Arene Clusters

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I. Introduction

The chemistry of carbonyl clusters has long since passed the point where only new metal geometries are of primary importance. Over the years, many specialist areas have been developed including the systematic study of organometallic cluster compounds. For example, an area within this field which has been extensively studied, and reviewed, is that concerning the interaction of acetylenes with clusters.[1,2] Recently, arene cluster chemistry has begun to emerge as an important entity within the field of organometallic cluster chemistry, although the roots of this subject date as far back as the late 1960s. There is a rich chemistry associated with the arene ligand in mono- and binuclear metal compounds, and complexes of virtually every transition metal have been prepared, and several important review articles concerned with the synthesis, structure, and theoretical aspects of these compounds have been previously published.[3-6] Until recently, however, relatively little effort had been directed toward the arene ligand and its interactions with cluster complexes, and the interest of the synthetic and structural

Dario Braga (left) graduated in Chemistry at the University of Bologna in 1977. He was postdoctoral fellow first at the University of Bologna and then at the University of North London working on the solid-state structure of high nuclearity transition metal clusters. He joined the Faculty of Science of the University of Bologna in 1982, where he is currently Associate Professor of General and Inorganic Chemistry. He was awarded the Raffaello Nasini Prize from the Inorganic Chemistry Division of the Italian Society of Chemistry in 1988 for his studies of the factors controlling molecular structure and fluxional behaviors. His research interests include the static and dynamic structure of organometallic molecules and clusters and the relationship between solid-state properties and molecular organization in organometallic crystalline materials.

Paul Dyson (center left) is currently a research fellow at the University of Edinburgh. He received his B.Sc. from the Hatfield Polytechnic (1990) together with a prize for his final year efforts. He moved to Fitzwilliam College, University of Cambridge, for his doctoral studies under the supervision of B. F. G. Johnson and transferred with his supervisor to the University of Edinburgh where he obtained his Ph.D. (1993). He will be soon taking up a lectureship at Imperial College, University of London. His research interests are concerned with arene clusters and polynuclear arene complexes without metal–metal bonds.

Fabrizia Grepioni (center right) graduated from the University of Bologna in 1985 and received her Ph.D. in Inorganic Chemistry in 1989. She is currently a research assistant at the Department of Chemistry of the University of Bologna. Her scientific interests are in the fields of inorganic and organometallic chemistry, empirical packing energy calculations, and molecular and crystal structure of transition metal clusters and complexes.

Brian Johnson (right) holds the Crum Brown Chair of Inorganic Chemistry at the University of Edinburgh. He received his B.Sc. (1960) and Ph.D. (1963) from the University of Nottingham. He then spent postdoctoral positions with Professor F. A. Cotton at M. I. T. and at the University of Manchester with Professor J. Lewis where he became a lecturer (1965). Lecturships were also held at University College London (1967–1970) and the University of Cambridge (1978–1990). In recognition of his research achievements he was elected as a Fellow of the Royal Society (1991) and Fellow of the Royal Society of Edinburgh (1992). He has also been awarded the Corday-Morgan Medal and Prize (1976) and the Award for the Royal Society of Chemistry. His major research interests are centered on the synthesis, spectroscopic characterization, and fluxional behavior of organometallic molecules and clusters.

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Table 1

arene–cluster compound	exp[a]	ref	arene–cluster compound	exp[a]	ref
		A. Nuclearity Three			
$Co_3(CO)_6(\mu_3\text{-}CR)(\eta^6\text{-arene})$ (R = F, Me, arene = $C_6H_4Me_2$, $C_6H_3Me_3$;	S	11	$\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2$	S,M	21
(R = Ph, arene = C_6H_6, C_6H_5Me, $C_6H_4Me_2$, $C_6H_3Me_3$)			$\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(CH_2Cl_2)\}RuB_{10}H_8(OEt)_2$	S,M	22
$Co_3(CO)_6(\mu_3\text{-}CPh)(\eta^6\text{-}C_6H_3Me_3)$	M	12	$Os_3(CO)_9(\mu_3\text{-}C_6H_6)$	S,M	27,28
$Co_3(\mu_3\text{-}CPh)(\eta^6\text{-}C_6H_3Me_3)_3$	S,M	13		C	29,33
$[Co_3(\mu_3\text{-}CO)_2(\eta^6\text{-}C_6H_6)_3]^+$	S	14	nucleophilic addition reactions		30a
	M	15	of the μ_3-ring		
$[CoCp]_3(\mu_3\text{-arene})$ (arene = α-methylstyrene, β-methylstyrene,	S	16	photoisomerization of		31
1,1-diphenylethane, stilbene, 4-methoxystilbene,			phosphine derivatives of		28
4-methylstyrene, 4-methoxystyrene, 1,1-diphenylpropene,			*ab initio* MO calculations		88
1-(4-anisyl)propene, β-ethylstyrene, 2-phenyl-2-butene)			$Ru_3(CO)_9(\mu_3\text{-}C_6H_6)$	S	24,32
$[CoCp]_3(\mu_3\text{-}\beta\text{-methylstyrene})$	M	16		M,RT	32
$[CoCp]_3(\mu_3\text{-}1,1\text{-diphenylethene})$	M	16		M,LT	33
$[CoCp]_3(\mu_3\text{-}1,1\text{-diphenylethane})$	M[b]	3		C	33,29
$[CoCp]_3(\mu_3\text{-}1,2\text{-diphenylethane})$	M[b]	3	Fenske–Hall calculations		28
$[CoCp]_3(\mu_3\text{-}2\text{-phenyl-}2\text{-butene})$	M[b]	3	$Os_3(CO)_8(\mu_3\text{-}C_6H_6)(\eta^2\text{-}CH_2CHR)$	S	34
$\{[CoCp]_3(\mu_3\text{-}\alpha\text{-methylstyrene})\}^+$	M[b]	3	(R = H, Me, Ph, Bu^t)		
$\{(\mu_3\text{-}H)[CoCp]_3(\mu_3\text{-}1,1\text{-diphenylethane})\}^+$	M[b]	3	$Os_3(CO)_8(\mu_3\text{-}C_6H_6)(\eta^2\text{-}CH_2CH_2)$	M	34
$[CoCp]_3(\mu_3\text{-}C_6H_6)$ (electronic structure)		17a	CPMAS NMR		34,35
$[RhCp]_3(\mu_3\text{-}C_6H_6)$	S,M	23	AAPEBC		36
$Fe_3(CO)_6(\mu_3\text{-}CX)(\mu_3\text{-}C\text{-}COOR)(\eta^6\text{-}C_6H_6)$	S,M	18	$Os_3(CO)_8(\mu_3\text{-}C_6H_6)(PPh_3)$	S,M	28
(X = Cl, R = C_2H_5; X = Br, R = CH_3)			$Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}C_2Me_2)$	S	37,38
$Ru_3(CO)_7(NPh)(\eta^6\text{-}C_6H_6)$	S,M	19		M	37
$[M_3S_2(p\text{-cymene})_3]^{2+}$ and $[M_3S_2(p\text{-cymene})_3]$ (M = Ru, Os)	S,M	20	AAPEBC		36
$[Ru_3S_2(\eta^6\text{-}p\text{-cymene})_3]^{2+}$	S,M	20	$Ru_3C(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}C_2R_2CO)$	S	38
$[Ru_3S_2(\eta^6\text{-}p\text{-cymene})_3]$	S,M	20	$Ru_3C(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}C_2R_2CO)$ (R = Ph)	S,M	38
		B. Nuclearity Four			
$Co_4(CO)_9(\eta^6\text{-arene})$ (arene = C_6H_5Me, $C_6H_4Me_2$, $C_6H_3Me_3$,	S	39	$Ru_4(CO)_9(PhC{=}CM)(\eta^6\text{-}C_6H_5Et)$	S	45
$C_6H_2Me_4$, C_5HMe_5, C_6Me_6, C_6H_5Et, C_6H_5OMe, C_6H_4MeOMe)			$[H_4Ru_4(\eta^6\text{-cymene})_4]^{2+}$	S	46
reactions of $Co_4(CO)_9(\eta^6\text{-}C_6H_2Me_4)$		40	$H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_6)$	S,M	47
$Co_4(CO)_9(\eta^6\text{-}C_6H_6)$ and $Co_4(CO)_9(\eta^6\text{-}C_6H_5Me)$	M	41	$Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$	S,M	47
$Co_4(CO)_9(\eta^6\text{-}C_{20}H_{14})$	S,M	42	$H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_5Me)$ and	S,M,C	48
$Co_4(CO)_6(\eta^6\text{-}C_6H_5Me)[HC(PPh_2)_3]$	S,M	43	$H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_4Me_2)$		
$Ru_4(CO)_9(\mu_4\text{-}C_6H_8)(\eta^6\text{-}C_6H_6)$	S,M	44			
		C. Nuclearity Five			
$Ru_5C(CO)_{12}(\mu_3\text{-}C_6H_6)$	S,M	49,50	$Ru_5C(CO)_{10}(\eta^6\text{-}C_6H_6)(\mu_2\text{-}C_6H_8)$	S,M	52
$Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$	S,M	49,50	$Ru_5(\mu_4\text{-}PPh)(CO)_{12}(\eta^6\text{-}C_6H_5Me)$	S,M	53
$Ru_5C(CO)_{13}(\eta^6\text{-}C_6H_6)$	S,M	50	$H_4Os_5(CO)_{11}(\eta^6\text{-}C_6H_6)$	S,M	54
$Ru_5C(CO)_{10}(\mu_3\text{-}C_6H_6)(\mu_2\text{-}C_6H_8)$	S,M	52	$H_4Os_5(CO)_{12}(\eta^6\text{-}C_6H_6)$	S,M	54
		D: Nuclearity Six			
$Ru_6C(CO)_{14}(\eta^6\text{-arene})$ (arene = C_6H_5Me, $C_6H_4Me_2$, $C_6H_3Me_3$)	S	55	$Ru_6C(CO)_{11}(\eta^6\text{-arene})(\mu_3\text{-}C_6H_6)$	S,M,C	61
$Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)$	M	56	(arene = C_6H_5Me, $C_6H_4Me_2$, $C_6H_3Me_3$)		
	C	48	$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}C_6H_6)$	S,M,C	61
$Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2)$	M	57	$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_4Me_2)(\mu_3\text{-}C_6H_6)$	S,M,C	61
$Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)$	M	58,48	$Ru_6C(CO)_{11}(\eta^6\text{-arene})(\eta^6\text{-}C_6H_6)$	S	61
$Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Et_3)$	S,M,C	57	(arene = C_6H_5Me, $C_6H_4Me_2$, $C_6H_3Me_3$)		
$Ru_6C(CO)_{14}(\mu_3\text{-}C_{16}H_{16})$	S,M,C	57	$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)(\eta^6\text{-}C_6H_6)$	M,C	65
$Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$	S	59,60	$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)_2$	S,M,C	65,66
		61,62			
	M	60			

$Ru_6C(CO)_{15}(\mu_2\text{-}C_6H_8)$	S,M	60	$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}C_6H_5Me)$	S,M	67
$Ru_6(\mu_4{:}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)$	S,M	63	$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)_2$	S	67
$HRu_6(CO)_{14}(\eta^7\text{-}\mu_2\text{-}C_6H_3Me_2CH_2)$	S,M	63	VTNMR (interconversion of the two isomers)		67
$Ru_6(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}C_6H_6)$	S	27,60			
	M	27	$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_4Me_2)_2$ (two forms)	S,M,C	68
	C	48	$Ru_6C(CO)_{11}(\eta^6\text{-}C_{16}H_{16})(\mu_3\text{-}C_{16}H_{16})$	S,M	69
$Ru_6(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_2\text{-}C_6H_8)$	S,M	60	$Ru_6C(CO)_{11}(\eta^4\text{-}C_6H_8)(\mu_3\text{-}C_{16}H_{16})$	S,M	69
$Ru_6(CO)_{11}(\mu_3\text{-}C_6H_6)(\mu_2\text{-}C_6H_8)$	S,M	60	$H_2Os_6(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}C_6H_6)$	S,M,C	71
$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2$	S,M	64	$Os_6(CO)_{12}(\eta^6\text{-}C_6H_6)_2$	S,M	72
$Ru_6C(CO)_{12}(\eta^6\text{-arene})(\mu_2\text{-}C_6H_8)$ (arene = C_6H_5Me, $C_6H_4Me_2$, $C_6H_3Me_3$)	S	61			
	E. Mixed-Metal Clusters				
$FeCo_2C(CO)_3(\mu_3\text{-}CO)_2(\eta^6\text{-}C_6H_3Me_3)_2$	S,M	73	$RuOs_3(CO)_9(\eta^6\text{-}C_6H_6)(R'C_2R'')$ ($R' = R'' =$ Me, Et, Ph; R' = Me, R'' = H, Et, Ph)	S	78
$FeCo_3(CO)_6(Cp)(\mu_4\text{-}C{=}CHCF_3)(\eta^6\text{-}C_6H_6Me)$	S,M	74	$RuOs_3(CO)_9(\eta^6\text{-}C_6H_6)(C_2Me_2)$	S,M	78
$H_3RhOs_3(CO)_9(\eta^6\text{-}C_6H_6)$	S,M	75,76	$H_4RuOs_4(CO)_{11}(\eta^6\text{-}C_6H_6)$	S,M	54
$H_3RhOs_3(CO)_9(\eta^6\text{-}C_6H_5Me)$	S,M	75,77	$RuOs_5(CO)_{15}(\eta^6\text{-}C_6H_6)$	S,M	79
	F. Nuclearity Higher than Six				
$Ru_7(CO)_{15}(\mu_4\text{-}PPh)_2(\eta^6\text{-}C_6H_5Me)$	S,M	53	$H_4Ru_8(CO)_{18}(\eta^6\text{-}C_6H_6)$	S,M	70
$Ru_8(\mu_8\text{-}P)(CO)_{19}(\mu_2\text{-}\eta^1\eta^6\text{-}CH_2C_6H_5)$	S,M	80	$Cu_2Ru_6(CO)_{18}(C_6H_5Me)_2$	S,M	82
$Ru_8(CO)_{17}(\mu_4\text{-}S)_2(\eta^6\text{-}C_6H_6Me)$	S,M	81			

[a] S = preparative path described; M = molecular structure determined by X-ray diffraction methods (if not otherwise specified); C = molecular organization in the crystal structure investigated; for AAPEBC, CPMAS, VTNMR, and other acronyms see Abbreviations. [b] Crystal structure determinations reported in ref 3 as unpublished results.

chemists has been mainly focused on arene clusters of cobalt, ruthenium, or osmium.

All early preparative approaches to arene cluster compounds implied essentially direct interaction of a metal carbonyl with the appropriate arene solvent under reflux. However, in recent years, the number of synthetic routes designed specifically for the formation of arene-clusters has risen significantly. It is not a straightforward task to classify the types of reactions used. For our purposes, we draw distinction between reactions in which the arene is added directly, and those in which other reagents are used in the first instance, and converted to an arene at a later stage in the synthesis. In general, the former are initiated by either thermolytic and photolytic means, and often involve a change of cluster nuclearity. The latter method is usually more selective, often with the cluster core remaining intact.

Reactivity of arene clusters has centered on both nucleophilic substitution reactions on the metal core, and nucleophilic addition reactions with the aromatic ring, these are also the primary reactions of monometallic complexes.

The *molecular structures* of arene clusters present some intriguing aspects which relate to the ability of the arene to replace three CO ligands over the cluster frame. Structural isomerism, for instance, arises from the availability of different coordination sites on the metal framework as well as from the different bonding modes available to the arene ligands.

The clusters produced are diverse. Many different bonding modes of the arene ligands have been observed directly: η^2, η^6, and μ_3-$\eta^2{:}\eta^2{:}\eta^2$,[3-5] and others postulated. In the latter mode each metal atom of a triangular face interacts with two C-atoms of the arene ring. Interconversion between the η^6 and μ_3-bonding modes has been studied in detail, induced both chemically and thermally. The μ_3-bonding type has been subjected to extensive chemical, structural, and theoretical investigations and is commonly found in clusters of nuclearity three, five, and six.

From the study of the *crystal structure* of cluster complexes much has been learned on the relationship between molecular shapes and organization in the solid.[7,8] It has been observed, for instance, that arene clusters tend to establish preferential arene–arene interactions in their crystals.[7] Structural non-rigidity of arene clusters and reorientational phenomena in the solid state have been the subject of many studies mainly by means of NMR spectroscopy and empirical potential barrier calculations.[9] It is by now well ascertained that the ease of reorientation of π-bound organic fragments in crystalline metal clusters and complexes depends essentially on the shape of the fragment, *viz.* on the intermolecular interlocking in the crystal structure.

The idea of metal clusters as models of chemisorption systems in surface chemistry is an attractive hypothesis which has been emphasized by numerous workers in recent years.[10a] In this review we shall examine possible boundary conditions to such a cluster–surface analogy. New insights for this work have been provided by the molecular chemistry of clusters containing benzene in the facial bonding mode.[10b]

This article is organized in five distinct sections. In the first section we deal with the synthesis of the arene clustes which have been characterized to date. The second section commences with an examination of the different types of bonding modes that arenes adopt on cluster frameworks with emphasis on the relationship between the apical (η^6) and the facial (μ_3-η^2:η^2:η^2) bonding modes. This section also reports a selection of the most representative structures. The third section examines the relationship between the *molecular* structure and the *crystal* structure of arene clusters, and the dynamic behavior of arene clusters in both solution and the solid state is reviewed in the fourth section. Finally, the fifth section is devoted to the cluster–surface relationship. All compounds discussed in these sections are listed in Table 1. References to the appropriate syntheses and structural papers are given.[11-82]

II. Synthesis and Reactivity

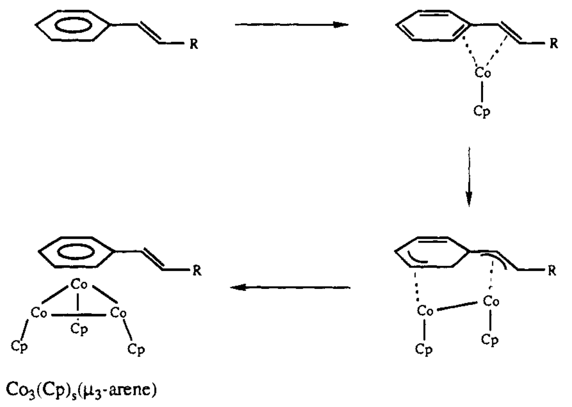
This section covers the methods used to prepare all the arene clusters reported to date. Where mechanistic information has been established, or proposed, it will also be included in the text.

A. Nuclearity Three

A large number of arene clusters possess trinuclear metal atom frameworks.[11-38] They comprise a very broad group of compounds in which both η^6- and μ_3-bonding modes have been observed and mono-, bis-, and tris-arene derivatives have all been prepared. Several trinuclear cobalt clusters containing η^6-arene ligands are known. A feature common to all of these species is that the metal triangle is capped (on at least one side) by a *triply*-bridging ligand such as MeC, PhC, or CO. For example, monoarene complexes of formula $RCCo_3(CO)_6(\eta^6\text{-arene})$ (R = F, Me, arene = $C_6H_4Me_2$, $C_6H_3Me_3$; R = Ph, arene = C_6H_6, C_6H_5Me, $C_6H_4Me_2$, $C_6H_3Me_3$) are prepared in good yield from the direct reaction of $RCCo_3(CO)_9$ with the appropriate arene.[11] The reaction is completely reversible, hence removal of carbon monoxide is essential for a good yield. The coordinated arene has been found to readily undergo exchange with other arenes, and there seems to be no restriction as to which arene will exchange with the one coordinated, providing it is in a large excess and high temperatures are used.

The tris(toluene) complex $Co_3(\mu_3\text{-}CC_6H_5)(\eta^6\text{-}C_6H_5Me)_3$ has been isolated in very low yield ($>1\%$) from the reaction of the toluene fragment $Co(\eta^6\text{-}C_6H_5Me)(MeCN)$ with toluene–cobalt cocondensates.[13] Large quantities of metallic cobalt are also isolated from the reaction. The tris(arene) cationic clusters $[Co_3(CO)_2(\eta^6\text{-arene})_3]^+$ (arene = C_6H_6, C_6H_5Me) were reported independently by both Chini and Fischer in 1958,[14] and were probably the first examples of arene cluster compounds. Chini's route involved the thermal reaction of $Co_2(CO)_8$ and $AlBr_3$ with either benzene or toluene. Fisher also used reductive conditions, heating $Hg[Co(CO)_4]_2$ with benzene in the presence of $AlCl_3$. In these clusters, the metal triangle is capped on either side by a *triply*-bridging CO group.[15]

Scheme 1. The Proposed Formation of $Co_3Cp_3(\mu_3\text{-arene})$ from $CpCo(C_2H_4)_2$ Fragments



A novel high-yielding synthetic approach has been applied to the preparation of μ_3-arene clusters of formula $Co_3Cp_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-arene})$ (Cp = C_5H_5).[16] The method is unusual in that the cluster assembles on the arene and involves a one-step reaction between a Jonas reagent, $CpCo(C_2H_4)_2$, and substituted styrenes, allylarenes, and 4-phenyl-1-butene. Benzene and simple arenes do not undergo reaction, and it would appear that the 1-alkenyl group on the central ring binds to the metal fragment in the first instance, before attack occurs on the aromatic π-system. Evidence for this suggestion arises from the isolation of mononuclear products in which the cobalt atom binds to a double bond of the ring and to that of the alkenyl. The second and third cobalt units must attack in a *syn* position, and a further intermediate has been proposed in which two cobalt fragments are attached to the arene. Scheme 1 depicts the postulated mechanistic pathway.

The rhodium analogue $[RhCp]_3(\mu_3\text{-}C_6H_6)$ of the cobalt cluster discussed above has been obtained by successive coordination on benzene in hexane of RhCp fragments generated photolitically from the thermally stable complex cyclopentadienylbis(ethene)rhodium.[23]

The reaction of the bis(alkylidene) triiron cluster $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ with AlX_3 (X = Cl and Br) in benzene affords the corresponding Fe cluster in which fluorine is replaced by chlorine or bromine.[18] Moreover, with alcohols an additional reaction occurs in which $Fe_3(CO)_6(\eta^6\text{-}C_6H_6)(\mu_3\text{-}X)(\mu_3\text{-}CCOOR)$ (X = Cl, R = C_2H_5, and X = Br, R = CH_3) is produced. The mechanism proposed involves the attack of $Fe_3(CO)_9(\mu_3\text{-}CCl)$ by a Lewis acid which causes a polarization of the C–X bond or, alternatively, formation of a cationic species. This is followed by migration of a carbonyl ligand to the electrophilic carbon atom and subsequent creation of a vacant coordination site on one of the iron atoms, with formation of the unsaturated cationic ketenylidene cluster $[Fe_3(CO)_8(\mu_3\text{-}CX)(\mu_3\text{-}CCO)]^+$. Uptake of benzene occurs at this vacant site with subsequent elimination of two carbonyl ligands affording $[Fe_3(CO)_6(\eta^6\text{-}C_6H_6)(\mu_3\text{-}CX)(\mu_3\text{-}CCO)]^+$. On reaction with alcohols nucleophilic addition of OR^- occurs leading to the formation of the observed product. As with the η^6-arene cobalt clusters described above, the metal triangle is capped above and below by the μ_3-alkylidene groups.

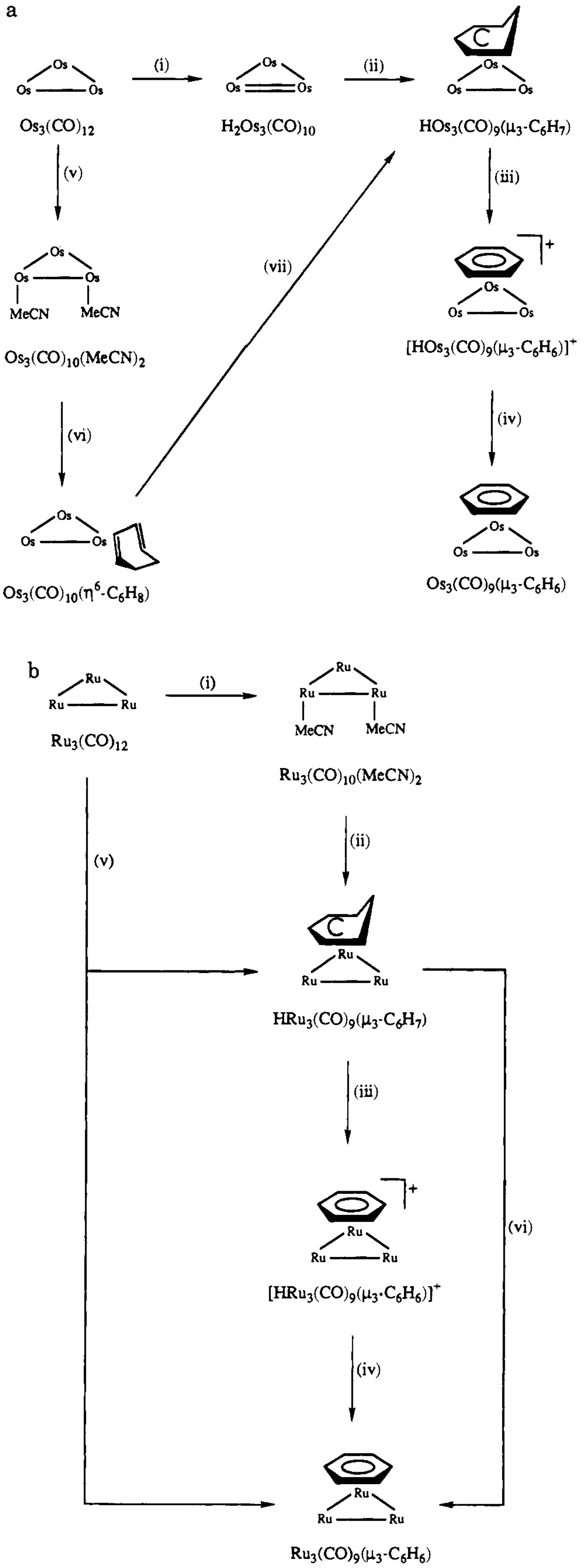
Interest in the industrially important carbonylation of nitrobenzene to give isocyanate or phenylcarbamate derivatives led to a reaction in which the triruthenium–benzene cluster $Ru_3(CO)_7(\mu_3\text{-}NPh)(\eta^6\text{-}C_6H_6)$ was isolated. The investigation centered on the reactions of $Ru_3(CO)_{12}$ since it had been found to be an efficient precatalyst. Part of this study included the reactions of $M_3(CO)_{12}$ (M = Fe, and Ru) with $PhNO_2$ in benzene in the presence of $Co_2(CO)_8$.[19] The reaction involving $Ru_3(CO)_{12}$ resulted in the isolation of the benzene cluster $Ru_3(CO)_7(\mu_3\text{-}NPh)(\eta^6\text{-}C_6H_6)$. Small amounts of the tetracobalt cluster $Co_4(CO)_9(\eta^6\text{-}C_6H_6)$ were also isolated from this reaction (see section II.B).[39] Although the formation of these benzene compounds was unintentional, the reaction demonstrated the relative ease in which benzene may be attached to a single ruthenium atom when the cluster is "held together" by a suitable *triply*-bridging ligand, in this case NPh.

