Trinuclear Benzene Clusters of Ruthenium and Osmium†

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The activated cluster $[Os_3(CO)_7(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(C_2H_4)(MeCN)]$ reacts with alkynes RC_2R' (R = R' = H, Ph or Me; R = H, R' = Ph; R = Me, R' = Et) to produce the new clusters $[Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}RC_2R')]$ in which the benzene molecule has migrated to a single osmium atom. In contrast, reaction of the ruthenium cluster $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ with similar alkynes RC_2R' (R = R' = H, Ph or Me; R = Ph, R' = H) yields the new clusters $[Ru_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}RC_2R'CO)]$ in which carbonyl insertion has occurred. The molecular structures of $[Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}C_2Me_2)]$ and of $[Ru_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}PhC_2PhCO)]$ have been established by single-crystal X-ray analysis. The C_6H_6 ligand is η^6-bonded to a single metal atom, while the C_2Me_2 and the PhC_2PhCO ligands lie above the metal triangles and are bonded to the three metal atoms *via* two σ interactions and one π interaction.

The use of discrete metal cluster complexes as models of chemisorption systems in surface chemistry is an attractive hypothesis and has been emphasised by Muetterties[1–7] and others.[8–11] The motivation for the work described in this paper came from our earlier studies whereby the molecular chemistry of a new class of arene carbonyl clusters was established.[12] The 'parent' cluster in those studies, *viz.* $[M_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (M = Os **1** or Ru **9**) contains benzene in an important new face-capping bonding mode which accurately models benzene adsorption at a three-fold site on the surface of a close-packed metal lattice.

We first reported the syntheses of the face-capping benzene-carbonyl clusters **1** and $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **2** in 1985.[12a] Subsequently we reported the preparation of the ruthenium analogue of **1**, $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **9** and, because of the high-quality crystals available,[12c] were able to establish that the C_6 ring shows in-plane Kekulè distortion and the bonding is related to that exhibited by C_6H_6 on the Rh(111) surface. More recently,[13] the highly efficient photoinduced isomerisation of **1** to the previously characterised μ_3-benzene complex $[Os_3H_2(CO)_9(\mu_3\text{-}\eta^2\text{-}C_6H_4)]$ **3** was observed. It would appear that photolysis generates a vacant site at osmium (mimicking the inherent co-ordinative unsaturation of a metal surface) and that this transformation offers a compelling model for the interconversion of associatively and dissociatively chemisorbed benzene. We would also note that a plausible primary intermediate in the surface-catalysed hydrogenation of benzene is suggested by our observation of the first well defined example of metal-to-arene hydrogen migration in a molecular complex. Hydrogen addition to a labile acetonitrile derivative of **1**, *viz.* $[Os_3(CO)_8(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(MeCN)]$ **4**, affords the dihydride compound $[Os_3H_2(CO)_8(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **5**, which undergoes either associative addition of CO, with migration of H to the C_6H_6 ligand, to yield the triply bridging cyclohexadienyl complex $[Os_3H(CO)_9(\mu_3\text{-}\eta^2:\sigma:\eta^2\text{-}C_6H_7)]$ **6** or CO addition with loss of H_2 to regenerate **1**.[14] The intermediacy of dienyl complexes in arene hydrogenation which has previously been postulated has therefore been shown to be viable from these studies.

In this work we have extended our studies of these model systems to embrace the displacement of benzene by alkyne which may represent an important stage in the cyclization of alkynes to arenes. In particular, the synthesis, chemical, spectroscopic and structural characterization in solution and the solid state of the new arene clusters $[Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}C_2Me_2)]$ **8c** and $[Ru_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}PhC_2PhCO)]$ **11b** are discussed.

Experimental

All experiments were carried out under an atmosphere of dry nitrogen, using dry, freshly distilled solvent, unless otherwise stated. Osmium tetraoxide and ruthenium trichloride were purchased from Johnson Matthey. The compounds $[Os_3(CO)_{12}]$ and $[Ru_3(CO)_{12}]$ were prepared following the published methods[15] with some modifications;[16] $[Os_3(CO)_9(C_6H_6)]$ and $[Ru_3(CO)_9(C_6H_6)]$ were also prepared by the published methods[12a,c] and were used for reactions after TLC separation.

