The Photoisomerisation Reactions of the Cluster $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ and Some of Its Derivatives

Brian F. G. Johnson,* Jacqueline G. M. Nairn, David B. Brown, Jack Lewis, Mark Gallop and David G. Parker

Abstract: The highly efficient photoinduced isomerisation of $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (**1**) to the previously characterised μ_3-benzyne complex $[H_2Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^1:\eta^1\text{-}C_6H_4)]$ (**2**) is described. We find that for the more electron-rich clusters $[Os_3(CO)_{9-n}(PPh_3)_n(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ ($n = 1$ or 2) the efficiency of the photolytic process is improved. We suggest that photolysis generates a vacant site at osmium (mimicking the inherent coordinative unsaturation of a metal complex) and that this transformation offers a compelling model for the interconversion of associatively and dissociatively chemisorbed benzene. Moreover, we can fine-tune our molecular "work function" (really the separation of HOMO/LUMO energies) by protonation or by phosphine substitution for CO at the metal. Thus, the cation $[HOs_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]^+$ does not undergo internal metalation, while photoisomerisation of the electron-rich phosphine derivatives proceeds more readily than for **1**. We find that these photolytic reactions are easily monitored by IR spectroscopy for samples suspended in polymethylmethacrylate films under ambient conditions. This method permits "matrix isolation" experiments under ideal conditions. Finally, we speculate that the mechanism of interconversion almost certainly involves the symmetric cleavage of a Os–Os bond ($\sigma-\sigma^*$ transition) to produce an extremely reactive diradical intermediate.

Keywords
benzene · benzyne · osmium clusters · photochemistry · polymer films

Introduction

Complementary to our studies of metal-based reactivity of face-capping arene cluster compounds that we have reported over recent years, we now wish to discuss the transformations we have observed for the $\mu_3\text{-}\eta^2:\eta^2:\eta^2$ ligands in the prototypical compound **1**. We find that the photoinduced isomerisation of

$[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$
1

the $Os_3(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ system provides a novel route into μ_3-benzyne complex chemistry. This reaction formally represents the intramolecular activation of two adjacent carbon–hydrogen bonds and may be considered as a molecular model for the interconversion of associatively and dissociatively chemisorbed states of benzene at a metal surface.

One of the problems that has frequently hampered the systematic development of metal cluster chemistry is that harsh reaction conditions are often required to effect rate-limiting ligand loss or metal–metal bond cleavage.[1] High temperatures preclude accumulation of all but the thermodynamically favoured pyrolysis products, and cluster fragmentation frequently competes with desired ligand-based transformations. Replacement of CO by a labile weak-field ligand such as MeCN to provide enhanced reactivity for coordinatively saturated clusters is now a well-established approach to cluster activation.[2–4] Associative pathways that rely on ambidentate ligands such as NO or SR[5,6] or on carbonyl insertion reactions[7,8] to provide a vacant coordination site are also known. Electron deficient clusters are particularly valuable synthetic intermediates (cf. the novel reaction chemistry associated with $[H_2Os_3(CO)_{10}]$[5,9]), but are difficult to generate in a systematic fashion. Although not extensively investigated as yet, the photoactivation of metal cluster complexes can provide a route to electron deficient species through dissociative ligand loss or metal framework rearrangement processes. Previous work has shown that photosubstitution reactions enable the synthesis of new clusters,[10–12] while mononuclear metal carbonyl derivatives are accessible by cluster fragmentation.[13–15] Cluster carbonyls have been shown to be pre-catalysts in several photoinduced catalytic transformations of organic substrates, including the polymerisation of acrylonitrile[16] and the isomerisation[17] and hydrogenation[18] of olefins. Recent mechanistic studies by Bentsen and Wrighton[21,22] indicate that the photochemistry of

---

[*] Prof. B. F. G. Johnson, J. G. M. Nairn, D. B. Brown
Department of Chemistry, The University of Edinburgh
West Mains Road, Edinburgh EH9 3JJ (UK)
Telefax: Int. code + (0131)650-6452
e-mail: BFGJohnson@ed.ac.uk
Prof. Lord Lewis, Dr. M. Gallop
University Chemical Laboratory
Lensfield Road, Cambridge CB2 1EW (UK)
Dr. D. G. Parker
ICI Wilton Centre
Middlesbrough, Cleveland TS6 8JE (UK)

$[M_3(CO)_{12}]$ (M = Os or Ru) is markedly wavelength and temperature dependent; this clarifies previous conflicting reports over the nature of the primary photoprocesses in these trinuclear complexes.[23–26]

Mann and co-workers[19,20] have demonstrated the photolability of η^6-arene ligands in the mononuclear complexes $[CpM(\eta^6\text{-arene})]^+$ (M = Fe, Ru); irradiation with visible light leads to efficient replacement of the arene by three monodentate ligands or one tridentate ligand. We were curious to see whether analogous photochemistry would be observed for the face-capping arene complex **1**, potentially a source of the unsaturated fragment "$[Os_3(CO)_9]$". We find no evidence for photolability of the C_6H_6 ligand in **1**, but report instead its novel photoisomerisation to a triply-bridging benzyne moiety. The mechanistic features of this transformation are not resolved as yet, though some useful insights have been obtained from a preliminary low-temperature matrix study.[27]

Results and Discussion

At 278 K in toluene solution, pyrex-filtered broad-band visible radiation from a 500 W tungsten-halogen lamp for around 13 h cleanly converted **1** to the isomeric triply-bridging benzyne (*ortho*-phenylene) cluster **2** in high yield (>90%). Complex **2** had

$[H_2Os_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_6H_4)]$
2

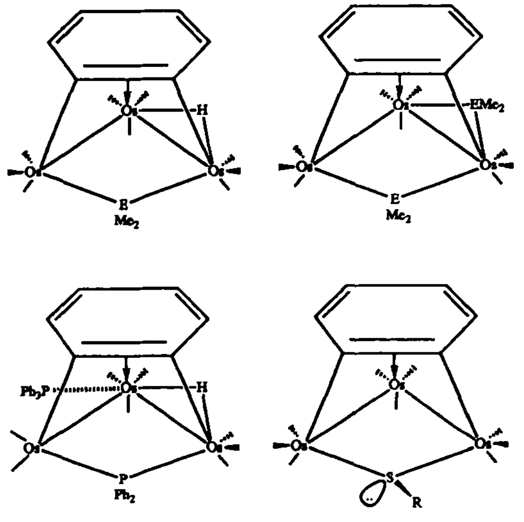
been previously obtained as a product from the reaction of benzene with $[Os_3(CO)_{12}]$ at around 463 K[28] or with $[Os_3(CO)_{10}(NCMe)_2]$ at 363 K, and was structurally characterised by single-crystal X-ray diffraction.[29] The benzyne ligand in **2** is planar and inclined at an angle of around 65° to the osmium triangle, with no significant variations in the C–C bond lengths being observed. The C_6H_4 fragment serves formally as a four-electron donor to the cluster and forms σ bonds to two Os atoms and a π interaction with the third osmium. While not directly located, the positions of the hydride ligand have been inferred from the distribution of the carbonyl groups in **2**. Benzyne ligands are commonly found in products of the thermolysis of a variety of aryl compounds with triosmium substrates. Thermolysis of $[Os_3(CO)_{11}(PMe_2Ph)]$ gives $[H_2Os_3(CO)_9(\mu\text{-}PMe_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_6H_4)]$, while $[Os_3(CO)_{10}(PMe_2Ph)_2]$ affords $[Os_3(CO)_7(\mu\text{-}PMe_2)_2(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_6H_4)]$ as a major product.[30,31] Related triply-bridging aryne clusters have been prepared from PPh_3,[31–33] $AsMe_2Ph$,[34,35] PEt_2Ph[36] and MeSPh.[37] Some representative structures are shown in Scheme 1.

