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## Invited Lecture

# Arene-cluster compounds *

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### Abstract

The synthesis and full characterization of a wide and diverse range of arene-clusters based on $M_3$, $M_4$, $M_5$ and $M_6$ metal-cluster units are described and their relevance to the chemisorption of arenes on to a metal surface is critically reviewed. Emphasis is placed on the cluster-sandwich compounds which are clearly related to Fischer's classic example bis(benzene)chromium. The molecular organization in crystals of a variety of arene clusters has been investigated and good evidence for substantial intermolecular interaction between adjacent arene moieties established. More recent studies of the interaction of a range of larger polycyclic systems with similar cluster precursors are also described, as are attempts to provide suitable monomeric arene-cluster subtrates for polymer formation. Finally, attempts to produce $Os_3(CO)_6(\mu_3\text{-}C_6H_6)_2$, an attractive analogue of $Cr(C_6H_6)_2$, are reported.

*Key words:* Chromium; Osmium; Cluster; Arene; π-Complexes

## 1. Introduction

The primary motivation for this account came from the seminal work of Professor E.O. Fischer and his group in Munich and their pioneering studies which led to the preparation of the classic sandwich molecule bis(benzene)chromium (Fig. 1) [1].

In our work we have devoted much effort to the synthesis of cluster analogues of this beautiful compound. We have also been influenced by the interest shown in the chemistry of transition metal cluster compounds and the proposition that they may, at least in part, be reasonable models of metal surfaces in the processes of chemisorption and catalysis. The use of discrete metal cluster complexes as models of chemisorption systems in surface chemistry is an attractive hypothesis [2–11] and we have found that this is especially true for the arene-cluster compounds recently prepared in our laboratories.

Several years ago, advances in the dynamic theory of low-energy electron diffraction (LEED) by ordered absorbate overlayers led to the structural characterization of several metal surface – benzene complexes by Somorjai and co-workers [12–16]. Optimized structures of the surface complexes $Rh^{III}\text{–}(3 \times 3)\text{–}C_6H_6 + 2CO$ [12], $Rh^{III}\text{–}c\{2(3)^{\frac{1}{2}} \times 4\}rect\text{–}C_6H_6 + CO$ [14], $Rh^{III}\text{–}\{2(3)^{\frac{1}{2}} \times 3\}rect\text{–}2C_6H_6$ [15] and $Pt^{III}\text{-}\{2(3)^{\frac{1}{2}} \times 4\}rect\text{–}2C_6H_6 + 4CO$ [13] are shown in Fig. 2. In each overlayer the benzene is chemisorbed intact and lies parallel to the close-packed metal surface. In **I** and **II**, adsorption occurs at a threefold hcp-type site, with an expanded $C_6$ ring showing in-plane Kekulé distortions; C–C distances alternate between 1.46(15) and 1.58(15) Å in **I** and between 1.31(15) and 1.81(15) Å in **II**, the short bonds lying above metal atoms while the long C–C bonds form bridges linking pairs of metal atoms. In both cases the C–H bond vectors point away from the surface.

In 1985, we described the synthesis and full characterization by single-crystal analysis of the benzene cluster $Os_3(CO)_9(\mu_3 : \eta^2 : \eta^2 : \eta^2\text{-}C_6H_6)$ (**1**) [17] The $\mu_3 : \eta^2 : \eta^2 : \eta^2\text{-}C_6H_6$ ligand in this novel complex bears a striking resemblance to benzene in overlayers **I** and

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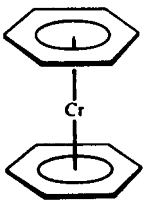
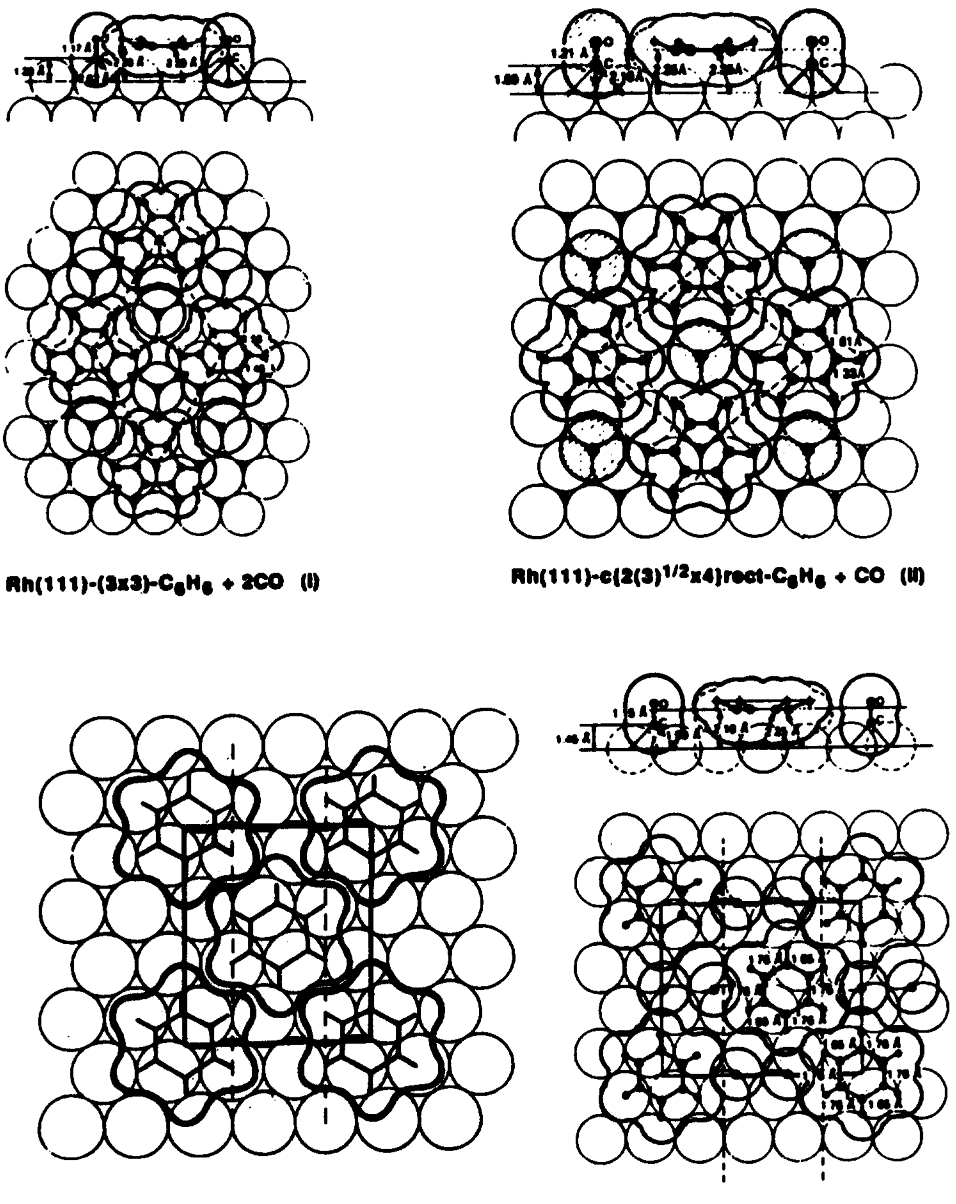
II, symmetrically capping trimetal faces and showing trigonal distortions towards the hypothetical cyclohexa-1,3,5-triene (on average, bond lengths alternate between 1.41(2) and 1.51(2) Å) (Fig. 3). This Kekulé distortion may be traced to an internal mixing of the benzene π-orbitals. Mixing between the highest occupied and the lowest unoccupied benzene π-orbitals is believed to account for small but significant trigonal distortions found in $\eta^6$-arene complexes of chromium [18], molybdenum and tungsten [19].



$Cr(\eta^6\text{-}C_6H_6)_2$

Fig. 1. Molecular structure of bis(benzene)chromium.