Infrared spectra were recorded on a Perkin-Elmer 983 or a 1710 FT instrument using carbon monoxide gas as calibrant, ^1H and ^{13}C NMR spectra on a Bruker WM250 or WM400 spectrometer. Mass spectra were recorded by electron-impact ionisation on a Kratos-AEI-MS 12 instrument, using tris(perfluoroheptyl)-s-triazene as calibrant or by fast atom bombardment on a FAB MS902 instrument. Thin-layer chromatography plates were pre-coated with a 0.25 mm layer of Merck Kieselgel 60F-254. Spectroscopic data for all species discussed herein are collected in Tables 1 and 2 for the osmium and ruthenium derivatives, respectively.

Preparations.—$[Os_3(CO)_7(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^2\text{-}C_2H_4)(MeCN)]$ **7**. A solution of Me_3NO (5.3 mg, 1.6 mol equivalents) in MeCN (0.5 cm^3) was added dropwise to $[Os_3(CO)_8(\eta^2\text{-}C_2H_4)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (40 mg, 0.04 mmol) in MeCN (2 cm^3) at room temperature under an argon atmosphere over a period of 5 min. After stirring for 30 min the solvent was evaporated under reduced pressure and the reactions with alkynes were carried out without any further purification. IR: ν_{CO}/cm^{-1} (MeCN) 2030m, 1992vs and 1927 (sh).

Compounds **8a–8e**. Essentially the same procedure was adopted for all five compounds. Details will be given for **8c**.

The compound $[Os_3(CO)_7(C_6H_6)(C_2H_4)(MeCN)]$ was

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Spectroscopic data for $[Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}RC_2R')]$

Complex	Alkyne	IR $\nu_{CO}(CH_2Cl_2)/cm^{-1}$	^1H NMR $\delta(CDCl_3)$	Mass spectrum *m/z* *
8a	R = R′ = H	2058m, 2032vs, 1974vs	5.94 (s, 6 H, C_6H_6) 9.73 (d, 1 H) 11.03 (d, 1 H)	876 (876)
8b	R = R′ = Ph	2063m, 2023vs, 1986s, 1952m, 1732w (br)	5.84 (s, 6 H, C_6H_6) 6.74–7.11 (m, 10 H, 2Ph)	Not observed
8c	R = R′ = Me	2054m, 2019vs, 1970s	2.24 (s, 3 H, Me) 2.69 (s, 3 H, Me) 5.94 (s, 6 H, C_6H_6)	904 (904)
8d	R = H, R′ = Ph	2057m, 2024vs, 1975s	**I**: 6.01 (s, 6 H, C_6H_6) 7.16–7.10 (m, Ph) 9.78 (s, 1 H) **II**: 6.02 (s, 6 H, C_6H_6) 7.16–7.10 (m, Ph) 11.13 (s, 1 H)	952 (952)
8e	R = Me, R′ = Et	2053m, 2018vs, 1970s		917 (917)

* Calculated values given in parentheses.

Table 2 Spectroscopic data for the compounds $[Ru_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}RC_2R'CO)]$

Complex	Alkyne	IR $\nu_{CO}(CH_2Cl_2)/cm^{-1}$	^1H NMR $\delta(CDCl_3)$	Mass spectrum *m/z* *
11a	R = R′ = Me	2066m, 2035vs, 1992s (br), 1870w	1.85 (s, 3 H, Me) 2.57 (s, 3 H, Me) 6.13 (6 H, C_6H_6)	660 (659)
11b	R = R′ = Ph	2069s, 2036vs, 1997s (br), 1887w	6.24 (s, 6 H, C_6H_6) 6.74–7.04 (m, 10 H, 2Ph)	780 (783)
11c	R = R′ = H	2072m, 2040vs, 1997s (br), 1882w	5.52 (d, 1 H, *J* = 7.6 Hz) 6.15 (s, 6 H, C_6H_6) 8.50 (d, 1 H, *J* = 7.6 Hz)	(631)
11d	R = Ph, R′ = H	2071m, 2040vs, 1998s, 1884w (br)	**I**: 6.21 (s, 6 H, C_6H_6) 7.15–7.30 (m, Ph) 8.62 (s, 1 H) **II**: 5.75 (s, 1 H) 6.18 (s, 6 H, C_6H_6) 7.15–7.30 (m, Ph)	(707)