Editorial Board Member:[*] *Professor Johnson was born in Northampton, England, and attended the Northampton School for Boys. From there he went to Nottingham University where he obtained both B. Sc. and Ph. D. degrees. Following a period with Professor F. A. Cotton as a postdoctoral fellow, he moved to lecturing posts at Manchester University and University College London before moving to Cambridge University in 1970 as a Lecturer in Inorganic Chemistry. At Cambridge he obtained an M. A. degree and became a Reader in Inorganic Chemistry and President and Acting Master of Fitzwilliam College. In 1976 he was awarded the Corday-Morgan Medal and Prize by The Royal Society of Chemistry, and in 1982 the same body gave him the Award for Chemistry and Electrochemistry of Transition Metals.*

Professor Johnson has served on a variety of committees concerned with the "welfare of chemistry". These include the new EPSRC, the SERC Inorganic Chemistry Sub-Committee, the Dalton Council and the Advisory Boards of Inorganica Chimica Acta, Organometallics and the RSC Materials Monograph Series. He has been Editor of Polyhedron and is an Editorial Board Member of the Journal of Cluster Science. At present he is a Member of the RSC Strategic Planning Committee and the Accreditation Panel.

In 1991, he took up the Crum Brown Chair of Inorganic Chemistry at The University of Edinburgh and is at present Head of the Department of Chemistry. Soon after he arrived in Edinburgh he was elected a Fellow of the Royal Society and a Fellow of the Royal Society of Edinburgh.

Very recently he has been elected to the Chair of Inorganic Chemistry at the University of Cambridge.



Scheme 1. Some structurally characterised benzyne–triosmium complexes (E = P, As). The carbonyl ligands in all structural formulae are omitted for clarity.

We found that appropriate derivatives of **1** also underwent photoisomerisation to give new μ_3-C_6H_4 complexes. While reaction of the olefin compounds $[Os_3(CO)_8(\eta^2\text{-}CH_2CHR)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ (R = H, Ph) was largely frustrated by photodecomposition pathways (presumably through loss of the relatively labile olefin ligands), virtually quantitative conversions of the phosphine and phosphite derivatives **3**, **4** and **5** was achieved under broad-band visible photolysis in toluene at

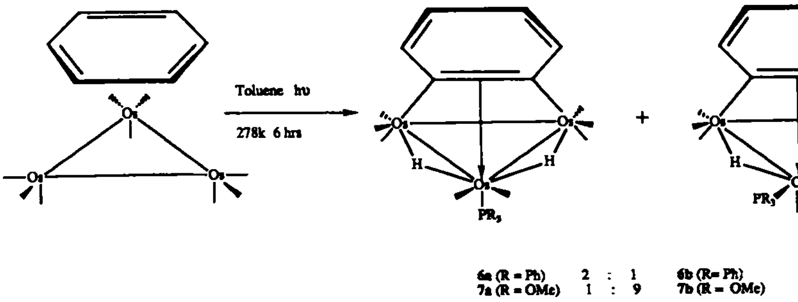
$[Os_3(CO)_8(PR_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ $[Os_3(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$
R = Ph (**3**), OMe (**4**) **5**

278 K. Markedly enhanced photoreaction rates were observed with increasing phosphine substitution; **3** and **4** were totally

---

[*] Members of the Editorial Board will be introduced to the readers with their first manuscript.

consumed after around 6 h of irradiation, while reaction of the bis-phosphine complex **5** was complete in 2.5 h. Photoisomerisation of **3** and **4** afforded benzyne complexes **6** and **7**, respectively, each as two chromatographically inseparable, interconvertible isomers that have been characterised by ^1H, ^{13}C and ^{31}P NMR spectroscopy (Scheme 2).



6a (R = Ph) 2 : 1 **6b** (R = Ph)
7a (R = OMe) 1 : 9 **7b** (R = OMe)

Scheme 2. Structural characterisation of compounds **6** and **7**.

Structural Characterisation of Compounds 6 and 7: The ^1H NMR spectrum of the major isomer of **6** (i.e., **6a**) is invariant over the temperature range 193–293 K and shows a single doublet resonance at high field ($J_{PH} \approx 9$ Hz) assigned to two equivalent hydride ligands locally mutually *cis* to PPh_3. The magnitude of the coupling constant $^1J(^{187}Os-^1H)$ of 30.5 Hz, measured from ^{187}Os satellites about the hydride resonance at 193 K, indicates that the hydride ligands are stereochemically rigid at this temperature. This rules out an alternative structure containing nonequivalent ligands for which rapid time-averaging by some intramolecular migration process leads to a single hydride environment. The C_6H_4 ligand shows an AA'XX' pattern; the two branches of the spectrum are centred at $\delta = 7.90$ and 6.85, and are consistent with a symmetrically *ortho*-disubstituted benzene moiety and equivalent hydride ligands. Identical spectral features have been previously reported for several μ_3-benzyne complexes in which low-energy fluxional processes associated with the ring or edge-bridging ligands introduce an effective plane of symmetry into the molecule (vide infra[29–31]).

Consistent with the C_s symmetry of **6a**, four sharp carbonyl resonances are observed in the $^{13}C\{^1H\}$ NMR spectrum below 253 K, each corresponding to two equivalent CO ligands. One resonance couples to phosphorus ($J_{PC} = 4.5$ Hz) and is assigned to carbonyls d, coordinated to the phosphorus-bearing Os atom (see Fig. 1). In the fully proton-coupled spectrum this resonance is further split by coupling to the *trans*-related hydrides. Carbonyls a also show *trans* coupling to the hydrides and may be assigned accordingly. The stereochemistry of **6a** is unequivocally defined by this data, assuming a ligand distribution that is isomorphic with all previously characterised μ_3-benzyne complexes. We note that **2**, **6** and **7** are the first benzyne clusters in which the two Os atoms forming σ interactions with C_6H_4 are otherwise unbridged.

Interestingly, the ^1H NMR spectroscopic features of the major isomer of **6** are reproduced for the minor isomer of the analogous $P(OMe)_3$ complex **7**. The converse applies to the minor and major isomers of **6** and **7**, respectively. At 203 K the equivalent hydride ligands in **7a** exhibit a doublet resonance ($\delta = -18.91$, $J_{PH} = 10.9$ Hz), and a doublet at $\delta = 3.64$ for the phosphite methyl protons is clearly visible. The expected AA'XX' spectrum for the C_6H_4 protons is obscured by the signals of the major isomer **7b** (Fig. 2). Three low-intensity singlets and one doublet resonance at low field in the $^{13}C\{^1H\}$ NMR spectrum of **7** at 186 K are attributed to the pairwise equivalent carbonyls of isomer **7b** (see Fig. 3).

The structural assignment of isomers **6b** and **7b** is more problematic. We propose, firstly, that these species are isostructural on the basis of the marked similarity of their ^1H and ^{13}C NMR spectra. At low temperatures **6b** and **7b** each exhibit two resonances at high field, split by either larger coupling (**6b**: $J_{PH} = 24.2$ Hz; **7b**: $J_{PH} = 38.8$ Hz) or smaller coupling (**6b**: $J_{PH} = 13.7$ Hz; **7b**: $J_{PH} = 14.5$ Hz) to phosphorus, and are assigned to nonequivalent hydrides located respectively *trans*- and *cis* to the phosphorus donor ligand. $^2J_{HH}$ must be less than 1 Hz and is not detected. ABXY ^1H NMR spectra are observed for the C_6H_4 ligands as has been found previously in the limiting spectra of nonsymmetrical μ_3-benzyne complexes.[30,31,37] In both **6b** and **7b** doublet resonances are observed for H_1 and H_4 (overlapping to give an apparent triplet in the latter complex) while pseudo-triplets (actually doublets of doublets) are found for H_2 and H_3 at higher field. The $^{13}C\{^1H\}$ NMR spectrum of **6b** recorded at 186 K shows the