$Rh(111)\text{-}(3x3)\text{-}C_6H_6 + 2CO$ (I)

$Rh(111)\text{-}c(2(3)^{1/2}x4)rect\text{-}C_6H_6 + CO$ (II)

$Rh(111)\text{-}(2(3)^{1/2}x3)rect\text{-}2C_6H_6$ (III)

$Pt(111)\text{-}(2(3)^{1/2}x4)rect\text{-}2C_6H_6 + 4CO$ (IV)

Fig. 2. LEED structures of metal surface–benzene adsorbate complexes.

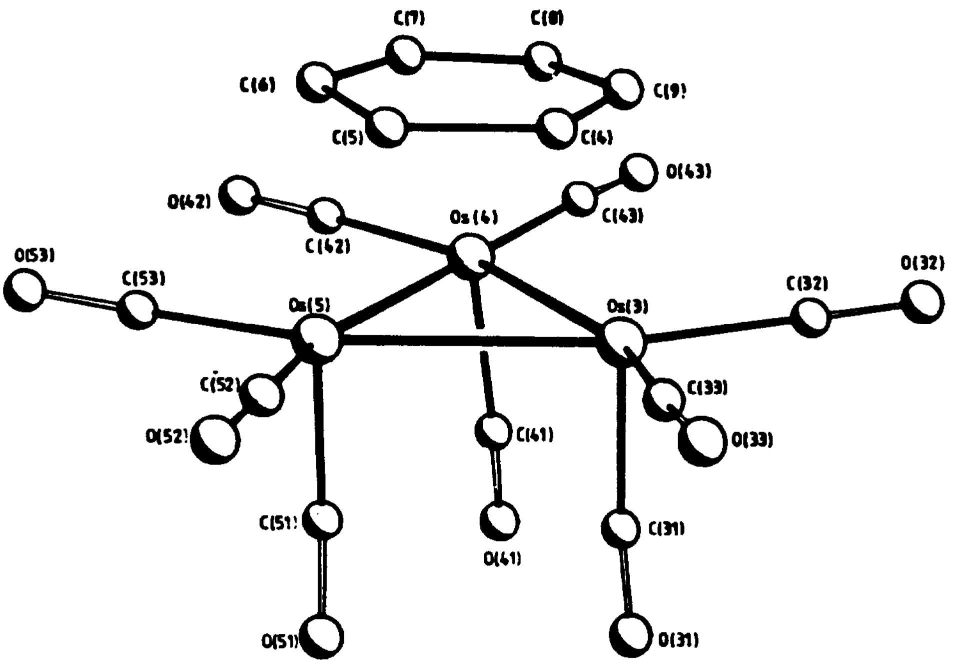


Fig. 3. Molecular structure of 1.

More recently, we have prepared the ruthenium analogue $Ru_3(CO)_9(\mu^3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ from the reaction of $Ru_3(CO)_{12}$ with $C_6H_8$ in the presence of the $Me_3NO$. For this compound better data were obtained from the single-crystal X-ray diffraction analysis and the aromatic H-atoms located. Significantly, in this case the benzene ring shows significant Kekulé distortion and the C–H vectors are observed to bend away from the $Ru_3$ triangle in total accord with the Somorjai viewpoint.

## 2. Substitution chemistry of $[Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$: synthesis and reactivity of $[Os_3(CO)_8(NCMe)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$

The formal triene-like representation of the face-capping ligand in $[Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (1) belies the remarkable robustness of this complex and harsh reaction conditions are typically required for arene displacement. The carbonyl substitution chemistry of 1 resembles that of the parent dodecacarbonyl $[Os_3(CO)_{12}]$ [20,21] with its thermally promoted reactions proceeding rather inefficiently and with low selectivity. Oxidative decarbonylation by trimethylamine *N*-oxide has been used extensively in the activation of the latter complex towards CO substitution; nucleophilic activation in the presence of weak-field ligand MeCN affords the labile derivatives $[Os_3(CO)_{11}(MeCN)]$ and $[Os_3(CO)_{10}(MeCN)_2]$ for the synthesis of many triosmium cluster compounds. We have applied this strategy to the derivatization of 1 and to the preparation of $[Os_3(CO)_8(NCMe)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (2).

## 3. Characterization of $[Os_3(CO)_8(NCMe)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$

Reaction of equimolar quantities of 1 and anhydrous $Me_3NO$ in acetonitrile affords the deep yellow complex $[Os_3(CO)_8(NCMe)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ as two isomers with either equatorial or axial MeCN in high yield. $^1H$ NMR spectroscopy confirms the formulation of this product and indicates high lability for the nitrile ligand: at 295 K, in $CD_3CN$ solution a broad singlet resonance at $\delta$ 4.34 is assigned to the fluxional $\mu_3$-benzene ligand, while a singlet at $\delta$ 1.97 is attributed to free MeCN, displaced from the cluster by exchange with the solvent. On recording the spectrum of a solution of 2 prepared at 195 K in the mixed solvent system $CD_2Cl_2$–$CD_3CN$ (10:1), three broadened singlets ($\delta$ 4.06, 3.94 and 3.68) attributed to the ring protons of the minor, equatorially substituted isomer 2 are observed (195 K) in addition to the single broad resonance ($\delta$ 4.4) of the major axially substituted **2a** (integrated intensities 1:5). Resonances at $\delta$ 2.80 and $\delta$ 2.33 for the minor and major isomers, respectively, rapidly lose intensity on warming to room temperature, being replaced by a sharp singlet at $\delta$ 1.97, consistent with the facile displacement of coordinated MeCN by deuterated donor molecules of the solvent. Evidently the barrier to benzene rotation is larger in **2b** (note that at 195 K the $^1$H spectrum more closely approaches the slow-exchange limit) and, interestingly, the rate of ligand exchange for this isomer is greater than for the axially substituted derivative **2a**. Intramolecular steric interactions may be the basis for both effects here.

## 4. Substitution by phosphorus donor ligands

Monophosphine and phosphite derivatives of the face-capping benzene cluster **1** are formed as single isomers in virtually quantitative yields from room-temperature substitution reactions of **2**. Phosphine substi-