The reaction between aqueous solutions of $Na_2S\cdot 9H_2O$ and the chloro-bridged dimeric species $[(p\text{-cymene})RuCl_2]_2$, followed by addition of excess KPF_6 affords the dicationic complex $[Ru_3S_2(\eta^6\text{-cymene})_3]^{2+}$, stabilized as the PF_6^- salt.[20] The metal triangle is capped on either side by the sulfur atoms. The same compound can also be prepared by reaction of the same dimer with NaSH in methanol. Reduction of this cluster to the isostructural neutral species $[Ru_3S_2(\eta^6\text{-cymene})_3]$ occurs on treatment with 2 equiv of Cp_2Co in acetonitrile.

Thermolysis has also been used to prepare the unusual bis(arene)triruthenium–decaborane "double-cluster" compound $[\{\eta^6\text{-}C_6Me_6)Ru_2H_4\}RuB_{10}H_8(OEt)_2]$.[21] Instead of heating a metal carbonyl in arene solvent, the arene-containing chloro-bridged dimer $\{Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2$ was heated in refluxing ethanol, in the presence of $[B_{10}H_{10}]^{2-}$. This leads to the aformentioned compound in modest yield. The complex may be described as a Ru_3 triangle in which the ethoxydecaborane moiety is connected to one ruthenium atom in an η^6-mode. The two remaining ruthenium atoms each carries an η^6-coordinated hexamethylbenzene ligand. A derivative of this compound has been produced by reaction with methylacetylene in dichloromethane. The product $[\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(CH_2Cl_2)\}RuB_{10}H_8(OEt)_2]$ contains a coordinated dichloromethane unit as well as acetylene.[22]

The triosmium complex $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ was the first example of a cluster found to contain a facially bound arene. It was first reported in 1985 together with the related hexaruthenium complex $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ (see section II.E).[27] Scheme 2, parts a and b, illustrates the various pathways to $M_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ (M = Os, Ru, respectively). The synthetic route to the triosmium cluster commences with the triply-bridging cyclohexadienyl complex $HOs_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^1{:}\eta^2\text{-}C_6H_7)$, first prepared several years earlier, from the reaction between the highly reactive cluster $H_2Os_3(CO)_{10}$ and cyclohexa-1,3-diene.[25] A hydride may be abstracted from the facially bound dienyl ring using the trityl cation, $[Ph_3C]^+$, yielding the cationic benzene cluster $[HOs_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]^+$. In turn, this may be treated with the noncoordinating base

Scheme 2. Preparation of (a) $Os_3(CO)_9(\mu_3\text{-}C_6H_6)$ and (b) $Ru_3(CO_9)(\mu_3\text{-}C_6H_6)$[a]



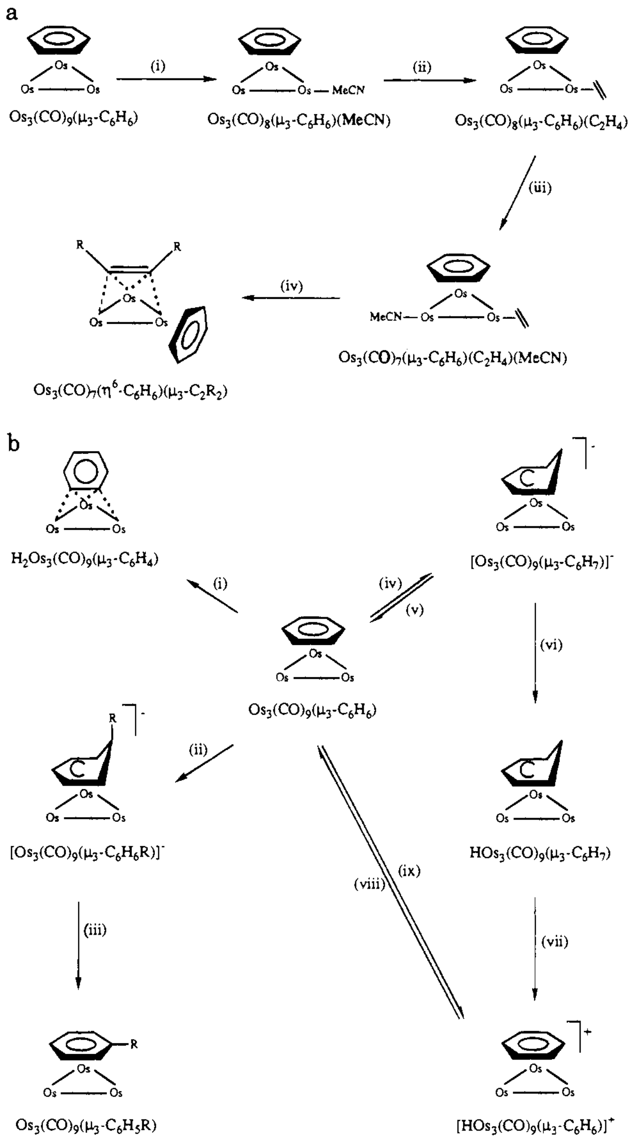
[a] Reagents: (a) (i) H_2, heating in octane, (ii) heating in octane/1,3-C_6H_8, (iii) $[Ph_3C][BF_4]$, (iv) DBU, (v) 2 equiv of Me_3NO/MeCN, (vi) 1,3-C_6H_8, (vii) heating in octane; (b) (i) 2 equiv of Me_3NO/MeCN, (ii) 1,3-C_6H_8, (iii) $[Ph_3C][BF_4]$, (iv) DBU, (v) 2 equiv of Me_3NO/1,3-C_6H_8, (vi) heating in hexane.

DBU resulting in deprotonation of the metal triangle, affording the neutral μ_3-benzene triosmium cluster.

The characterization of the novel μ_3-η^2:η^2:η^2-coordination mode stimulated extensive studies probing the nature of this ring, as well as prompting a search for a synthetic route to the analogous ruthenium complex. Five years later the ruthenium analogue was indeed prepared.[32] The synthetic route was based on the use of the activated cluster $Ru_3(CO)_{10}(MeCN)_2$ since the hydrido analogue of the osmium cluster $H_2Os_3(CO)_{10}$, namely $H_2Ru_3(CO)_{10}$, is not available. Treatment of the bis(acetonitrile) complex with cyclohexa-1,3-diene affords the dienyl complex $HRu_3(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_7)$.[32] From here, the synthesis of $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ parallels that developed for the osmium complex. In a more convenient route, $Ru_3(CO)_{12}$ is treated with the oxidative decarbonylation reagent trimethylamine *N*-oxide (Me_3NO) in the presence of cyclohexa-1,3-diene; this yields both $HRu_3(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_7)$ and $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ in a single step.[24] The overall yield of the benzene complex can be increased by thermolysis of the dienyl complex in hexane. The corresponding osmium compound, $Os_3(CO)_{12}$, does not react in the same way, but from the reaction of the activated cluster, $Os_3(CO)_{10}(MeCN)_2$, with cyclohexa-1,3-diene the intermediate compound $Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)$ has been isolated.[24,25b] This intermediate may be converted to the triply-bridging dienyl species, $HOs_3(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_7)$ by thermolysis in octane. On the basis of these observations, it has been postulated that the reaction of $Ru_3(CO)_{10}(MeCN)_2$ with cyclohexa-1,3-diene also proceeds via a similar diene intermediate, *viz.* $Ru_3(CO)_{10}(\eta^4\text{-}C_6H_8)$ but that it is less stable than the corresponding osmium compound, eliminating a CO ligand to form the coordinatively unsaturated intermediate "$Ru_3(CO)_9(\eta^4\text{-}C_6H_8)$" which then undergoes C$-$H bond cleavage to generate the known dienyl complex.

Scheme 3, parts a and b, illustrates the reactions carried out on the triosmium benzene cluster. Substitution reactions on the triosmium benzene cluster framework usually involve the initial substitution of acetonitrile for a carbonyl group by reaction with Me_3NO in the presence of MeCN yielding $Os_3(CO)_8(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(MeCN)$. Treatment of this activated complex with two-electron donor ligands such as tertiary phosphines or alkenes results in the displacement of the acetonitrile ligand and formation of derivatives in which equatorial substitution has occurred on the metal frame. Significantly, the coordination mode of the face-capping benzene ligand is retained. In a typical reaction, ethylene may be introduced to form the alkene complex $Os_3(CO)_8(\eta^2\text{-}C_2H_4)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ in which an equatorial carbonyl group is replaced by a symmetrically coordinated ethylene molecule.[34]

Scheme 3. (a) Substitution Reactions of $Os_3(CO)_9(\mu_3\text{-}C_6H_6)$ and (b) Reactions of the Ring in $Os_3(CO)_9(\mu_3\text{-}C_6H_6)$[a]



[a] Reagents/reactions: (a) (i) 1 equiv of Me_3NO/MeCN, (ii) C_2H_4, (iii) 1 equiv of Me_3NO/MeCN, (iv) C_2R_2; (b) (i) $h\nu$, (ii) LiR, (iii) $[Ph_3C][BF_4]$, (iv) $Li(BHEt_3)$ or $[NEt_4][BH_4]$, (v) $[Ph_3C][BF_4]$, (vi) $HBF_4{\cdot}Et_2O$, (vii) $[Ph_3C][BF_4]$, (viii) DBU, (ix) $HBF_4{\cdot}Et_2O$.

This substituted complex, $Os_3(CO)_8(\eta^2\text{-}C_2H_4)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$, undergoes further carbonyl substitution on reaction with an additional aliquot of Me_3NO in the presence of acetonitrile, thereby affording $Os_3(CO)_7(\eta^2\text{-}C_2H_4)(MeCN)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$. This activated species readily reacts with alkynes (C_2RR') to form the complexes $Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}C_2RR')$ (R = R′ = H, Ph, or Me; R = H, R′ = Ph; R = Me, R′ = Et) in which the benzene has migrated to a terminal position, and the osmium triangle is now capped on one side by the acetylene moiety.[37] Direct reaction of $Os_3(CO)_8(\eta^2\text{-}C_2H_4)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ with alkynes leads to extensive decomposition, and only small amounts of $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ may be recovered. Although the triruthenium complex $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ does not readily undergo substitution reactions, treatment with alkynes in refluxing dichloromethane affords the clusters $Ru_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}RC_2R'CO)$ (R = R′ = Me, Ph, or H; R = Ph, R′ = H).[38] In the diphenylacetylene derivative $Ru_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}PhC_2(PhCO))$ it has been established that one of the Ru$-$C σ-bonds has undergone carbonyl insertion to generate an acyl derivative.[38]

We shall now focus on the reactivity of benzene in its μ_3-η^2:η^2:η^2-coordination mode. A detailed study concerning reactions of the benzene moiety in the triosmium cluster $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ has been carried out.[30a] The metal-induced electrophilic nature of the benzene ring in $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ favors nucleophilic addition reactions with suitable reagents. Good hydride donors such as $Li[BHEt_3]$ or $[NEt_4][BH_4]$ react readily in tetrahydrofuran at −78 °C to afford the anionic dienyl cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_7)]^-$. *Exo* attack of the hydride has been established by deuterium labeling experiments. The benzene complex may be regenerated by abstraction of hydride from the anionic cluster on treatment with $[Ph_3C][BF_4]$ in dichloromethane at −78 °C. The anionic complex can also be protonated with $HBF_4{\cdot}Et_2O$ affording the neutral dienyl complex $HOs_3(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_7)$, which upon treatment with $[Ph_3C][BF_4]$ undergoes hydride abstraction of the dienyl moiety forming the cationic complex $[HOs_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]^+$. Alternatively, this cationic benzene cluster can be generated from $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ by treatment with $HBF_4{\cdot}Et_2O$, and the reaction reversed with DBU.

The cluster $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$, also undergoes reaction with the nucleophilic reagents methyl- or phenyllithium in thf at −78 °C, affording the functionalized cyclohexadienyl complexes $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_6R)]^-$ (R = Me or Ph) as a result of *exo* addition. Further treatment with $HBF_4{\cdot}Et_2O$ results in the neutral hydrido cluster $HOs_3(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_6R)$.

These reactions display a marked similarity between nucleophilic addition to the face-capping ligands and to the η^6-arenes found in mononuclear metal complexes.

An important reaction which models the interconversion of the associatively and dissociatively chemisorbed states of benzene on low Miller index surface planes of a metallic surface (see Section VI) has been achieved by the photoinduced isomerization at 278 K of the osmium species $Os_3(CO)_{9-n}(L)_n(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ [n = 0, 1, or 2; L = CO, PPh_3, or $P(OMe)_3$] affording the μ_3-benzyne compounds $H_2Os_3(CO)_{9-n}(L)_n(\mu_3\text{-}\sigma{:}\eta^2{:}\sigma\text{-}C_6H_4)$.[30b]

B. Nuclearity Four

A series of arene derivatives based on the tetracobalt cluster $Co_4(CO)_{12}$ have been isolated.[39-43] The preparation of compounds $Co_4(CO)_9(\eta^6\text{-arene})$ (arene = C_6H_6, C_6H_5Me, $C_6H_4Me_2$, $C_6H_3Me_3$) is straightforward; thermolysis of $Co_2(CO)_8$ or $Co_4(CO)_{12}$ in the appropriate arene solvent (or a 2−3-fold excess of the arene in hexane) affords the arene clusters in good yield.[39] The triptycene derivative has also been prepared by direct reaction with $Co_4(CO)_{12}$.[42] Although no direct mechanistic evidence has been established, one can envisage the stepwise expulsion of carbonyl ligands, and the simultaneous addition of the arene ring.

Two types of reaction have been studied with the tetracobalt system. The first involves reaction with strong nucleophilic reagents which results in cleavage of the Co−arene bonds. The second reaction involves carbonyl substitution by phosphines. With triphenylphosphine only one ligand can be substituted, while the tripod ligand $HC(PPh_2)_3$ readily replaces three carbonyl groups on $Co_4(CO)_9(\eta^6\text{-}C_6H_5Me)$, yielding $Co_4(CO)_6(\eta^6\text{-}C_6H_5Me)(HC(PPh_2)_3)$.[43] It is significant that in this reaction arene displacement by the tertiary phosphine is not observed.

Thermolysis of $Ru_3(CO)_{12}$ in a solution of octane containing excess cyclohexa-1,3-diene results in the isolation of several products, including $Ru_4(CO)_9(\eta^6\text{-}C_6H_6)(\mu_4\text{-}C_6H_8)$.[44] The four ruthenium atoms adopt a "butterfly" arrangement, the C_6H_8 ligand lying between the wings. The benzene ligand coordinates in the η^6-mode to a "hinge" metal atom. It has been found that the diene cluster $Ru_4(CO)_{12}(C_6H_8)$ may be isolated from the thermolysis of $Ru_3(CO)_{12}$ with cyclohexa-1,3-diene in refluxing cyclohexane, benzene, or hexane. This can subsequently be converted into $Ru_4(CO)_9(\eta^6\text{-}C_6H_6)(\mu_4\text{-}C_6H_8)$ by treatment with an excess of cyclohexa-1,3-diene in octane heated to reflux for several hours.

Thermolytic action upon $Ru_3(CO)_{12}$ has also been used in the preparation of a tetraruthenium "butterfly" complex with an η^6-ethylbenzene ligand. $Ru_3(CO)_{12}$ is refluxed with an excess of styrene in cyclohexane, methylcyclohexane, or octane; two major products isolated from these reactions were characterized spectroscopically as the tetranuclear clusters $Ru_4(CO)_{12}(PhC_2H)$ and $Ru_4(CO)_9(PhC_2H)(\eta^6\text{-}C_6H_5Et)$.[45] The proposed structures of these complexes involve a Ru_4 butterfly configuration, in which the PhC_2H group lies between the wings, interacting with all four ruthenium atoms. The ethylbenzene is believed to coordinate in an η^6-mode to one of the hinge ruthenium atoms, although the precise isomer is not known.

Ultrasound has been used to stimulate the heterogeneous reduction of the chloro-bridged dimeric species $[(\text{cymene})RuCl_2]_2$, in the presence of zinc.[46] When the reaction is carried out under an atmosphere of hydrogen, cluster formation occurs, and one such product has been tentatively formulated as the tetrakis(arene) cluster $[H_4Ru_4(\eta^6\text{-cymene})_4]^{2+}$ on the basis of spectroscopic evidence.

A detailed study of tetranuclear arene clusters based on derivatives of the hydrido cluster $H_4Os_4(CO)_{12}$ has been undertaken.[47,48] Treatment of $H_4Os_4(CO)_{12}$ with 2 equiv of Me_3NO in the presence of acetonitrile yields the activated bis(acetonitrile) species $H_4Os_4(CO)_{10}(MeCN)_2$. Heating this activated cluster in dichloromethane−cyclohexa-1,3-diene results in the formation of several products including $H_3Os_4(CO)_{11}(\mu\text{-}\sigma{:}\eta^2\text{-}C_6H_9)$, the diene complex, $H_2Os_4(CO)_{11}(\eta^4\text{-}C_6H_8)$, the benzene species $H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_6)$, and the benzene−diene cluster $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$.[47]

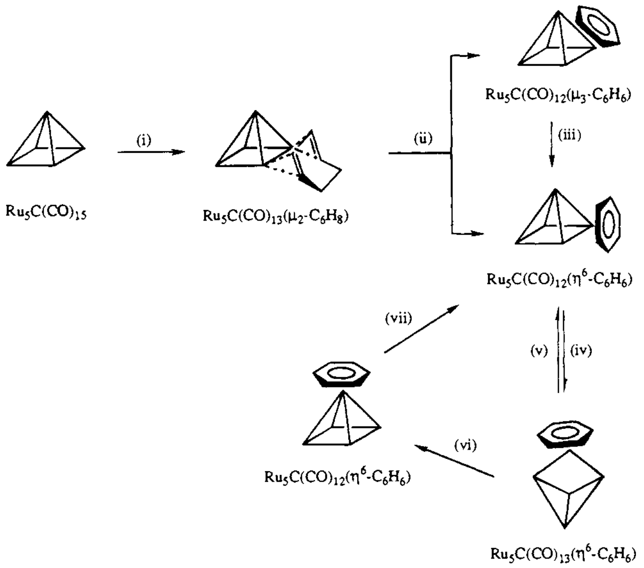
Toluene and xylene analogues of the benzene cluster, with the formula $H_2Os_4(CO)_{10}(\eta^6\text{-arene})$ have also been prepared.[47] In the case of the toluene derivative $H_4Os_4(CO)_{10}(MeCN)_2$ is reacted with dihydrotoluene in refluxing dichloromethane. The xylene (and also the toluene) species is prepared by arene exchange;[48] an important phenomenon which has received wide attention for mononuclear metal complexes. In this reaction the benzene cluster $H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_6)$ is heated in the appropriate arene (or an octane−arene solution) for a prolonged period, resulting in substitution of the benzene moiety by the appropriate arene in reasonable yield. In contrast to the Co_4 derivatives described earlier the reverse reaction is not observed. It would thus appear that the exchange process is controlled primarily by electronic factors.

C. Nuclearity Five

For ruthenium, work has centered largely on benzene derivatives of the square-pyramidal carbido cluster $Ru_5C(CO)_{15}$, in which three interconvertable isomers of formula $Ru_5C(CO)_{12}(C_6H_6)$ have been isolated and characterized.[49] Scheme 4 illustrates the synthesis and interconversion of these compounds. The synthetic strategy employed involves the initial replacement of two CO ligands on the cluster by cyclohexadiene, followed by the "dehydrogenation" of the organic ring, and the expulsion of another CO group, to afford the required benzene species. The cluster $Ru_5C(CO)_{15}$ undergoes reaction with either cyclohexa-1,3-diene[50] or cyclohexa-1,4-diene[51] upon treatment with 2 equiv of Me_3NO in dichloromethane. In either case, this results in the formation of the diene cluster $Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)$, in which the cyclohexadiene ligand spans a basal edge of the metal framework.[50,51] The simplest mechanistic pathway might be taken to involve the sequential removal of a carbonyl ligand followed by the stepwise addition of the diene. No isomerization of cyclohexa-1,4-diene to the more common 1,3-diene is observed upon coordination.

The diene species, $Ru_5C(CO)_{13}(\mu_3\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)$ reacts with a further aliquot of Me_3NO, again in dichloromethane, to afford two isomeric benzene derivatives $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ and $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$,[49,50] in which the benzene is facially and terminally bound, respectively. Mild thermolysis results in the irreversible conversion of the former isomer into the latter. This thermally induced arene migration process also requires simultaneous carbonyl rearrangement. The fact that the facial benzene migrates to a terminal site (and not *vice versa*) suggests that $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ is initially formed in the reaction. The first step in the conversion of $Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)$ to the two benzene coordinated isomers is believed to take place by the creation of a vacant coordination site within the Ru_5C unit by oxidation of a further carbonyl ligand to CO_2. This is followed by the oxidative addition of a C−H bond of the diene to generate a hydrido−hexadienyl cluster of formula $HRu_5C(CO)_{12}(C_6H_7)$. The second C−H bond cleavage must occur by an alternative route since only 1 equiv of Me_3NO is required. Here the route is proposed to occur via an initial rearrangement of the cluster core, probably the customary square-pyramid ↔ bridged-butterfly interconversion during which an activated coordination site is generated. This is followed by the necessary second C−H bond cleavage. By this means the second possible intermediate $H_2Ru_5(CO)_{12}(C_6H_6)$ is generated. Loss of H_2 would be accompanied by reformation of the square-pyramidal unit, and the dienyl derivative would be expected to lie facially over a triruthenium face.

Scheme 4. Synthesis of Benzene Derivatives of $Ru_5C(CO)_{15}$[a]



[a] Reagents: (i) 2 equiv of $Me_3NO/1,3\text{-}C_6H_8$, (ii) 1 equiv of Me_3NO/CH_2Cl_2, (iii) heating in hexane, (iv) CO/CH_2Cl_2, (v) remove CO source, (vi) allow to stand under CO atmosphere for 24 h and then remove CO source, (vii) heating in hexane.

Treatment of $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ with carbon monoxide at room temperature produces the bridged-butterfly cluster $Ru_5C(CO)_{13}(\eta^6\text{-}C_6H_6)$.[50] The addition of the carbon monoxide occurs at the basal ruthenium atom to which the benzene is attached reflecting the lower electron density on this atom with respect to the $Ru(CO)_3$ groups. On standing, freshly prepared samples of $Ru_5C(CO)_{13}(\eta^6\text{-}C_6H_6)$ readily revert back to the precursor, $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$, via CO loss.[50] However, if the bridged-butterfly species is stored at −20 °C for 24 h under a carbon monoxide atmosphere, then, on removal of CO, a third isomer of formula $Ru_5C(CO)_{12}(C_6H_6)$ results. This new isomer is believed to contain the benzene ligand η^6-bound to the apical ruthenium atom of the square-pyramidal cluster. Upon thermolysis in hexane, this new isomer reverts back to the cluster in which the benzene ligands coordinates in an η^6-fashion to a basal ruthenium atom.

In an extension of the Me_3NO activation route, $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ and $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ have been treated with Me_3NO in dichloromethane−cyclohexa-1,3-diene to yield the isomers $Ru_5C(CO)_{10}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)$ and $Ru_5C(CO)_{10}(\eta^6\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)$.[52] Unlike the former isomeric pair, conversion of the facial benzene into the terminally bound complex occurs under more aggressive conditions, accompanied by extensive decomposition. As yet, no bis(benzene) complexes have been derived from these complexes.

The pentanuclear cluster $Ru_5(\mu_4\text{-}PPh)(CO)_{12}(\eta^6\text{-}C_6H_5Me)$ has been isolated from the thermolysis of $Ru_3(CO)_{12}$ with $PPhH_2$ in toluene.[53] The five metal atoms also adopt a square pyramidal geometry, the square base being capped by the phenylphosphinidene moiety. The toluene ligand is coordinated in an η^6-fashion to a basal metal atom.

A pair of pentaosmium arene clusters have been prepared by the ionic coupling of the readily available dianionic tetraosmium cluster $[H_4Os_4(CO)_{11}]^{2-}$ with an osmium−benzene fragment. Reduction of $H_4Os_4(CO)_{12}$ by excess potassium−benzophenone in tetrahydrofuran yields the dianionic cluster $[H_4Os_4(CO)_{11}]^{2-}$ which on treatment with the capping species $[Os(C_6H_6)(MeCN)_3]^{2+}$ results in the formation of two major products, *viz.* $H_4Os_5(CO)_{11}(\eta^6\text{-}C_6H_6)$ and $H_4Os_5(CO)_{12}(\eta^6\text{-}C_6H_6)$.[54] The former complex is based on a trigonal-bypyramidal arrangement of Os atoms, while the metal core of the latter species constitutes an edge-bridged tetrahedron. Although these two compounds have not been found to undergo interconversion, the same intermediate compound, $H_4Os_5(CO)_{11}(\eta^6\text{-}C_6H_6)(MeCN)$, which contains an edge-bridged tetrahedral core has been suggested,[54] explaining how the two compounds are formed: $H_4Os_5(CO)_{12}(\eta^6\text{-}C_6H_6)$ may be trapped from $H_4Os_5(CO)_{11}(\eta^6\text{-}C_6H_6)(MeCN)$ by scavenging of CO or loss of MeCN, with metal core rearrangement affords $H_4Os_5(CO)_{12}(\eta^6\text{-}C_6H_6)$. This type of mechanism could be general for such coupling reactions, more of which will be discussed in due course.

