Photoisomerisation of Benzenetriosmium Cluster Complexes: a Model for Arene Activation on Flat Metal Surfaces

Mark A. Gallop,[a] Brian F. G. Johnson,[a] Jack Lewis,*[a] Andrew McCamley,[b] and Robin N. Perutz[b]
[a] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.*
[b] *Department of Chemistry, University of York, York YO1 5DD, U.K.*

The photoinduced dimetallation of face-capping benzene ligands in triosmium carbonyl complexes is presented as a cluster analogue for benzene activation in adsorbate overlayers on transition metal surfaces.

The chemistry of molecular chemisorption at the gas–metal interface is the focus of considerable interest in surface science, and important structure–reactivity correlations are now becoming apparent.[1] For example, under ultra-high vacuum conditions, benzene is adsorbed molecularly at ambient temperature on atomically flat surfaces of the later transition metals Rh[2a,b] and Ni and Pt,[3] while intrinsic topographical features of stepped metal surfaces favour dissociative benzene chemisorption.[3] It seems likely that planar co-ordination of the arene parallel to terraces on such surfaces provides for close approach of its hydrogen atoms to the step atoms of other terraces, facilitating C–H bond cleavage. An attractive cluster model for this process is provided by the μ_5-benzyne complex $[Ru_5(CO)_{13}(\mu_4\text{-PPh})(\mu_5\text{-}C_6H_4)]$, containing five ruthenium atoms arranged as in a step site on a (111) surface.[4] We are currently developing the chemistry of triosmium carbonyl clusters containing benzene in a face-capping bonding mode, $(\mu_3\text{-}\eta^2 : \eta^2 : \eta^2\text{-}C_6H_6)$,[5] that accurately models the non-dissociative chemisorption of benzene at a three-fold site on the surface of a closed-packed metal lattice.[2] This communication describes the efficient photoinduced isomerisation of the complexes $[Os_3\text{-}(CO)_{9-n}(L)_n(\mu_3\text{-}\eta^2 : \eta^2 : \eta^2\text{-}C_6H_6)]$ [n = 0, 1, or 2; L = CO, PPh_3, or $P(OMe)_3$] to the μ_3-benzyne compounds $[H_2Os_3\text{-}(CO)_{9-n}(L)_n(\mu_3\text{-}\eta^1 : \eta^2 : \eta^1\text{-}C_6H_4)]$, offering a cluster analogue

for the interconversion of associatively and dissociatively chemisorbed states of benzene on low Miller index surface planes of a metallic lattice.

At 278 K in toluene solution, pyrex-filtered broad-band visible radiation from a 500 W tungsten–halogen heat lamp for 13 h quantitatively converts $[Os_3(CO)_9(\mu_3\text{-}\eta^2 : \eta^2 : \eta^2\text{-}C_6H_6)]$ (1) into the isomeric triply-bridging benzyne (*ortho*-phenylene) cluster $[H_2Os_3(CO)_9(\mu_3\text{-}\eta^1 : \eta^2 : \eta^1\text{-}C_6H_4)]$ (2) (Scheme 1). Benzyne ligands are commonly found in thermolysis products of a variety of aryl compounds with triosmium substrates:[6] the C_6 fragment is invariably planar and inclined at an angle of *ca.* 60—70° to the metal triangle, forming σ-bonds to two Os atoms and having a π-interaction with the third osmium. The complex (2) has been previously obtained in modest yields from the reaction of benzene with $[Os_3(CO)_{12}]$ at *ca.* 463 K (ref. 7) or with $[Os_3(CO)_{10}(NCMe)_2]$ at 363 K, and has been structurally characterised by X-ray diffraction.[8]

Appropriate derivatives of (1) also undergo photoisomerisation to give new μ_3-benzyne compounds in high yields (*ca.* 90%). Photolysis of $[Os_3(CO)_8(PR_3)(\mu_3\text{-}\eta^2 : \eta^2 : \eta^2\text{-}C_6H_6)]$ [R = Ph (3) or OMe (4)] affords the complexes $[H_2Os_3(CO)_8\text{-}(PR_3)(\mu_3\text{-}\eta^1 : \eta^2 : \eta^1\text{-}C_6H_4)]$ [R = Ph (5) or OMe (6)], each as two chromatographically inseparable, interconvertible isomers that have been fully characterised by ^1H, ^{13}C, and ^{31}P