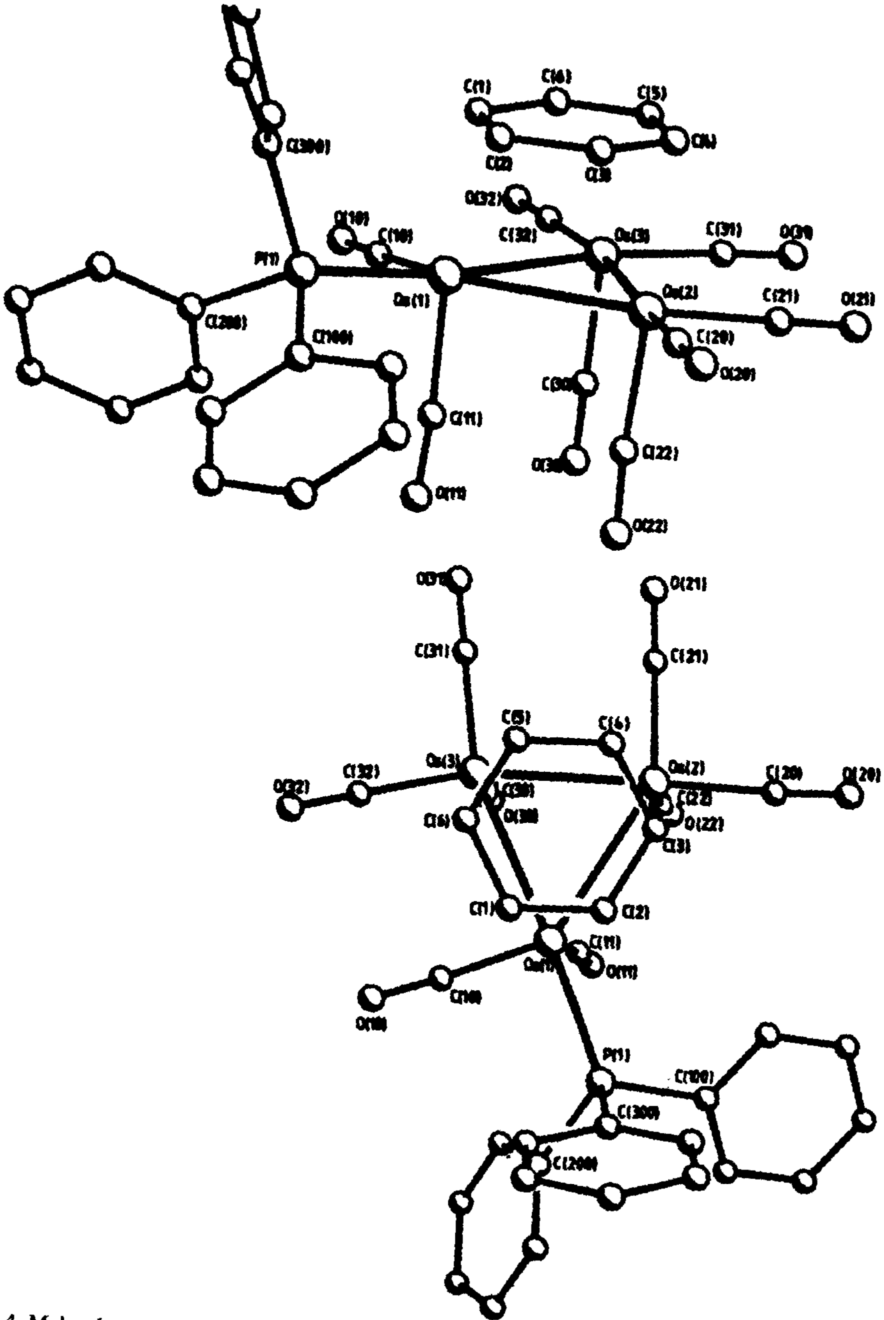


Fig. 4. Molecular structure of [$Os_3(CO)_8(PPh_3)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$].

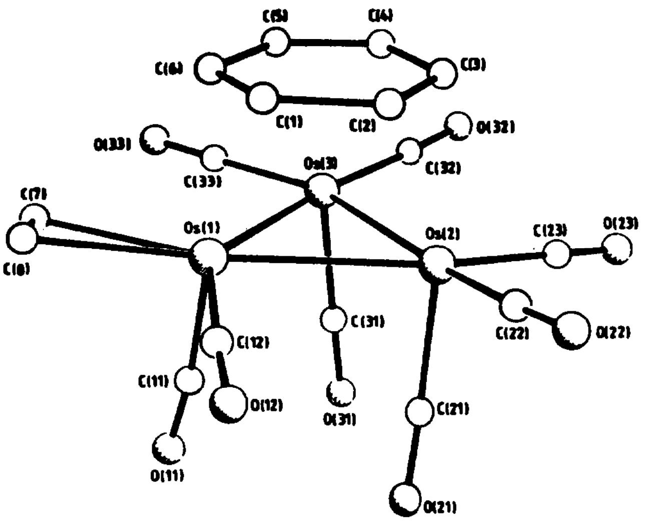
tution for CO in $[Os_3(CO)_{12}]$ invariably occurs at an equatorial site [21,22] and a single-crystal X-ray diffraction study reveals equatorial coordination of triphenylphosphine in the $\mu_3$-benzene complex $[Os_3(CO)_8(PPh_3)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (**3**). The molecular structure of **3** is shown in Fig. 4 together with some relevant metrical parameters.

## 5. Substitution by $\pi$-alkene ligands

$\eta^2$-Alkene–triosmium complexes are not widely encountered since the $\pi$-bound alkenes are typically labile and/or susceptible to oxidative-addition reactions [21,23]. $\eta^2$-Ethylene [24], fluoroalkene [25,26] and chelating vinyl acetate [27] ligands have previously been crystallographically characterized in $Os_3$ systems and in every case the olefin ligand occupies an equatorial coordination site and is approximately coplanar with the $Os_3$ triangle.

The MeCN ligand in **2** is easily substituted by simple olefins in high-yielding reactions to afford $\eta^2$-alkene complexes that retain the face-capping benzene ligand. Specifically, we have characterized the olefin–triosmium complexes $[Os_3(CO)_8(\eta^2\text{-}CH_2CHR)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (R = H, Me, Ph, ${}^tBu$, F and $CH{=}CH_2$) through extensive $^1H$ and $^{13}C$ NMR studies, and for the $\pi$-ethylene complex a single-crystal X-ray analysis has been undertaken [28].

The molecular structure is shown in Fig. 5, together with some important bond parameters [29]. The structure is derived from that of **1** with an equatorial carbonyl ligand on one metal atom being replaced by a $\pi$-bound ethylene ligand. The $C_6$ ring is strictly planar and lies parallel to the metal triangle (tilt angle 0.8°) at a distance of 2.17 Å above the plane. Although the high estimated standard deviations associated with the C–C distances preclude an accurate assessment of the bonding within the ring, the apparent bond length alternation is again consistent with the Kekulé-type distortion of the benzene ligand. Mean "coordinated" and "non-coordinated" C–C bond lengths of 1.41(3) and 1.46(3) Å may be compared with the corresponding distances of 1.41 and 1.51 Å in the parent complex. The ethylene group is symmetrically coordinated and is displaced slightly from the $Os_3$ plane towards the benzene ligand (deviations: C(7) = 0.18 Å, C(8) = 0.46 Å). The C(7)–C(8) vector is twisted by 14° with respect to the triosmium plane, minimizing unfavourable interactions between proximal ethylene and benzene protons.



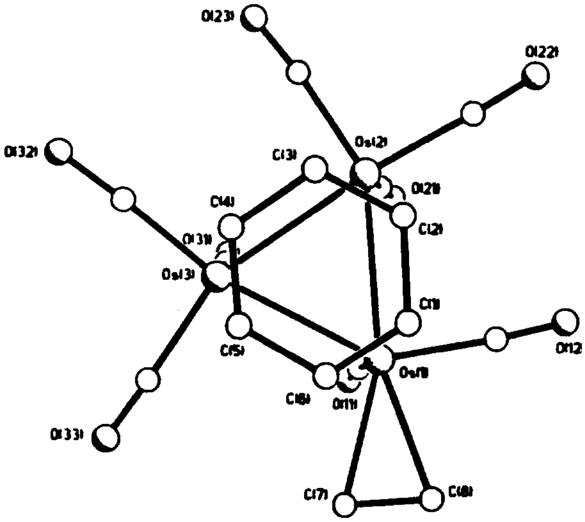


Fig. 5. Molecular structure of $[Os_3(CO)_8(\eta^2\text{-}CH_2{=}CH_2)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$.

We have discovered that stereodynamic processes are associated with both the benzene and olefin ligands in this olefin complex. In particular, the observation of limiting slow exchange $^1H$ and $^{13}C$ NMR spectra for this compound has permitted mechanistic analysis of the fluxionality of the face-capping arene ligand through two-dimensional exchange spectroscopy. The important result is that nuclei of the $\mu_3$-benzene ligand are equilibrated via (1, 2) shifts of the $C_6H_6$ moiety relative to the basal $Os_3$ triangle [30].