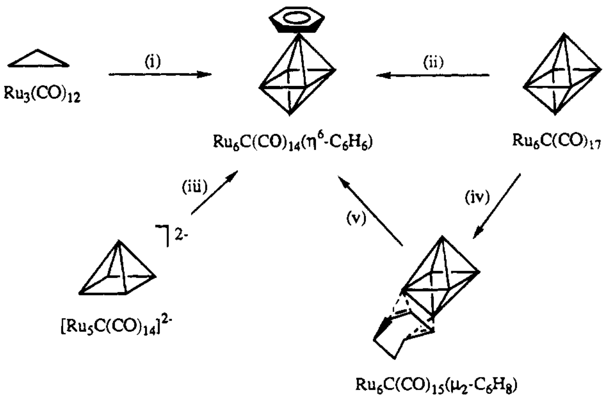
D. Nuclearity Six

The mono(arene) derivatives $Ru_6C(CO)_{14}$(arene) were among the earliest examples of arene clusters. The various methods by which they can be prepared are shown in Scheme 5, with regard to the benzene.[55-63] The original preparation involves the direct reaction of $Ru_3(CO)_{12}$ with the appropriate arene under reflux, which yields $Ru_6C(CO)_{14}(\eta^6\text{-arene})$ (arene = C_6H_6, C_6H_5Me, $C_6H_4Me_2$, $C_6H_3Me_3$, $C_6H_3Et_3$) and $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$ ($C_{16}H_{16}$ = [2.2]paracyclophane).

Investigations into the mechanisms by which the formation of these products occurs has been carried out with reference to the mesitylene complex.[55] In this study, the direct reaction of $Ru_3(CO)_{12}$ with mesitylene was performed in heptane (10% mesitylene, v/v). The previously isolated complex $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)$ was formed together with two new compounds $Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)$ and $HRu_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\mu_2\text{-}\sigma{:}\eta^6\text{-}C_6H_3Me_2CH_2)$.[63] In the former complex, $Ru_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)$, the metal framework is defined by a tetrahedral Ru_4 arrangement with two edge-bridging ruthenium atoms. The mesitylene ligand adopts the conventional η^6-terminal bonding mode. $HRu_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)(\mu_2\text{-}\sigma{:}\eta^6\text{-}C_6H_3Me_2CH_2)$ has a trigonal-bipyramidal metal core with an additional ruthenium atom bridging an apical-equatorial edge. In this compound the mesitylene ligand has undergone a hydride shift from a methyl group to the metal framework. The hydride triply bridges a ruthenium face, while the $C_6H_3Me_2CH_2$ group adopts an $\mu_2\text{-}\sigma\text{-}\eta^6$-bonding mode in which the benzyl ligand bridges two ruthenium atoms. It is noteworthy that this type of bonding has been observed for toluene adsorbed onto a Pt(111) surface.[83] The thermolysis of $Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)$ in mesitylene results in conversion to $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)$, demonstrating it to be an intermediate in the formation of the octahedral carbido cluster.

A high-yielding route to $Ru_6C(CO)_{14}(\eta^6\text{-arene})$ (arene = C_6H_6, C_6H_5Me, $C_6H_4Me_2$, and $C_6H_3Me_3$) comprises the ionic coupling between the preformed ruthenium–arene fragment $[Ru(\eta^6\text{-arene})(MeCN)_3]^{2+}$ (arene = C_6H_6, C_6H_5Me, $C_6H_4Me_2$ and $C_6H_3Me_3$) and the pentanuclear dianion $[Ru_5C(CO)_{14}]^{2-}$.

Scheme 5. Routes to $Ru_6C(CO)_{14}(\mu_3\text{-}C_6H_6)^a$

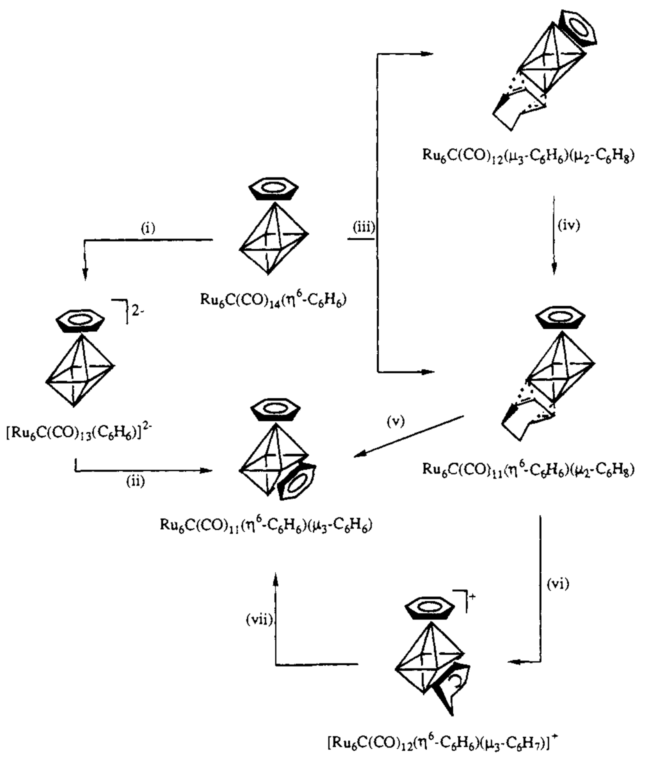


[a] Reagents: (i) heating in benzene, (ii) 1,4-C_6H_8 or 1,3,5-cyclohexatriene, heating in sealed system, (iii) $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$, (iv) 2 equiv of Me_3NO/C_6H_8, (v) 1 equiv of Me_3NO/CH_2Cl_2.

The benzene species $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$ has also been prepared from a variety of other nonaromatic reagents. These reactions commence with the parent cluster $Ru_6C(CO)_{17}$.[84,85] Activation of this cluster with 2 equiv of Me_3NO in dichloromethane containing an excess of cyclohexa-1,3-diene or cyclohexa-1,4-diene yields both the diene and benzene complexes $Ru_6C(CO)_{15}(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)$ and $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$.[60] The diene always coordinates with a 1,3-double-bond arrangement irrespective of the diene employed in the reaction. The coordinated diene may be converted into an η^6-benzene, *i.e.* $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$, by the addition of one further molecular equivalent of Me_3NO. Hence, it would appear that the diene cluster is initially formed, by a mechanism paralleling that described for the pentaruthenium analogue. Abstraction of dihydrogen from the coordinated C_6H_8 must occur spontaneously (this being thermodynamically favorable) driven by the creation of a further coordination site on the metal framework when an additional carbonyl group is removed by excess Me_3NO. It is believed that the dehydrogenation involves two steps, the first involving removal of a proton from the ring yielding an hydrido–hexadienyl intermediate, *viz.* $HRu_6C(CO)_{13}(C_6H_7)$, followed by elimination of a hydride, and hence, formation of the benzene cluster. It is unlikely that isomerization of the cyclohexa-1,4-diene would occur by a similar intermediate (as established in the mononuclear organometallic chemistry of iron and ruthenium). It is therefore postulated that isomerization occurs via an allylic type transition state.[51] The autoclave reaction between $Ru_6C(CO)_{17}$ and cyclohexa-1,4-diene or 1,3,5-hexatriene also yields the benzene cluster $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$ in moderate yield.[64,62] Other products isolated from the former reaction will be discussed shortly.

The routes used in the preparation of the mono(benzene) complex $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$ have been extended to the synthesis of bis-substituted clusters and are illustrated in Scheme 6. For instance, reduction of $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$ with Na_2CO_3/MeOH affords the dianionic species $[Ru_6C(CO)_{13}(C_6H_6)]^{2-}$, which on treatment with an aliquot of $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ affords $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}$

Scheme 6. Synthetic route to $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}C_6H_6)$[a]



[a] Reagents: (i) $MeOH/Na_2CO_3$, (ii) $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$, (iii) 2 equiv of Me_3NO/C_6H_8, (iv) heating in hexane, (v) 1 equiv of Me_3NO/CH_2Cl_2, (vi) $[Ph_3C][BF_4]$, (vii) DBU.

C_6H_6).[27,60] In this cluster one of the benzene rings adopts the commonly observed η^6-coordination mode, while the other acquires the μ_3-face-capping mode.

Alternatively, reaction of $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$ with 2 equiv of Me_3NO in dichloromethane containing excess cyclohexa-1,3-diene or cyclohexa-1,4-diene results in the isolation of three products. These being the two diene–benzene species $Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)$ and $Ru_6C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)$ and the bis(benzene) cluster $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$.[60]

The proposed mechanism by which $Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)$ is formed is similar to that described earlier. The formation of the other benzene–diene isomer, in which the benzene adopts a face-capping coordination mode is less obvious, but since there is no evidence for the starting material being contaminated with an isomer of $Ru_6C(CO)_{14}(C_6H_6)$ in which the benzene is μ_3-coordinated, the migration of the η^6-benzene ligand to a face-capping site must occur upon substitution of the cyclohexadiene ligand. The migration of benzene from a facial site to terminal position readily occurs when this compound is heated in hexane, hence generating $Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)$.[60] Both the mixed benzene–diene clusters may be converted to $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ by treatment with an additional aliquot of Me_3NO. The cluster $Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)$ has also been treated with $[Ph_3C][BF_4]$, which abstracts a hydride from the diene ring, affording the cationic benzene–dienyl complex $[Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C_6H_7)]^+$. Deprotonation of this cationic cluster with DBU affords the bis(benzene) cluster $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ in good yield.

The reaction of $Ru_6C(CO)_{17}$ with cyclohexa-1,4-diene in a closed system yields both $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ and a second isomeric form of the bis(benzene) cluster, *viz.* $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2$ in which the two benzene moieties "sandwich" the cluster core.[64] A third isomer in which the two benzene ligands coordinate to *cis*-ruthenium atoms has also been identified spectroscopically.[65] These observations are not unique to the bis(benzene) complex and will be elaborated in the following.

The mixed arene–benzene clusters $Ru_6C(CO)_{11}(\eta^6\text{-arene})(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ (arene = C_6H_5Me, $C_6H_4Me_2$, and $C_6H_3Me_3$) are prepared in reasonable yield by the Me_3NO activation route, commencing with $Ru_6C(CO)_{14}(\eta^6\text{-arene})$.[61] Treatment with 2 equiv of Me_3NO in dichloromethane in the presence of cyclohexa-1,3-diene or cyclohexa-1,4-diene affords, as the major product, $Ru_6C(CO)_{12}(\eta^6\text{-arene})(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)$ and as a minor product the arene–benzene compounds, in a similar manner to that described earlier. Addition of a further equivalent of Me_3NO to the arene–diene clusters generates the bis(arene) complexes, thus improving the overall yield.[61]

On standing at −25 °C in dichloromethane for a prolonged period, these arene–benzene compounds undergo conversion to afford the new isomers $Ru_6C(CO)_{11}(\eta^6\text{-arene})(\eta^6\text{-}C_6H_6)$ (arene = C_6H_5Me, $C_6H_4Me_2$, and $C_6H_3Me_3$) in which the aromatic ligands bind to ruthenium atoms which are *cis* to one another on the cluster framework.[65] The ease of isomerization occurs according to the series mesitylene–benzene > xylene–benzene > toluene–benzene > benzene–benzene. These new isomers may be converted back to their original form by heating in hexane for a few hours.

Other bis(arene) derivatives have also been prepared by the analogous method to that described above, merely exchanging cyclohexadiene for the appropriate dihydroarene in the reaction. The bis(mesitylene) analogue $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)_2$ has only been observed to exist in one form, that being the sandwich structure.[66] The bis(toluene) complex $Ru_6C(CO)_{11}(C_6H_5Me)_2$ has been found to exist in a temperature dependent equilibrium between the $\eta^6/\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ and *trans*-η^6 structural forms (see section V.A).[67]

An hexaosmium bis(benzene) cluster may be synthesized from the pentanuclear complex $H_4Os_5(CO)_{11}(\eta^6\text{-}C_6H_6)$. Removal of two protons using DBU, affording the dianionic cluster $[H_2Os_5(CO)_{11}(\eta^6\text{-}C_6H_6)]^{2-}$, followed by ionic coupling with the osmium cationic fragment $[Os(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ yields $H_2Os_6(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$.[71] When $[Os_5(CO)_{12}(\eta^6\text{-}C_6H_6)]^{2-}$ is reacted with the osmium fragment $[Os(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ the product is similar, except for that the two benzene ligands are attached to the cluster in terminal η^6-mode forming $Os_6(CO)_{12}(\eta^6\text{-}C_6H_6)_2$.[72]

E. Mixed-Metal Clusters

The majority of mixed-metal arene clusters reported to date[54,73–79] are similarly produced in that the arene is introduced into the cluster system via a metal fragment, which is added to a cluster of different metal atoms.

The reaction of metal atoms vapors generally leads to the formation of mononuclear species. This can be attributed to the conditions normally employed, since excess ligand favors the production of mononuclear complexes. Alternatively, one would anticipate that, if a high metal-to-ligand ratio is used, metal aggregation should be favored. A reduction in cluster formation has also been observed to occur when metal atoms are in excess, since catalytic decomposition of already formed complexes on active metal sites can occur. However, these effects have been reduced in order to optimize cluster formation by the reaction of metal atoms directly with organometallic compounds. The trinuclear bis(mesitylene) cluster $FeCo_2(CO)_5(\eta^6\text{-}C_6H_3Me_3)_2$ was isolated in low yield from the cocondensation of Co atoms with mesitylene and $Fe(CO)_5$ at −196 °C.[73] An improved yield was obtained by vaporizing the Co atoms directly into a solution of $Fe(CO)_5$ and mesitylene in methyl cyclohexane at −120 °C. In both reactions the formation of the bis(arene) complex of Co is a reasonable intermediate in the initial step of the reaction.

Thermolysis of $FeCo_3(\eta^5\text{-}C_5H_5)(CO)_9(\mu\text{-}C_2HCF_3)$ in toluene for several hours affords $FeCo_3(\eta^5\text{-}C_5H_5)(CO)_6(\mu\text{-}C{=}CHCF_3)(\eta^6\text{-}C_6H_5Me)$.[74] The metal atom framework constitutes that of a butterfly, with the "wingtip" Co atom bearing the toluene ligand. This species is formed by the replacement of a tricarbonyl unit by the arene.

The reaction between the reactive osmium cluster $H_2Os_3(CO)_{10}$ and the cobalt fragment $(\eta^5\text{-}C_5H_5)Co(CO)_2$, in the presence of hydrogen, results in the formation of the tetranuclear cluster $H_3CoOs_3(CO)_9(\eta^5\text{-}C_5H_5)$. Attempts to prepare the rhodium analogue gave only very small amounts of a paramagnetic substance. It was found that if the reaction was carried out in an aromatic solvent, the cyclopentadienyl moiety exchanged with the arene, affording $H_3RhOs_3(CO)_9(\eta^6\text{-arene})$ (arene = C_6H_6 and C_6H_5Me).[75-77] Both derivatives contain a $RhOs_3$ tetrahedral core, with the arene bound to the rhodium atom in an η^6-fashion.

The mixed metal clusters $RuOs_3(CO)_9(\eta^6\text{-}C_6H_6)(R'C_2R'')$ (R′ = R″ = Me, Et, and Ph; R′ = Me, R″ = H, Et, and Ph) were prepared in good yield from the treatment of the dianion $[Os_3(CO)_9(R'C_2R'')]^{2-}$ in dichloromethane with a molar equivalent of $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ in acetone at −78 °C.[78]

The pentanuclear osmium−ruthenium complex $H_4RuOs_4(CO)_{11}(\eta^6\text{-}C_6H_6)$ can be prepared from the reaction between $[H_4Os_4(CO)_{11}]^{2-}$ and the same capping reagent $[Ru(C_6H_6)(MeCN)_3]^{2+}$ in a similar manner to that just described.[54] Similarly, ionic coupling of the pentaosmium dianionic cluster $[Os_5(CO)_{15}]^{2-}$ with an equiv of the dicationic benzene fragment $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ results in the formation of two hexanuclear isomeric species $RuOs_5(CO)_{15}(\eta^6\text{-}C_6H_6)$.[79]

F. Nuclearity Higher than Six

From the thermolysis of $Ru_3(CO)_{12}$ with $PPhH_2$ in toluene which produced the pentanuclear cluster $Ru_5(CO)_{12}(\mu_4\text{-}PPh)(\eta^6\text{-}C_6H_5Me)$ the heptaruthenium complex $Ru_7(CO)_{15}(\mu_4\text{-}PPh)(\eta^6\text{-}C_6H_5Me)$ was also obtained, although only in extremely low amounts.[53] As in the pentaruthenium complex, the toluene ligand bonds to one of the basal ruthenium atoms in an η^6-coordination mode. In a similar reaction between $Ru_3(CO)_{12}$ and PPh_2H in refluxing toluene the octaruthenium complex $Ru_8(CO)_{19}(\mu_8\text{-}P)(\mu_2\text{-}\eta^1{:}\eta^6\text{-}C_6H_5CH_2)$ was isolated as a minor product.[80,81] In this cluster the benzyl group bridges two ruthenium atoms.

On heating a solution of $Ru_3(CO)_{12}$ in octane containing C_6H_{10} three major products have been obtained, *viz.* the known species $Ru_4(CO)_{12}(C_6H_8)$ and $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$ together with the octaruthenium cluster $H_4Ru_8(CO)_{18}(\eta^6\text{-}C_6H_6)$.[70]

The octaruthenium complex $Ru_8(CO)_{17}(\mu_4\text{-}S)_2(\eta^6\text{-}C_6H_5Me)$ may be prepared by dropwise addition of $Ru_3(CO)_{10}(\mu_3\text{-}S)$ in toluene into a solution of $Ru_3(CO)_{12}$ in toluene heated to reflux. After heating for a while, the cluster is isolated in moderate yield.[82] The mixed-metal species $Cu_2Ru_6(CO)_{18}(\eta^1\text{-}C_6H_5Me)(\eta^2\text{-}C_6H_5Me)$[83] has been prepared by reacting $[Ru_6(CO)_{18}]^{2-}$ with $[Cu(MeCN)_4]^-$ in dry acetone. The toluene groups are apparently introduced into the system during the crystallization of the initial product (presumably replacing acetonitrile or acetone ligands).

III. Molecular Structures

The molecular structures of the most pertinent arene clusters will now be described. All known structures have been determind in the solid state by single-crystal X-ray diffraction. The most representative molecules are shown in "ball-and-stick" style: large and small filled atom balls represent the metal and hydrogen atoms, respectively. The hydrogen atoms are shown only when coordinates are available in the original structural reports or in the Cambridge Structural Database System.[84]

Before illustrating the individual structures, it is of some importance to discuss the relationship between apical and facial bonding modes in detail.

A. Apical and Facial Bonding Modes

The examplar clusters in the series of face-capped $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$-arene species are the trinuclear complexes $M_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ [M = Ru,[32] and Os[27]]. Diffraction data for the ruthenium cluster have been collected at both room temperature and 193 K,[33] thus allowing for comparisons both of the ruthenium and osmium clusters and of the structural features of the ruthenium complex at the two temperatures. A detailed analysis of the atomic motion about equilibrium positions has also been carried out (see section V.B). The molecular structures of the two complexes are shown in Figure 1, parts a and b, for M = Ru and M = Os, respectively.

Prior to this discussion it is necessary to describe the isostructural complexes $HM_3(CO)_9(\mu_3\text{-}\sigma\text{-}\eta^2{:}\eta^2\text{-}C_6H_7)$ [M = Ru,[26,32] and Os[25]] from which the benzene products are derived as one can appreciate from the position of the dienyl ring above the metal triangle prior to conversion to benzene (see Figure 2). The cyclohexadienyl ligand interacts in $\mu_3\text{-}\sigma\text{-}\eta^2{:}\eta^2$ mode with the metal atoms contributing a total of five

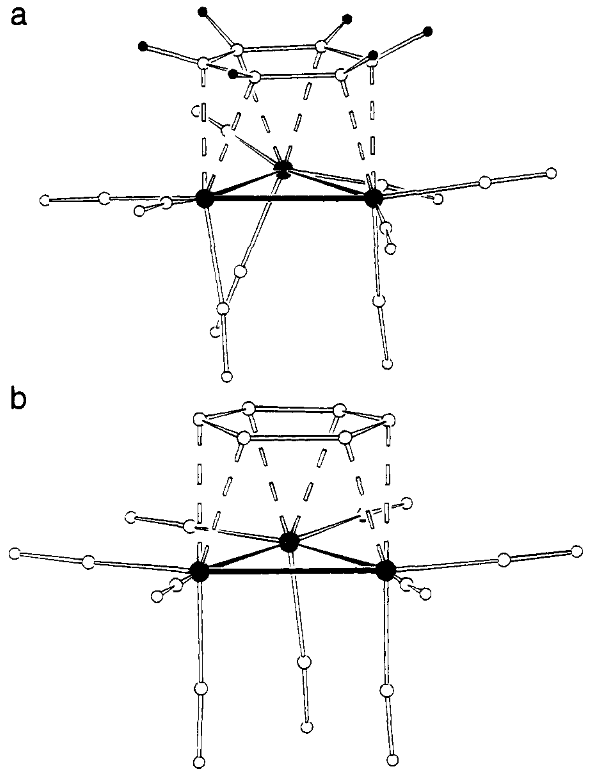


Figure 1. The molecular structure of (a) $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ and (b) of $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ in the solid state. (Note that only for the ruthenium species the hydrogen atom positions are experimentally determined.)

electrons to the cluster. The ligand lies almost parallel to the cluster although slightly shifted in order to manage one σ-interaction as well as two π-interactions with the metal atoms. In the ruthenium complex the bond length distribution within the ligand is in good agreement with a 1,4-localization of the double bonds, with two short bonds for the two π-interactions [1.39(1) Å] and two longer distances involving the carbon atom σ-bonded to the cluster [1.45(1) Å].[32] As in the case of the benzene cluster the H atoms of the ligand show a clear out-of-plane bending. The position of the H(hydride) atom has been located almost coplanar with the ruthenium triangle. A similar bonding distribution is present in the osmium derivative.[25] The five carbon atoms interacting with the cluster are coplanar within 0.01 Å, while the $C(CH_2)$ atom lies 0.32 Å above the ring plane. As in the ruthenium complex one Os—Os bond is much longer than the other two and is believed to carry the H bridge.

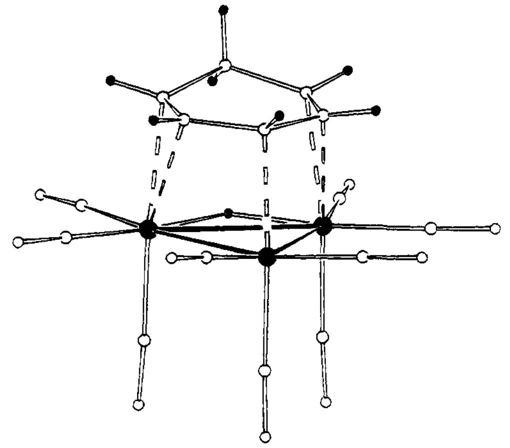


Figure 2. The molecular structure of $HRu_3(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_7)$ in the solid state. (The filled small atom spheres represent the hydrogen atoms, including the experimentally determined hydride atom.)

From the dienyl clusters the benzene species are derived, *viz.* $Me_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ (M = Ru, Os). The most striking feature of the face-capping benzene

Table 2. Relevant Bond Distances (Å) for Trinuclear Clusters Carrying Facial Arenes

compound notes	M—M range[a] M—M(mean)[d]	M—C(benz) range[b] M—C(mean)[d]	C=C, C—C[c] C—C(mean)[d]
$Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ from 193K determination	2.827–2.855(1)	2.288–2.379(5)	1.41–1.45(1)
	2.837(1)	2.332(5)	1.43(1)
$Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$	2.856–2.878(1)	2.27–2.39(2)	1.41–1.51(4)
	2.865(1)	2.33(2)	1.44(3)
$Os_3(CO)_8(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^2{:}CH_2CH_2)$	2.839–2.858(1)	2.27–2.34(2)	1.41–1.46(3)
	2.847(1)	2.32(2)	1.44(3)
$Os_3(CO)_8(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(PPh_3)$	2.829–2.936(1)	2.27–2.36(1)	1.40–1.43(2)
	2.879(1)	2.32(1)	1.42(2)
$[RhCp]_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$	2.625–2.625(1)	2.144–2.159(9)	1.424–1.453(13)
	2.625(1)	2.152(9)	1.439(13)
$[CoCp]_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}\beta\text{-methylstyrene})$	2.496–2.503(1)	2.017–2.059(3)	1.420–1.446(5)
	2.500(1)	2.029(3)	1.433(5)
$[CoCp]_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-1,1-diphenylethene})$	2.489–2.506(1)	2.000–2.057(3)	1.418–1.449(5)
	2.497(1)	2.016(3)	1.433(5)
$[CoCp]_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-1,1-diphenylethane})$	2.489–2.522(1)	2.021–2.070(5)	1.403–1.448(6)
	2.504(1)	2.034(5)	1.427(6)
$[CoCp]_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-1,2-diphenylethane})$	2.490–2.533(1)	2.018–2.046(5)	1.408–1.453(8)
	2.507(1)	2.035(5)	1.429(8)
$[CoCp]_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-2-phenyl-2-butene})$	2.495–2.517(1)	2.017–2.060(9)	1.39–1.48(1)
	2.502(1)	2.029(9)	1.43(1)
$\{(\mu_3\text{-}H)[CoCp]_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-1,1-diphenylethane})\}^+$	2.588–2.613(1)	2.026–2.142(7)	1.40–1.46(2)
	2.599(1)	2.063(7)	1.43(2)
$\{[CoCp]_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}\alpha\text{-methylstyrene})\}^+$	2.424–2.494(1)	2.001–2.179(5)	1.405–1.515(8)
	2.458(1)	2.080(5)	1.432(8)

[a] M—M bond length ranges indicate the extent of deformation of the metal triangles. [b] M—C(benzene) range gives a measure of deviation from exact eclipsing of the C—C bond midpoints over the metal atoms. [c] C=C, and C—C are the average "short" and "long" C—C bond lengths within the facially bound ring. [d] Average M—M and M—C(arene) bond lengths; values in bracket are the average ESDs on the individual values (all values are taken from the original structural reports).

ligand in the ruthenium and osmium complexes is the alternation of long and short bonds within the C_6 ring, which resembles that of the hypothetical 1,3,5-cyclohexatriene molecule. This deviation from the idealized D_{6h} symmetry of "free" benzene to a "Kekulé-type" structure mimics that observed for benzene chemisorbed at the surface metal atoms in low Miller index planes of close-packed arrays of a metallic lattice (see section VI). Relevant structural information for all trinuclear species carrying face-capping arenes is grouped in Table 2.