* Calculated values given in parentheses.

prepared by using $[Os_3(CO)_8(C_6H_6)(C_2H_4)]$ (40 mg, 0.044 mmol) as starting material, and following the literature procedure[14] described above. Excess of dimethylacetylene was then added to the dry complex, separated from the reaction mixture without purification. Dichloromethane (5 cm^3) was added and the solution stirred at room temperature for 30 min. Separation by TLC eluting with CH_2Cl_2 (40%)–hexane (60%) afforded four bands. The orange band corresponding to **8c** was extracted with CH_2Cl_2 and, after removal of the solvent *in vacuo*, yellow microcrystals (8 mg, 0.008 mmol) were obtained. Attempts fully to identify the other reaction components have not yet been successful.

Compounds **11a–11d**. Again essentially the same synthetic method was adopted for all compounds **11a–11d**. The preparation of **11b** will serve as a typical example.

Excess of diphenylacetylene in CH_2Cl_2 (5 cm^3) was added as solid to a Carius tube containing a solution of $[Ru_3(CO)_9(C_6H_6)]$ **9** (20 mg, 0.03 mmol) in CH_2Cl_2 (15 cm^3). The tube was sealed and heated at *ca.* 37 °C for 4 h. The solvent was then evaporated at reduced pressure. After purification by TLC, eluting with CH_2Cl_2 (30%)–hexane (70%), three complexes were isolated. The dark red complex **11b** was isolated as a major product (10 mg, 0.013 mmol) and crystallised from CH_2Cl_2–hexane.

Structural Characterisation.—Crystal data for cluster **8c**. $C_{17}H_{12}O_7Os_3$, *M* = 899, triclinic, space group $P\bar{1}$, *a* = 8.09(1), *b* = 8.374(1), *c* = 15.139(7) Å, α = 101.67(2), β = 92.00(7), γ = 106.82(6)°, *U* = 956.6 Å^3, *F*(000) = 796, *Z* = 2, D_c = 3.12 g cm^{-3}, μ(Mo-Kα) = 191.3 cm^{-1}, *R* = 0.056 (*R′* = 0.061) for 2938 out of 3252 independent reflections $[I_o > 2\sigma(I_o)]$.

An absorption correction was applied by azimuthal scan of 12 reflections (χ > 80°) (minimum transmission factor 46%) and subsequently by the Walker and Stuart method[17] (correction range 0.89–1.31).

Crystal data for cluster **11b**. $C_{28}H_{16}O_8Ru_3 \cdot 0.5CH_2Cl_2$, *M* = 826, monoclinic, space group $P2_1/n$, *a* = 12.850(1), *b* = 14.637(1), *c* = 14.874(3) Å, β = 89.35(1)°, *U* = 2797 Å^3, *Z* = 4, D_c = 1.96 g cm^{-3}, *F*(000) = 1604, μ(Mo-Kα) = 15.75, θ range 2.5–27°, *R* = 0.020 (*R′* = 0.022), for 3982 out of 4617 independent reflections $[I_o > 2\sigma(I_o)]$.

No absorption correction was applied.