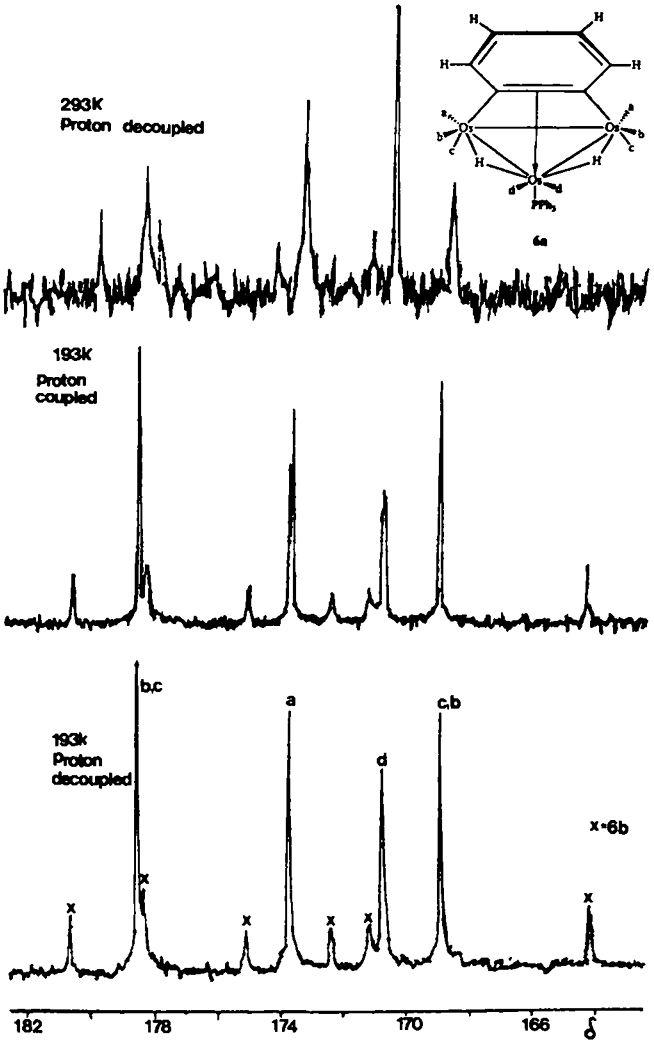


Fig. 1. Variable-temperature ^{13}C NMR spectra of **6**.

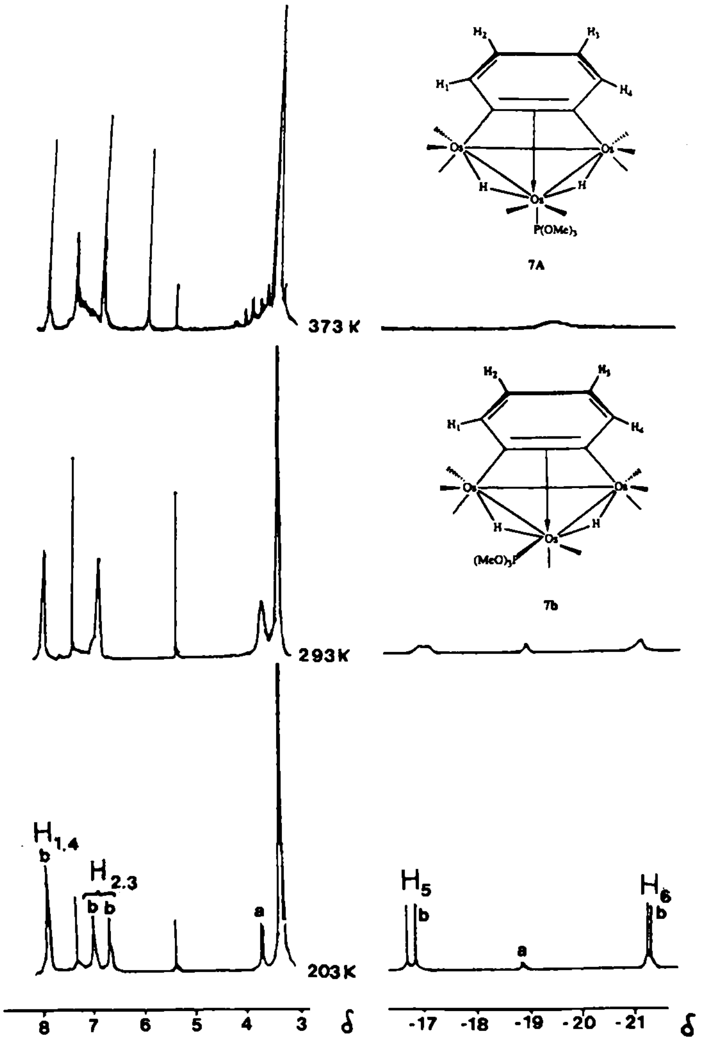


Fig. 2. Variable-temperature ^1H NMR spectra of 7.

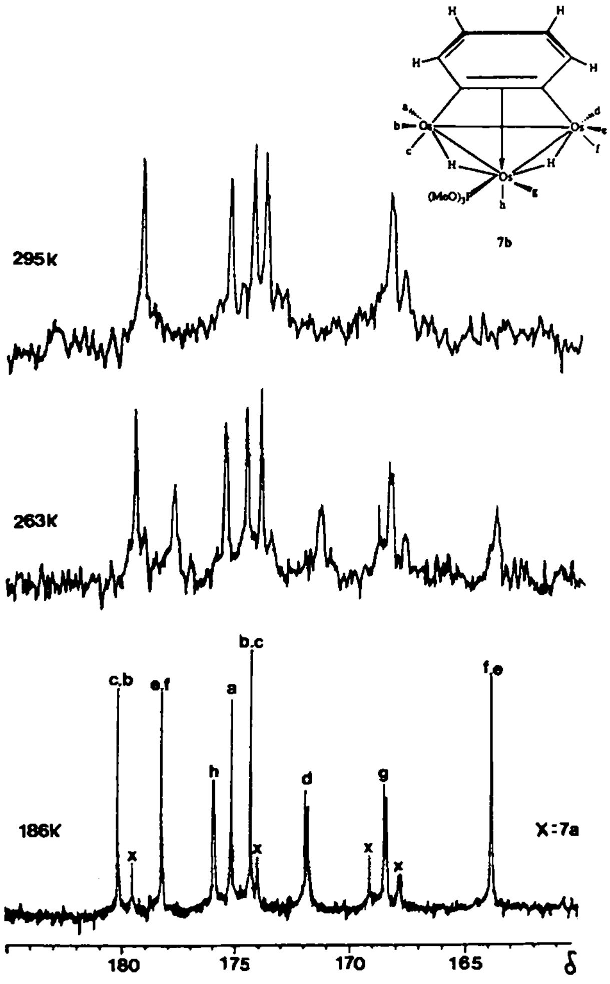


Fig. 3. Variable-temperature $^{13}C\{^1H\}$ NMR spectra of 7.

eight carbonyl resonances anticipated for the nonsymmetrical complex; three are doublets resulting from two two-bond couplings and one three-bond (i.e., *trans*) coupling to phosphorus. Selective proton-decoupling enables partial assignment of the spectrum. The limiting $^{13}C\{^1H\}$ spectrum in the carbonyl region for complex **6b** is qualitatively similar to that of the phosphite analogue, although two signals are apparently obscured by resonances of the major isomer **6a**.

Three distinct representations of the nonsymmetrical isomers **6** and **7** consistent with this data are tenable (Fig. 4). Several lines of reasoning would suggest, however, that **6b** and **7b** adopt structure A:

1) We anticipate that substitution as in C should be particularly unfavourable since carbonyl substitution by a relatively bulky tertiary phosphine or phosphite ligand should introduce destabilising steric interactions with the benzyne ring protons (recalling that the C_6H_4 ligand is inclined *toward* this coordination site).