In the case of $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ "long" and "short" C—C bonds average 1.45(1), 1.40(2), and 1.45(1), 1.41(1) Å at room temperature and 193 K, respectively, the short bonds being those interacting directly with the Ru atoms.[33] The difference between the two sets of bonds (0.05 Å) is much smaller than that observed in the osmium complex [long 1.51(4), short 1.41(3) Å, Δ = 0.10 Å]. The poorer quality of this latter data set, however, makes this difference less significant than in the ruthenium species. In the tricobalt cluster $(CpCo)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}trans\text{-}\beta\text{-}$methylstyrene)[16] (see Figure 3) the same distortions are apparent, but the differences even smaller [Δ = 0.03 Å]. In $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ Ru—C interactions also alternate in length [mean 2.361(5) and 2.303(5) Å, respectively] accompanying a slight rotation (approximately 4.5°) of the benzene moiety with respect to exact eclipsing of the short C=C bond midpoints over the ruthenium atoms. This effect is not seen in the osmium species.

Direct location of the benzene H-atoms in $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ also allowed for the direct observation of out-of-plane bending of the C—H bonds away from the ruthenium atoms. The average bending with respect to the C_6 plane is 21.1° and 21.5° at room temperature and at 193 K, respectively. The benzene and Ru_3 planes are almost parallel.

These structural features indicate a certain degree of localization of the multiple bonds in the face-capping benzene ligand, and the electronic bases for this bonding has been probed via the Fenske—Hall quantum chemical method by using $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ to model the osmium species.[28] The results were consistent with the observed C—C bond length alternation showing that the interaction between the ligand and the trimetal unit is enhanced if out-of-plane bending (away from the metal core) of the C—H bonds is allowed, accompanied with an expansion of the C_6 ring. In good agreement with the observed values a bending of 10—20° was predicted.[28] Displacement of hydrogen atoms from the arene plane is commonly observed in mononuclear complexes, the displacement being both toward and away from the metal centre. This displacement has been attributed to a reorientation of the benzene molecular orbitals for more effective overlap with metal-based orbitals.[86a]

The bonding in the species $Ru_5C(CO)_{12}(C_6H_6)$ and $Ru_6C(CO)_{11}(C_6H_6)_2$ has also been investigated using extended Hückel calculations.[87] The relative stability of the known isomeric pairs $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ and $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$, $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2$ and $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ has been related to the chemically characterized interconversion process occurring in solution. The calculations have shown that the apical isomers are more stable than those carrying benzene bound in facial mode, although the local benzene—ruthenium interaction is stronger in these latter isomers. This is in agreement with the observation that apical isomers are always the final product of the reaction and subsequent interconversion process (see below). The calculations also confirm that in $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ coordinated benzene rings the hydrogens atoms should bend out of the plane of the carbon atoms, as this leads to stronger benzene—cluster bonds.

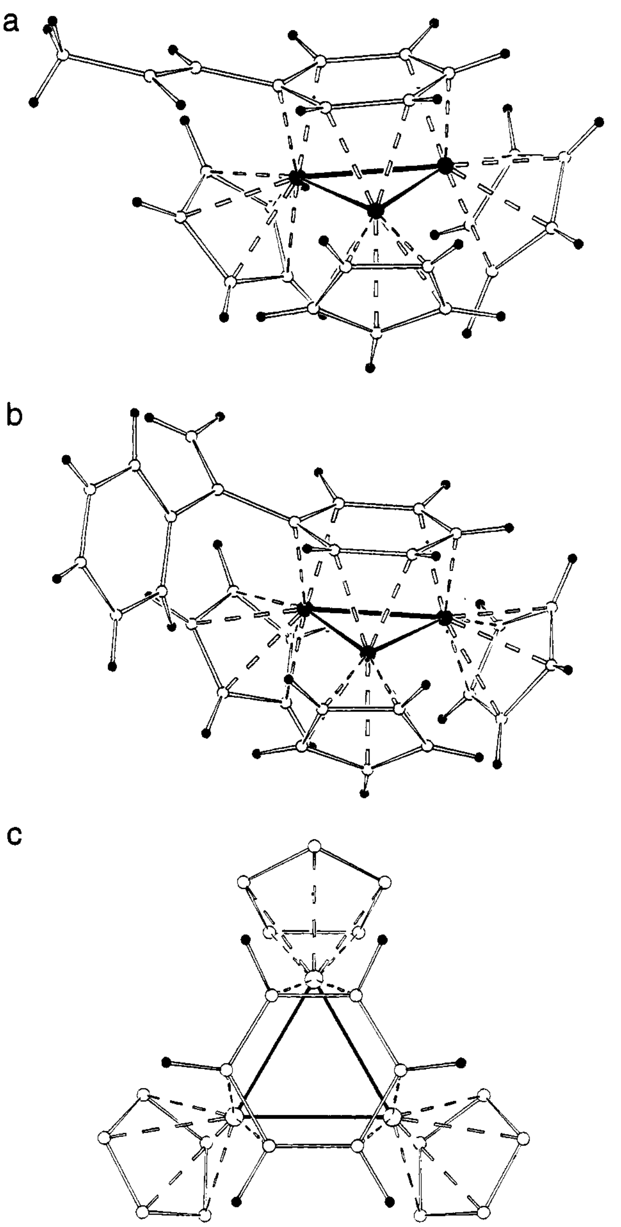


Figure 3. The molecular structures of $[CoCp]_3(\mu_3\text{-}\beta\text{-}$methylstyrene) (a), $[CoCp]_3$(1,1-diphenylethene) (b), and $[RhCp]_3(\mu_3\text{-}C_6H_6)$ (c) in the solid state. [H(Cp)-atoms omitted in c for clarity.]

The electronic structure of tricobalt derivatives based on the model complex $(CpCo)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ has also been investigated by Fenske—Hall quantum chemical calculations.[17] The input molecular geometry was derived from the solid-state structure of $(CpCo)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}trans\text{-}\beta\text{-}$methylstyrene)[16] shown in Figure 3a. The molecular symmetry was idealized to C_3. Because of the isolobal relationship between the CpCo and the $(CO)_3Fe$ fragments the sequence of frontier orbitals was found to be similar to that obtained earlier by extended-Hückel molecular orbital calculations on the hypothetical complex $[(CO)_3Fe_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$.[86b] In $(CpCo)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ the main interaction arises from π-donation from benzene orbitals accompanied by back-donation from the $(CpCo)_3$, *viz.* benzene acts as both a π-acceptor and a π-donor ligand. The calculations reproduced well some of the structural details which have been observed in face-capped arene clusters, such as C–H bending and alternation of C–C bond lengths.

The electronic structure of the osmium complex $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ has been subjected to an *ab initio* calculation and MO analysis.[88] It has been shown that the interaction of benzene with the $Os_3(CO)_9$ fragment can be described in terms of donation and back-donation which is favored by CH bending. The origin of the Kekulé distorsion of benzene has been attributed to an enhanced back-donation and a decrease in exchange repulsion due to the π-electrons of benzene. The barrier to internal rotation of benzene over the osmium triangle has been estimated to be 66.5 kJ mol^{-1}.[88]

Arenes bound to cluster atoms in η^6-bonding mode show features that are in common with those shown by mononuclear arene complexes. The bonding and electronic structure of mono(arene) derivatives has been extensively studied by various theoretical approaches in the recent past. The reader is referred to a number of excellent reviews and papers which are available.[3,6]

B. Trinuclear Clusters

Several derivatives of the triosmium benzene cluster $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ have been characterized in the solid state. The structure of $Os_3(CO)_8(\eta^2\text{-}CH_2CH_2)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ (see Figure 4a) is similar to that of the parent molecule in which an equatorial CO is replaced by an η^2-bound ethylene ligand, symmetrically coordinated with Os–C distances of 2.29(3) and 2.27(3) Å.[34] The benzene ligand is parallel to the metal triangle and slightly tilted from exact eclipsing of the C=C midpoints over the osmium atoms [Os–C(benzene) range from 2.27 to 2.34(2) Å].

The structure of the phosphine-substituted species $Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ is similar to that of the ethylene derivative, the triphenyl phosphine ligand being equatorially bound in place of the ethylene ligand. Os–Os distances show a greater variation than in $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ [2.828–2.938(1) *vs* 2.856–2.878(1) Å].[28] The benzene lies parallel to the metal plane, the separation between the two planes being 2.17 Å. Only a small difference between coordinated and uncoordinated C–C bonds is observed [1.40(2) *vs* 1.43(2) Å].

In the alkyne-substituted derivative $Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\sigma{:}\eta^2{:}\sigma\text{-}C_2Me_2)$, the benzene has migrated to a terminal site (see Figure 4b) and is bound in η^6-fashion with an average Os–C distances of 2.25(1) Å, while the C_2Me_2 ligand bridges the triangle via two σ-interactions [mean 2.12(1) Å] and one π-interaction [mean of the two Os–C distances 2.23(1) Å].[38] It has been pointed out that the formal electron distribution over the three metal centers is uneven, since the three osmium atoms formally receive from the ligands nine, ten, and eleven electrons, respectively. Os–C(benzene) and C–C(benzene) bonds are shorter in their mean values than in the face capped species [2.25(1), 1.39(1) Å in $Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\sigma{:}\eta^2{:}\sigma\text{-}C_2Me_2)$ *versus* 2.33(2), 1.44(3) Å in $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ and 2.32(2), 1.46(3) Å in $Os_3(CO)_7(\eta^2\text{-}CH_2CH_2)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$]. These differences indicate that benzene establishes substantially different bonding interactions when coordinated to one or three metal centers.

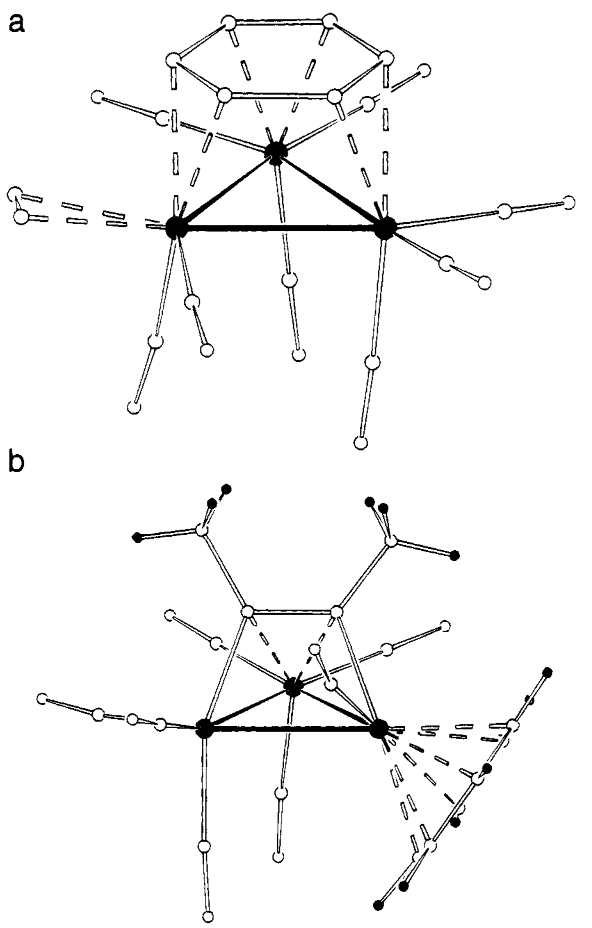


Figure 4. The molecular structures of (a) $Os_3(CO)_8(\mu_3\text{-}C_6H_6)(\eta^2\text{-}CH_2CH_2)$ and (b) $Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}C_2Me_2)$ in the solid state.

The structure of $Ru_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\sigma{:}\eta^2{:}\sigma\text{-}PhC_2PhCO)$ is related to that of $Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\sigma{:}\eta^2{:}\sigma\text{-}C_2Me_2)$. The benzene ligand is terminally bound to one corner of the cluster, whereas the ligand PhC=C(Ph)CO is bound to the three metal atoms via two σ and one π interactions. The ligand can be seen as formally derived from the insertion of a CO group into one Ru–C(alkyne) σ interaction. Metal–carbon(benzene) distances [mean 2.306(3) Å] are, as in the osmium case, shorter than in the corresponding facial derivative [2.331(4) Å]. The Ru atom carrying the apical benzene also bears a slightly bent terminal CO ligand pushed toward semibridging position.[38]

The only other class of trinuclear complexes known to possess arene ligands bound in a μ_3-fashion is that of the trinuclear cobalt clusters containing the [Cp-

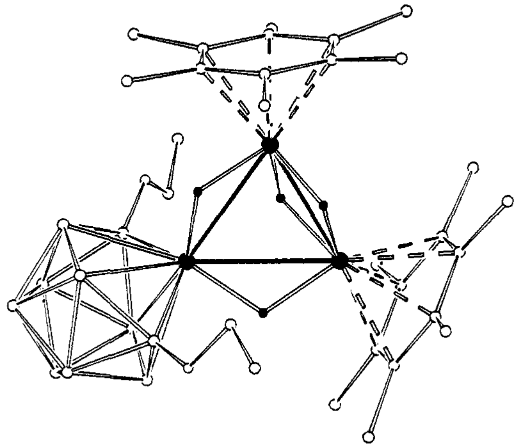


Figure 5. The molecular structure of $\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2$ in the solid state. (Only the H(hydride) atoms are shown for sake of clarity.)

Co]$_3$ fragment [Cp = C_5H_5].[16] $(CpCo)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}$*trans*-β-methylstyrene) is constituted of an equilateral triangle of Co atoms with the arene ligand lying almost parallel to the metal triangle as shown in Figure 3a. Only a slight difference [Δ = 0.03 Å] is detected between the C−C bonds overlapping the Co atoms and those above the triangle edges. Each Co atom bears an η^5-coordinated C_5H_5 ligand so that the complex is isoelectronic with the triangular arene clusters $M_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ of ruthenium and osmium. In the cobalt complex the side chain extends in a *trans* configuration coplanar with the benzene fragment. A possible intermediate in the synthesis of this complex, namely the dinuclear complex $(CpCo)_2(\mu\text{-}Ph(CH)_6Ph)$, has also been structurally characterized.[17b] The complex bears a diphenylhexatriene ligand in a twisted conformation. The ligand is $\mu_2\text{-}\eta^3{:}\eta^3$-coordinated and donates six electrons to the Co−Co system.

The structure of $(CpCo)_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}1,1\text{-}$diphenylethene) is closely related to that of the methylstyrene derivative,[16] as shown in Figure 3b. In both complexes the *ipso* carbon atoms are slightly displaced from the plane defined by the other five ring atoms. The olefinic planes of the side chain are at a dihedral angle of 17° (styrene) and 28° (ethene) with respect to the arene rings. In the diphenylethene complex, C−C bond alternation is also fairly small [mean 1.449(5) and 1.418(5) Å, Δ = 0.031 Å]. The structures of the derivatives containing 1,1-diphenylethane, 1,2-diphenylethane, and 2-phenyl-2-butene have also been reported to be similar to those of the above complexes but no structural details are available.

The solid-state molecular structure of the arene cluster $[RhCp]_3(\mu_3\text{-}C_6H_6)$ (Figure 3c) shows that the benzene ligand interacts with the three metal atoms each carrying a Cp ligand. As in the cobalt and ruthenium cases the bond lengths within the arene slightly alternate, and the C−H bonds bend away from the metal centers.[23]

All other trinuclear clusters studied to date contain the arene coordinated in terminal (η^6) bonding mode.

Two mesitylene ligands are coordinated in η^6-apical mode to two Ru atoms in the trinuclear cluster $\{(\eta^6\text{-}C_6H_3Me_3)_2Ru_2H_4\}RuB_{10}H_8(OEt)_2$ (see Figure 5).[21] The third ruthenium atom is part of a $\{2,3\text{-}(OEt)_2\text{-}$*isocloso*-$1\text{-}RuB_{10}H_8\}$ subcluster. Metal−metal bond distances range from 2.684(4) to 2.827(4) Å, the shortest bond connecting the arene-substituted Ru atoms. Each Ru−Ru bond is spanned by a hydrido ligand; a fourth hydride ligand triply bridges the metal triangle.

A similar structure is shown by the derivative $\{(\eta^6\text{-}C_6Me_6)_2Ru_2H_2(CH_2Cl_2)\}RuB_{10}H_8(OEt)_2$.[22] Metal−metal bond distances range from 2.815(3) to 2.896(2) Å, the longest being bridged by a hydride ligand and connecting the arene-substituted Ru atoms. The second hydride triply bridges the Ru triangle, with the two Cl atoms asymmetrically bridging the Ru−Ru edges opposite to the arene ligands and formally replacing the two hydrides of the parent molecule.

The trinuclear species $[(p\text{-cymene})_3M_3S_2]^{2+}$ and $(p\text{-cymene})_3M_3S_2$ [M = Ru, Os; cymene = 4-isopropyltoluene] have been prepared, but only the Ru species have been structurally characterized.[20] The dicationic cluster can be described either as a sulfido-bicapped metal triangle or as a *closo* trigonal bipyramid, with Ru−Ru distances ranging from 2.763(3) to 2.796(1) Å and an average Ru−S distance of 2.338(2) Å, while in the neutral species a metal−metal bond has been broken to generate an open triangle of Ru atoms, *i.e.* a *nido* framework, with Ru−S distances elongated with respect to the *closo* cluster. In both species each Ru atom bears an η^6-coordinated *p*-cymene ligand. The rotameric conformation of each arene with respect to the Ru_3 plane is different in both molecules.

An η^6-apical benzene ligand is present in $Ru_3(CO)_7(NPh)(\eta^6\text{-}C_6H_6)$.[19] The ruthenium atoms constitute an almost equilateral triangle with Ru−Ru bond distances ranging from 2.695(2) to 2.726(2) Å, the shortest bond being opposite to the Ru atom bearing the η^6-benzene ligand. The triangle is triply bridged on opposite sides by a CO group and by the NPh group.

The compound $Fe_3(CO)_6(\mu_3\text{-}CCl)(\mu_3\text{-}CCOOC_2H_5)(\eta^6\text{-}C_6H_6)$ contains a triangle of iron atoms triply bridged on opposite sides by the CCl and $CCOOC_2H_5$ ligands, while the benzene fragment is bound in η^6-apical fashion to one of the metals.[18] Metal−metal bond distances range from 2.500(2) to 2.522(2) Å. Contrary to the ruthenium cluster mentioned above the longest bond is the one opposite to the Fe atom bearing the benzene ligand.

The asymmetric unit of crystalline $Co_3(\mu_3\text{-}CC_6H_5)(\eta^6\text{-}C_6H_5Me)_3$[13] comprises two independent molecules; the cobalt triangle [Co−Co bond lengths range from 2.405(2) to 2.431(2) Å] is triply bridged by the benzylidine group, while the toluene ligands are η^6-coordinated one to each metal atom as shown in Figure 6a.

Three benzene ligands are similarly bound in η^6-apical mode one to each Co atom in the monocation $[Co_3(\mu_3\text{-}CO)_2(\eta^6\text{-}C_6H_6)_3]^+$. The Co atoms form a scalene triangle [Co−Co range 2.386(4)−2.426(4) Å], triply bridged on both sides by the two CO ligands (see Figure 6b).[15]

The molecular structure of $Co_3(\mu_3\text{-}CC_6H_5)(CO)_6(\eta^6\text{-}C_6H_3Me_3)$ shows a triangular metal frame capped on one side by the CC_6H_5 ligand.[12] The mesitylene

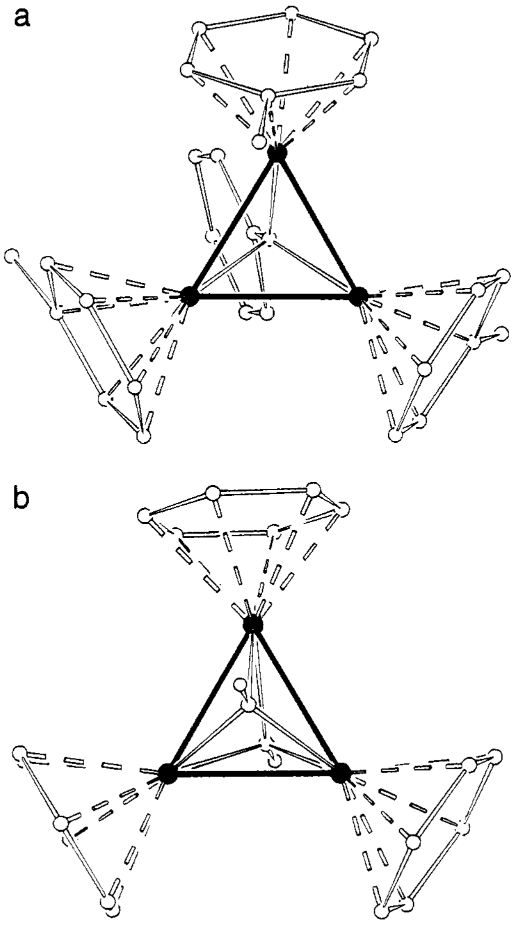


Figure 6. The solid-state molecular structures of (a) $Co_3(\mu_3\text{-}CPh)(\eta^6\text{-}C_6H_3Me_3)_3$ and (b) of $[Co_3(\mu_3\text{-}CO)_2(\eta^6\text{-}C_6H_6)_3]^+$.

ligand is η^6-apically coordinated to one Co atom, while each of the other two metal atoms bears three terminal CO groups. Co–Co bond distances range from 2.441(2) to 2.477(3) Å, the longest one being opposite to the arene-substituted metal atom.

C. Tetranuclear Clusters

Tetranuclear arene clusters with face-capping arenes have not been synthesized up to date. Therefore, all species described in the following carry the arene in apical bonding mode.

Three mono(arene) species derived from the tetranuclear cluster $Co_4(CO)_{12}$ have been structurally characterized, *i.e.* the species of general formula $Co_4(CO)_9(\eta^6\text{-arene})$ [arene = C_6H_6, $C_6H_4Me_2$, $C_{20}H_{14}$ (triptycene)].[41,42] All compounds contain a tetrahedron of Co atoms; the apical cobalt atom bears the η^6-coordinated arene moiety, while the three basal Co atoms are bound each to two terminal and two bridging CO groups. No relevant distortion of the six-membered ring has been observed in the benzene and xylene derivatives. The xylene complex presents two independent molecules in the asymmetric unit: one molecule contains an *o*- and the other a *m*-xylene ligand. The crystal can then be regarded as a mixed crystal, of the type observed for the crystals of $H_2Os_4(CO)_9(\eta^6\text{-xylene})$ described below.[48] In the triptycene derivative the arene ligand is terminally bound to one Co atom through one of its three six-membered rings (see Figure 7). The presence of the CO ligands causes deformation of the triptycene framework, detected in the spreading of the angle between the plane of the coordinated ring and the plane of the ring closest to two terminal CO ligands of the basal metal plane.

Figure 7. The solid-state molecular structure of $Co_4(CO)_9(\eta^6\text{-}C_{20}H_{14})$.

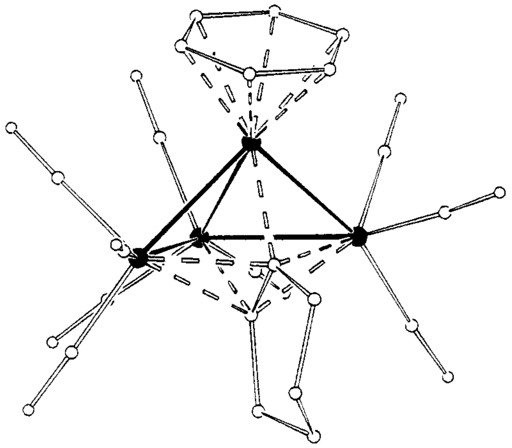


Figure 8. The solid-state molecular structure of $Ru_4(CO)_9(\eta^6\text{-}C_6H_6)(\mu_4\text{-}C_6H_8)$.

Another derivative of $Co_4(CO)_{12}$ containing an η^6-arene ligand is the complex $Co_4(CO)_6(\eta^6\text{-}C_6H_5Me)\{HC(PPh_2)_3\}$.[43] The basal triangle of the tetrahedral core bears three bridging CO's and is capped by the tripod ligand $HC(PPh_2)_3$, whereas the η^6-toluene ligand is carried by the apical cobalt atom.

In the butterfly species $Ru_4(CO)_9(\eta^6\text{-}C_6H_6)(\mu_4\text{-}C_6H_8)$ (see Figure 8) the benzene ligand is coordinated to one of the hinge atoms, while the other one carries three terminal CO ligands. Ru–Ru bond lengths range between 2.643(3) and 2.809(3) Å.[44] The C_6H_8 moiety interacts with all four ruthenium atoms of the cluster, occupying the central part of the butterfly between the two wings. The ligand is bound in a way very similar to that observed with acetylenic or cyclooctadienyl derivatives.