It is interesting to compare the stabilities of ethylene complex and the $\pi$-adduct of the parent dodecacarbonyl, *viz.* $[Os_3(CO)_{11}(\eta^2\text{-}CH_2CH_2)]$. Whereas $CH_2Cl_2$ solutions are not appreciably air-sensitive and are thermally stable to 50°C, the compound is highly labile in the absence of external ethylene and is converted on thermolysis into the hydride-vinylidene species $[H_2Os_3(CO)_9(\mu\text{-}CCH_2)]$ [22]. It seems likely that the greater basicity of the $[Os_3(CO)_8(C_6H_6)]$ fragment relative to the undecacarbonyl triosmium moiety accounts for this reactivity difference, with more extensive $\pi$-back donation to the olefin ligand in the former complex enhancing the stability of the metal–olefin interaction

## 6. Temperature-dependent NMR spectroscopy of $[Os_3(CO)_8(\eta^2\text{-}CH_2CHR)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$

Variable-temperature $^1H$ and $^{13}C$ NMR studies on several face-capping arene–triosmium-cluster complexes illustrate that the $\mu_3$-ligands in these compounds are characteristically fluxional. In the neutral complexes $[Os_3(CO)_8(L)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (L = NCMe, py, $PR_3$), the barrier to benzene rotation is sufficiently low as to preclude the observations of limiting, static solution spectra, whereas for the dihydride complex $[H_2Os_3(CO)_8(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ and the cluster cation $[HOs_3(CO)_8(L)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)][BF_4]$ (L = CO, $PR_3$), slow exchange spectra may be observed below 200 K. We have examined the temperature dependence of the $^1H$ NMR spectra of the $\pi$-olefin derivatives $[Os_3(CO)_8(\eta^2\text{-}CH_2CHR)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (R = H, Me, Ph and $^t$Bu) and found that in every case limiting spectra can be obtained by *ca.* 180 K.

At ambient temperature the six inequivalent ring protons in each of these complexes see time-averaged environments, showing broadened singlet resonances at *ca.* 4.0 ppm. Irradiating at the resonance frequency for free benzene ($\delta$ 7.35) in these spectra does not lead to saturation transfer to the coordinated ligand, demonstrating that the equilibrations are strictly intramolecular processes. The four protons in the ethylene derivative show a single resonance at $\delta$ 2.03.

## 7. Photo-induced transformation $\mu_3$-benzene → $\mu_3$-benzene

At 278 K in toluene solution, Pyrex-filtered broadband visible radiation from a 500 W tungsten–halogen lamp for *ca.* 13 h cleanly converts $[Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (**1**) into the isomeric triply-bridging benzyne (*o*-phenylene) cluster $[H_2Os_3(CO)_9(\mu_3:\eta^1:\eta^2:\eta^1\text{-}C_6H_4)]$ in high yield (> 90%).

This benzyne complex has been previously obtained as a product from the reaction of benzene with $[Os_3(CO)_{12}]$ at 463 K [31] or with $[Os(CO)_{10}(NCMe)_2]$ at 363 K and has been structurally characterized by single-crystal X-ray diffraction [32]. The benzyne ligand is planar and inclined at an angle of *ca.* 65° to the osmium triangle, with no significant variations in the C–C bond distances being observed. The $C_6H_4$ fragment serves formally as a four-electron donor to the cluster, forming $\sigma$-bonds to two Os atoms and a $\pi$-interaction with the third osmium. Although not directly located, the positions of the hydride ligands have been inferred from the distribution of the carbonyl groups.

Benzyne ligands are commonly found in products of thermolysis of a variety of aryl compounds with triosmium substrates. Thermolysis of $[Os_3(CO)_{11}(PMe_2Ph)]$ gives $[H_2Os_3(CO)_9(\mu\text{-}PMe_2)(\mu_3:\eta^1:\eta^2:\eta^1\text{-}C_6H_4)]$ while $[Os_3(CO)_{10}(PMe_2PH_2)]$ affords $[Os_3(CO)_7(\mu\text{-}PMe_2)_2(\mu_3:\eta^1:\eta^2:\eta^1\text{-}C_6H_4)]$ as the major product. Related triply-bridging aryne clusters have been prepared from $PPh_3$, $AsMe_2Ph$, PEtPh and MeSPh.

We find that appropriate derivatives of **1** also undergo photoisomerization to give new $\mu_3\text{-}C_6H_4$ complexes. While reaction of the olefin compounds $[Os_3(CO)_8(\eta^2\text{-}CH_2CHR)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (R = H, Ph) is largely frustrated by photo-decomposition pathways (presumably via loss of the relatively labile olefin ligands), virtually quantitative conversions of the phosphine and phosphite derivatives $[(Os_3(CO)_8(PR_3)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (R = Ph, OMe) and $Os_3(CO)_7(PPh_3)_2(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ are achieved under broad-band visible photolysis in toluene at 278 K. Markedly enhanced photo-reaction rates are observed with increasing phosphine substitution.

Photoisomerization of these complexes affords benzyne complexes $[H_2Os_3(CO)_8(PR_3)(\mu_3:\eta^1:\eta^2:\eta^1\text{-}C_6H_4)]$ (R = Ph, OMe), each as two chromatographically inseparable, interconvertible isomers that have been characterized by $^1H$, $^{13}C$ and $^{31}P$ NMR spectroscopy.

## 8. Thermal conversion $\mu_3$-benzene → $\mu_3$-benzyne

Prolonged thermolysis in toluene solution at 388 K converts the $\mu_3$-benzene complexes $[Os_3(CO)_{9-n}(PPh_3)_n(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ ($n$ = 0, 1, 2) into the corresponding $\mu_3$-benzyne compounds $[H_2Os_3(CO)_{9-n}(PPh_3)_n(\mu_3:\eta^1:\eta^2:\eta^1\text{-}C_6H_4)]$. The rate of intramolecular oxidative-addition increases with phosphine substitution (*i.e.* with increasing electron richness of the cluster). There is no evidence for the reversibility of this isomerization and the dimetallated complexes apparently represent the thermodynamically favoured species here. We now consider some mechanistic aspects of the photo-reaction.

## 9. Mechanism for photo-isomerization

Although a mechanistic study of the $\mu_3$-benzene → $\mu_3$-benzyne conversion is not available, some prelimi-

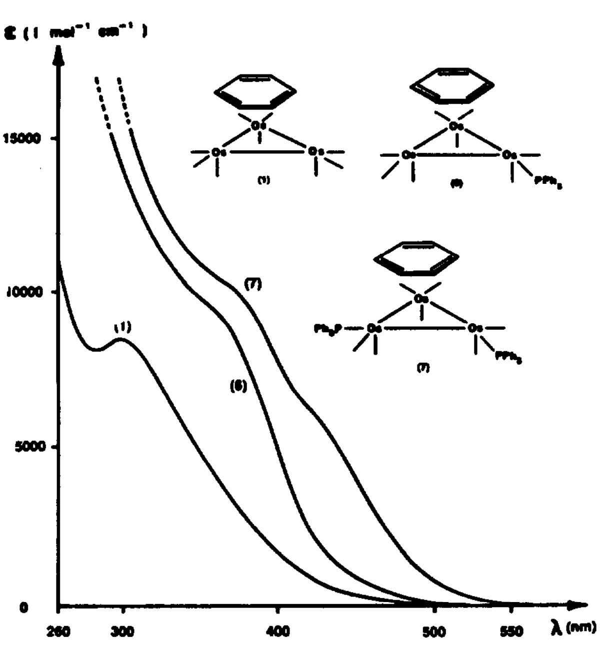


Fig. 6. UV-visible spectra of $[Os_3(CO)_{9-n}(PPh)_n(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$.

nary observations seem relevant to the formation of a speculative description of this photochemistry.

The electronic absorption spectra of the complexes, recorded in cyclohexane solution at 298 K, are shown in Fig. 6. Phosphine substitution leads to a bathochromic shift of the 312 nm absorption maximum in **1**. It is clear from preliminary low-temperature matrix photolysis studies that irradiation in the near-UV-visible range initiates the photoisomerization reaction. Thus, at 20 K in Ar, $CH_4$ and CO matrices, irradiation with $\lambda > 365$ nm yields no net photochemistry whereas $\lambda > 290$ nm gives efficient photoisomerization to the benzyne complex. The observed rate enhancements may reflect a real increase in quantum yield for this reaction on increasing substitution of $PPh_3$ for CO. There are several candidates for the primary activation process.

### *9.1. Radical initiation*

Homolysis of an Os–Os bond in **1** (and its derivatives), insertion of the diradical into two C–H bonds of the $\mu_3$-benzene ligand and subsequent rearrangement could generate the benzene fragment.