2) Substitution at the alternative pseudo-equatorial site as in B may, to some extent, relieve unfavourable steric pressure between the ligands, but accounts rather unsatisfactorily for the variable-temperature behaviour of the ^{13}C NMR spectra. For the symmetrical isomer **6a** (and possibly for **7a** also) a localised trigonal-twist process exchanges carbonyl ligands a, b and c, as evidenced by the broadening of their resonances at 293 K. The doublet resonance of carbonyl d remains sharply resolved at this temperature; this reflects a higher barrier to ligand interchange in the unique osmium atom. Khattar has reported similar behaviour in ^{13}C NMR studies of related μ_3-alkyne complexes

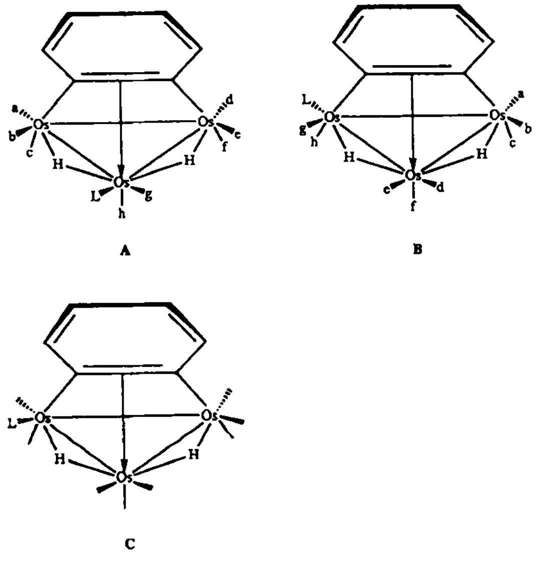
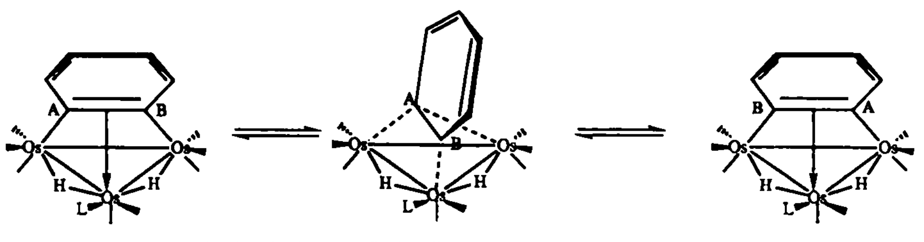


Fig. 4. Representations of the nonsymmetrical isomers 6 and 7 (L = PPh_3, $P(OMe)_3$).

$[Os_3(CO)_9(L)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)]$ where exchange among the ligand set x, y and z is invariably the lowest-energy process detected.[39] This is presumably a consequence of the electronic requirements of π coordination of the organic ligand (but undoubtedly also of steric hindrance to rotation on PR_3 substitution) in **6**.



Scheme 3. Proposed mechanism for benzyne fluxionality.

On warming from 186 to 295 K, three CO resonances of **7** broaden and coalesce with the baseline as a result of "turnstile" carbonyl exchange. From selective decoupling studies it is clear that this interchange involves the unique carbonyl located *trans* to both the phosphorus ligand and the hydride (i.e., CO d above). This would imply that carbonyl exchange at the "front" osmium atom is more facile than interchange of ligands a, b or c for B, in contrast to the findings of Khattar[39] above. We favour structure A and account for the rigidity of carbonyls a, b and c at 295 K on the basis of steric hindrance to rotation from the adjacent ligand L. The barrier to localised scrambling of carbonyls d, e and f is apparently lower in **6b** and **7b** than in the symmetrical isomers and may result from increased electron density of the "back" Os atom when the phosphorus ligand rather than CO occupies the *trans*-coordination site. The ability of phosphine and phosphite ligands to lower the activation barrier to "turnstile" exchange at an adjacent metal centre has been noted previously.[40] One rationalisation invokes the weakening of metal–metal bonds through population of a LUMO that is antibonding with respect to the metal framework, thereby facilitating rotation of the $M(CO)_3$ unit as a *whole* with respect to the rest of the cluster.[41,42]

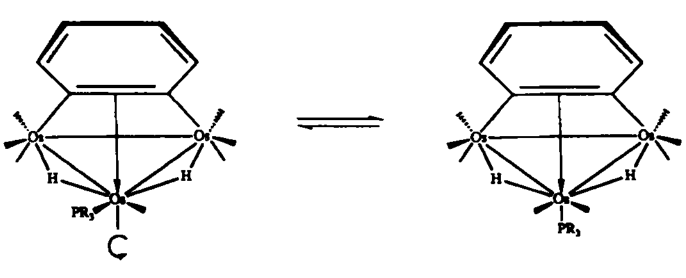
3) Finally, it may be significant that in the structurally characterised complex $[HOs_3(CO)_7(PPh_3)(\mu\text{-}PPh_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_6H_4)]$ the PPh_3 ligand chooses to occupy a pseudo-equatorial coordination site of the osmium atom forming the π interaction with C_6H_4, in direct correspondence with the proposed structure A for **6b** and **7b** above. The different relative proportions of symmetrical and nonsymmetrical isomers formed on photolysis of **3** and **4** may reflect the subtle interplay of electronic and steric effects in this chemistry. Pseudo-equatorial coordination of the phosphorus ligand may be intrinsically favoured on electronic grounds (perhaps π back bonding to the axial CO is enhanced by donation from the benzyne moiety), but destabilised by steric interaction with the C_6H_4 ligand. This would explain the greater preference of the smaller phosphite ligand to coordinate equatorially, with the more bulky PPh_3 preferentially adopting the axial configuration. In $[HOs_3(CO)_7(PPh_3)(\mu\text{-}PPh_2)(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_6H_4)]$, steric pressure between $\mu\text{-}PPh_2$ and PPh_3 would presumably destabilise the axial isomer.

Isomer Interconversion and Benzyne Fluxionality: On warming from the low temperature limit, the resonances of the benzyne ligand in the ^1H NMR spectra of both isomers of **6** and **7** broaden and coalesce. Similar behaviour is found for the hydride resonances. The benzyne signals of the nonsymmetrical isomers **6b** and **7b** broaden at a much greater rate than the resonances of either the C_6H_4 ligand in **6a** and **7a** or the hydrides in both isomers; for example, the C_6H_4 resonances of **6b** have coalesced by 293 K, while the hydride signals of **6a** and **6b** are still sharp at this temperature.

Clearly two processes are operative. The lower energy pathway produces a plane of symmetry through the benzyne ligand of the nonsymmetrical isomers without averaging the inequivalent hydride environments or equilibrating with the symmetric forms. We propose the rotation/flipping mechanism shown below to account for this behaviour (Scheme 3). This process is a variation of the Deeming mechanism[31,34] for facile equilibration of the bridging arsenide ligands in $[Os_3(CO)_7(\mu\text{-}AsMe_2)_2(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_6H_4)]$ without permutation of the C_6H_4 moiety. The intermediacy of the species having a benzyne carbon coordinated to only one osmium atom is a feature common to both mechanisms and this bonding motif has been characterised[36] in the complex $[Os_3(CO)_9(\mu\text{-}PEt)(\mu_3\text{-}C_6H_4)]$. Our mechanism is the converse of the Deeming process, however, since we symmetrise the ring without equilibrating the other bridging ligands. It seems entirely reasonable that an analogous rotation/flipping mechanism operates in the C_s isomers **6a** and **7a**, though the inherent symmetry of these species does not permit its detection.

The higher energy process results in the interconversion of the symmetrical and nonsymmetrical isomers of **6** and **7**. Spin saturation transfer experiments at 323 K clearly demonstrate the exchange of protons H_β in **6a** with the time-averaged β protons of **6b**. Thus irradiating at the low field resonance of **6a** leads to a denuding of the corresponding resonance for **6b** (obscured by PPh_3 signals), while slight enhancement of the higher field peak of **6a** arises from cross-relaxation (i.e., Overhauser effect enhancement). Weak NOE transfer to H_γ of **6b** is also evident. Similarly, irradiation of the high-field resonance of either **6a** or **6b** leads to spin saturation of the other, and direct or transferred NOE to the β protons. Complete saturation of the hydride resonances in both isomers is achieved on irradiation of each of the three doublets. Interestingly, no saturation transfer between the hydrides and benzyne ligand is found here, even at 373 K; this indicates that the rapid, reversible proton transfer between ring and metal sites noted by Shapley et al.[43] for the aryne complexes $[H_2Os_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_6H_2R_2)]$ is not important for **6** (the added complication associated with isomer interconversion means that we would not have detected weak saturation transfer here).