Details common to both species. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer by the ω–2θ scan method. The structures were solved by direct methods; light atoms were located by subsequent Fourier difference syntheses. All non-H atoms were allowed to vibrate anisotropically. A weighting scheme of the form $w = K/[\sigma(F) + gF^2]$ was used. The H atoms of the methyl and benzene groups in complex **8c** and of the phenyl groups in **11b** were added in calculated positions (C–H 1.08 Å) and refined 'riding' on their respective C atoms; common isotropic thermal parameters were also refined (in the order: 0.16, 0.08 and 0.08 Å^2); the benzene H atoms in **11b** were located from the Fourier difference maps and refined with constraints on the C–H distances. The SHELX 76[18] package of crystallographic programs was used in all calculations. Fractional atomic coordinates for **8c** and **11b** are reported in Tables 3 and 4, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Recently we demonstrated that cluster **1** readily undergoes reaction with Me_3NO–MeCN to produce the activated species $[Os_3(CO)_8(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(MeCN)]$ **4** from which a range of derivatives of the type $[Os_3(CO)_8L(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$[19] ($L = PR_3$, *etc.*) and $[Os_3(CO)_7(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)(C_2H_4)(MeCN)]$ **7** may be obtained (see Scheme 1). In an earlier communication we further reported that **7** reacts with alkynes (RC_2R') ($R = R' = H$, Ph or Me; $R = H$, $R' = Ph$; $R = Me$, $R' = Et$) to yield $[Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}RC_2R')]$ **8** in which the benzene is now bonded to a single osmium atom. The migration of the benzene from a $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2$ bonding site to a single metal atom is the reverse of that previously observed and is another indication of the ease with which the C_6H_6 unit (or arenes in general) may modify its co-ordination mode.

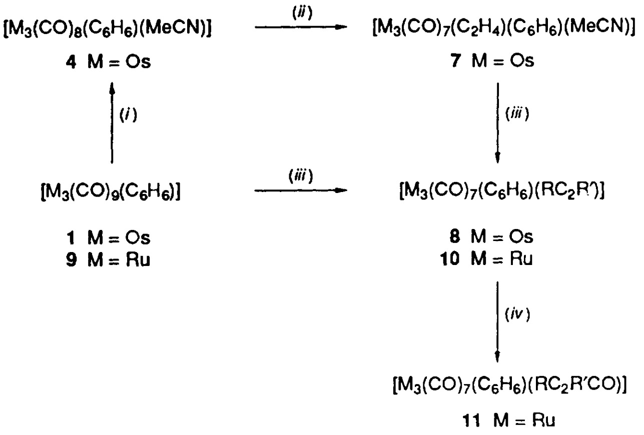
Table 3 Fractional atomic coordinates for compound **8c**

Atom	*x*	*y*	*z*
Os(1)	0.070 10(7)	0.036 88(6)	0.717 19(3)
Os(2)	0.372 08(6)	0.269 62(6)	0.675 26(3)
Os(3)	0.224 03(6)	0.336 55(6)	0.837 14(3)
C(1)	−0.069 1(20)	0.100 6(22)	0.633 4(11)
O(1)	−0.146 8(19)	0.151 2(20)	0.585 9(10)
C(2)	0.037 6(18)	−0.185 9(15)	0.643 0(10)
O(2)	0.018 9(20)	−0.316 6(17)	0.603 2(9)
C(3)	−0.113 6(21)	−0.049 8(21)	0.787 2(11)
O(3)	−0.203 1(18)	−0.086 8(19)	0.837 5(11)
C(4)	0.377 1(24)	0.044 3(20)	0.643 5(11)
O(4)	0.411 7(21)	−0.081 7(15)	0.625 8(10)
C(5)	0.403 8(19)	0.537 3(18)	0.895 0(9)
O(5)	0.520 4(16)	0.657 9(16)	0.927 8(8)
C(6)	0.060 9(20)	0.441 5(21)	0.798 8(9)
O(6)	−0.029 2(16)	0.510 6(17)	0.775 3(9)
C(7)	0.114 5(24)	0.315 6(20)	0.945 1(11)
O(7)	0.051 7(20)	0.294 8(21)	1.008 0(9)
C(8)	0.286 9(22)	−0.016 4(21)	0.891 4(10)
C(9)	0.273 1(18)	0.078 5(16)	0.816 5(9)
C(10)	0.422 0(16)	0.210 8(17)	0.802 7(9)
C(11)	0.596 8(18)	0.257 7(25)	0.847 5(11)
C(12)	0.550 0(18)	0.537 7(17)	0.688 8(11)
C(13)	0.386 3(20)	0.547 9(18)	0.669 4(10)
C(14)	0.280 6(19)	0.432 8(18)	0.595 5(10)
C(15)	0.345 3(21)	0.322 1(19)	0.535 7(9)
C(16)	0.513 3(20)	0.320 2(21)	0.555 7(10)
C(17)	0.616 3(20)	0.424 4(19)	0.632 7(10)