Decomposition of a triplet excited state by insertion reactions of a ligand-centred radical intermediate might also be a feasible process here (compare the Cr → $C_6H_6$ transition responsible for the radical-initiated photodecomposition of $\eta^6\text{-}C_6H_6Cr(CO)_3$).

### *9.2. Activation via CO dissociation*

Photo-induced dissociative carbonyl ligand loss is an important primary photoprocess. Activation of a benzene C–H bond by an electron-deficient species formed through rate-determining CO loss from **1** should be strongly inhibited by external carbon monoxide. We find that visible photolysis of **1** in toluene (standard conditions) in the presence of CO (1 atm) affords the benzene derivative (*ca.* 80% yield) and $Os_3(CO)_{12}$ (*ca.* 5%) through displacement of $C_6H_6$. While the concentration of dissolved CO in this inhibition experiment is undoubtedly rather low, it seems unlikely that dissociative CO loss is directly relevant to this photochemistry.

### *9.3. "Non-dissociative" activation*

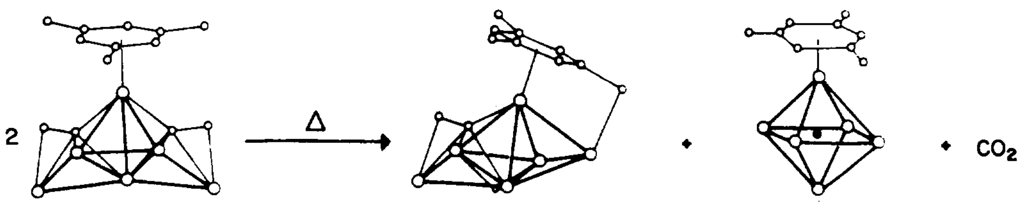
Ring slippage of monometallic $\eta^6$-arene complexes is thought to play an important role in arene-exchange reactions of these compounds, viz.,

$$\eta^6\text{-arene-M} \rightleftharpoons \eta^2\text{-arene-M}$$

A related transformation of **1** could be a plausible elementary step in its photoisomerization, creating a metal-centered vacancy, with metallation and subsequent rearrangement.

### *9.4. Reaction of $Ru_3(CO)_{12}$ with arenes*

In contrast to $Os_3(CO)_{12}$ or $Os_3(CO)_{10}(MeCN)_2$, the reaction of either $Ru_3(CO)_{12}$ or $Ru_3(CO)_{10}(MeCN)_2$ with arenes produces the carbido-hexaruthenium clusters $Ru_6C(CO)_{14}(arene)$ (arene = $C_6H_6$, $C_6H_5Me$, $C_6H_4Me_2$ or $C_6H_3Me_3$) [33,34]. In the case of the mesitylene derivative the $\eta^6$-coordination mode was soon afterwards established by single-crystal X-ray analysis [35]. The source of the carbido atom was established as CO and in subsequent studies we were



$[Ru_6(CO)_{15}(C_6H_3Me_3)]$ $[HRu_6(CO)_{14}(C_6H_3Me_2CH_2)]$ $[Ru_6C(CO)_{14}(C_6H_3Me_3)]$

Scheme 1. Products of the reaction of $Ru_3(CO)_{12}$ with $C_6H_3Me_3$.

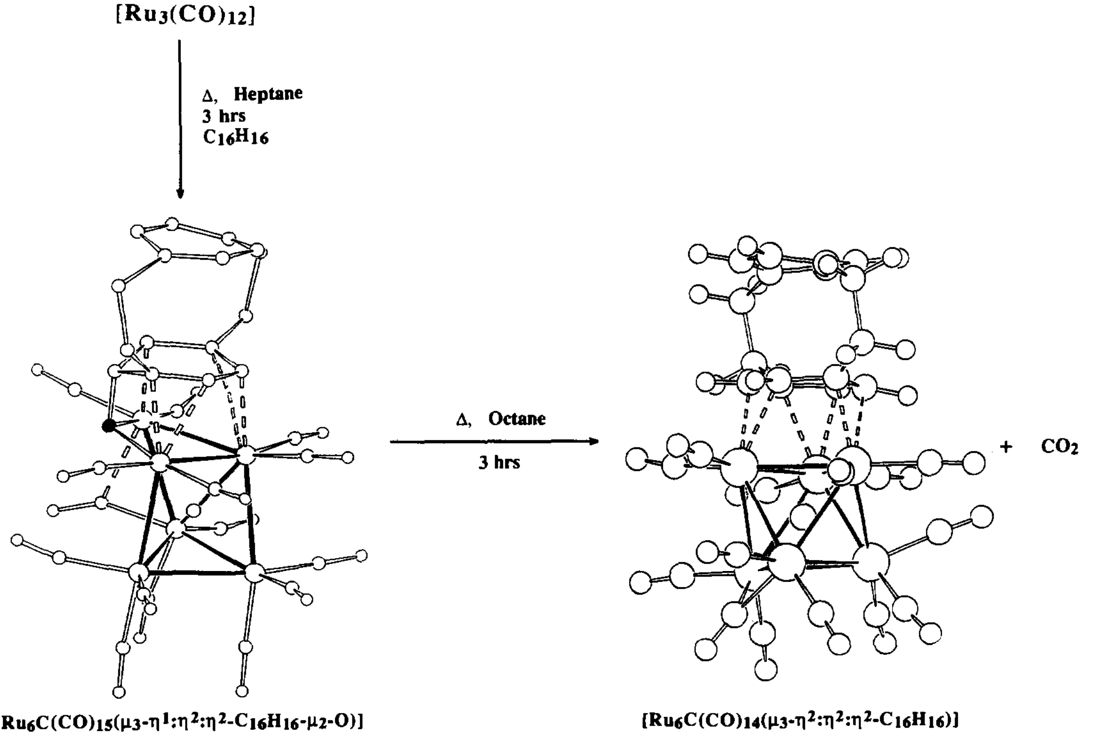
able to isolate a series of intermediate complexes which shed a fascinating light on the overall course of the reaction [36]. This sequence is illustrated in Scheme 1.

The reaction of $Ru_3(CO)_{12}$ was monitored and we observed that the previously isolated cluster $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3)$ was formed, together with the two additional compounds $Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3)$ and $HRu_6(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\mu_2\text{-}\eta^7\text{-}C_6H_3Me_2CH_2)$. In the former the metal complex corresponds to a $Ru_4$ tetrahedron with two edge-bridging Ru units. The mesitylene ligand adopts the conventional $\eta^6$-bonding mode on the apical atom of the $Ru_4$ tetrahedron and the two "butterfly" $Ru_4$ arrangements support a CO ligand bonded through both the C and O atoms, thereby generating a substantially weakened ligand C–O linkage. On heating, this complex undergoes transformation to the established carbido derivatives, $Ru_6C(CO)_{14}(\eta_6\text{-}C_6H_3Me_3)$, thereby illustrating that it is an intermediate compound on route to the formation of the carbido atom.

Very recently we have examined [36] the reaction of paracyclophane with $Ru_3(CO)_{12}$. Our objective was to produce derivatives of the type $Ru_3(CO)_9(C_6H_4(CH_2)_2C_6H_4)$ which would serve as precursors to polymeric materials with $Ru_3$ clusters spanned by the cyclophane ligand. In the course of these studies we also prepared the $Ru_6$ derivatives $Ru_6C(CO)_{14}(C_6H_4(CH_2)_2C_6H_4)$ and $Ru_6C(CO)_{15}(C)(O)(C_6H_4(CH_2)_2C_6H_4)$. A single-crystal X-ray structure analysis combined with detailed study of the $^1H$ and $^{13}C$ NMR spectra for samples in solution revealed the structures shown in Scheme 2. Both an "isolated" carbon and oxygen atom have been located in the compound $Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_{16}H_{16}\text{-}\mu_2\text{-}O)]$ and, significantly, the compound undergoes quantitative conversion to $Ru_6C(CO)_{14}(C_6H_4(CH_2)_2C_6H_4)$ on heating, with the evolution of $CO_2$. We believe that these studies clearly identify the reaction pathway involving the cleavage of C–O by cluster rearrangement.