n.m.r. spectroscopy† (Scheme 1). Photoisomerisation of the bistriphenylphosphine derivative $[Os_3(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (7) provides the benzyne complex $[H_2Os_3(CO)_7(PPh_3)_2(\mu_3\text{-}\eta^1:\eta^2:\eta^1\text{-}C_6H_4)]$ (8) as a single isomer. Its stereochemistry has not been unequivocally determined, though the ^1H n.m.r. spectrum† is consistent with structure (8) containing two non-equivalent hydride ligands located cis to respectively one and two PPh$_3$ ligands. These transformations may also be effected with much lower efficiency by prolonged thermolysis in toluene. There is no evidence for reversibility of the isomerisations and the dimetallated complexes apparently represent the thermodynamically favoured species here.
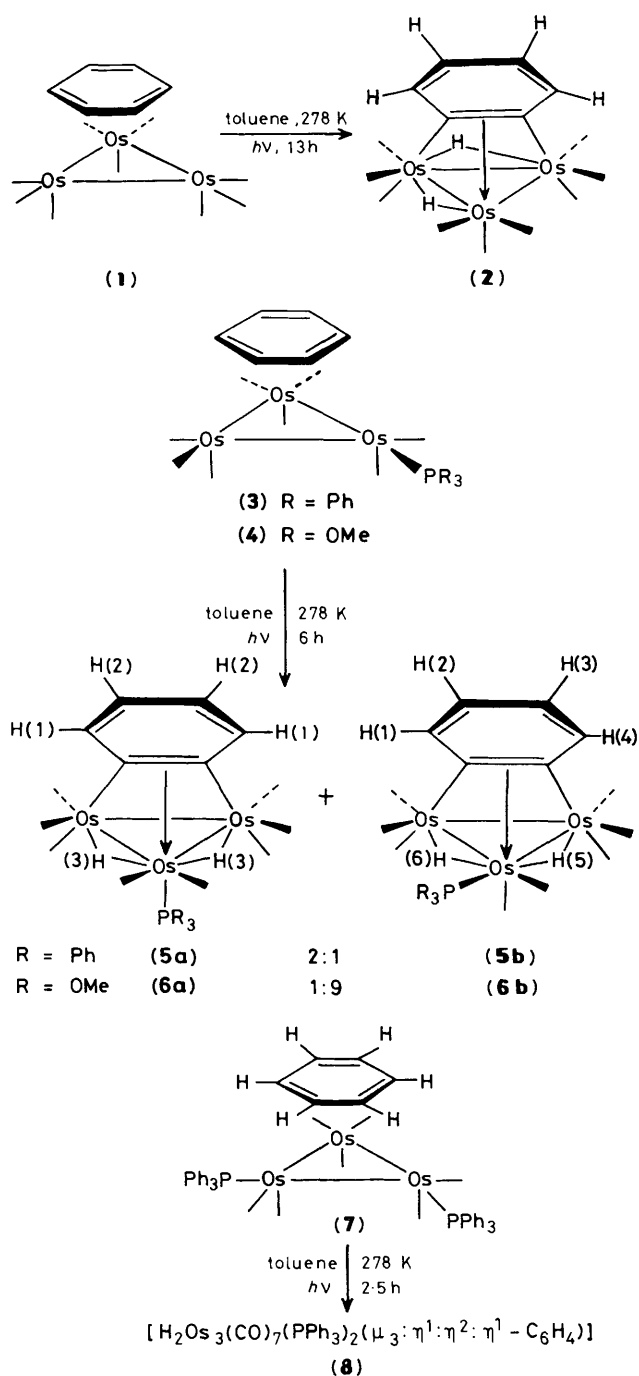
The clusters (5) and (6) are stereochemically non-rigid in solution. A lower energy benzyne rotation/flip process[9] $[\Delta G^*_{293}$ ca. 55 kJ mol^{-1} for (5)] produces a plane of symmetry through the C_6H_4 ligand of the non-symmetrical isomers (5b) and (6b) without averaging the inequivalent hydride environments or equilibrating with the symmetric forms (5a) and (6a). 'Turnstile' ligand interchange at the phosphorus-substituted osmium atom interconverts the C_1 and C_s isomers of (5) and (6) in a higher energy pathway $[\Delta G^*_{373}$ ca. 70 kJ mol^{-1} for (5)].

The electronic absorption spectra of the complexes (1), (3), and (7) in cyclohexane solution at 293 K are shown in Figure 1.