The benzene cluster $H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_6)$ shown in Figure 9 contains a tetrahedral metal framework with Os–Os distances ranging from 2.758(1) to 2.979(1) Å, the two longest bonds being spanned by H(hydride) bridges.[47] The benzene is η^6-bound to a tetrahedral apex with an average Os–C distance of

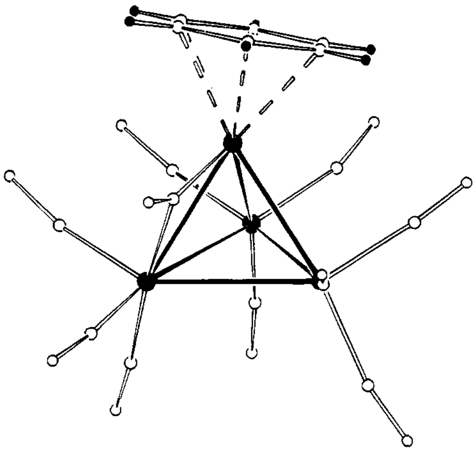


Figure 9. The molecular structure $H_2Os_4(CO)_{14}(\eta^6\text{-}C_6H_6)$ in the solid state.

2.24(2) Å. The toluene and xylene derivatives $H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_5Me)$ and $H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_4Me_2\text{-}1,2)$ and $H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_4Me_2\text{-}1,3)$ have also been structurally characterized.[48] Both complexes are essentially isostructural with the benzene derivative. Os–Os distance range from 2.763(1) to 2.963(1) and from 2.755(3) to 2.966(3) Å [average 2.833(1) and 2.828(4) Å in the toluene and xylene derivatives, respectively]. Os–C(ring) distances average 2.25(2) and 2.27(4) Å, respectively. As in the benzene species the "long" Os–Os bonds are believed to be bridged by the H(hydride) atoms. In all these species the osmium atom carrying the arene ligand also participates in the bonding with a single semibridging CO ligand.

The ligand distribution in $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$ can be derived from that of the complexes described above merely by replacing two CO ligands by an η^4-cyclohexadiene group.[48] The enhanced steric crowding in $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)$ is reflected in the presence of two further CO groups in bridging position. The mean Os–C(benzene) [2.25(1) Å] and Os–C(cyclohexadiene) [2.22(2) Å] distances are comparable to those observed in $H_2Os_4(CO)_{10}(\eta^6\text{-arene})$ (arene = C_6H_6, C_6H_5Me, and $C_6H_4Me_2$).

D. Pentanuclear Clusters

The diene cluster $Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,3)$[50] and $Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)$[51] are the intermediates in the synthesis of benzene derivatives of $Ru_5C(CO)_{15}$. The 1,3-C_6H_8 derivative contains a cyclohexadiene ligand bound in radial position with respect to the cluster square base (see Figure 10a). The ligand interacts in a $\mu_2\text{-}\eta^2\text{:}\eta^2$ bridging mode formally replacing two CO's from the parent molecule. The 1,3-topology of the diene is reflected in the C–C distances, which average 1.39(2) Å for the double bonds and 1.46(2) Å for the single bonds. The structure of $Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)$[51] has also been determined and is shown in Figure 10b for comparison with that of the isomer $Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,3)$. From these cyclohexadiene adducts, the isomeric pair $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ and $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ is obtained.[49,50] Both clusters retain the square-pyramidal metal framework of the precursor. The main difference between the two structures arises from the benzene coordination. In the former complex the benzene adopts a face-capping bonding mode, while in the latter the ring is apically bound to one of the basal Ru atoms (see Figure 11a,b). The coordination of benzene in $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ is essentially of the same type as discussed previously for $M_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ (M = Ru, Os) and $(CpCo)_3(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}$*trans*-$\beta$-methylstyrene). C–C bond length alternation is clearly observable with mean values of 1.36(2) Å and 1.44(2) Å, for the C=C bonds overlapping the Ru atoms and for those nearly parallel to the Ru–Ru bonds, respectively, out-of-plane bending of the hydrogen atoms is also observed. The metal atom polyhedron is slightly smaller and much more distorted in the apical isomer than in the facial one as indicated by the average Ru–Ru bond distance [2.812(2) *vs* 2.840(2) Å] and by the spread in length in the two complexes [2.744–2.865(2) *vs* 2.800–2.845(1) Å]. The Ru–C(benzene) distances indicate that the ligand is slightly closer to the metal atoms when in η^6-apical bonding mode than in μ^3-facial bonding [mean Ru–C 2.23(1) *vs* 2.26(1) Å]. The C(carbide) atom is off-centered with respect to the center of the square base showing a shorter bond from the Ru atom carrying the apical benzene ligand than from the other atoms [1.93(2) and 1.86(2) *vs* an average of 2.03(2), and 2.06(2) Å for the two independent molecules present in the asymmetric unit of crystalline $Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)$].

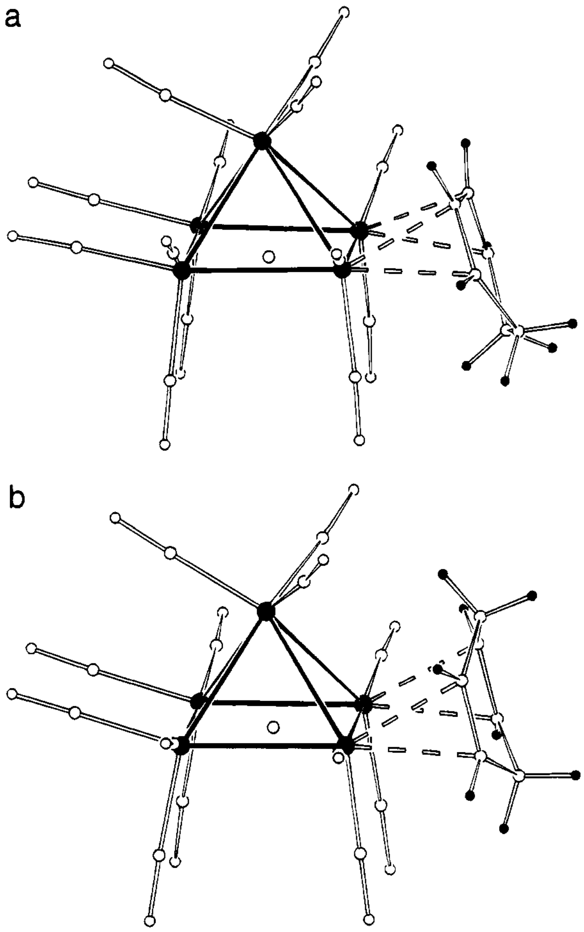


Figure 10. The molecular structures (a) of $Ru_5C(CO)_{13}(\mu_2\text{-}C_6H_8\text{-}1,3)$ and (b) of $Ru_5C(CO)_{13}(\mu_2\text{-}C_6H_8\text{-}1,4)$ in the solid state.

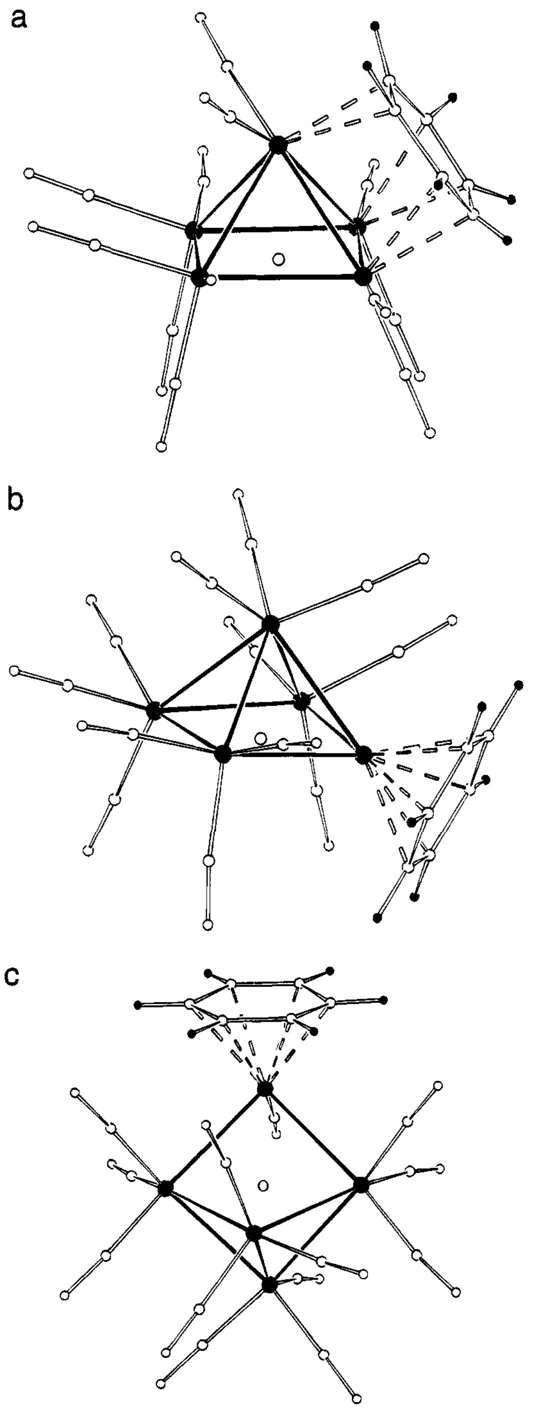


Figure 11. The molecular structures of (a) $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$, (b) of $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$, and (c) $Ru_5C(CO)_{13}(\eta^6\text{-}C_6H_6)$ in the solid state.

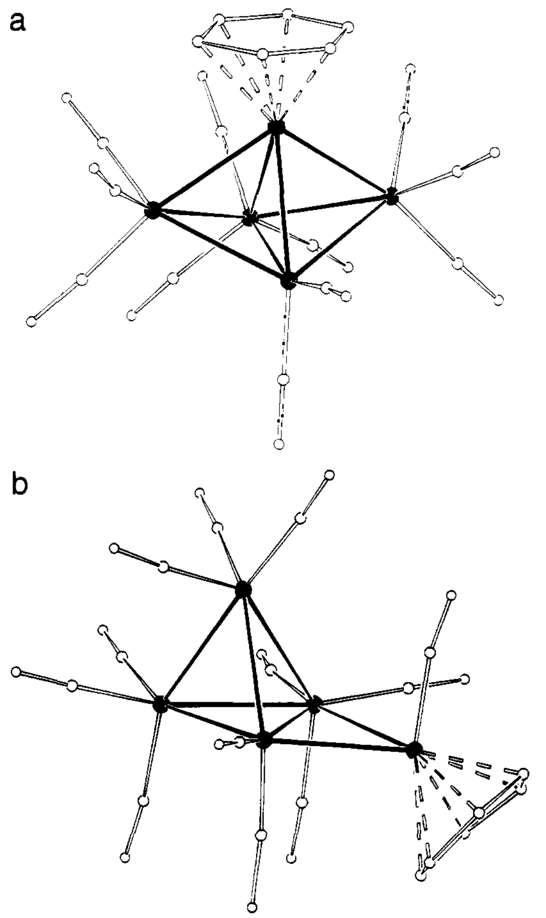


Figure 12. The molecular structures of (a) $H_4Os_5(CO)_{11}(\eta^6\text{-}C_6H_6)$ and of (b) $H_4Os_5(CO)_{12}(\eta^6\text{-}C_6H_6)$ in the solid state.

The Ru_5 polyhedron undergoes conversion from square pyramidal to bridged butterfly upon addition of CO to $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$. The product, $Ru_5C(CO)_{13}(\eta^6\text{-}C_6H_6)$ (see Figure 11c) can be seen as derived from the square-pyramidal geometry by opening up one apex-to-base bond upon CO insertion.[50] In this way the benzene ligand and the CO ligand are bond to the Ru atom bridging the Ru_4 butterfly. Ru–Ru bonds are slightly longer than in the precursor $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ [mean 2.844(2) *vs* 2.840(2) Å]. The C(carbide) displacement toward the arene coordinated metal atom, observed in $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ and in other carbide clusters of ruthenium carrying apical arenes (see section III.E), is not seen in $Ru_5C(CO)_{13}(\eta^6\text{-}C_6H_6)$. The C(carbide) drift, in fact, is only observed when complete substitution of CO ligands on a metal [as in $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$] deprives the metal atom of electron density. In $Ru_5C(CO)_{13}(\eta^6\text{-}C_6H_6)$ the extra CO ligand bonded to the benzene-substituted Ru atom appears to compensate for the presence of the poor π-acceptor benzene ligand.

The structures of $Ru_5C(CO)_{10}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,3)$ and $Ru_5C(CO)_{10}(\eta^6\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,3)$ are closely related. The two complexes form an isomeric pair differing essentially in the mode of coordination of the benzene ligand. In $Ru_5C(CO)_{10}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,3)$ this ligand caps the square-pyramid triangular face opposite to the Ru–Ru bond bridged by the $\mu_2{:}\eta^2{:}\eta^2$-cyclohexadiene ligand, while in $Ru_5C(CO)_{10}(\eta^6\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,3)$ the benzene ligand adopts an η^6-coordination mode.[52] In both molecules the cyclohexadiene ligand spans one basal edge taking the place of two radial CO ligands with respect to the parent molecule $Ru_5C(CO)_{15}$. Metal–metal bonds range from 2.804(1) to 2.881(1) Å in $Ru_5C(CO)_{10}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,3)$ and from 2.744(1) to 2.856(1) Å in $Ru_5C(CO)_{10}(\eta^6\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,3)$. The benzene ligand in this latter complex is disordered over two sites, with site occupation ratio 7:3. This disorder is, very likely, dynamic in nature, since benzene cannot be easily locked in place by the surrounding molecules in the crystal.[9] From atom–atom potential energy barrier calculations (see section V.B), a low

Table 3. Relevant Bond Distances (Å) for Mono- and Bis(arene) Derivatives of $Ru_6C(CO)_{17}$

compound reference, notes	M—M(range)[a] M—M(average)[b]	M—C(carbide) vs av M″—C(carbide)[c]	M—C(arene)[d] (mean)
$Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$	2.825–2.999(1) 2.888(1)	1.935(6) vs. 2.064(6)	2.221(8)
$Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)$	2.815–2.955(1) 2.892(1)	1.937(7) vs. 2.067(7)	2.25(1)
$Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2)$ Mol.1	2.836–3.006(2) 2.894(2)	1.914(5) vs. 2.074(5)	2.258(7)
Mol.2	2.822–2.975(2) 2.892(2)	1.926(6) vs. 2.069(6)	2.247(7)
$Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)$	2.846–2.961(1) 2.881(1)	1.90(1) vs. 2.04(1)	2.24(1)
$Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Et_3)$	2.853–2.962(1) 2.894(1)	1.919(4) vs. 2.074(4)	2.270(5)
$Ru_6C(CO)_{14}(\mu_3\text{-}C_{16}H_{16})$ [$C_{16}H_{16}$ = 2,2-paracyclophane]	2.794–2.990(1) 2.902(1)		2.285(9)
trans-$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2$	2.811–2.974(1) 2.868(1)	1.963(7) vs. 2.028(7)	2.225(1)
trans-$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)_2$	2.796–3.089(1) 2.895(1)	1.97(1) vs. 2.07(1)	2.26(1)
cis-$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_3Me_3)$	2.816–3.013(2) 2.902(2)	1.94(1) vs. 2.11(1)	2.23(1) bz 2.25(1) mes
$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}C_6H_6)$	2.819–3.006(1) 2.889(1)	1.948 vs. 2.062(1)	2.23(1) η^6 2.27(1) μ_3
$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}C_6H_6)$	2.798–2.950(1) 2.884(1)	1.94(1) vs. 2.04(1)	2.246(7) tol 2.260(6) bz
$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_4Me_2)(\mu_3\text{-}C_6H_6)$	2.805–2.980(1) 2.891(1)	1.92(1) vs. 2.04(1)	2.25(1) xyl 2.27(1) bz
$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}C_6H_5Me)$	2.814–3.014(1) 2.885(1)	1.93(1) vs. 2.07(1)	2.23(1) η^6 2.28(1) μ_3

[a] M—M bond length ranges indicate the extent of deformation of the metal triangles. [b] Average M—M bond lengths (see footnote *e* to Table 2). [c] M′—C(carbide) distances are given (M′ = η^6-arene substituted metal atom) against average of M″—C(carbide) distances (M″ = μ_3-arene and/or CO substituted metal atom) as a measure of the C(carbide) atom "drift". [d] M—C(arene) average values are given separately for different arene types and/or different coordination modes; bz = benzene, tol = toluene, xyl = xylene.

reorientation barrier for jumps of the benzene atoms was estimated (*ca.* 6 kJ mol^{-1}).

The pentanuclear species $H_4MOs_4(CO)_{11}(\eta^6\text{-}C_6H_6)$ (M = Ru, Os) are isostructural and their crystals isomorphous.[54] Both contain a trigonal bipyramidal metal framework (see Figure 12a) with M—M bond lengths ranging from 2.744(2) to 2.888(2) for both species. The (MC_6H_6) fragment (M = Ru, Os) occupies an equatorial site. The CO distribution is uneven: the two apices of the trigonal bipyramid and one equatorial atom bear three terminally bonded CO's each while the third equatorial atom bears two CO's only.

The cluster $H_4Os_5(CO)_{12}(\eta^6\text{-}C_6H_6)$ presents a more unusual metal atom framework (see Figure 12b): the Os atom carrying the η^6-bound benzene also bears a terminally bound CO; this Os atom effectively bridges one edge of an Os_4 tetrahedron. The H(hydride) atoms were located by potential energy calculations in all three complexes.[54]

E. Hexanuclear Clusters

A large number of mono- and bis(arene) derivatives of $Ru_6C(CO)_{17}$ have been structurally characterized by X-ray diffraction. All relevant structural information for this family of arene clusters is summarized in Table 3. A feature common to all these compounds is the low-energy scrambling of the CO ligands around the metal framework in solution (see section V.A). In the solid this is reflected in an almost continuous distribution of metal—CO bonding geometries from symmetric bridges, via asymmetric bridging and "bent-terminal" to linear terminal ligands around the metal frame.

Both the η^6-terminal and $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$-bonding modes have been observed in these species. The μ_3 coordination on a triangular face of the metal octahedron is characteristic of the benzene fragment. However, in only two cases is this coordination mode adopted by a substituted ring, *e.g.* by paracyclophane in $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$ and by toluene in $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5Me)$. Xylene, mesitylene, and triethylbenzene have only been found to adopt η^6-coordination modes.

The metal atom framework for the hexaruthenium derivatives is that of an octahedron, encapsulating a C(carbide) atom, similar to that established for $Ru_6C(CO)_{17}$.[84,85] A systematic C(carbide) drift toward the Ru atom(s) bearing the arene ligand(s) is detected in these complexes (see Table 3). This may be attributed to a compensatory effect due to substitution of arene groups for CO ligands.

In the mono(arene) derivatives $Ru_6C(CO)_{14}(\eta^6\text{-arene})$ (arene = C_6H_6, C_6H_5Me, $C_6H_4Me_2$, $C_6H_3Me_3$, $C_6H_3Et_3$) the arene fragments formally replace three apical CO ligands of the parent cluster $Ru_6C(CO)_{17}$, thus adopting the η^6-apical bonding mode. The solid-state structure of the prototypical molecule $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$[60] is shown in Figure 13. In all the mono(arene) derivatives the CO ligand distribution is similar and is characterized by the presence of one bridging CO spanning one Ru—Ru bond in the plane parallel to the arene plane. In general, two other

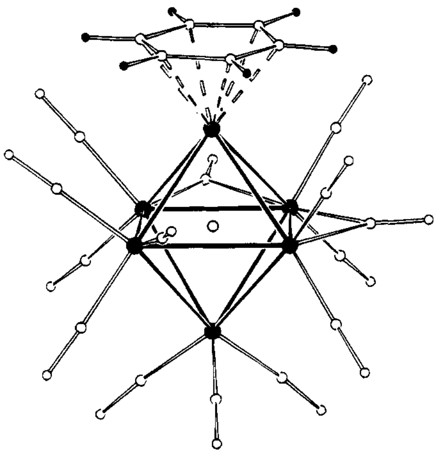


Figure 13. The molecular structure of $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$ in the solid state.

CO's lie within the same plane and are bound in asymmetric bridging position. Each ruthenium atom in the equator also carries two terminal CO's while the apical atom opposite to the one carrying the arene bears three terminal CO's. The arenes, as well as the apical tricarbonyl units, do not show any marked conformational preference with respect to the cluster or to the other ligands.

In keeping with this general behavior, two molecules of the xylene derivative $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2)$[57] are present in the asymmetric unit. The two units possess different rotameric conformations of the xylene ligands with respect to the bridged equator (see Figure 14). One methyl group in the first molecule is almost eclipsed by the *quasi*-symmetric bridging CO ligand, while the xylene ligand in the second molecule is rotated by *ca.* 120°. Therefore the crystal of $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2)$ can be regarded as a mixed crystal, in which two structural isomers have cocrystallized. A third conformer of $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2)$ has been found in the cocrystal of the mono- and the bis(xylene) derivatives (see also below).[68]

A more "crowded" arene moiety is present in the compound $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Et_3)$.[57] The three ethyl groups on the arene point "upwards" with respect to the metal frame, thus minimizing intramolecular repulsions between the CH_3 groups and the CO ligands, and favoring optimization of the intermolecular interlocking in the crystal (see section IV).

The only example of a mono(arene) derivative presenting facial coordination is the [2.2]paracyclophane complex $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$.[57] The paracyclophane ligand is bound through one of its two C_6 aromatic rings to one triangular face of the metal octahedron as shown in Figure 15. Its coordination geometry is not appreciably different from that of benzene in face-capping bonding mode. Long–short C–C bond alternation within the ring bound to the cluster has not been detected. The CO ligand distribution is similar to that observed for most arene derivatives in this family, with the bridging ligand placed opposite to the arene-capped ruthenium face.

The benzene–cyclohexadiene complexes $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,3)$ and $Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,3)$[61] (intermediate in the formation of bis(benzene) complexes) constitute another isomeric pair in this class of complexes. In both molecules the cyclohexadiene ligands show the bridging coordination common to all other Ru_5 and Ru_6 clusters, while the benzene moiety is in apical and facial bonding modes, respectively. Similar ligand distribution is also shown by the molecular structure of the complex $Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,3)$ in which the paracyclophane moiety adopts a facial bonding mode as in the mono adduct $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$.[57]

Three different structural forms of bis(arene) derivatives based on the hexaruthenium carbido cluster have been established. These correspond to the general formulae *trans*-$Ru_6C(CO)_{11}(\eta^6\text{-arene})_2$, *cis*-$Ru_6C(CO)_{11}(\eta^6\text{-arene})_2$, and $Ru_6C(CO)_{11}(\eta^6\text{-arene})(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-arene})$. Some of these forms are known to interconvert according to a precise scale of relative stability (see section V.A). Only in a couple of cases, however, could isomers of the same arene derivative be crystallized and characterized structurally.

Trans-η^6 isomers are known for the species $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2$[64] and $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)_2$ (see Figure 16, parts a and b).[65] The rings in the bis(benzene) complex are staggered and almost parallel to each other and to the equatorial plane containing the bridging CO ligand. In contrast, the mesitylene ligands adopt an almost eclipsed conformation. The planes of the two aromatic rings form angles of 5.6° and 4.4° with respect to the molecular equatorial plane. The methyl groups on both arene fragments are slightly bent above the C_6-ring planes. In both

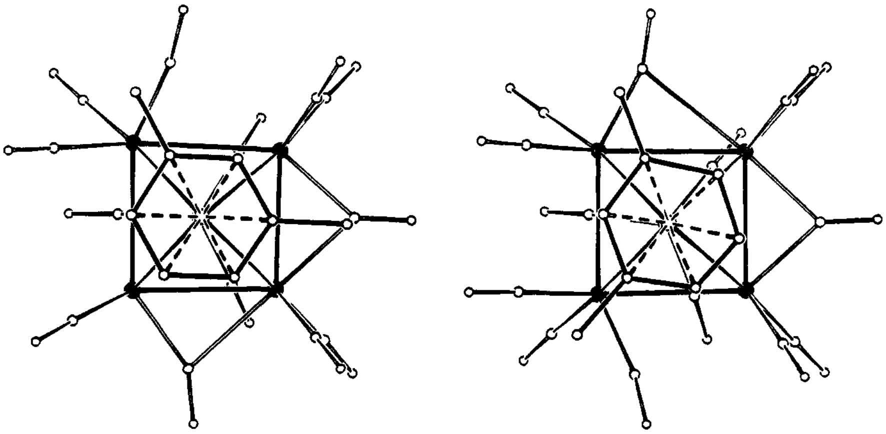


Figure 14. The two independent molecular units present in the asymmetric unit of crystalline $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2)$ showing the different rotameric conformations of the xylene ligands with respect to the CO-bridged equator.

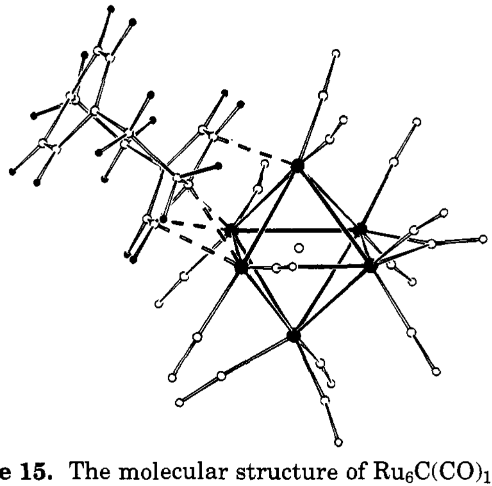


Figure 15. The molecular structure of $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{16}H_{16})$ in the solid state.