## 10. Synthesis of hexaruthenium bis(arene) clusters

Several years ago we demonstrated that the arene derivatives $Ru_6C(CO)_{14}$(arene) undergo reaction with NaOH–MeOH to generate the dianionic clusters $[Ru_6C(CO)_{13}(\text{arene})]^{2-}$, which undergo subsequent reaction with the arene dication $[Ru(C_6H_6)(MeCN)_3]^{2+}$ to form the bis-arene derivatives $Ru_6C(CO)_{17}(\eta^6\text{-arene})(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$. This reaction was unex-



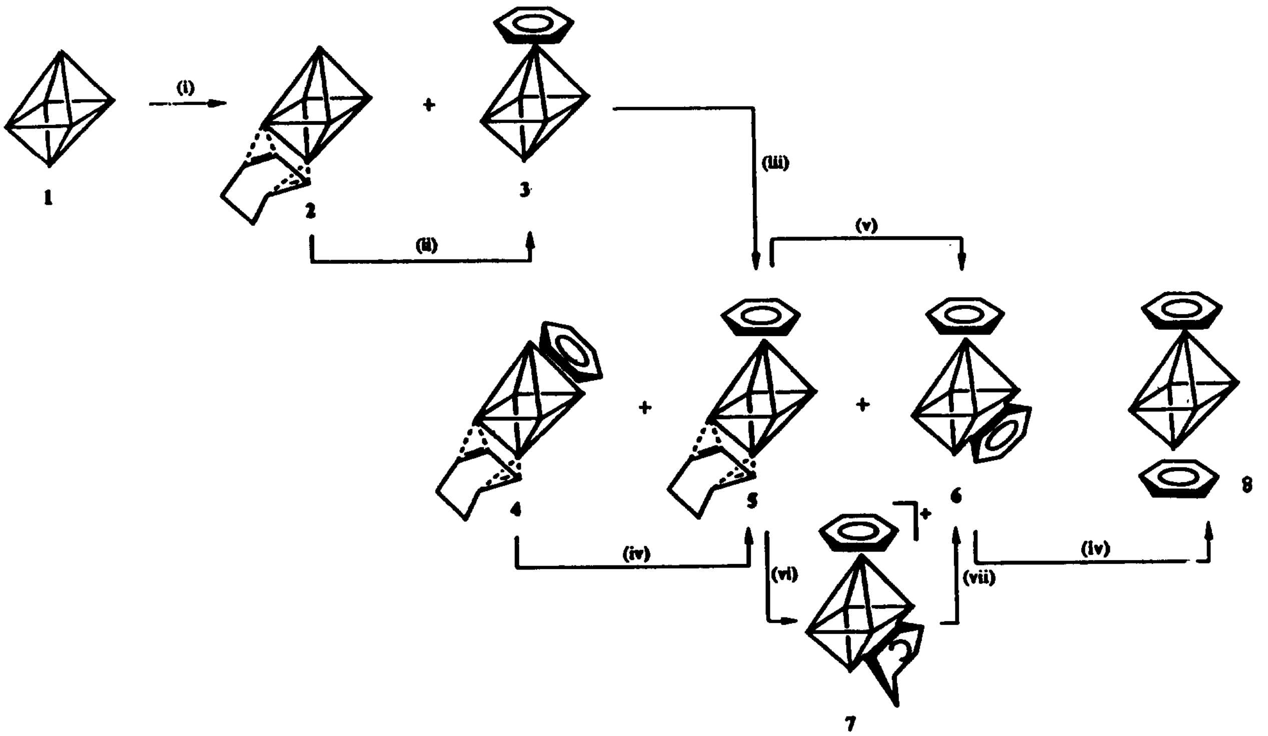
Scheme 2. Reaction of $Ru_3(CO)_{12}$ with cyclophane.

pected since we considered that the combination of these two ionic species would yield a $Ru_7C$ cluster. Lately we have been ivestigating new synthetic routes to these compounds and have devised [37] the novel reaction sequence illustrated in Scheme 3.

Treatment of $Ru_6C(CO)_{14}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)$ with two equivalents of $Me_3NO$ in $CH_2Cl_2$ in the presence of $1,3\text{-}C_6H_8$ yields the mixed arene–diene derivative $Ru_6C(CO)_{12}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(\eta^4\text{-}C_6H_8)$. Further reaction of this cluster with $Me_3NO\text{-}CH_2Cl_2$ produces $Ru_6C(CO)_{12}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$, which on standing is converted into a second isomer $Ru_6C(CO)_{12}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)(\eta^6\text{-}C_6H_6)$. In a similar sequence of reactions a whole matrix of compounds containing $C_6H_6$, $C_6H_5Me$, $C_6H_4Me_2$ and $C_6H_3Me_3$ have been obtained and the method established as completely general. In particular, *trans*-$Ru_6C(CO)_{12}(1,3,5\text{-}C_6H_3Me_3)_2$ and *trans*-$Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)_2$, the first examples of cluster sandwich molecules, have been established by this route. Further, the investigation of the crystal structures of some of these carbonyl–arene clusters has afforded insight into the factors controlling the reorientational motion of the arene fragments in the solid state. In the case of $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ in particular, we have found that the two benzene fragments establish graphitic-like interactions throughout the crystal lattice [38]. In crystalline $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)(\eta^6\text{-}C_6H_6)$ the benzene and mesitylene ligands of one molecule are almost face to face with the benzene and mesitylene ligands belonging to next-neighbouring molecules, as shown in Fig. 7. By these means moleuclar "snakes" are created. The distance between the arene planes is *ca.* 3.6 Å, *i.e.* only slightly longer than in graphite itself. Similar behaviour is noted in the two closely related compounds $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)_2$ (Fig. 7(a)) and $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_3Me_3)_2$ (Fig. 7(b)).

## 11. Bis-substituted 1,3-$C_6H_8$ and $C_6H_6$ derivatives of $Ru_5C(CO)_{15}$

Following essentially the same synthetic approach, a comprehensive range of diene- and arene-substituted derivatives have been prepared. These are shown in Scheme 4. A remarkable feature of these arene derivatives is the range of isomers they show. Thus, all possible coordination sites have been observed for $\eta^6$- and $\mu^3$-bonded benzene in $Ru_5C(CO)_{12}(C_6H_6)$. These rearrangements and interconversions have been monitored by $^1H$ NMR and spectroscopy activation energies calculated. Of significance, $Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)$,



Scheme 3. Reaction of $Ru_6(CO)_{17}$ with cyclohexadiene.