Isomer interconversion in **6** and **7** is easily understood in terms of a "turnstile" ligand exchange process at the phosphorus-substituted osmium atom (Scheme 4). By 373 K we observe coalescence of the resonances of the exchanging carbonyl ligands and broadening of the PPh_3 resonances in the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra for **6**, as required by this mechanism.



Scheme 4. Proposed mechanism for isomer interconversion.

Activation barriers to C_6H_4 rotation/flip and $Os(CO)_2(PR_3)$ rotation are clearly lower in **7** than in **6** (we estimate very approximately $\Delta G^{\ddagger}_{293\,K} \approx 55\,kJ\,mol^{-1}$ and $\Delta G^{\ddagger}_{373\,K} \approx 70\,kJ\,mol^{-1}$ for the two processes in **6**), and this reflects, presumably, the greater steric hindrance to fluxionality for the latter complex.

Photoisomerisation of 5: Cluster **5** was converted on visible photolysis to a single isomer of the benzyne complex **8** in high

$$[H_2Os_3(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_6H_4)]$$

8

in high yield. The ^1H NMR spectrum of **8** at room temperature exhibits one doublet ($J_{PH} = 10.3$ Hz) and one triplet ($J_{PH} = 8.8$ Hz) at high field attributed to two nonequivalent hydrides located *cis* to respectively one and two PPh_3 ligands. The C_6H_4 ligand resonances form an apparent AA′XX′ pattern. Complex **8** has not been exhaustively characterised, but four plausible structures are given in Figure 5. We favour structure G for **8**, since steric repulsion between C_6H_4 and the bulky phosphine ligands should be minimised here (cf. the structure of the phosphine–phosphido cluster above).

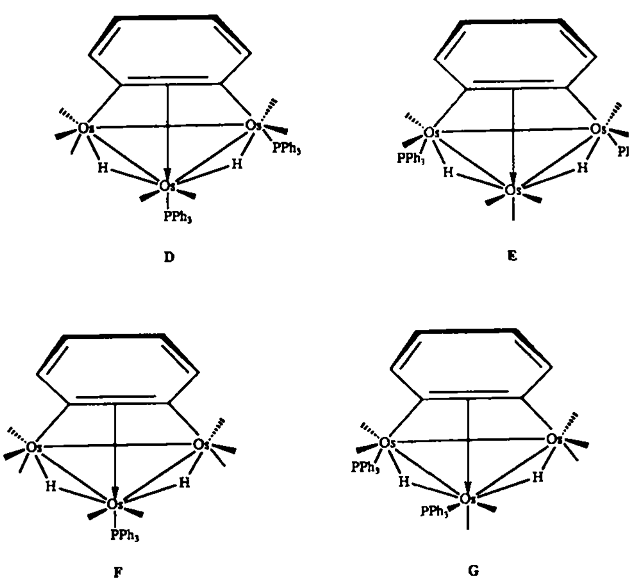


Fig. 5. Possible structures of complex **8**.

Thermal Conversion of μ_3-Benzene to μ_3-Benzyne: Prolonged thermolysis in toluene solution at 388 K converted the μ_3-benzene complexes $[Os_3(CO)_{9-n}(PPh_3)_n(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ [$n = 0$ (**1**), 1 (**3**), 2 (**5**)] to the corresponding μ_3-benzyne compounds $[H_2Os_3(CO)_{9-n}(PPh_3)_n(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^1\text{-}C_6H_4)]$. The rate of intramolecular oxidative addition increased with phosphine substitution (i.e., with increasing electron richness of the cluster). Thus **1** afforded **2** in about 70% yield after 41 h; **3** gave **6** in around 80% yield after 16 h; **5** gave **8** in around 50% yield after 8 h. Visible light was not excluded in these reactions, and contributory photolysis cannot be totally discounted here. Isomers **6a** and **6b** were obtained from the thermolysis of **3** in the same proportions found for photolytic conversion, while low intensity signals at high field in the ^1H NMR spectrum of thermally derived **8** may be due to trace amounts of a second isomer. Several other uncharacterised pyrolysis products of **5** were formed in low yields, possibly through metalation of one or more phenyl groups of a PPh_3 ligand. *ortho*-Metalation of phenyl phosphines on a triosmium framework is well known[32,33] and Deeming[44] has demonstrated the stepwise degradation of coordinated PPh_2R to μ_3-C_6H_4 by a metalation/elimination/metalation sequence.

Photolysis clearly provides a more efficient and selective synthesis of the triply-bridging benzyne clusters than thermal conversion in this system. There is no evidence for the reversibility of this isomerisation and the dimetalated complexes apparently represent the thermodynamically favoured species here. We now consider some mechanistic aspects of the photoreaction.

A Mechanism for Photoisomerisation: Although a detailed mechanistic study of the μ_3-benzene→μ_3-benzyne conversion is not available, some preliminary observations seem relevant to the formation of a speculative description of this photochemistry.

The electronic absorption spectra of complexes **1**, **3** and **5**, recorded in cyclohexane solution at 293 K, are shown in Figure 6. Phosphine substitution leads to a bathochromic shift of the absorption maximum at 312 nm in the spectrum of **1**; the corresponding feature in **3** and **5** are incompletely resolved from the tailing of the higher energy metal-to-ligand charge transfer band(s). An additional shoulder at 432 nm is evident in the spectrum of the bis-phosphine complex **5**. A red shift of in-plane (metal) bonding to antibonding transitions in the electronic spectra of phosphine derivatives of $[Os_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$ has been found previously.[45,46]

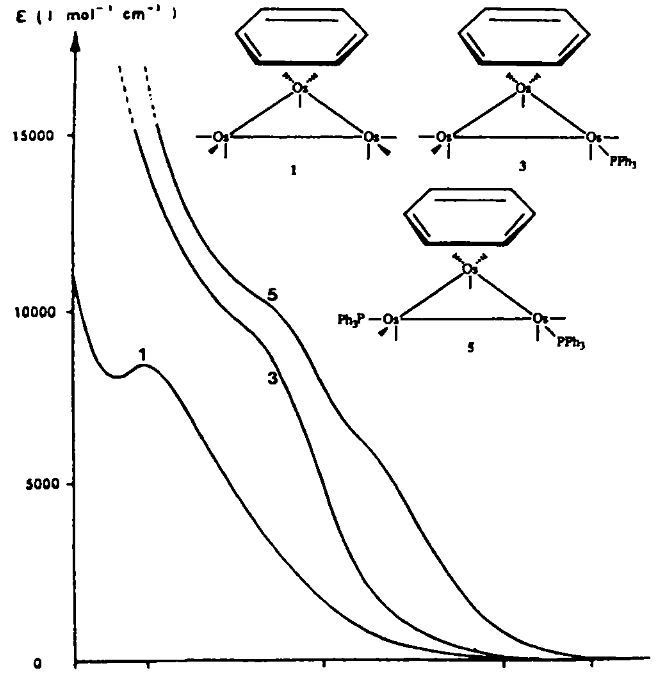


Fig. 6. UV/Vis spectra of **1**, **3** and **5** in cyclohexane solution.

It is clear from preliminary low temperature matrix photolysis studies (vide infra) that irradiation into these near UV/visible absorptions initiates the photoisomerisation reaction. Thus at 20 K in Ar, CH_4 and CO matrices, irradiation at $\lambda > 365$ nm yields no net photochemistry, while $\lambda > 290$ nm gives efficient photoisomerisation to the benzyne complex **2**. The observed rate enhancements (i.e., conversion rates for **5** > **3** > **1**) may reflect a real increase in quantum yield for this reaction on increasing substitution of PPh_3 for CO and/or result simply from the tungsten-halogen source providing a greater photon flux at more appropriate (i.e., higher) wavelengths for efficient isomerisation of the substituted compounds **3** and **5**.