Although we have previously observed that compound **1** undergoes substitution reactions, it does not react with alkyne even at high temperatures. The reaction of $[Os_3(CO)_8L(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ ($L = C_2H_4$ or MeCN) leads to extensive decomposition and only small amounts of **1** may be isolated. In contrast, treatment of **7** with alkyne (RC_2R') at ambient temperature leads to the formation of the new complexes $[Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}RC_2R')]$ ($R = R' = H$ **8a**; $R = R' = Ph$ **8b**; $R = R' = Me$ **8c**; $R = H$, $R' = Ph$ **8d**; $R = Me$, $R' = Et$ **8e**). Very small amounts of other, as yet uncharacterised, products were also obtained.

Apart from compound **8b** all the new compounds **8a**–**8e** exhibit a similar IR spectrum in the ν_{CO} region (see Table 1). Compound **8b** exhibits a spectrum which, to some extent, resembles that of the ruthenium complex **11b** at least in the ν_{CO} region. However, in the absence of structural data, it is difficult to make hypotheses on the molecular structure.

The ^1H NMR spectra of compounds **8a**–**8e** are also similar (see Table 1). All exhibit a singlet resonance at *ca.* δ 5.8–6.0, which may be assigned to a co-ordinated C_6H_6 molecule. Shifts in this region are characteristic of benzene in a η^6 co-ordination mode.[10] The ^1H NMR spectrum ($CDCl_3$) of **8c** is completely in



Scheme 1 The formation of $[Os_3(CO)_7(C_6H_6)(RC_2R')]$ and $[Ru_3(CO)_7(C_6H_6)(RC_2R'CO)]$: (*i*) Me_3NO–MeCN; (*ii*) Me_3NO–C_2H_4; (*iii*) RC_2R'; (*iv*) CO. Formation of compound **11** is believed to proceed *via* the intermediate formation of the ruthenium analogue **10** of the previously characterised osmium complex **8**