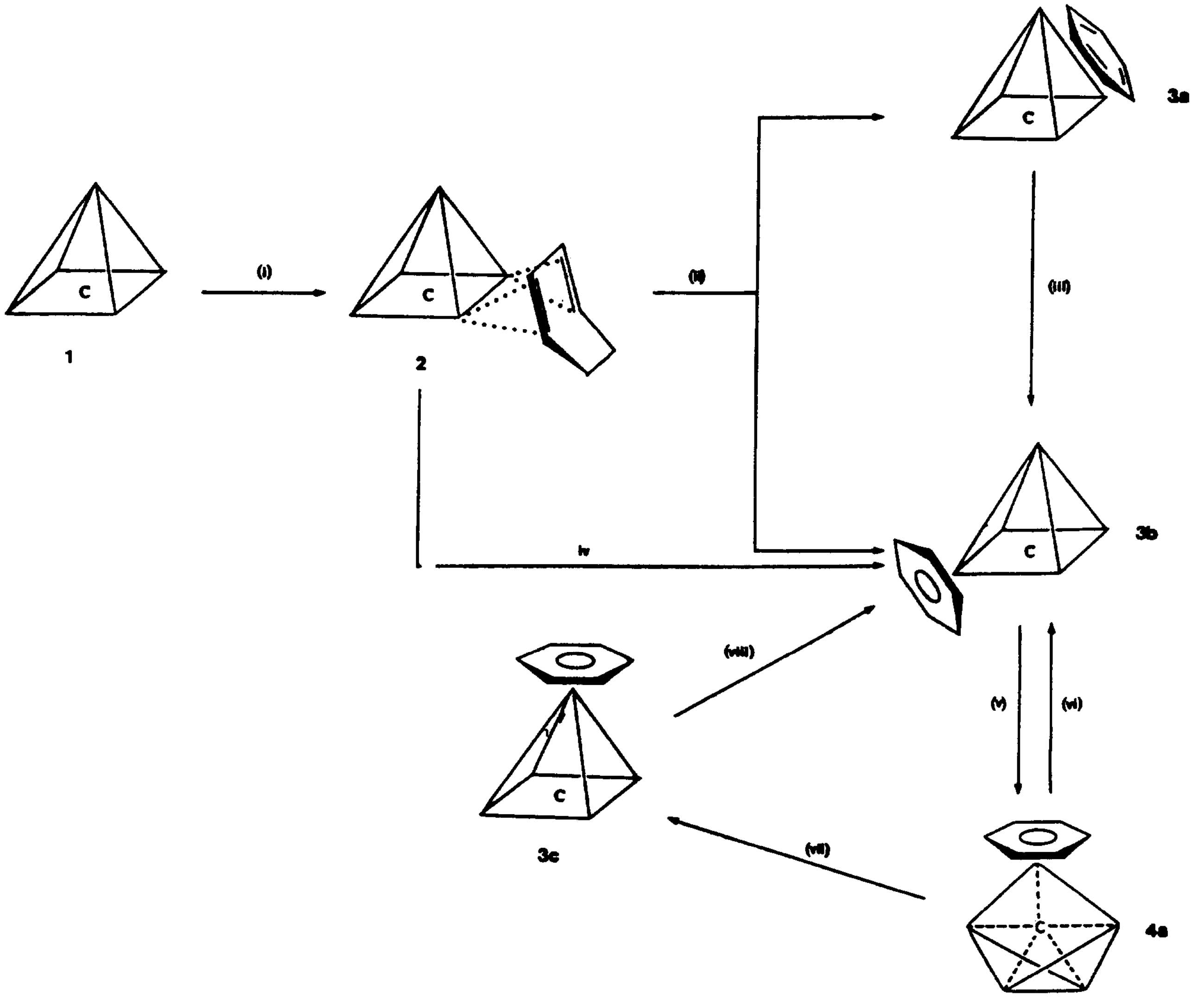
with $C_6H_6$ occupying an equatorial site, reacts reversibly with CO and in so-doing leads to the formation of the compounds with $\eta^6$-$C_6H_6$ at the apical site.

## 12. Substituted 1,3-$C_6H_8$ and $C_6H_6$ derivatives of $H_2Os_4(CO)_{13}$

Extension of the synthetic method to the chemistry of $H_4Os_4(CO)_{12}$ and $H_2Os_4(CO)_{13}$ has permitted the synthesis of a range of related $Os_4$–diene and $Os_4$–benzene derivatives (see Scheme 5). In this case, however, no evidence for the formation of $\mu_3$-$C_6H_6$-bonded clusters has been found. We have noted similar behaviour with the corresponding derivatives of $Co_4(CO)_{12}$. Again, substantial evidence has been accumulated from X-ray crystallographic data for arene–arene interaction between next-neighbouring molecules. In this instance ribbon-like distributions are formed. Our eventual goal is the synthesis of $Os_4(\eta^6$-$C_6H_6)_4$ derivatives with arene–arene interactions with all four tetrahedral directions!

## 13. Attempted synthesis of $Os_3(CO)_6(\mu_3$-$C_6H_6)_2$

This work has led us to consider the possibility of synthesising the *parent* cluster sandwich, *viz.* $Os_3(CO)_6(\mu_3$-$C_6H_6)_2$. To date we have not succeeded, but the extent of our studies may be of interest. Reaction of $Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2$-$C_6H_6)$ with $Me_3NO$–



Scheme 4. Reaction of $Ru_5C(CO)_{15}$ with cyclohexadiene.

$CH_2Cl_2$ in the presence of 1,3-$C_6H_8$ yields first $Os_3(CO)_8(\mu_3:\eta^2:\eta^2:\eta^2$-$C_6H_6)(\eta^2$-$C_6H_8)$ and then $Os_3(CO)_7(\mu_3:\eta^2:\eta^2:\eta^2$-$C_6H_6)(\eta^4$-$C_6H_8)$. Further reaction of this mixed arene–diene complex has produced a new, as yet uncharacterized, compound, possibly $Os_3(CO)_6(\mu_3:\eta^2:\eta^2:\eta^2$-$C_6H_6)_2$.

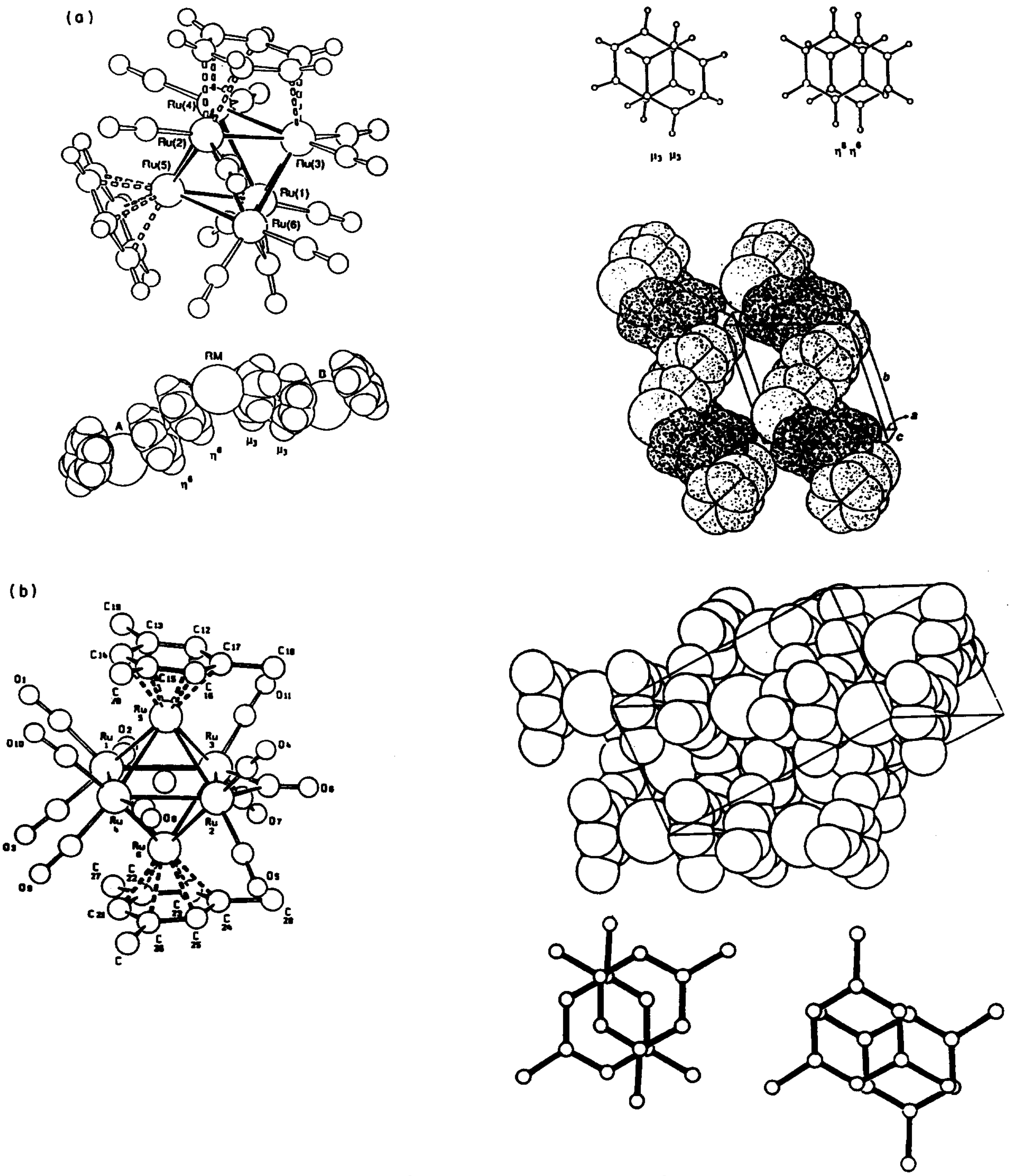
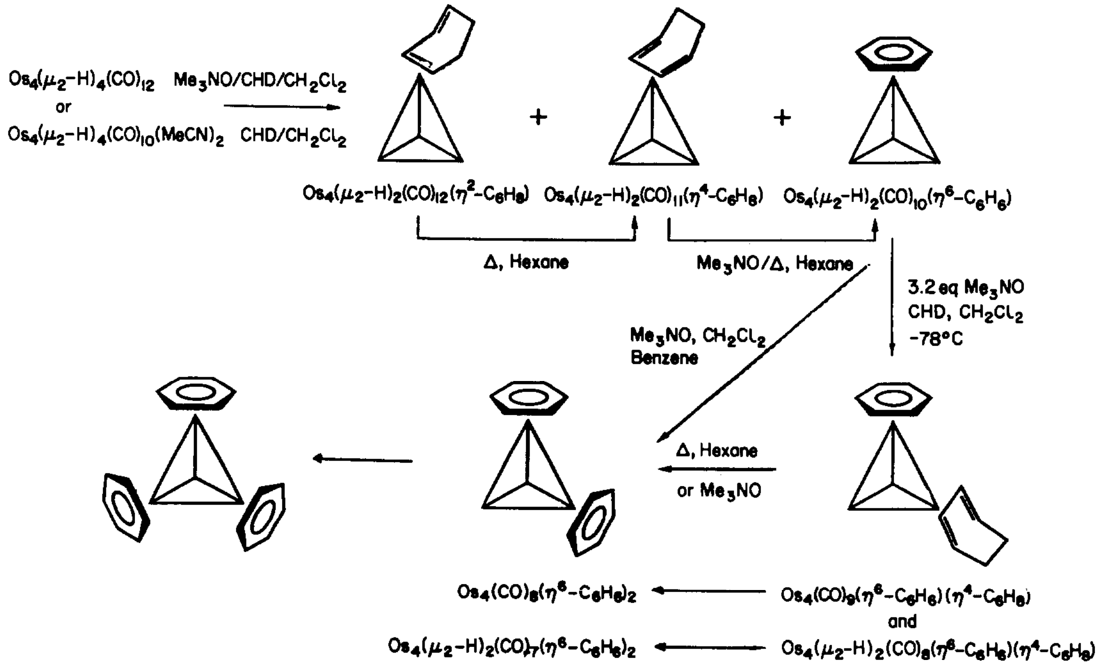