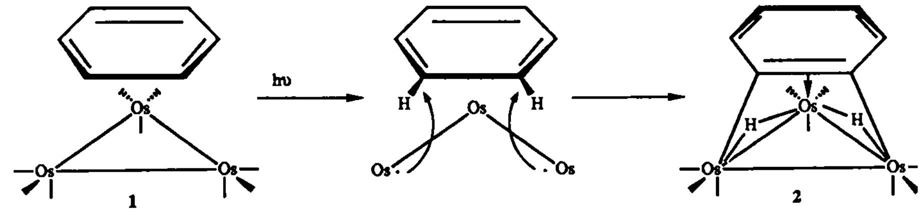
We may speculate as to the nature of the orbitals associated with these low-energy transitions by recalling the results of a Fenske–Hall quantum chemical calculation undertaken for the hypothetical model complex $[Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$. The scheme predicts that the dipole-allowed transitions of lowest energy are $E \rightarrow A_2$ (3.4 eV) and $A_1 \rightarrow E$ (4.6 eV) and should be compared with the experimentally observed transition energy of 3.9 eV (i.e., 312 nm). It is interesting to note that the former transition is between a doubly-degenerate orbital that is predominantly bonding with respect to the metal triangle and the cluster LUMO, which is mainly metal–metal antibonding and is again directed along the Ru–Ru edges. This transition is apparently the analogue of the $\sigma \rightarrow \sigma^*$ transition responsible for the photofragmentation and associative substitution reactivity in $[Os_3(CO)_{12}]$. Substitution of PPh_3 for an equatorial carbonyl ligand is expected to stabilise the in-plane LUMO and may account for the observed red-shifting of the low energy electronic transitions in **3** and **5**.

We now consider several candidates for the primary activation process responsible for the photochemistry of the face-capping benzene complexes:

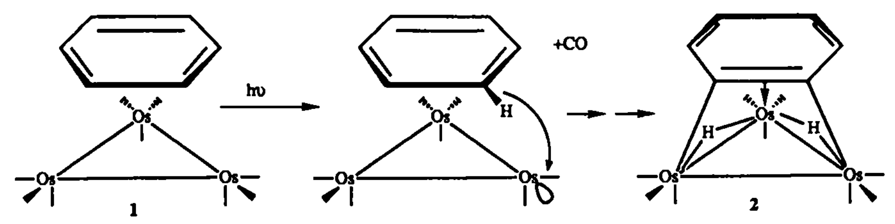
1) *Radical Initiation*: Homolysis of an Os–Os bond in **1** (and its derivatives), insertion of the diradical into two C–H bonds of the μ_3-benzene ligand and subsequent rearrangement could generate the μ_3-benzyne fragment (Scheme 5). Decomposition of a triplet excited state by insertion reactions of a ligand-centred radical intermediate might also be a feasible process here (compare the $Cr \rightarrow C_6H_6$ transition responsible for the radical-initiated photodecomposition of $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$).[48]

Dinuclear complexes have been shown to undergo fragmentation to mononuclear species on photolysis by homolytic cleavge of the metal–metal bond, and the trapping of metal radicals $M^{\cdot}$ by chlorocarbons to give the respective chlorides M–Cl appears to be a diagnostic test for the diradical pathway.[47] Photolysis of **1** in toluene solution at 278 K for 13 h in the presence of 2 M CCl_4 afforded benzyne complex **2** (ca. 70% yield) and a purple-brown toluene-insoluble residue that remained uncharacterised. It is unclear, though, whether this material represents a primary photolysis product, since small quantities were also recovered on photolysing pure $[Os_3(CO)_{12}]$ under identical reaction conditions. Nevertheless, the intermediacy of a diradical species that is sufficiently long-lived to undergo intramolecular insertion or be trapped (less efficiently) by CCl_4 in an intermolecular reaction cannot be discounted here.

2) *Activation by CO Dissociation*: Photoinduced dissociative carbonyl ligand loss is an important primary photoprocess (vide supra). Activation of a benzene C–H bond by an electron-deficient species formed through rate-determining CO loss from **1**, according to Scheme 6, should be strongly inhibited by external carbon monoxide. We found that visible photolysis of **1** in toluene (standard conditions) in the presence of CO (1 atm) afforded **2** (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 was undoubtedly rather low, it seems unlikely that dissociative CO loss is directly relevant to this photochemistry.



Scheme 5. Radical initiation.



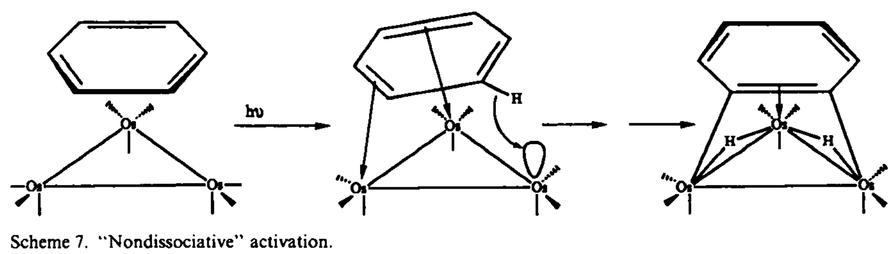
Scheme 6. Activation by CO dissociation.

3) *"Nondissociative" Activation*: Ring slippage [Eq. (a)] of monometallic η^6-arene complexes is thought to play an important role in arene exchange reactions of these compounds.

$$\eta^6\text{-arene–M} \rightleftharpoons \eta^4\text{-arene–M} \rightleftharpoons \eta^2\text{-arene–M} \qquad (a)$$

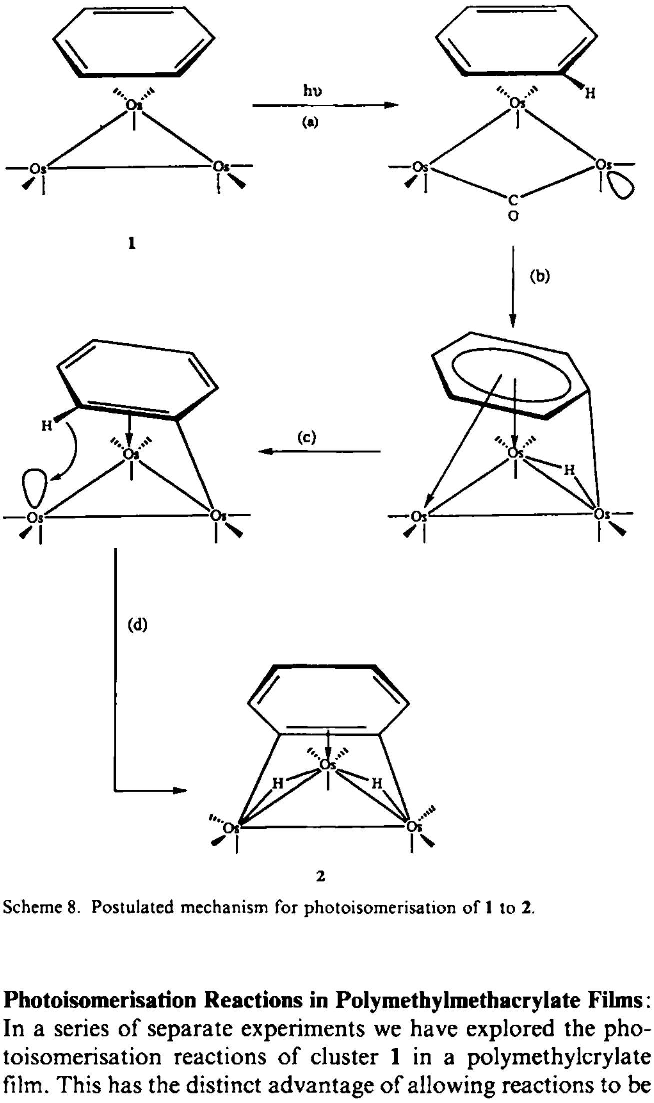
A related transformation of **1** could be a plausible elementary step in its photoisomerisation, creating a metal-centred vacancy; metalation and subsequent rearrangement then afford **2** (Scheme 7). Several photosubstitution studies of mononuclear iron η^4-diene complexes by PR_3 have indicated, however, that the quantum efficiency for $\eta^4 \rightarrow \eta^2$ binding is very low, particularly for dienes locked in an *s-cis* conformation, since the reverse action between the vacant coordination site and the uncoordinated double bond is facile. It is not clear whether extrapolation to the photoisomerisation reaction is entirely valid, as the step subsequent to ring slippage here is an intra- rather than intermolecular addition.