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† *Spectroscopic and analytical data* for the new benzyne complexes: (5) i.r. ν_{CO}/cm^{-1} (CH$_2$Cl$_2$) 2078(m), 2044(vs), 2032(sh), 1995(s), 1973(m), and 1940(w); ^1H n.m.r. δ (CD$_2$Cl$_2$) (indicates the presence of two isomeric benzyne complexes in the ratio 2:1), major isomer (5a) (293 K) 7.94 (m, 2 H-1) and 6.89 (m, 2 H-2) (AA'XX'), 7.10—7.55, (m, 15H, PPh$_3$), −18.09 (d, J_{PH} 9.2 Hz, 2 H-3); (193 K) 7.92 (m, 2 H-1) and 6.84 (m, 2 H-2) (AA'XX'), 7.1—7.5 (m, 15H, PPh$_3$) and −18.30 [d, J_{PH} 8.4 Hz, J (^{187}Os–^{1}H) 30.5 Hz (from satellite spectrum); 2 H-3]; minor isomer (5b) (293 K) 7.10—7.55 (m, 15H, PPh$_3$) (benzyne resonances exchange-broadened into baseline) −16.14 (d, J_{PH} 24.2 Hz, H-5), and −19.87 (d, J_{PH} 14.2 Hz, H-6); (193 K) 7.55 (d) and 7.09 (d) $J_{1,2} \simeq J_{3,4} \simeq 8.0$ Hz, H-1 and -4), 7.1—7.5 (m, 15H, PPh$_3$), 6.72 (pt) (pt = pseudotriplet) and 6.07 (pt) (J_{obs} 7.5 Hz, H-2 and H-3), −16.02 (d, J_{PH} 24.2 Hz, H-5 and −20.16 (d, J_{PH} 13.7 Hz, H-6); $^{13}C\{^1H\}$ n.m.r. (carbonyl resonances only) δ (CD$_2$Cl$_2$), major isomer (5a) (293 K) 174.5 (br. s), 169.3 (br. s), 166.4 (d, J_{PC} 4.5 Hz), and 164.5 (br. s); (193 K) 178.6 (s, 2 C), 173.7 (s, 2, C), 170.7 (d, J_{PC} 4.5 Hz, 2 C), and 168.9 (s, 2 C); minor isomer (5b) (293 K) obscured by resonances of major isomer; (193 K) only six of eight expected resonances visible, viz. 180.7, 178.4, 175.0, 172.4, 171.2, and 164.2; $^{31}P\{^1H\}$ n.m.r. δ (CD$_2$Cl$_2$) (193 K) −145.93 (major isomer) and −153.14 (minor isomer). (Found: C, 33.7; H, 1.7; P, 2.55. $C_{32}H_{21}O_8Os_3P$ requires C, 33.9; H, 1.85; P, 2.7%).

(6) I.r. ν_{CO}/cm^{-1} (CH$_2$Cl$_2$) 2080m, 2044s, 1944s, and 1974sh, ^1H n.m.r. δ (CDCl$_3$) (indicates the presence of two isomeric benzyne complexes in the ratio 9:1), major isomer (6b) (293 K) 7.82 (br. d, H-1 and -4), 6.77 (br. s, H-2 and -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) $J_{1,2} = J_{3,4} = 6.9$ Hz, H-1 and -4), 6.93 (pt) and 6.63 (pt) ($J_{2,3}$ 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} 38.8 Hz, H-5 and −21.28 (d, J_{PH} 14.5 Hz, H-6), minor isomer (6a) [only P(OMe)$_3$ and hydride resonances identified] (293 K) 3.66 [br. s, P(OMe)$_3$], −18.80 (br. s, 2 H); (203 K) 3.64 [d, J_{PH} 12.2 Hz, P(OMe)$_3$], and −18.91 (d, J_{PH} 10.9 Hz, 2 H); $^{13}C\{^1H\}$ n.m.r. δ (CD$_2$Cl$_2$) (carbonyl resonances only), major isomer (6b) (186 K) 180.1 (s), 178.2 (s), 175.9 (d, J_{PC} 7.7 Hz), 175.1 (s), 174.3 (s), 171.8 (d, J_{PC} 12.2 Hz), 168.4 (d, J_{PC} 11.7 Hz), and 163.8 (s); minor isomer (6a) (186 K) 179.5 (s, 2 C), 174.0 (s, 2 C), 169.1 (s, 2 C), and 167.8 (d, 2 C), M^+ 1002 (as required). (Found: C, 20.9; H, 2.0; P, 3.8. $C_{17}H_{15}O_{11}Os_3P$ requires C, 20.5; H, 1.5; P, 3.1%).

(8) i.r. ν_{CO}/cm^{-1} (CH$_2$Cl$_2$) 2053m, 2027s, 1996m, and 1978m; ^1H n.m.r. δ (CD$_2$Cl$_2$) 7.50 (m, H-1 and -4), 7.0—7.5 (m, 30H, 2PPh$_3$), 6.68 (m, H-2 and -3), −17.20 (t, J_{PH} 8.8 Hz, H-5) and −17.83 (d, J_{PH} 10.3 Hz, H-6). (Found: C, 43.55; H, 2.5; P, 4.4. $C_{49}H_{36}O_7Os_3P_2$ requires 43.0; H, 2.6; P, 4.5%).