Table 4 Fractional atomic coordinates for compound **11b**

Atom	*x*	*y*	*z*
Ru(1)	0.588 77(2)	0.159 39(2)	0.361 43(1)
Ru(2)	0.665 34(2)	0.128 96(2)	0.186 87(1)
Ru(3)	0.477 02(2)	0.053 65(1)	0.249 32(2)
C(1)	0.530 1(2)	0.173 9(2)	0.478 1(2)
O(1)	0.502 7(2)	0.182 0(2)	0.550 8(2)
C(2)	0.702 7(3)	0.234 7(2)	0.397 5(2)
O(2)	0.770 9(2)	0.278 1(2)	0.420 3(2)
C(3)	0.639 8(2)	0.041 3(2)	0.388 9(2)
O(3)	0.675 3(2)	−0.027 0(2)	0.411 5(2)
C(4)	0.551 5(2)	0.139 2(2)	0.109 5(2)
O(4)	0.501 9(2)	0.157 3(2)	0.048 8(2)
C(5)	0.381 7(3)	0.034 6(2)	0.154 5(2)
O(5)	0.324 4(2)	0.024 6(3)	0.098 9(2)
C(6)	0.382 7(2)	0.002 7(2)	0.334 2(2)
O(6)	0.327 9(2)	−0.032 1(2)	0.383 1(2)
C(7)	0.546 8(2)	−0.062 8(2)	0.234 0(3)
O(7)	0.586 0(2)	−0.131 1(2)	0.223 3(3)
C(8)	0.610 5(2)	0.257 5(2)	0.218 3(2)
O(8)	0.659 2(2)	0.324 6(1)	0.194 8(2)
C(9)	0.442 6(2)	0.190 1(2)	0.282 1(2)
C(10)	0.510 4(2)	0.265 1(2)	0.270 4(2)
C(11)	0.333 7(2)	0.210 9(2)	0.312 7(2)
C(12)	0.267 3(2)	0.250 6(2)	0.250 6(2)
C(13)	0.164 3(3)	0.269 0(2)	0.272 5(3)
C(14)	0.125 7(3)	0.250 2(2)	0.357 6(3)
C(15)	0.190 3(2)	0.211 2(2)	0.419 8(2)
C(16)	0.293 0(2)	0.190 6(2)	0.397 5(2)
C(17)	0.476 7(2)	0.360 8(2)	0.293 3(2)
C(18)	0.449 8(3)	0.418 3(2)	0.222 5(3)
C(19)	0.416 6(3)	0.507 3(2)	0.239 3(3)
C(20)	0.410 2(3)	0.539 1(2)	0.324 8(3)
C(21)	0.435 3(3)	0.484 3(2)	0.395 1(3)
C(22)	0.469 6(3)	0.394 2(2)	0.379 3(2)
C(23)	0.822 9(2)	0.079 6(3)	0.247 2(2)
C(24)	0.784 7(2)	0.006 5(2)	0.195 8(3)
C(25)	0.760 9(3)	0.020 5(2)	0.107 2(2)
C(26)	0.774 7(3)	0.105 4(3)	0.068 2(2)
C(27)	0.811 9(3)	0.178 3(3)	0.116 0(3)
C(28)	0.835 2(2)	0.166 8(3)	0.206 8(3)
C(A)	0.943 3(7)	0.040 4(7)	0.481 0(6)
C(B)	1.090 5(4)	−0.106 5(5)	0.518 8(4)
C(C)	1.077 7(11)	0.015 7(8)	0.511 0(12)
C(D)	0.956 0(10)	0.083 2(9)	0.475 0(10)

accord with this structure: a singlet resonance of relative intensity six is observed at δ 5.94 in agreement with the presence of an η^6-bonded C_6H_6 molecule. In addition two singlet methyl resonances are observed at δ 2.69 (3 H) and 2.24 (3 H); this is as expected for the bonded Me_2C_2 moiety, in which the Me groups are rendered inequivalent by the asymmetry of the molecule **8c**. Compound **8d** appears to exist in two isomeric forms. Despite the fact that the IR spectrum exhibits only three ν_{CO} bands, in the ^1H NMR spectrum the resonances which may be assigned to the co-ordinated benzene molecule are observed at δ 6.10 (s) and 6.02 (s). In the phenyl region a complex multiplet is observed but signals assigned to an alkynic proton are observed at δ 9.78 (s) and 11.13 (s). We believe that these two isomers possess the structures shown in Fig. 1 (**I** and **II**). The resonance observed for the alkynic protons at δ 11.13 (s) we thereby assign to isomer **II** in which the alkynic proton is adjacent to the benzene ring. In this connection it is important to note that for compound **8a** two proton resonances are observed at δ 9.73 (d) and 11.03 (d).

I **II**

Fig. 1 Probable structures of the two isomeric forms (**I** and **II**) of compound **8d**

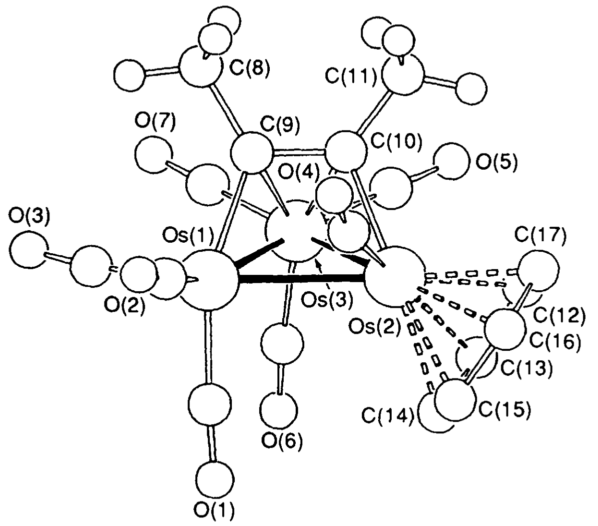


Fig. 2 The molecular structure of compound **8c**, showing the atomic labelling scheme; H atoms are omitted for clarity. The C atoms of the CO groups bear the same numbering as the corresponding O atoms

Crystallisation of compound **8c** from dichloromethane–hexane gave orange rhombic crystals which were subject to a single-crystal X-ray analysis (see Fig. 2).