We believe that perhaps the most likely pathway for photoisomerisation of **1** requires a vacancy formed by carbonyl insertion into an Os–Os bond as the primary photoprocess. Our com-



Scheme 7. "Nondissociative" activation.

plete mechanism as proposed is given in Scheme 8. Step (a) is directly analogous to the formation of coordinatively unsaturated $M_3(CO)_{11}$ proposed by Wrighton and Ford to explain the associative substitution and fragmentation chemistry of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. Significantly, the nature of the electronic transition responsible for the generation of $Os_3(CO)_{11}$ may, as indicated, closely resemble the transition promoted in this photoisomersiation. Step (b) represents metalation of the face-capping ligand to give an intermediate π-aryl species of the type recently implicated in a study of ring-to-metal proton exchange in triosmium aryne complexes.[46] Subsequent ring slippage (possibly photoassisted) and metalation would afford benzyne complex **2** as shown.



Scheme 8. Postulated mechanism for photoisomerisation of **1** to **2**.

Photoisomerisation Reactions in Polymethylmethacrylate Films: In a series of separate experiments we have explored the photoisomerisation reactions of cluster **1** in a polymethylcrylate film. This has the distinct advantage of allowing reactions to be monitored (by IR spectroscopy) under ambient conditions and does *not* involve the complexities normally encountered with matrix isolation studies. As far as we have been able to judge, the interconversion of **1** to **2** follows precisely the same course, although possibly at a slightly faster rate.

In a typical experiment, the polymer precursor was dissolved in toluene, and cluster **1** was then added. After removal of the solvent by slow evaporation, the resulting film was subjected to irradiation from a medium-pressure mercury lamp. The photolytic reaction was monitored by following the observed infrared spectrum (ν_{CO}) with time. As in the alternative matrix isolation experiments, the formation of the second isomer **2** was followed by observing the appearance of two carbonyl peaks at 2109 (w) and 2050 (s) cm^{-1}.

This method of "matrix isolation" is clearly extremely convenient especially when compared with other more usual matrix isolation methods and has been previously applied by us to a range of other cluster systems. A full report of these additional studies will be made in due course.

Experimental Procedure

Photolysis of $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (1): A solution of **1** (30 mg) in toluene (15 mL) in a pyrex vessel was cooled to 5 °C and subjected to unfiltered visible irradiation from a 500 W heat lamp positioned around 5 cm from the reaction vessel. After 13 h irradiation, the solvent was removed in vacuo, the residue taken up in CH_2Cl_2 and separated by TLC (eluent: CH_2Cl_2 (35%)/hexane (65%). Extraction of a pale yellow band ($R_f \approx 0.8$) and crystallisation from CH_2Cl_2/hexane gave microcrystals of the benzyne complex $[H_2Os_3(CO)_9(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_6H_4)]$ (**2**) (27 mg, 90% yield), identified by comparison with an authentic sample.

Photolysis of $[Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (3): Following the procedure described above for the photoisomerisation of **1**, 5 h irradiation of **3** afforded yellow microcrystalline $[H_2Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_6H_4)]$ (**6**) in 94% yield. IR: $\tilde{\nu}_{CO}/cm^{-1}$ (CH_2Cl_2): 2078 (m), 2044 (vs), 2032 (sh), 1995 (s), 1973 (m), 1940 (w). ^1H NMR (CD_2Cl_2) indicates the presence of two isomeric benzyne complexes in the ratio 2:1: Major isomer **6a**, 293 K: $\delta = 7.94$ (m, $2H_1$) and 6.89 (m, $2H_2$) form an AA'XX' system, 7.10–7.55, (m, 15H, PPh_3), −18.09 (d, $J_{PH} = 9.2$ Hz, $2H_3$); 193 K: $\delta = 7.92$ (m, $2H_1$) and 6.84 (m, $2H_2$) form an AA'XX' system, 7.1–7.5 (m, 15H, PPh_3), −18.30 (d, $J_{PH} = 8.4$ Hz, $J(^{187}Os-^1H) = 30.5$ Hz (from satellite spectrum), $2H_3$). Minor isomer **6b**, 293 K: $\delta = 7.10-7.55$, m (15H, PPh_3), benzyne resonances exchange-broadened into baseline, −16.14 (d, $J_{PH} = 24.2$ Hz, H_5), −19.87 (d, $J_{PH} = 14.2$ Hz, H_6); 193 K: $\delta = 7.55$ (d) and 7.09 (d, $J_{12} \approx J_{34} \approx 8.0$ Hz, H_1 and H_4), 7.1–7.5 (m, 15H, PPh_3), 6.72 (pt) and 6.07 (pt, $J_{obs} = 7.5$ Hz, H_2 and H_3), −16.02 (d, $J_{PH} = 24.2$ Hz, H_5), −20.16 (d, $J_{PH} = 13.7$ Hz, H_6). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, only carbonyl resonances reported): Major isomer **6a**, 293 K: $\delta = 174.5$ (br s), 169.3 (br s), 166.4 (d, $J_{PC} = 4.5$ Hz), 164.5 (br s); 193 K: $\delta = 178.6$ (s, 2C, b or c), 173.7 (s, 2C, a), 170.7 (d, $J_{PC} = 4.5$ Hz, 2C, d), 168.9 (s, 2C, b or c). Minor isomer **6b**, 293 K: spectrum obscured by resonances of major isomer; 193 K: only 6 of 8 expected resonances visible, namely, $\delta = 180.7$, 178.4, 175.0, 172.4, 171.2, 164.2. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 193 K: $\delta = -145.93$ (major isomer), −153.13 (minor isomer). $C_{32}H_{21}O_8Os_3P$: found (calcd): C 33.72 (33.86), H 1.73 (1.85), P 2.55 (2.73).

Photolysis of $[Os_3(CO)_8(P(OMe)_3)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_4)]$ (4): Following the procedure described above for the photoisomerisation of **1**, 6 h irradiation of **4** afforded yellow microcrystalline $[H_2Os_3(CO)_8(P(OMe)_3)(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_6H_4)]$ (**7**) in 83% yield. IR: $\tilde{\nu}_{CO}/cm^{-1}$ (CH_2Cl_2): 2080 (m), 2044 (s), 1994 (s), 1974 (sh). ^1H NMR (CD_2Cl_2) indicates the presence of two isomeric benzyne complexes in the ratio 9:1: Major isomer **7a**, 293 K: 7.82 (br d, H_1 and H_4), 6.77 (br s, H_2 and H_3), 3.34 (d, $J_{PH} = 12.0$ Hz, 9H, $P(OMe)_3$), −16.85 (br d, H_5), −20.95 (br d, H_6); 203 K: 7.81 (d) and 7.78 (d, $J_{12} = J_{34} = 6.9$ Hz, H_1 and H_4), 6.93 (pt) and 6.63 (pt, $J_{23} = 6.9$ Hz, H_2 and H_3), 3.25 (d, $J_{PH} = 12.0$ Hz, 9H, $P(OMe)_3$), −16.80 (d, $J_{PH} = 3.8$. Hz, H_5), −21.28 (d, $J_{PH} = 14.5$ Hz, H_6). Minor isomer **7b**: only $P(OMe)_3$ and hydride resonances identified, 293 K: 3.66 (br s, $P(OMe)_3$), −18.80 (br s, 2H); 203 K: 3.64 (d, $J_{PH} = 12.2$ Hz, $P(OMe)_3$), −18.91 (d, $J_{PH} = 10.09$ Hz, 2H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, only carbonyl resonances reported): Major isomer **7a**, 186 K: 180.1 (s, b or c), 178.2 (s, e or f), 175.9 (d, $J_{PC} = 7.7$ Hz, h), 175.1 (s, a), 174.3 (s, b or c), 171.8 (d, $J_{PC} = 12.2$ Hz, d), 168.4 (d, $J_{PC} = 11.7$ Hz, g), 163.8 (s, e or f). Minor isomer **7b**, 186 K: 179.5 (s, 2C, b or c), 174.0 (s, 2C, a), 169.1 (s, 2C, b or c), 167.8 (d, 2C, d). MS: *m/z*: 1002 (M^+, as required). $C_{17}H_{15}O_{11}Os_3P$: found (calcd): C 20.91 (20.48); H 2.01 (1.50); P 3.77 (3.11).