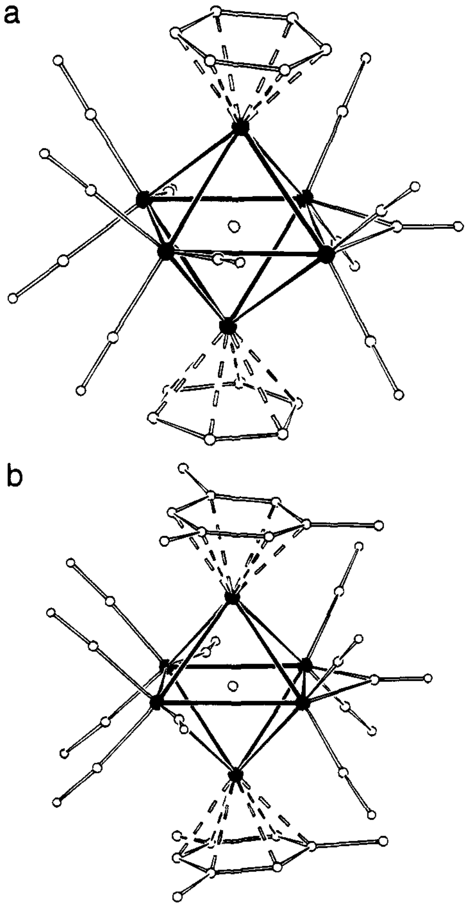


Figure 16. The molecular structures of (a) *trans*-$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2$ and (b) *trans*-$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)_2$ in the solid state.

cases Ru–C(carbide) distances involving the substituted Ru atoms are substantially shorter than those involving the equatorial Ru atoms, see Table 3, causing an appreciable distortion of the octahedron along the arene–cluster coordination axis.

Two structural forms of the bis(xylene) derivative $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_4Me_2)_2$ have been observed[68] which differ in the relative conformation of the xylene ligands. One of these belongs to a cocrystal containing also the mono adduct $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2)$ (see below).

The *cis* form has been found in the mesitylene–benzene cluster $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_3Me_3)$ (see Figure 17).[65] The two arene ligands are coordinated in η^6-apical mode to *contiguous* sites over the Ru_6-octahedral framework. The two arene planes form an angle of *ca.* 90°, with the methyl group of the mesitylene ligand directed toward the neighboring benzene slightly displaced above the ring plane [elevation 0.21 Å]. The C(carbide) atom is appreciably displaced from the octahedron center toward the two metal atoms carrying the arene ligands.

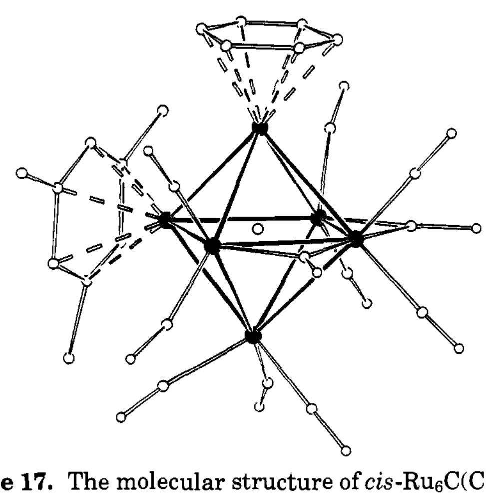


Figure 17. The molecular structure of *cis*-$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_3Me_3)$ in the solid state.

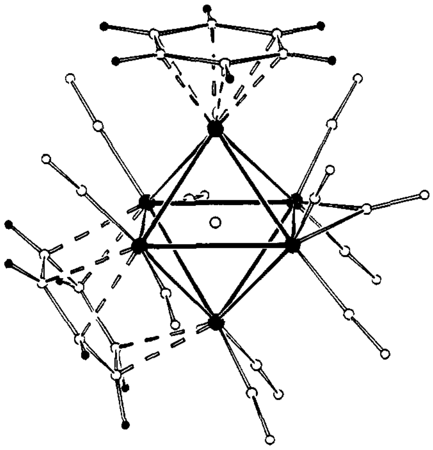


Figure 18. The molecular structure of $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ in the solid state.

A second example of *cis* isomer has been characterized. The structure of $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_4Me_2)(\eta^6\text{-}C_6H_5Me)$ is similar to that illustrated above.

The apical–facial structural form is characteristic of the complexes of formula $Ru_6C(CO)_{11}(\eta^6\text{-arene})(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ (arene = C_6H_6,[27] C_6H_5Me,[61] $C_6H_4Me_2$[61]). In these complexes one of the rings adopts the η^6-apical coordination, while the other ring is bound in $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$-capping mode to one triangular face of the octahedral metal framework. In the mixed-arene derivatives, the methyl-substituted ring always adopts the terminal coordination mode. The structure of the prototype of these molecules, namely $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$, is shown in Figure 18.

The molecule of the $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_4Me_2)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ and the two independent molecules of the $Ru_6C(CO)_{11}(\eta^6\text{-arene})(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ derivative possess different rotameric conformations of the η^6 ligands.[61] As previously suggested for other η^6-apical derivatives, the conformational choice of the apical

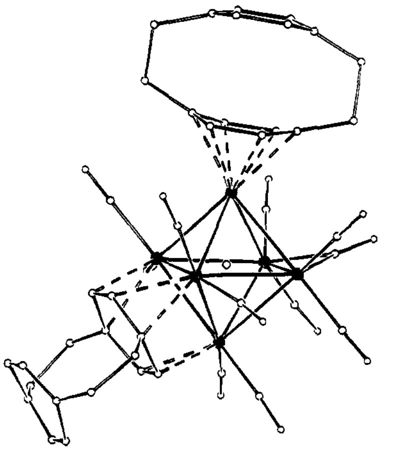


Figure 19. The molecular structure of $Ru_6C(CO)_{11}(\eta^6\text{-}C_{16}H_{16})(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$ in the solid state.

ligands can be ascribed to optimization of intermolecular packing interactions (see section IV). In both compounds the hydrogen atoms of the μ_3-capping benzene are bent out-of-plane with respect to the ring plane and the metal triangle, as previously observed in $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$.

The bis(paracyclophane) derivative $Ru_6C(CO)_{11}(\eta^6\text{-}C_{16}H_{16})(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_{16}H_{16})$ has been structurally characterized (see Figure 19).[69] The gross features of the complex structure are similar to those of the bis(benzene) derivative. The ligand in η^6-coordination mode does not differ appreciably from free paracyclophane,[90] whereas the facial ligand is "flattened" over the surface of the cluster. Interestingly, the face-capping ligand is rotated substantially with respect to expected eclipsing of the C–C midpoints over the cluster triangular face. The rotation is such that the relative conformation is closer to eclipsing rather than to staggering of the ring carbon atoms with respect to the ruthenium atoms.

The η^6-coordination of an arene fragment to a ruthenium atom has been also found in the 88-electron cluster $Ru_6(\eta^2\text{-}\mu_4\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)$.[63] The metal framework is a tetrahedron of ruthenium atoms with two additional ruthenium atoms bridging two consecutive edges of the basal plane. The "apical" ruthenium atom bears an η^6-mesitylene group; two CO ligands are triply–bridging two triangular faces of the tetrahedron and interact, through carbon and oxygen, with the edge-capping ruthenium atoms. Metal–metal bond distances range from 2.628(1) to 2.843(1) Å, while Ru–C(mesitylene) range from 2.256(8) to 2.303(8) Å.

From the same reaction the 86-electron cluster $HRu_6(\eta^2\text{-}\mu_4\text{-}CO)(CO)_{13}(\mu_2\text{-}\eta^1{:}\eta^7\text{-}C_6H_3Me_2CH_2)$ is obtained. The cluster possesses a trigonal-bipyramidal structure with a sixth ruthenium atom bridging an apical–equatorial edge.[63] The 3,5-dimethylbenzyl ligand does not adopt the conventional η^6-bonding mode as in the related species, but it undergoes a hydride shift from a methyl group to the metal frame, which is σ-connected [Ru–C 2.21(3) Å] to a second Ru atom (see Figure 20). Metal–metal bond distances range from 2.716(2) to 2.858(2) Å; Ru–C(arene) distances range from 2.28(2) to 2.31(2) Å.

The hexanuclear family has been enriched with the novel osmium complexes $Os_6(CO)_{12}(\eta^6\text{-}C_6H_6)_2$[72] and $H_2Os_6(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$.[71] In these complexes the two conventional η^6- and $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$-bonding modes of benzene are observed on a metal framework derived from that of the 84-electron binary carbonyl $Os_6(CO)_{18}$,[91] *viz.* a bicapped tetrahedron, with which both arene derivatives are isoelectronic. In $Os_6(CO)_{12}(\eta^6\text{-}C_6H_6)_2$ the two terminally bound ligands occupy sites with different chemical environment.[72] One benzene is coordinated to one osmium atom belonging to the central tetrahedron; this atom does not carry other ligands, while the second benzene is bound to one apex atom which is also involved in the bonding with one bridging CO. In the second complex the replacement of the bridging CO by two hydrides is associated with the "slippage" of one benzene ligand to a face-capping arrangement,[71] similar to that observed in $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$. The limited precision of the data set prevented an analysis of the delocalization within the ring. It has been pointed out, however, that the orientation of the ring is such that the midpoints of alternate C–C bonds are eclipsed with the osmium atom of the capped face. The H(hydride) positions were obtained, from potential energy calculations, along the shortest Os–Os bonds in the structure. This behavior contrasts with the usual bond lengthening associated to the presence of bridging hydrides. On the other hand, the three metal–metal bonds interacting with the benzene ligand are significantly longer [2.842(3) Å] than those belonging to the uncapped faces [mean 2.776(3) Å]. Os–C(η^6-benzene) distances range from 2.17(5) to 2.26(5) Å, while Os–C(μ_3-benzene) distances range from 2.23(5) to 2.34(5) Å. It has been argued that the presence of a face-capping benzene in the hydridic species may be due to an electronic effect.[71,72] The H(hydride) atoms, in fact, can donate electrons to the cluster in a more delocalized way than a CO ligand, thus inducing the arene ligand to donate electron density to three metal atoms rather than to one, *i.e.* to adopt a facial instead of an apical coordination mode.

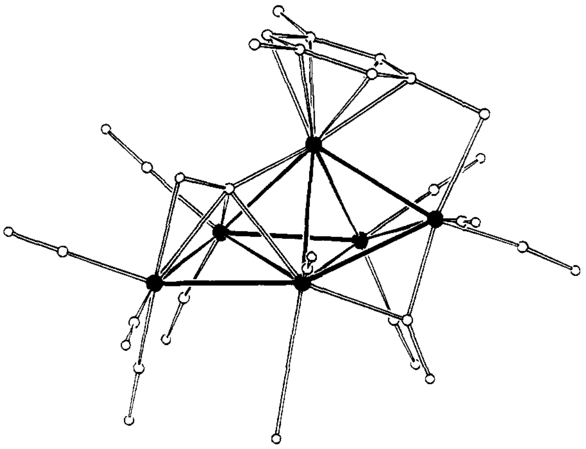


Figure 20. The molecular structure of $HRu_6(CO)_{14}(\eta^7\text{-}\mu_2\text{-}C_6H_3Me_2CH_2)$ in the solid state.

F. Mixed-Metal Clusters

The trinuclear complex $FeCo_2(CO)_3(\mu_3\text{-}CO)_2(\eta^6\text{-}C_6H_3Me_3)_2$ consists of a triangle of metal atoms bridged by two face-capping CO-ligands.[73] The mesitylene ligands are bound to the cobalt atoms, the distances from the midpoint of the two rings being 1.635(4) Å and 1.645(4) Å, respectively.

The metal core of $H_3RhOs_3(CO)_9(\eta^6\text{-}C_6H_5Me)$ is a tetrahedron in which the osmium atoms bear three terminal CO's each, while the rhodium atom carries the apical toluene ligand.[77] The toluene ligand is found disordered over three sites corresponding to eclipsing of the methyl group with each osmium atom. The "average" disordered molecular structure conforms to the 3-fold symmetry of the $Os_3(CO)_9$ fragment. The H(hydride) atoms are believed to bridge the three equivalent Os−Os bonds. The structural parameters of the benzene analogue $H_3RhOs_3(CO)_9(\eta^6\text{-}C_6H_6)$[76] are strictly comparable to those of the toluene derivative. The ring atoms show extensive displacement in the plane of the ring indicating that the ligand lies in smooth potential surface and is very probably able to reorientate in the solid state with a small energy barrier.[9] Rh−C(arene) distances are in the range 2.271(8)−2.230(8) Å and 2.257(29)−2.308(18) Å for the benzene and toluene derivatives, respectively. The arene derivatives are isoelectronic with the cyclopentadienyl species $H_2Os_3Rh(CO)_{10}(\eta^5\text{-}C_5H_5)$, in which the C_5H_5 ligand is also coordinated to the corresponding rhodium atom, while two Os−Os edges are H-bridged and an additional CO is found bridging the Rh−Os edge.

A butterfly geometry is shown by the cluster core of $RuOs_3(CO)_9(\mu_4\text{-}C_2Me_2)(\eta^6\text{-}C_6H_6)$.[78] The ruthenium atom carrying the benzene ligand occupies the wingtip position, while the C_2Me_2 ligand spans the butterfly hinge. Each osmium atom carries three terminal CO groups. Ru−C(benzene) distances fall in the range 2.17(3)−2.26(3) Å with no significant differences attributable to the presence of three independent molecules in the asymmetric unit.

$FeCo_3(C_5H_5)(\mu_4\text{-}\eta^2\text{-}C{=}CHCF_3)(CO)_6(\eta^6\text{-}C_6H_5Me)$ is also based on a butterfly of metal atoms whose wingtips are occupied by the iron atom coordinated to the C_5H_5 ligand and by a cobalt atom interacting with the η^6-toluene ligand.[74] The space between the wings is occupied by the $C{=}CHCF_3$ ligand that is bound to all four metal atoms via the C-terminus and interacts in η^2 fashion with the Co atom carrying the toluene ligand.

The hexanuclear cluster $RuOs_5(CO)_{15}(\eta^6\text{-}C_6H_6)$[79] possesses the bicapped tetrahedron of metal atoms characteristic of $Os_6(CO)_{18}$. This structure is related to those of the bis(benzene) species $H_2Os_6(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ and $Os_6(CO)_{12}(\eta^6\text{-}C_6H_6)$ that are also based on the bicapped tetrahedral metal core. In the ruthenium derivative the benzene ligand is bound to the heteroatom occupying one vertex of the cluster cage as shown in Figure 21.

G. High Nuclearity

The chemistry of arene clusters with nuclearity higher than six has not been well developed, hence only a few arene clusters derivatives have been structurally characterized in the solid state.[53,80−83] Furthermore, since no systematic study has been reported only a brief account of the salient structural features for the known compounds will be given.

The heptanuclear cluster $Ru_7(CO)_{15}(\mu_4\text{-}PPh)_2(\eta^6\text{-}C_6H_5Me)$ has been obtained together with the pentanuclear species $Ru_5(CO)_{12}(\mu_4\text{-}PPh)(\eta^6\text{-}C_6H_5Me)$.[53] In the former species the seven ruthenium atoms define a condensed polyhedron consisting of two square pyramidal Ru_5 units sharing a triangular face, with the two basal planes capped by the μ_4-PPh ligands (see Figure 22a). The toluene ligand coordinates in an η^6-mode to one basal Ru atom. This structure is strictly related to that of the pentanuclear derivative obtained from the same reaction. This latter species contains a square-pyramidal core bridged by the μ_4-PPh ligand and carries the arene ligand on one basal atom as in the heptanuclear species.

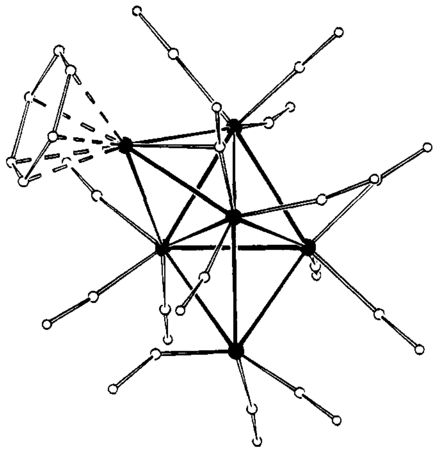


Figure 21. The molecular structure of $RuOs_5(CO)_{15}(\eta^6\text{-}C_6H_6)$ in the solid state.

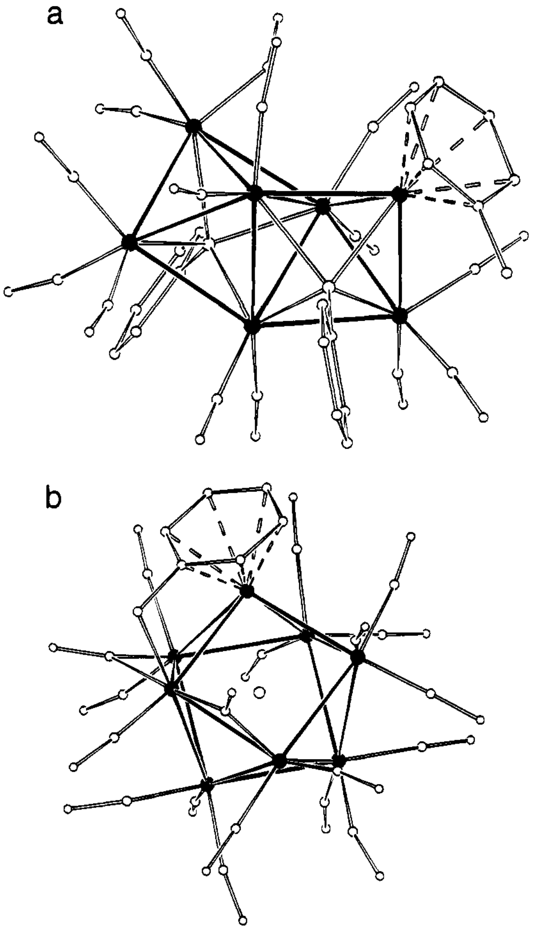


Figure 22. The molecular structures of (a) $Ru_7(CO)_{15}(\mu_4\text{-}PPh)_2(\eta^6\text{-}C_6H_5Me)$ and (b) $Ru_8(\mu_8\text{-}P)(CO)_{19}(\mu_2\text{-}\eta^1\eta^6\text{-}CH_2C_6H_5)$ in the solid state.

The metal core in $Ru_8(\mu_8\text{-}P)(\mu_2\text{-}CO)_2(CO)_{17}(\mu_2\text{-}\eta^1,\eta^6\text{-}CH_2C_6H_5)$ is that of a square-antiprismatic polyhedron encapsulating a phosphorus atom.[81] The benzyl ligand is coordinated to two ruthenium atoms via a direct σ interaction with the methylenic C atom and via η^6-coordination of the C_6 ring (see Figure 22b). Ru−C distances are found in the range 2.20−2.29(3) Å for the phenyl ring while the benzylic carbon is at 2.19(4) Å from its Ru atom.

In a second example of an octaruthenium cluster, *viz.* $Ru_8(\mu_4\text{-}S)(CO)_{17}(\eta^6\text{-}C_6H_5Me)$[82] the central metal unit contains two fused square pyramids of ruthenium atoms bridged by the four S atoms. The toluene ligand is coordinated in terminal η^6-mode to a Ru atom that does not bear CO ligands. The toluene ligand exhibits 2-fold rotational disorder.

The complex $H_4Ru_8(CO)_{18}(\eta^6\text{-}C_6H_6)$ is the only example of hydrido−carbonyl arene−Ru_8 cluster characterized up to date.[70] The cluster is an octahedron capped by two additional metal atoms on two triangular faces sharing a common vertex. The benzene ligand is η^6 bound to the only octahedron vertex not belonging to the capped triangular faces. Two out of 18 CO ligands are symmetrically bridging two opposite Ru edges, while the remaining 16 CO's are terminally bound. The four H(hydride) atoms are located on the cluster surface.

The mixed-metal species $Cu_2Ru_6(CO)_{18}(\eta^2\text{-}C_6H_5\text{-}Me)_2$ contains an octahedral ruthenium core bicapped on opposite faces by the copper atoms.[82] Each copper atom bears a toluene ligand bound in η^2 fashion. Disorder in the orientation of these ligands has been observed.

IV. Crystal Structure of Arene Clusters

Neutral transition metal cluster molecules aggregate in the solid state in typical van der Waals fashion.[91] Molecular size and shape control the way in which molecules interlock and generate crystal structures.[92] Furthermore, it is well known that packing forces affect the molecular structure observed in the solid state.[7] The relationship between the structure of the individual molecular entity and that of the crystal is, however, very elusive. Although much progress has been made in recent years in the understanding of the crystal packing of molecules, the nature of the intermolecular forces is far from being fully understood. This aspect of crystal structure studies becomes particularly intriguing when dealing with molecules that possess an extensive degree of structural freedom.[9] The molecular structure of flexible molecules in the solid state is not necessarily identical to that in solution or in the gas phase, since crystal forces, *i.e. intermolecular bonding*, makes a significant contribution to the global energy of the system. Arene clusters are highly fluxional since arene reorientation combines with CO scrambling over the cluster framework to yield extremely flexible structural systems. In these cases the environment, whether constituted of the same molecule packed in an ordered way in the crystal structure or by rapidly tumbling solvent molecules in solution, is not simply a spectator but can have great influence on the structural features that are observed by crystallographic or spectroscopic techniques.[93,94]

In this section we focus on the interplay between molecular and crystal structure for some of the arene clusters described in section III. Attention is directed toward the relationship between the type of arene fragment and the molecular organization in the solid state. The method of analysis is worth mentioning, since it has been used for virtually all the crystals examined thus far. The crystal structure of a given compound can be *decoded* by studying the distribution and interaction of the nearest-neighbor molecules among the molecules surrounding the one arbitrarily chosen as reference. Methods based on empirical packing potential energy calculations within the pairwise atom−atom approach[95] or packing analysis based on graphical methods[96] are used to identify the nearest neighbor molecules (*i.e.* those forming the so called "enclosure shell", ES hereafter) and to study the number, distribution, and interactions between these molecules. These procedures have been shown to yield an accurate knowledge of the immediate molecular environment and of the intermolecular interlocking.

Arene clusters are particularly well suited for studying the relationship between molecular and crystal structure because of the simultaneous presence of both flat and cylindrical ligands, *viz.* the arenes and the carbonyl groups, on the same molecule. These two different atomic groupings, with their specific spacial requirements, pose problems in the optimization of the intermolecular interlocking that control crystal cohesion and stability. Furthermore, there exists the likelihood that crystal packing forces may alter, at times significantly, the structure of the molecule, and control the separation and crystallization of other isomeric forms.

This discussion commences by looking at the changes in the crystal structure which arise when the same arene is bound to clusters differing in the number or type of constituent metal atoms. We shall then proceed to systems in which the arene is varied on the same cluster unit.

Although $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ and $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ are *almost* isostructural in the solid state, their crystals differ substantially in terms of intermolecular organization.[33] This can be appreciated from a comparison of the distribution of the first neighboring molecules in the two crystal structures. The "enclosure shell" in crystalline $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ consists of 12 molecules distributed in *anti*-cuboctahedral arrangement (*A/B/A* sequence of layers, Figure 23a). The cluster crystallizes in the space group $P2_1$ with $Z = 2$.[33] The osmium analogue, $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$, crystallizes in the space group *Im* with one and a half molecules in the asymmetric unit.[27,28] The ES's of the two independent molecules in crystalline $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ differ substantially from that of $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$. The two groups of 12 molecules organize themselves in cuboctahedral ES's (*A/B/C* sequence of layers, Figure 23b). We have shown in section III that, in terms of molecular structures, the two complexes differ essentially in the orientation of the benzene ligand with respect to the metal triangle

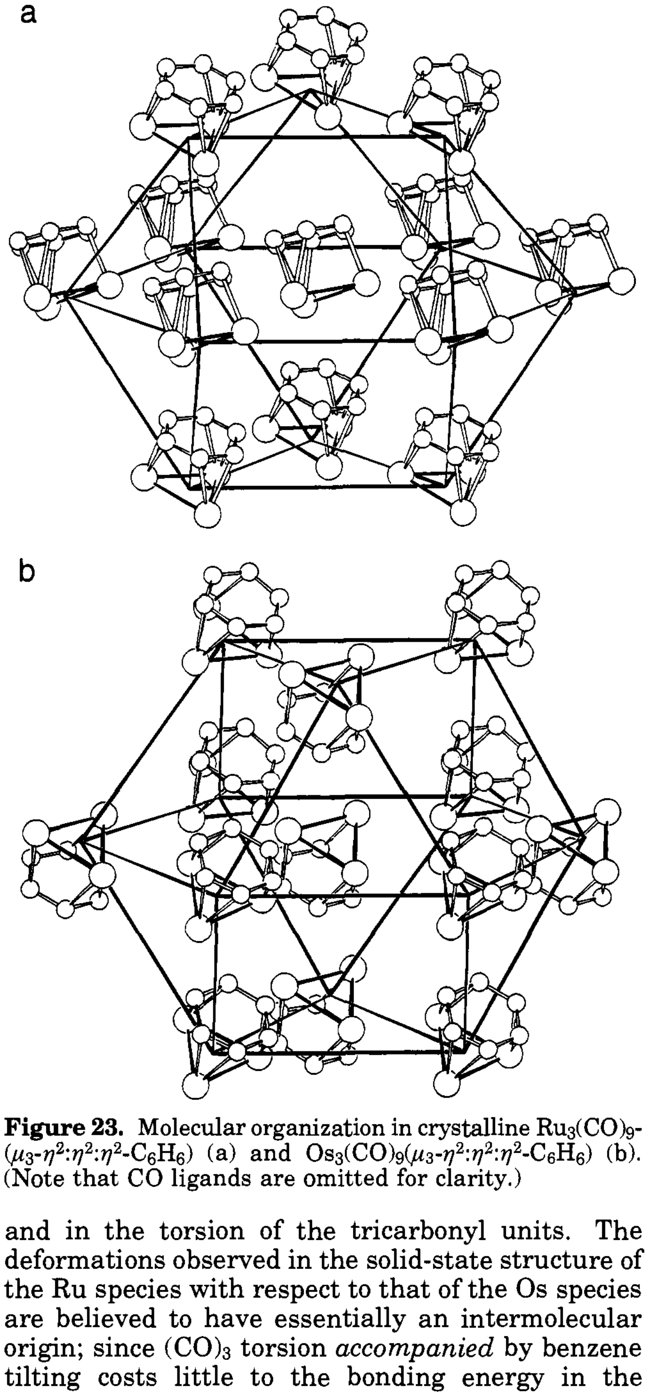


Figure 23. Molecular organization in crystalline $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ (a) and $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ (b). (Note that CO ligands are omitted for clarity.)

and in the torsion of the tricarbonyl units. The deformations observed in the solid-state structure of the Ru species with respect to that of the Os species are believed to have essentially an intermolecular origin; since $(CO)_3$ torsion *accompanied* by benzene tilting costs little to the bonding energy in the complex, the optimization of the intermolecular interactions becomes important. The differences in structure *and* packing between the two molecules and between their respective crystals have been explained by assuming that the two crystal structures represent two *alternative solutions* to the minimization of the "global" energy (*i.e.* inter- and intramolecular energy) of the system molecule-crystal. The crystals of the two benzene clusters can thus be regarded as a sort of polymorphic modification, whose existence might be due to the difference in intermolecular cohesion caused by substitution of Ru for Os.