(1) (2)

(3) R = Ph
(4) R = OMe

toluene 278 K
hν 6 h

R = Ph (5a) 2:1 (5b)
R = OMe (6a) 1:9 (6b)

(7)

toluene 278 K
hν 2·5 h

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

(8)

Scheme 1. Photoisomerisation of face-capping benzene cluster complexes.

Phosphine substitution leads to a bathochromic shift of the 312 nm absorption maximum in (1), with the corresponding feature in (3) and (7) being 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 bisphosphine compound (7). Fenske–Hall molecular orbital calculations[5c] for the model complex $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ predict that the lowest energy dipole-allowed transition occurs between (i) a doubly-degenerate orbital that is predominantly bonding with respect to the metal triangle and (ii) the cluster LUMO, which is
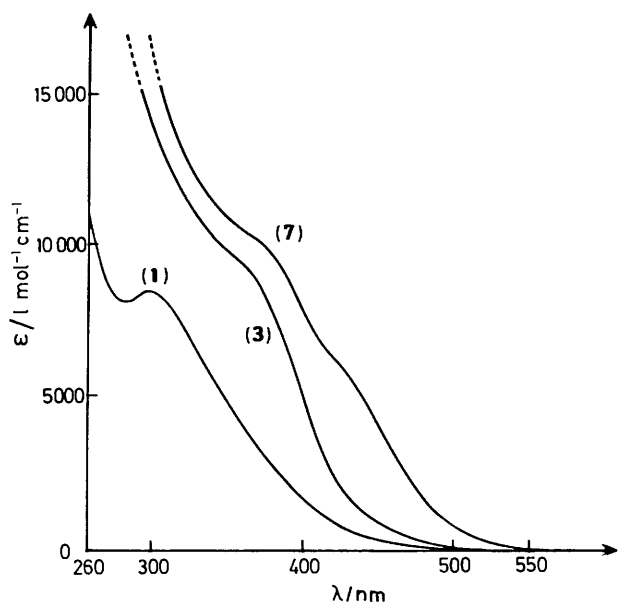
Figure 1. U.v.–visible spectra of $[Os_3(CO)_{9-n}(PPh_3)_n(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ [n = 0 (**1**), 1 (**3**), or 2 (**7**)] in cyclohexane solution.

mainly metal–metal antibonding and is directed along the Ru–Ru edges. Substitution of PPh_3 for an equatorial carbonyl ligand is expected to stabilise the in-plane LUMO[10] and may account for the observed red-shifting of the low-energy electronic transitions in (**3**) and (**7**).

It is clear from preliminary low temperature matrix photolysis studies in Ar, CH_4, and CO matrices that irradiation into these near-u.v.–visible absorptions initiates photoisomerisation. Thus, at 12—20 K, irradiation of (**1**) with light of wavelength >365 nm yields no net photochemistry, while irradiation above 290 nm gives substantial conversion to products in all three matrices (typically 40% conversion after 135 min). Initially a photo-sensitive species having an all-terminal CO ligand set is observed, which on prolonged photolysis is consumed to give a product whose ν_{CO} bands closely match those of the benzyne complex (**2**) in alkane solution.‡ The observation that only trace quantities of photo-ejected CO are detected in Ar and CH_4 matrices, and that (**1**) is photolysed in neat CO indicate that (**1**) is isomerised to (**2**) without undergoing CO loss. It seems probable that the photoreaction is a two-stage process, with the two C–H bonds being activated sequentially in the matrix. The nature of this intermediate species and of the primary photoprocess leading to its formation are unknown. C–H activation could occur

directly in an excited state of (**1**), or alternatively, at a vacant co-ordination site formed by arene 'ring-slippage'[11] or (less likely) by CO insertion into an Os–Os bond.[12,13] We hope to address these questions in further investigations of wavelength, medium, and ligand effects on this reaction in both matrix and solution phases.

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‡ *I.r. spectroscopic data* for (**1**) and its photo-products in CH_4 matrices. (**1**): ν_{CO} 2083, 2041, 2034, 2013, 2011, 2008, 1987, 1984, 1979, 1976, 1972, 1968, 1965, 1959 cm⁻¹. First photo-product: ν_{CO} 2050, 2023, 1955 cm⁻¹. Second photo-product (**2**): ν_{CO} 2111, 2105, 2069, 2059, 2025, 2005, 2000, 1985 cm⁻¹.