Photolysis of $[Os_3(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (5): Following the procedure described above for the photoisomerisation of **1**, 2.5 h irradiation of **5** afforded bright yellow crystalline $[H_2Os_3(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_6H_4)]$ (**8**) in 86% yield. IR: $\tilde{\nu}_{CO}/cm^{-1}$ (CH_2Cl_2): 2053 (m), 2027 (s), 1996 (m), 1978 (m). ^1H NMR (CD_2Cl_2): $\delta = 7.50$ (m, H_1 and H_4); 7.0–7.5 (m, 30H, $2PPh_3$); 6.68 (m, H_2 and H_3); −17.20 (t, $J_{PH} = 8.8$ Hz, H_5); −17.83 (d, $J_{PH} = 10.3$ Hz, H_6). $C_{49}H_{36}O_7Os_3P_2$: found (calcd): C 43.55 (42.99); H 2.50 (2.63); P 4.44 (4.52).

Acknowledgements: We wish to thank NATO, The University of Edinburgh, BP Chemicals, ICI and the EPSRC for financial support.

Received: October 24, 1994 [F 5]

---

[1] J. A. Connor, *Top. Curr. Chem.* **1977**, *71*, 71.
[2] M. Tachikawa, J. R. Shapley, *J. Organomet. Chem.* **1977**, *124*, C19.
[3] B. F. G. Johnson, J. Lewis, D. A. Pippard, *J. Chem. Soc. Dalton Trans.* **1981**, 407.

[4] G. A. Foulds, B. F. G. Johnson, J. Lewis, *J. Organomet. Chem.* **1985**, *296*, 147.

[5] B. F. G. Johnson, J. Lewis, *Adv. Inorg. Radiochem.* **1981**, *24*, 225.

[6] R. D. Adams, L.-W. Yang, *J. Am. Chem. Soc.* **1983**, *105*, 235.

[7] E. D. Morrison, G. L. Geoffroy, A. L. Rheingeld, W. C. Fultz, *Organometallics* **1985**, *4*, 1413.

[8] G. Lavigne, N. Lugan, J. J. Bonnett, *Inorg. Chem.* **1987**, *26*, 2345.

[9] A. J. Deeming, *Adv. Organomet. Chem.* **1986**, *26*, 1.

[10] P. F. Hevelolt, B. F. G. Johnson, J. Lewis, P. R. Raithby, G. M. Sheldrick, *J. Chem. Soc. Chem. Commun.* **1978**, 340.

[11] R. D. Adams, I. T. Horvath, H.-S. Kim, *Organometallics* **1984**, *3*, 548.

[12] R. D. Adams, J. E. Babin, H.-S. Kim, *J. Am. Chem. Soc.* **1987**, *109*, 1414.

[13] B. F. G. Johnson, J. Lewis, M. V. Twigg, *J. Organomet. Chem.* **1974**, *67*, C75.

[14] F.-W. Grevels, J. G. A. Reuvers, J. Takats, *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 452.

[15] M. R. Burke, J. Takats, F.-W. Grevels, J. G. A. Reuvers, *J. Am. Chem. Soc.* **1983**, *105*, 4092.

[16] C. H. Bamford, M. U. Mahmud, *J. Chem. Soc. Chem. Commun.* **1972**, 762.

[17] J. L. Graff, R. D. Sanner, M. S. Wrighton, *Organometallics* **1982**, *1*, 837.

[18] Y. Doi, S. Tamura, K. Koshizuka, *J. Mol. Catal.* **1983**, *19*, 213.

[19] T. P. Gill, K. R. Mann, *Organometallics* **1982**, *1*, 485.

[20] J. L. Schrenk, A. M. McNair, F. B. MCormick, K. R. Mann, *Inorg. Chem.* **1986**, *25*, 3501.

[21] J. G. Bentsen, M. S. Wrighton, *J. Am. Chem. Soc.* **1987**, *109*, 4518.

[22] J. G. Bentsen, M. S. Wrighton, *J. Am. Chem. Soc.* **1987**, *109*, 4530.

[23] D. R. Tyler, M. Altobelli, H. B. Gray, *J. Am. Chem. Soc.* **1980**, *102*, 3022.

[24] J. Malito, S. Markiewicz, A. J. Po, *Inorg. Chem.* **1982**, *21*, 4335.

[25] A. J. Po, C. V. Sekhar, *J. Am. Chem. Soc.* **1986**, *108*, 3673.

[26] M. F. Desrosiers, D. A. Wink, R. Trautman, A. E. Friedmann, P. C. Ford, *J. Am. Chem. Soc.* **1986**, *108*, 1917.

[27] S. T. Belt, R. N. Perutz, University of York, private communication **1987**.

[28] A. J. Deeming, M. Underhill, *J. Chem. Soc. Dalton Trans.* **1974**, 1415.

[29] R. J. Goudsmit, B. F. G. Johnson, J. Lewis, P. R. Raithby, M. J. Rosales, *J. Chem. Soc. Dalton Trans.* ***1983***, 2257.

[30] A. J. Deeming, R. S. Nyholm, M. Underhill, *J. Chem. Soc. Chem. Commun.* **1972**, 224.

[31] A. J. Deeming, R. E. Kimber, M. Underhill, *J. Chem. Soc. Dalton Trans.* **1973**, 2589.

[32] C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, R. S. Mason, *J. Chem. Soc. Chem. Commun.* **1972**, 87.

[33] G. J. Gainsford, J. M. Guss, P. R. Ireland, R. S. Mason, C. W. Bradford, R. S. Nyholm, *J. Organomet. Chem.* **1972**, *40*, C70.

[34] A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, J. D. J. Backer-Dirks, *J. Chem. Soc. Dalton Trans.* **1981**, 1879.

[35] A. J. Arce, A. J. Deeming, *J. Chem. Soc. Dalton Trans.* **1982**, 1155.

[36] S. C. Brown, J. Evans, L. E. Smart, *J. Chem. Soc. Chem. Commun.* **1980**, 1021.

[37] R. D. Adams, D. A. Katahira, L.-W. Yang, *Organometallics* **1982**, *1*, 235.

[38] R. G. Bergman, *Science.* **1984**, *233*, 902.

[39] R. Khattar, Ph. D. Thesis, University of Cambridge, **1987**.

[40] E. Band, E. L. Muetterties, *Chem. Rev.* **1978**, *78*, 639.

[41] B. K. Teo, M. B. Hall, R. F. Fenske, L. F. Dahl, *J. Organomet. Chem.* **1977**, *70*, 413.

[42] S. Aime, L. Milone, R. Rossetti, P. L. Stanghellini, *Inorg. Chim. Acta.* **1977**, *25*, 103.

[43] H.-J. Kneuper, J. R. Shapley, *Organometallics* **1987**, *6*, 2455.

[44] A. J. Deeming, S. E. Kabir, N. I. Powell, P. A. Bates, M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.*, **1987**, 1529.

[45] D. R. Tyler, R. A. Levenson, H. B. Gray, *J. Am. Chem. Soc.* **1978**, *100*, 7888.

[46] B. Delley, M. C. Manning, D. E. Ellis, J. Berkowitz, W. C. Trogler, *Inorg. Chem.* **1982**, *21*, 2247.

[47] M. S. Wrighton, D. S. Ginley, *J. Am. Chem. Soc.* **1975**, *97*, 4246.

[48] C. H. Bamford, K. G. Al-Lamee, C. J. Konstantinov, *J. Chem. Soc. Faraday Trans. 1*, **1977**, *73*, 1406.