Fig. 7. Molecular organization in (a) $Ru_6C(CO)_{11}(\eta^6$-$C_6H_6)_2$ and (b) $Ru_6C(CO)_{11}(\eta^6$-$C_6H_3Me_3)_2$.



Scheme 5. Reaction of $H_4Os_4(CO)_{12}$ with cyclohexadiene.

## 14. Precursors to polymeric arene-cluster systems

As mentioned above, our primary objective in synthesizing the $Ru_3$ and $Ru_6$ cyclophane derivatives was to provide precursors to a range of polymeric materials in which redox-active clusters are linked through $\pi$-delocalized bridging units. We have extended this idea to derivatives containing the $C_6H_5(CH_2)_nC_6H_5$ ($n = 0$, 1 or 2) unit. So far the compounds shown in Fig. 8 have been synthesized and fully characterized by single-crystal X-ray analysis. Further, they have been shown to undergo further reactions with a range of mononuclear and polynuclear reagents to provide new polymeric materials which we shall describe elsewhere.

## 15. Conclusions

In this account we have attempted to give an overview of investigations into the chemistry of arene metal clusters. General synthetic pathways have been

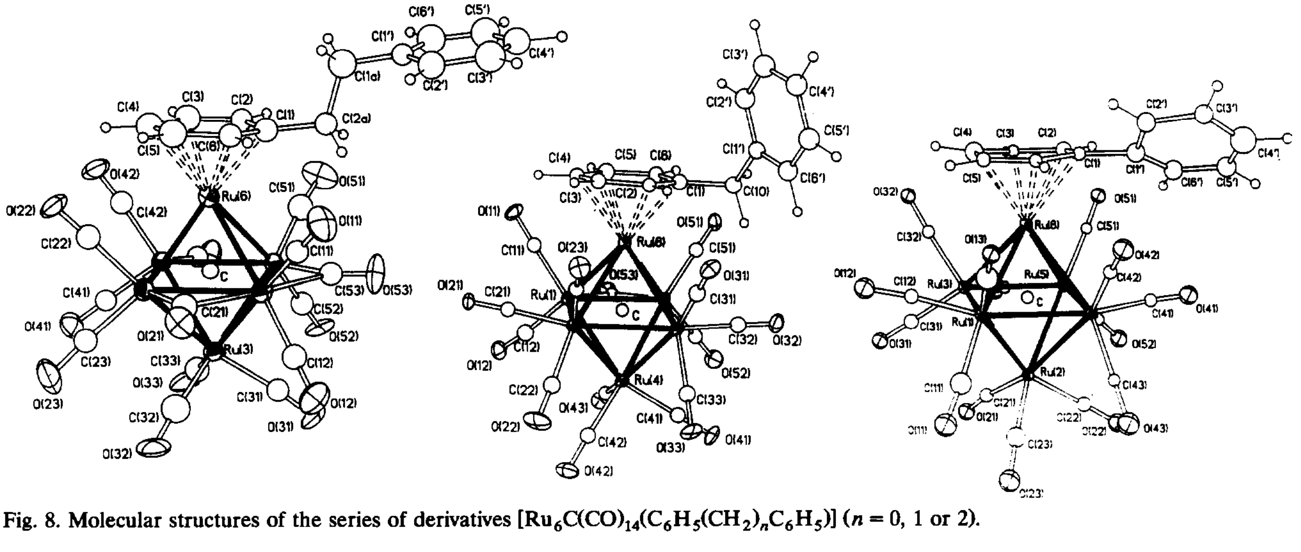


Fig. 8. Molecular structures of the series of derivatives $[Ru_6C(CO)_{14}(C_6H_5(CH_2)_nC_6H_5)]$ ($n = 0$, 1 or 2).

developed to mono- and bis-diene and arene clusters based on $M_3$, $M_4$, $M_5$ and $M_6$ (M = Ru or Os) systems and a wide range of new compounds prepared and characterized. These compounds appear to be highly appropriate models for arenes on the metal surface and the chemistry they undergo parallels that observed on the surface. We have been able to establish that two types of bonding modes predominate, *viz.* the bonding to a single metal atom ($\eta^2$) and to a triangle of metals ($\mu_3:\eta^2:\eta^2:\eta^2$). These two modes apparently interconvert readily with moderately low energy barriers to change or isomerization.

For some systems, especially $Os_3(CO)_9(C_6H_6)$ and its derivatives $Os_3(CO)_8L(C_6H_6)$ ($L = PR_3$), photodissociation of C–H bonds is observed to generate benzene (or related) derivatives. Bond activation of this sort would appear to be unique to cluster derivatives. The interaction between arene moieties to produce polymers is apparent in the crystallographic lattice. There are clear indications that these interactions approximate to those observed in graphite. Many of these compounds also serve as precursors to polymers in which clusters which are redox active are linked through aromatic bridges. There is clearly much to be done here.

Finally, we have put considerable effort into the preparation and characterization of the first cluster-sandwich compound *trans*-$Ru_6C(CO)_{11}(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)$. Despite much effort the parent cluster sandwich $M_3(CO)_6(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)_2$ still evades us, but we believe that at last we have good evidence for this elusive compound.

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