Another type of packing is present in crystalline $H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_6)$ and $H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_5Me)$.[48] The reference molecules in the two crystals are surrounded by 14 first neighbors. In spite of the presence of different arene ligands, the two molecules pack in nearly the same way in their solids. The arene ligands form *ribbons* generated by the interlocking of two rows of arene fragments in a chevron like fashion as shown in Figure 24. This packing feature has been found again in the crystal structure of the hexanuclear species $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)$.[48] In spite of the rather different molecular geometry and of the different size of the molecules, the packing in the crystal of this latter species is similar to that observed in the two Os_4 clusters since the toluene ligands form analogous ribbons throughout the lattice. The relative orientation of the arene ribbons is of the "herringbone" type, *i.e.* similar to that commonly observed in crystals of condensed arenes, such as naphthalene, anthracene, coronene and even benzene itself. The "herringbone" pattern is also present in some mononuclear arene complexes such as $(C_6H_6)_2Cr$ (see Figure 25).[92b]

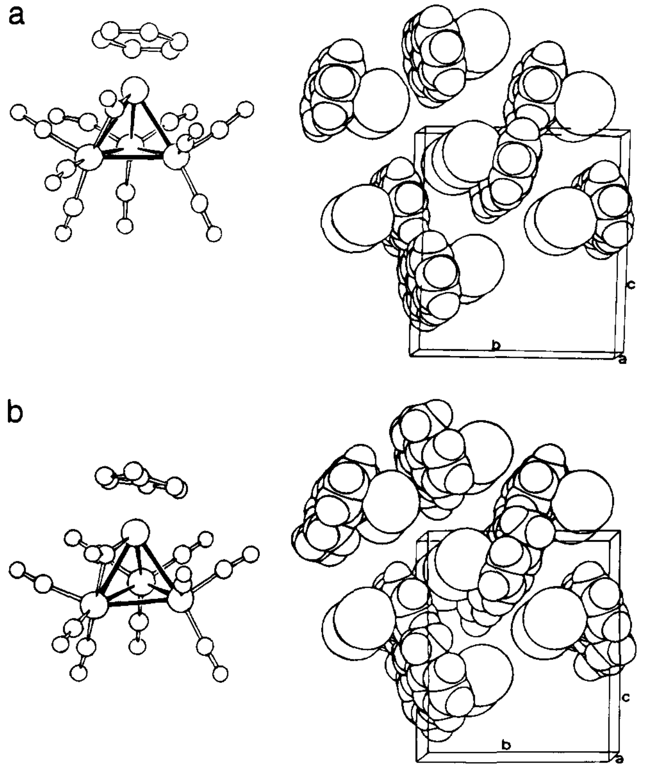


Figure 24. Molecular organization in crystalline $H_2Os_4(CO)_{14}(\eta^6\text{-}C_6H_6)$ (a) and $H_2Os_4(CO)_{14}(\eta^6\text{-}C_6H_5Me)$ (b). (Reprinted from ref 9. Copyright 1992 American Chemical Society.)

A strict analogy also exists between mononuclear and polynuclear systems. Most mono(arene) derivatives of the type $Ru_6C(CO)_{14}(\eta^6\text{-arene})$ form molecular piles in their crystals structures. These piles are "held together" by the interaction between the arene fragments and the apical tricarbonyl units of neighboring molecules (see Figure 26). Molecules such as $(C_6H_6)Cr(CO)_3$ and $(C_6Me_6)Cr(CO)_3$ establish extremely similar packing patterns in their respective crystal structures.[92b] These crystals are not adequately described as close-packed structures (*i.e.* of the *hcp* or *ccp* type), rather the crystals are formed by close-packed molecular rods (or piles) as shown in Figure 27. The intermolecular interaction along the pile is, as for the polynuclear systems described above, based on arene–$(CO)_3$ interactions.[92b]

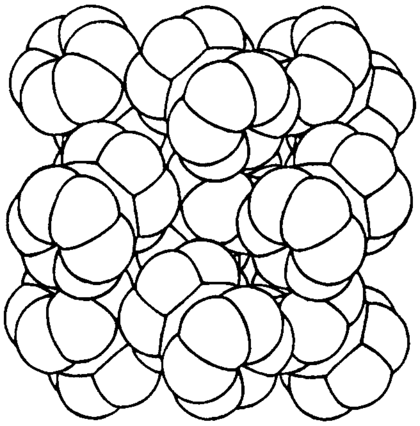


Figure 25. Molecular organization in crystalline $(C_6H_6)_2$-Cr showing the "herringbone" pattern established by the benzene rings. (Hydrogen atoms are omitted for clarity.) (Reprinted from ref 92b. Copyright 1992 American Chemical Society.)

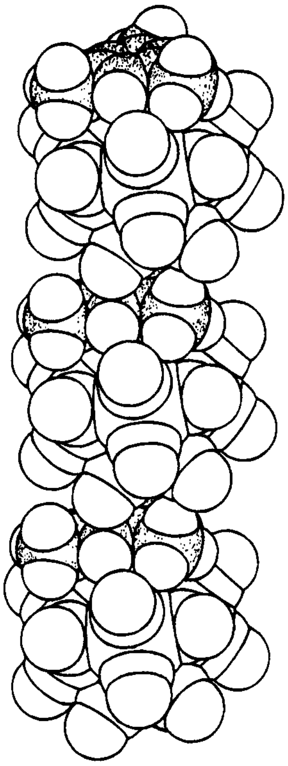


Figure 26. Mono(arene) cluster complexes often form molecular piles in the crystal structure. The intermolecular interlocking is based on direct interactions between the arene fragment and the tricarbonyl unit of a next neighboring molecule.

While the arene fragments in mono(arene derivatives establish herringbone patterns this is not so for most bis(arene) clusters. The most representative example is given by the isomeric pair of bis(benzene) clusters $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ and $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2$.[48] In both crystals the benzene ligands face each other in graphitic-type arrangements forming molecular "snakes" and "rods", respectively, as shown in Figure 28, parts a and b. In the case of $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ the molecule does not self-assemble in a close packed arrangement. The reference molecule interacts with two next-neighboring molecules generated by crystallographic centers of symmetry. The separation between the carbon rings is 3.29 and 3.56 Å for the η^6/η^6 and μ_3/μ_3 interactions, respectively, *i.e.* strictly comparable to separation in graphite itself (see Figure 29, parts a and b, respectively). In crystalline *trans*-$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2$ the benzene fragments belonging to next neighboring molecules along a row adopt a nearly staggered orientation (see Figure 29c) at a distance of 3.52 Å. The crystal is thereby composed of parallel molecular rods each formed by a sequence of molecules linked together *via* benzene–

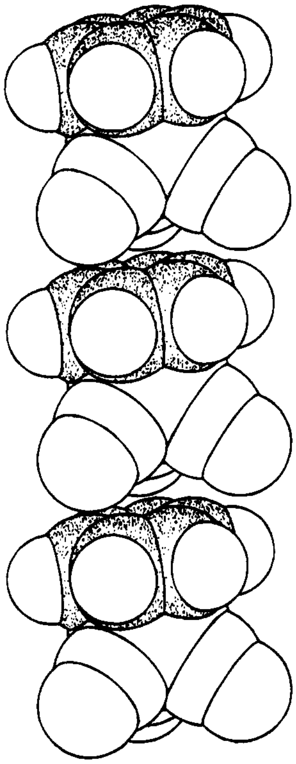


Figure 27. Molecular piles of the type shown in Figure 26 for mono(arene) clusters are also present in crystalline $(C_6H_6)Cr(CO)_3$. (From ref 92b. Copyright 1992 American Chemical Society.)

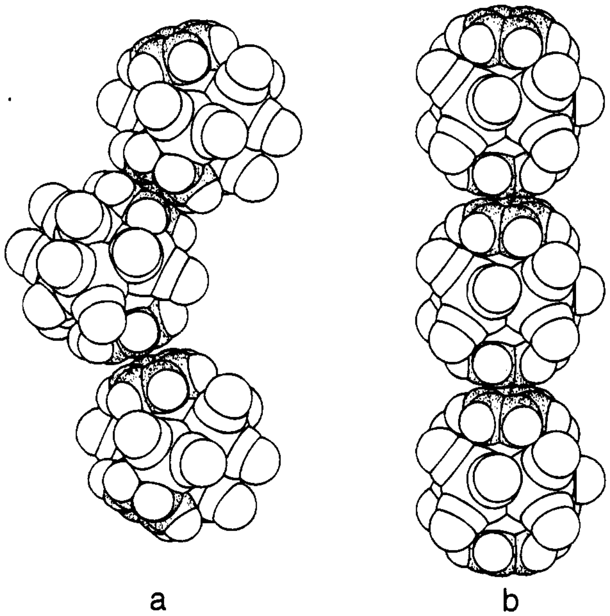


Figure 28. Comparison of the interaction between the benzene ligands in crystalline $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ (a) and *trans*-$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2$ (b).

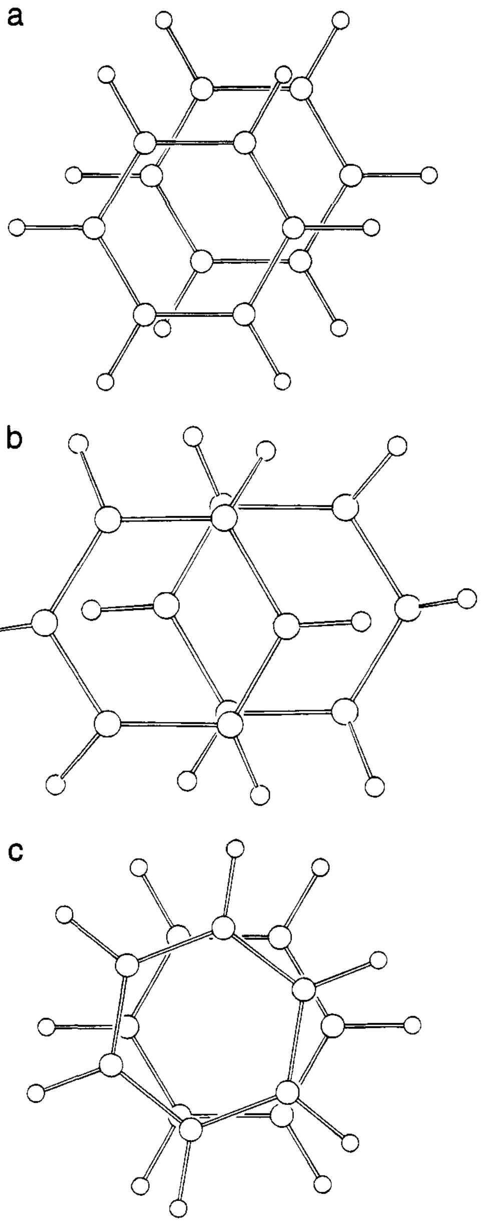


Figure 29. Projection of next-neighboring benzene fragments in $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ for the η^6-η^6 (a) and μ_3-μ_3 (b), and in $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2$ (c).

benzene intermolecular interactions.

This general trend has also been recognized in the study of the crystal structure of the bis(benzene) species $H_2Os_6(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$,[71] which, in spite of the different geometry of the cluster core, *viz.* a bicapped tetrahedron *vs* an octahedron, forms snakes of arene-linked molecules extending in the 111 direction of the monoclinic crystal.

This behavior is not confined to the bis(benzene) cluster but it is also observed with other bis(arene) derivatives. A study of the molecular organization in crystalline *cis*-$[Ru_6C(CO)_{11}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(\eta^6\text{-}C_6H_6)]$ and *trans*-$[Ru_6C(CO)_{11}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2]$ shows that, in both cases, the arene ligands establish graphitic-like intermolecular interactions.[65] In crystalline *cis*-$[Ru_6C(CO)_{11}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(\eta^6\text{-}C_6H_6)]$ the benzene and the mesitylene ligands belonging to the reference molecule are almost face-to-face with, respectively, the mesitylene and benzene ligands belonging to next neighboring molecules as shown in Figure 30a. In a similar manner, in crystalline *trans*-$[Ru_6C(CO)_{11}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2]$ the mesitylene fragments are paired throughout the lattice as sketched in Figure 30b. Each molecule is related to the next along the piles by crystallographic centers of inversion. The distance between the arene planes is *ca.* 3.6 Å, *i.e.* only slightly longer than in graphite itself.

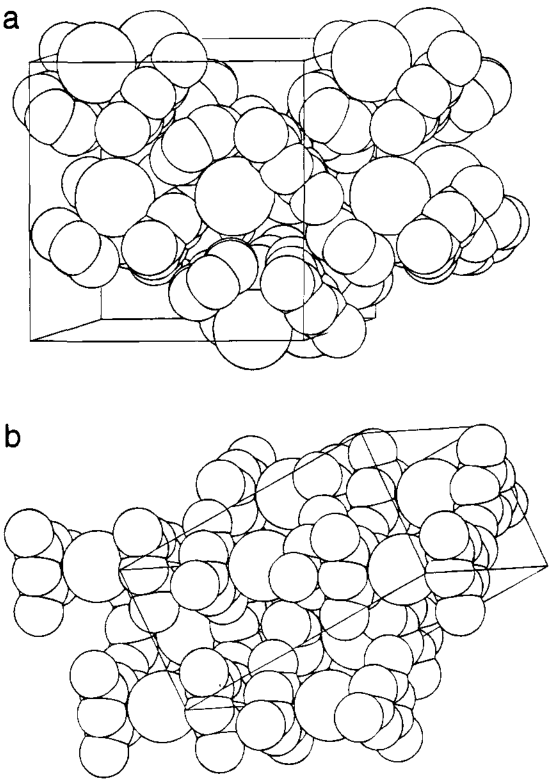


Figure 30. Molecular organization in crystalline *cis*-$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_3Me_3)$ (a) and *trans*-$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)_2$ (b). (Large spheres represent the cluster cores. CO ligands and hydrogen atoms are omitted for clarity.) (From ref 65. Copyright 1992 American Chemical Society.)

Molecular snakes are also present in crystalline $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$.[61] The toluene and benzene fragments belonging to next neighboring molecules face each other in the chain, although the presence of the methyl group on the toluene fragment prevents the two arenes from being parallel as, for example, in the bis(benzene) analogue. In crystalline $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_4Me_2)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ the packing is otherwise constituted of "dimers" of benzene–benzene interacting molecules.[62] The solvent molecules of cocrystallization (CH_2Cl_2) are wedged in between the two benzene fragments, while the xylene ligands tend to form ribbons throughout the crystal lattice. This packing motif is reminiscent of that observed in crystalline $H_2Os_4(CO)_{10}(\eta^6\text{-arene})$ (arene = benzene, toluene) and $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_5Me)$.

The crystal structure of $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Et_3)$ deserves close examination, since all three ethyl groups on the arene ring point "upwards", as shown in Figure 31a. This arrangement allows minimization of the *intramolecular repulsions* between the outermost CH_3 groups and the carbonyl ligands and an efficient *intermolecular interlocking* in the crystal structure.[57]

In $Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})$ the paracyclophane ligand adopts a μ_3-$\eta^2:\eta^2:\eta^2$-bonding mode.[57] The

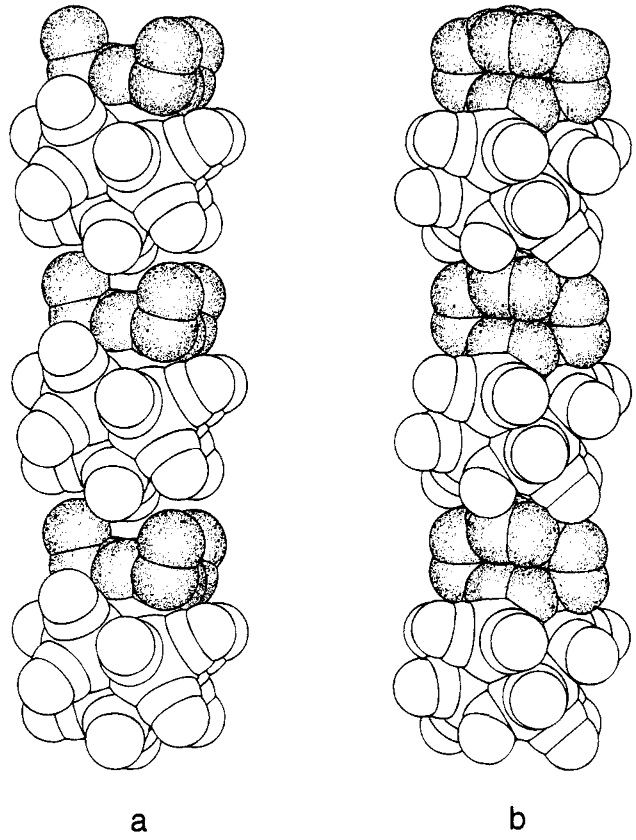


Figure 31. A molecular pile in crystalline $Ru_6(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}C_6H_3Et_3)$ (note how the "upward" orientation of the outer CH_3 groups provides an efficient clamping unit to lock a neighboring molecule and (b) intermolecular interlocking in crystalline $Ru_6C(CO)_{14}(\mu_3\text{-}C_{16}H_{16})$ (note how the paracyclophane ligand interacts with the CO ligands bound to the opposite face of a neighboring molecule along the pile).

molecular arrangement in the crystal structure is based on a direct interaction between the "free" ring of the paracyclophane ligand and the CO groups bound to the opposite face of a neighboring molecule (see Figure 31b), as observed in crystalline $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Et_3)$.

These studies indicate that the packing choice in crystalline arene clusters is governed by the need of optimizing the intermixing in the crystal structure of the flat arene fragments and the CO ligands protruding from the cluster surface. By grouping the arene fragments together in ribbons or snakes, optimum CO⋯CO interlocking is preserved. This tendency is maintained on changing the arene type and the arene coordination mode. With mono(arene) derivatives packing optimization is achieved by forming arene ribbons or layers through the lattice, while with bis(arenes) this is better achieved by placing the ligands face to face.

Mono(arene) hexanuclear clusters and, to some extent the bis(arene) derivatives interlock in the three-dimensional network by inserting the unique bridging ligand in the middle of the cavity generated by four terminal ligands of a neighboring molecule. In this way molecular rows are formed in which the individual clusters are all linked via this type of "key–keyhole" interaction. The same fundamental packing motif has been found in both crystals of $Ru_6C(CO)_{17}$.[84,85] The intermolecular separation between next neighboring molecules is *ca.* 9.5 Å, which usually corresponds to a cell axis translation. The molecular rows present in the crystals of $Ru_6C(CO)_{14}(\eta^6\text{-arene})$ (arene = C_6H_6, $C_6H_3Me_3$) are compared in Figure 32.

It is worth mentioning in this section that the crystal structure of $HRu_3(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_7)$[26] revealed the existence of a network of CH⋯O(CO) interactions between the H atoms belonging to the C_6H_7 ligand and the carbonyl groups. Since then, CH⋯O interactions have been detected in a number of other systems.[97] The role of CH⋯O(CO) interactions in contributing to crystal cohesion has been discussed in a comprehensive way by Desiraju.[98] Their influence on the packing mode observed may be decisive, although their importance in the crystallization process is still far from being understood.

The crystal structures of the isomeric pairs $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ and $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$, $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2$ and $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ have also been investigated by empirical packing potential energy calculations and compared with the results of extended Hückel calculations (see section III.A).[87] Hydrogen bonds of the CH⋯OC type have been detected in crystals of the apical isomers of both the Ru_5 and Ru_6 clusters.

V. Dynamics in Solution and the Solid State

A. Dynamics in Solution

As with most organometallic complexes,[99] arene clusters exhibit a variety of rearrangement processes. All undergo fluxional behavior, and arene rotation is a common feature of most, if not all, the systems examined to date. Isomerization is also frequently observed, but arene exchange, at least under relatively mild conditions, is rarely seen.

Barriers to arene rotation in mononuclear systems are small and usually of the order of a few kilojoules per mole (kJ mol^{-1}).[100] In all cluster systems studied to date which contain η^6-bonded arenes similar rotational barriers are observed. Given the greater complexity of the cluster systems and the presence of other supporting ligands, somewhat higher barriers might have been anticipated. However, as detailed investigations of the molecular structures of these materials in the solid state have shown, the degree of steric constraint is minimized and it is conceivable that, as far as we can judge, the motion of the arene is concerted with the motion of other ligands present, especially when those other ligands are carbonyls.

Higher barriers are observed for the μ_3-bonding mode. Investigations into these systems have revealed barriers in the range 12 – 20 kJ mol^{-1}.[101] It is tempting to associate these higher barriers with the triene bonding mode indicated by the variation in C–C bond distances around the arene ring. Such suppositions are probably misplaced and the barrier may rise simply from the increasased interaction with adjacent ligands, again, the CO ligand. In some compounds, and the best examples are probably $Os_3(CO)_8(\eta^2\text{-}CH_2CHR)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ (R = H, Me, Bu, and Ph) the motion of the ring is apparently

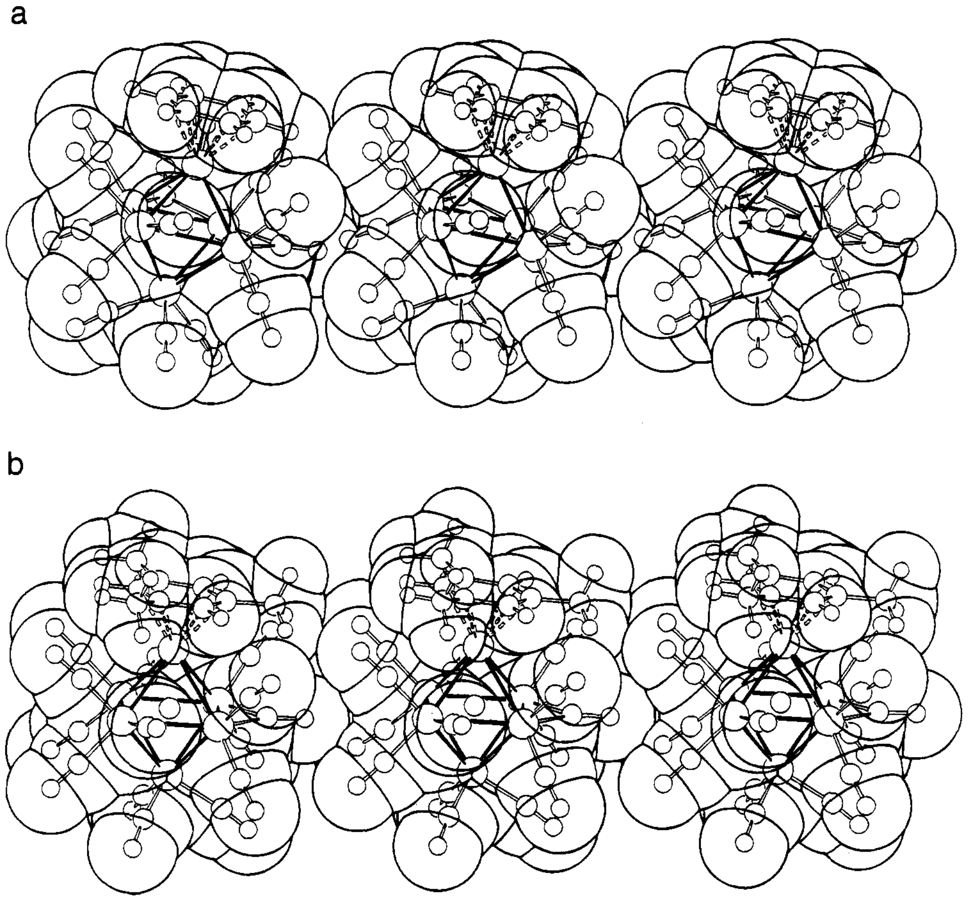


Figure 32. "Key–keyhole" interaction along the molecular rows present in the crystals of $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$ (a) and $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)$ (b).

synchronized with the rotation of the alkene and the CO ligands.[101,102]

We have commented in sections II and III on the wide variety of isomers observed for many of these compounds, especially for those clusters based on the Ru_5C and Ru_6C central units. Terminally bonded arenes may coordinate to different sites within the cluster unit, *e.g.* apical and basal in Ru_5C. Where two (or more) arenes are present in the Ru_6C derivatives then *cis* and *trans* geometrical isomers have been observed, and when both facial and terminal arene complexes form, additional geometrical isomers are apparent. The problem is more complicated when substituted arenes such as toluene, xylene, and mesitylene are employed: additional conformational isomer variations may arise depending on mutual orientations of arenes and $M(CO)_3$ units. This type of isomerization is a feature emerging from systems of this type, but for reasons outlined above, because of the low barriers to rotation, such conformational isomers are only likely to exist in the solid.

Interconversion of terminal–facial ligands may also occur with relative ease, and here again, provided that two different arenes are employed, different isomeric possibilities are available. From the studies reported to date, it would appear that in all cases of isomer interconversion a dissociative (or at least an external exchange process) may be excluded.

This leads us to the final aspect of these rearrangement phenomena, *viz.* arene exchange with external arenes. In the cases observed at present which are restricted to derivatives of Co_4 and Os_4 such exchange does not occur easily and usually requires moderately forcing conditions. Detailed studies have not been conducted, but given the nature of the replacement, *viz.* a six-electron donor by a six-electron donor we would assume that the exchange process occurs via an associative mechanism. Further studies are essential here.

Fluxionality, isomerization, and exchange phenomena have been most conveniently studied by NMR spectroscopy and a whole range of NMR techniques have been employed. Given the diagnostic value for the chemical shifts of both the η^6- and μ_3-coordination modes such studies are relatively easy to carry out. In selected examples the variation in $\nu(CO)$ may also serve as a reliable method of monitoring exchange phenomena, particularly isomerization.

Evidence that arene ligands undergo reorientational motions is shown by NMR in which, for example, protons of benzene exhibit a singlet, consistent with the same chemical environment. This suggests that the ligand is free to rotate, although no direct evidence is available to say whether rotation occurs *via* a dissociative or nondissociative process. The chemical shifts derived from the NMR spectra of $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ are equally diagnostic exhibiting singlets at δ 5.54 and 4.14 ppm in the ^1H NMR spectrum, for the terminal and facial ligands, respectively.[27] These values are typical for arenes coordinated to neutral transition metal clusters. For example, the ^1H NMR of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ shows a singlet at δ 4.42 ppm. The ^{13}C NMR spectrum of this compound has also been

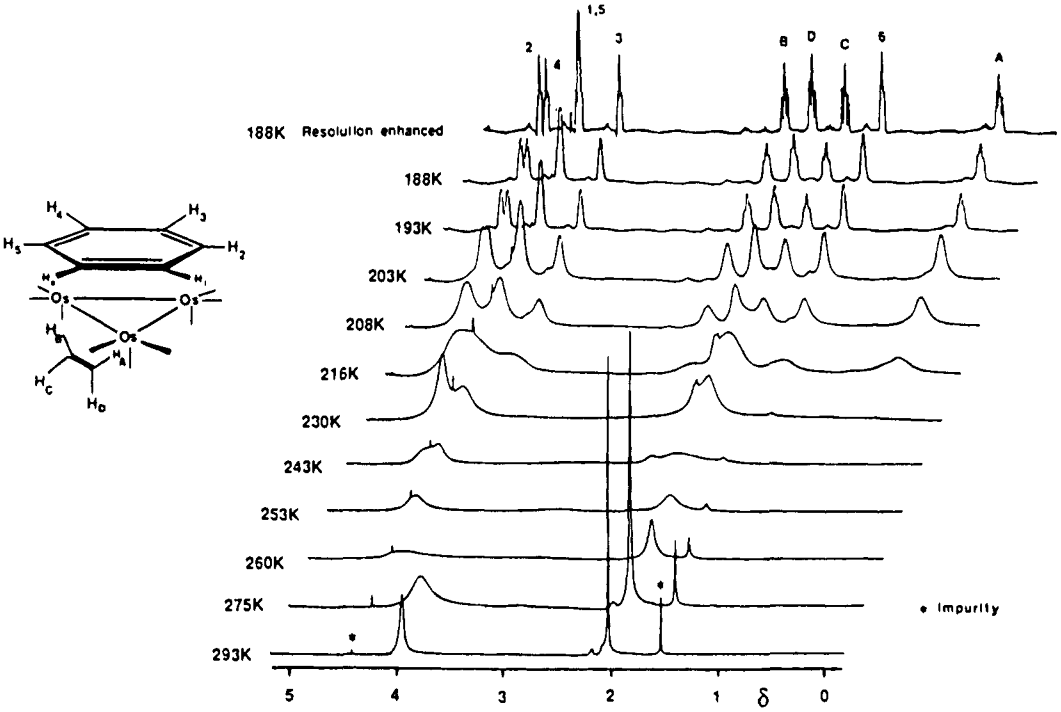


Figure 33. The variable-temperature solution ^{1}H NMR of $Os_3(CO)_8(\eta^2\text{-}CH_2CH_2)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ recorded between 293 and 188 K. The assignments of the molecule is displayed. (From ref 34. Copyright 1992 American Chemical Society.)

recorded, and a single resonance for the ring carbons is observed at δ 38.15 ppm. This value is considerably shifted to lower frequencies, when compared to free benzene or even a terminal ligand. For example, two isomers of $RuOs_5(CO)_{15}(\eta^{\circ}\text{-}C_6H_6)$ display singlets in their ^{1}H and ^{13}C NMR spectra at δ 5.92, 5.84 and 86.3, 85.6 ppm, respectively.

As anticipated, the vibrational spectra of both the terminal and face-capping arenes show marked spectroscopic differences. Infrared spectroscopic studies indicate that ν_{C-H} modes for terminal and face-capping arene ligands occur at significantly different wavelengths. In $Ru_6C(C)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ values of the vibrational modes for the terminal and facial benzene are observed at 3125, 3118 and 3100, 3065 cm^{-1}, respectively.

Although systematic VTNMR studies to detect arene motion over a cluster surface are rare, most systems which have been studied show no evidence for this. A variable-temperature ^{1}H NMR study[67] of the complex $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_5Me)$ reveals that in solution the complex exists in two isomeric forms, namely, that observed in the solid state (**A**) with one terminal and one face-capping toluene, and also as *trans*-$Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)_2$ (**B**).

$$\underset{\mathbf{A}}{[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_5Me)]} \Leftrightarrow \underset{\mathbf{B}}{\textit{trans}\text{-}[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_5Me)_2]}$$

At 295 K the ratio **A**:**B** is estimated to be 9:1. This ratio changes to 1:1 at 385 K. On cooling the sample back to 295 K the ratio of **A**:**B** returns to approximately 8:1.

In a separate experiment a solution of the bis(toluene) complex in $C_6D_5CD_3$ was allowed to stand for several weeks at room temperature. No appreciable exchange of bonded toluene with toluene-d_8 was recorded over this period indicating that the interconversion process takes place by a nondissociative mechanism.[67]

In an additional experiment the mixed-complex $Ru_6C(CO)_{11}(\eta^6\text{-}C_6D_5CD_3)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_5Me)$ was prepared. On monitoring the ^{1}H NMR of this compound scrambling of the toluene ligand between the two potential sites was observed. These observations are consistent with a unimolecular process.[67]

The variable-temperature solution ^{1}H NMR spectra of $Os_3(CO)_8(\eta^2\text{-}CH_2CH_2)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ recorded between 293 and 188 K are shown together with the assignments in Figure 33.[101] At ambient temperature the six inequivalent ring protons see time-averaged environments and a broadened singlet is observed at δ 3.92 ppm. The four ethylene protons give rise to a singlet at δ 2.03 ppm. On cooling, these resonances broaden and collapse until sharp. In the limiting spectrum 10 distinct protons are observed, and their assignment was achieved with the aid of 2D (COSY) and nOe spectroscopy. Strong nOe enhancements between proximal benzene and ethylene protons H_6 and H_B effectively label the resonances at δ 1.73 and 0.72 ppm, respectively, and form the basis of the remaining assignments. The fluxional processes occurring in this molecule have led to the benzene and ethylene ligands being described as rotors which undergo "helicopter-like" motions.[101] The above spectra, coupled with information gained from ^{13}C NMR and ^{13}C 2D-exchange spectroscopy of $Os_3(CO)_8(\eta^2\text{-}CH_2CH_2)(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)$ demonstrate that five fluxional processes occur in solution. The two tricarbonyl units undergo localized "turnstile" rotation that is not completely frozen out even at 145

K.[102] A trigonal-twist process allows movement of the alkene between equatorial sites within the $Os(CO)_2(CH_2CH_2)$ unit, exchanging via the axial position. A Cramer-type alkene rotation also occurs about the $Os-(C_2H_4)$ axis, and lastly a 1,2-ring-hopping motion permutes the nuclei of the μ_3-benzene ligand.

The side arm in the tricobalt clusters, $[CoCp]_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-arene})$, provides additional information concerning the rotation of the ring over a trimetal face. The exchange process in $[CoCp]_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5R)$ species has been analyzed in detail by 2D EXSY NMR spectroscopy (EXSY = exchange spectroscopy). Successive 1,2-shifts of the cobalt atoms with respect to the ring atoms could be directly observed.[3] The hindered motion has interesting stereochemical consequences because clusters of the type $[CoCp]_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5R)$ are asymmetric, although isomer interconversion can be caused by a rotational motion of the arene (or cluster) frame. Variable-temperature NMR studies[3] have shown that at low temperature a separate signal for each Cp ligand is distinguishable, hence, rotation is slow, and the dynamical process probably involves 1,2-shifts. As temperature is raised, a single signal is obtained for the Cp groups, thus, the ring rotates rapidly, effectively averaging these Cp groups.

B. Dynamics in the Solid State

Very little spectroscopic information is available on the dynamics of arene clusters in the solid state. This is largely due to the difficulty of preparing large quantities of samples for studies of spin–lattice proton relaxation times or for ^{13}C CPMAS NMR. It is now well ascertained that unsaturated organic fragments coordinated to metal centers with substantial bonding delocalization can undergo rotational jumping motion in the solid state as a function of the shape of the fragment: *i.e.* the more regular the shape, the lower the reorientational barrier.[9] The relationship between fragment shape and ease of reorientation can be transferred to larger polymetallic systems. Differences between mononuclear and polynuclear species arise mainly at the *intramolecular* level and will be briefly illustrated in the following.

CPMAS experimental results are available only for solid $Os_3(CO)_8(\eta^2\text{-}C_2H_4)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$.[102] The CPMAS spectra recorded in the range 220–335 K indicate the occurrence of exchange processes involving both the face-capping C_6H_6 ligand and the η^2-bound C_2H_4 fragment: reorientation of the two fragments (over the triangular metal frame and about the $Os-C_2H_4$ coordination axis, respectively) gives rise to two resonances between 245 and 296 K for the two groups of C atoms. Multiple resonances are resolved on cooling from 245 to 220 K. Above 270 K and up to 335 K progressive broadening on the CO resonances is also observed, suggesting that the CO ligands within the $Os(CO)_3$ units can interchange by "turnstile" rotation. Benzene and ethene reorientational motions have the same activation energy (55 kJ mol^{-1}).[102] Atom–atom potential energy barrier calculations (AAPEBC) have been used to show that the two reorientational processes are correlated, *viz.* reorientation of the C_2H_4 fragment is possible only if accompanied by benzene jumps over the cluster surface.[103] In other words benzene and ethene rotations are correlated in "helicopter-like" fashion as observed in solution.[101] In the solid state and in solution the process is, therefore, mainly under *intramolecular* control and occurs with a potential barrier of about 50 kJ mol^{-1}.[103]

The dynamic behavior of many other arene clusters has been approached by AAPEBC showing that benzene reorientation can occur irrespective of the cluster nuclearity and of the mode of bonding of the ring (whether $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ or η^6).[9] The potential barrier to reorientation of C_6H_6 fragments is between 9 and 36 kJ mol^{-1}. No systematic differences can be detected between face-capping and terminal bonding modes. This is in agreement with the highly fluxional behavior of these species in solution (see section V.A). In crystalline $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$, for instance, the calculated potential barrier is 18.8 and 26.4 kJ mol^{-1} at room temperature and 193 K, respectively.[33] In crystalline $Os_3(CO)_7(\mu_3\text{-}\eta^2\text{-}C_2Me_2)(\eta^6\text{-}C_6\text{-}H_6)$ benzene reorientation occurs with a potential barrier of 8.8 kJ mol^{-1}, while, not surprisingly, reorientation of the C_2Me_2 ligand is forbidden.[103] Analogously, in crystalline $Ru_3(CO)_7(\mu_3\text{-}\eta^2\text{-}PhC_2PhCO)(\eta^6\text{-}C_6H_6)$ benzene reorientation requires 10.9 kJ mol^{-1}.

As the molecular complexity increases (*i.e.* with increasing nuclearity of the cluster) intramolecular steric (nonbonding) interactions become important and contribute to determine the total reorientational barrier to the motion in the solid state. Thus, for example, the reorientational barrier in $H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_6)$ increases to 36.0 kJ mol^{-1}, while in solid $Ru_6C(CO)_{11}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(\eta^6\text{-}C_6H_6)$ reorientation of the two benzene ligands requires 11.7 and 20.5 kJ mol^{-1} for the η^6-benzene and the μ_3-benzene, respectively.

In general, given that ligand-to-cluster bonding interactions are substantially delocalized in nature, the ease with which reorientation may occur is essentially a function of the *shape* of the fragment, *viz.* disklike benzene (but also cyclopentadienyl, hexamethylbenzene ligands, *etc.*) are always able to reorientate in any crystal lattice. On the contrary, when the fragments are less regular and present side arms and cavities (*viz.* toluene or mesitylene) the intermolecular assembly is able to lock in the fragment and thereby prevent full rotational freedom. Thus ligand reorientation in solid $H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_5Me)$, $H_2Os_4(CO)_{10}(\eta^6\text{-}C_6H_4Me_2)$, and $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)$ has been shown to be prevented by the high potential barriers due to both intramolecular and intermolecular interlocking.[48]

Additional information on the dynamic behavior of atoms and molecules in the solid state can be obtained by studying how the atoms behave in their displacement motion about equilibrium positions.[104] This can be done, when diffraction data of reasonable quality are available, by means of thermal motion analysis.[105] $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ represents a good example of the application of thermal motion analysis to transition metal clusters.[33] It has been shown that the molecule behaves as a rigid body in its motion about equilibrium only in first approximation, since both benzene and CO groups have appreciable additional motion with respect to the metal frame. Both rigid body and additional motions increase with temperature, although the librational freedom of benzene around the idealized molecular 3-fold axis is larger than that of the equatorial CO's. The additional motion of the O atoms is larger than that of the C atoms belonging to the CO ligands, this indicating that some bending motion of the Ru—O axes is convoluted in the observed ADP.

VI. Relevance to Chemisorbed Benzene

Continued interest in the chemistry of transition metal cluster complexes is in part due to the proposition that these discrete, molecular compounds may be reasonable models of metal surfaces in the processes of chemisorption and catalysis.[106] The use of discrete metal cluster complexes as models of chemisorption systems in surface chemistry is an attractive hypothesis, then, and has been emphasized by Muetterties and others.[106,110] Here we examine possible boundary conditions to such a cluster—surface analogy.

Heterogeneous catalysis forms the basis of many industrially important chemical processes, yet our understanding of the associated surface chemistry is generally poorly developed at a molecular level.[109] Structural characterization of the chemisorbed state represents a formidable challenge, as the physical techniques of X-ray diffraction and NMR spectroscopy, used routinely by molecular chemists to define the essential stereochemical features of a molecule, are not generally applicable to these heterogeneous systems. Low-energy electron diffraction (LEED), angle-resolved UV photoelectron spectroscopy (ARUPS), high-resolution electron energy loss spectroscopy (HREELS), and Auger electron spectroscopy (AES) are among the techniques employed by surface scientists to define the crystallography of chemisorbed atoms and molecules on extended surfaces.[108] These methods do not offer the precision available in molecular structural analysis however, and the experimental and theoretical details of their implementation are by no means trivial.

Advances in the dynamical theory of low-energy electron diffractin (LEED) by ordered adsorbate overlayers has led to the structural characterization of several metal surface—benzene complexes by Somorjai, Van Hove, and coworkers.[110] The technique relies on the fitting of calculated diffraction intensities to the experimental data set and differs fundamentally from the X-ray diffraction method in that the "correct" structure must initially be anticipated. Optimized structures of the surface complexes Rh(111)-(3×3)-C_6H_6+2CO (a), Rh(111-c[$2(3)^{1/2}\times4$]rect-C_6H_6+CO (b), Rh(111)-[$2(3)^{1/2}\times3$]rect-2C_6H_6 (c), and Pt(111)-[$2(3)^{1/2}\times4$]rect-2C_6H_6+4CO (d) have been obtained.[109,110] In each overlayer, benzene is chemisorbed intact and lies parallel to the close-packed metal surface. In a and b absorption occurs at a 3-fold site with an expanded C_6 ring showing in-plane Kekulé distortions: C—C bond distances alternate between 1.46(15) and 1.58(15) Å in a and between 1.31(15) and 1.81(15) Å in b, the short bonds lying above single metal atoms while the long C—C bonds form bridges linking pairs of metal atoms.[110] Although the CO-free structure c has not been analyzed in detail the principal features are known; the superlattice contains two benzene molecules per unit cell occupying 2-fold bridging sites. Bridge site occupancy has been substantiated in the ordered Pt(111) structure d, with the suggested distortion in molecular symmetry to C_{2v}. CO site symmetry for the CO—adsorbate systems parallels the benzene orientation in each case.

The metal skeletons of high nuclearity carbonyl cluster compounds are frequently structurally comparable to fragments of bulk metallic lattices: e.g. $[Rh_{13}(CO)_{24}H_3]^{2-}$,[111a] $[Os_{10}C(CO)_{24}]^{2-}$,[111b] and $[Rh_{14}(CO)_{25}]^{4-}$ [111c] may be recognized as fragments of hexagonal close-packed, cubic close-packed and body-centered cubic structures, respectively. Smaller carbonyl clusters are typically deltahedra and their metal core configurations may be regarded as microscopic fragments of a (hypothetical) close-packed lattice. The role of the ligand sphere in stabilizing these bulklike geometries should be appreciated however, since 5-fold symmetry is commonly observed for small, "naked" crystallites in preference to the 6-fold symmetry of close-packed structures of the bulk metal.

Structural comparisons between the chemisorbed state and metal clusters have been made when there is correspondence in the metal, ligands, ligand coverage of the cluster or surface, and the crystallography. Detailed structural analysis of the gas—metal interface is currently only feasible at metal crystals having well-defined flat surfaces. For chemisorption on these low Miller index surface planes, the metal—ligand and metal—metal connectivity is respectively smaller and larger than for the clusters, although on higher planes the metal coordination number decrease at irregular features such as step and kink sites and the crystallography approaches that of certain cluster species.

In the limiting case, the single-crystal metallic surface may be regarded as being composed of approximately close-packed planar arrays of spheres extending infinitely in two dimensions. A consequence of this long-range periodicity is that the local atomic and electronic structure will be influenced by more distant atoms in both the surface and the bulk of the metal. There is a fundamental caveat, then, to any analogy between cluster species and the bulk metallic interface, since any collective electronic and structural phenomena characteristic of the latter state may have no counterparts among discrete molecular systems. Modeling adsorption processes via small clusters invokes a localization of the adsorbate—adsorbent interaction, and we shall see that, depending on the criteria by which the relationship is assessed, the limitations imposed by this constraint may or may not lead to a breakdown of the analogy.

The scheme of the preceding discussion has been one of cautious assent for a cluster—surface analogy based on localized bonding descriptions of the cluster—ligand, surface—adsorbate interactions. A comparison of reactivity patterns for clusters and surfaces represents, perhaps, the most stringent test of the analogy, and it is here that the correspondence is poorest. The catalytic properties of these systems are vastly different implying that the spatial extent of bonding is not the salient characteristic determining the chemistry of surfaces. There is a growing body of evidence that the dissociative adsorption essential to heterogeneous catalysis occurs at "ensembles" of free metal atoms, readily provided by the coordinatively flexible metal surface. The required substrate binding sites are not available in coordinatively saturated cluster complexes (analogous to saturation coverage of a surface) and ligand dissociation is typically accompanied by structural reorganization or cluster breakdown.

Fundamental to our understanding of the bonding of arenes to clusters, small metal particles or indeed the bulk metallic lattice is an appreciation of the way in which the bonding arrangement of the arene moiety varies as the nature of the metal substrate undergoes change in size and in structure. Such considerations must be concerned mainly with bonding modes other than the more commonly observed η^6 arrangement, but even here variations are to be expected. As shown in this article the η^6-bonding mode has been observed in clusters of metal atoms with a range of different (metal−metal) connectivities. This is clearly exemplified by the derivatives $Ru_5C(CO)_{13}(\eta^6\text{-}C_6H_6)$ (connectivity two), $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ (basal; connectivity three), and $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$ (apical; connectivity four). There is no good reason for supposing that the cluster−arene interaction will remain constant (*i.e.* similar bond energy or geometry) in each situation, and a knowledge of such possible variations is important if we are to more fully appreciate the phenomena on a surface.

For the μ_3-bonding mode, interaction with three metal atoms obviously remains constant. Here the concern is with the role of the additional metal atoms in affecting the nature of the μ_3 interaction. As discussed above, the benzene ring in a hollow site of coordination is expanded and exhibits in plane Kekulé distortions. In the surface complexes $Rh(111)\text{-}(3\times3)\text{-}C_6H_6{+}2CO$, C−C bond distances alternate between 1.31(15) and 1.81(15) Å.[110] These features are remarkably similar to those shown by benzene in μ_3-bonding mode although there are differences in the extent of localization. It is interesting to note that the difference between "long" and "short" bonds is *ca.* 0.04 Å in $Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$. This difference increases to 0.08 Å in $Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$, becoming *ca.* 0.09 Å in the hexaruthenium clusters carrying facial benzenes. Although these observations are confined to a limited number of cases and the differences close to experimental errors, there is a clear trend showing that, as the nuclearity increases, the Kekulé distortion in the ring increases accordingly.

In general, on coordination, arenes adopt a bonding mode in which the C−H vector points away from the cluster surface. In valence bond language this corresponds to a change from carbon sp^2 toward sp^3 hybridization on combination with the metal center. However, such observations are usually made in relation to low oxidation state metal systems. Examples are known where the reverse is observed.[112] Even with low oxidation state metal clusters, *e.g.* $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$ cleavage of a C−H bond can be brought about, in this case by selective irradiation, implying that at some stage a strong metal−H interaction must be induced. We must therefore keep an open mind about the interaction of arenes with clusters and particles and plan ahead a full and detailed study of a multitude of systems embracing not only different structural types and molecularities, but also different metals and combinations of metals throughout the transition series. In this connection it is important to recognize that most studies have been preoccupied with the late, heavier transition metals. Studies of the earlier transition metals would be of significant interest.

VII. Conclusions

We have shown in this review article that, after a rather slow start in the early 1960s, the chemistry of arene carbonyl clusters is now being studied extensively. With the combined efforts of synthesis and spectroscopic investigations in solution and the solid state, as well as of crystallographic studies, entire new *families* of complexes have been characterized to the extent that arene clusters constitute by themselves a new class of organometallic compounds. The study of this field of research has involved the development of a whole host of specialized synthetic techniques targeting such compounds. Early preparations of arene clusters usually involved the direct reaction of a cluster with an appropriate arene under thermal conditions. New techniques are much more selective and can be divided into two general categories. These being preparations which involve direct reaction with arenes, and employ reaction with activated species, or arene−metalla fragments which undergo condensation under a variety of conditions. Secondly, indirect methods which involve the initial coordination of molecules such as hexatriene or cyclohexadiene which are then modified chemically to yield a coordinated arene. Nucleophilic addition, the prime reaction of mononuclear arene species, seems to dominate also in clusters, even with the μ_3 bonded arenes. Arene exchange phenomena, although well established in mononuclear complexes, are rare in cluster systems.

The nuclearity of the clusters so far isolated ranges between three and eight. These clusters may bear one or more arene ligands bound in essentially two coordination geometries, namely the apical bonding mode (η^6 coordination), in which the carbon atoms of the arene ring interact with a single metal center, and the facial bonding mode ($\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ coordination) in which benzene interacts with three metal atoms forming a triangle. In this latter coordination geometry the midpoints of alternating C−C bonds around the ring are usually eclipsed, or very nearly so, with the metal atoms.

Most arene clusters have been characterized by single-crystal X-ray diffraction experiments in the solid state. The molecular structures of these complexes present some intriguing aspects arising from the availability of different coordination sites on the metal framework as well as from the different bonding modes available to the arene ligands. This gives rise to the presence of structural isomers which differ in site and type of coordination. In square-pyramidal pentaruthenium arene clusters, for instance, the arene can bind either apically, to one of the four basal atoms of the cluster, or to its vertex, facial bonding is also possible on one of the cluster triangular faces. Similar isomerism is possible in hexanuclear octahedral clusters. The number of possible isomers increases when more than one arene is coordinated. In ruthenium clusters of nuclearity three, five, and six, as well as in trinuclear osmium clusters, interconversion between isomers can be induced both chemically and thermally.

It has also been shown that the molecular organization in the *crystal structure* of arene cluster complexes results from a complex optimization of the interlocking of the flat arene fragments with the other ligands present on the cluster surface, *viz.* carbon monoxide in terminal or bridging bonding geometry. In general, preferential arene–arene interactions of the graphitic type are established in crystals of bis(arene) derivatives while mono(arene) derivatives form ribbons in the so called "herringbone" pattern. These studies have afforded insights into the "cluster–surface" analogy, related to the interaction of specific fragments with metal surfaces. The molecular chemistry of clusters containing benzene in the facial mode has provided model systems for the interaction of arene molecules with metallic surfaces. New insight into chemisorption phenomena has been provided in keeping with early suggestions that metal clusters could represent a bridge between material and molecular chemistry.

Molecular size and shape not only dictate how the crystal is organized but also are intimately related to the occurrence of dynamic phenomena in the solid state. This is particularly important in organometallic chemistry because many unsaturated ligands are able to bound to metal centers in a delocalized manner, the absence of well-defined conformational minima for the ligands being responsible for the occurrence of low-energy reorientational processes both in solution and the solid state. Reorientational processes in the solid state have been assessed by NMR spectroscopy and substantiated by empirical potential barrier calculations. It has been pointed out, in this review, that organic fragments bound in delocalized manner in mononuclear and polynuclear complexes undergo reorientational motion in the solid state irrespective of the mode of coordination. The great variety of arene fragments employed in the most recent studies (from toluene, to xylene, to mesitylene, to paracyclophanes, *etc.*) allows a deeper understanding of the factors controlling the intermolecular interlocking and the ease of reorientational motion in the solid state.

VIII. Abbreviations

AAPEBC	atom–atom potential energy barrier calculations
ADP	anisotropic displacement parameters
AE	activation energy
Cp	cyclopentadienyl (C_5H_5)
CPMAS	^{13}C cross-polarization magic-angle spinning NMR
CSA	chemical shift anisotropy
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
Me_3NO	trimethylamine *N*-oxide
PB	potential barrier
thf	tetrahydrofuran
VTNMR	variable-temperature NMR spectroscopy

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X. References

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