In contrast to the osmium cluster **1**, the ruthenium analogue **9** does not undergo substitution reaction, at least under comparable conditions. However, on heating with alkynes RC_2R' (R = R' = Me, Ph or H; R = Ph, R' = H) in dichloromethane under reflux a deep red cluster is obtained as the major product. Crystallisation of the cluster $[Ru_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2\text{-}PhC_2(PhCO)]$ **11b** obtained from the reaction with C_2Ph_2 from a solution in CH_2Cl_2–hexane gave dark red rhombic crystals, which were found to be suitable for X-ray analysis.

The spectroscopic data for the new clusters **11a**–**11d** given in Table 2 are consistent with this structure. In particular, the IR band at ≈ 1880 cm^{-1} may be assigned to the ketonic CO of the bonded $RC_2R'(CO)$ unit. The ^1H NMR data show a singlet resonance in all cases in the region δ 6.13–6.24, which may be reliably assigned to the η^6-co-ordinated benzene molecule. It is noteworthy that, although these spectra resemble that observed

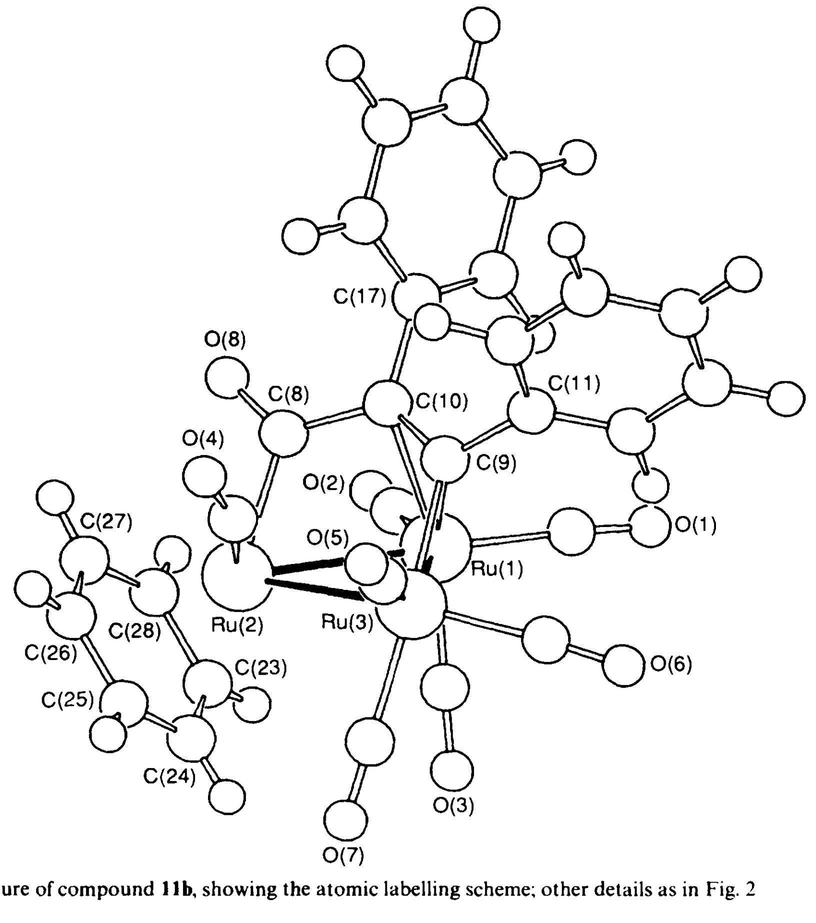


Fig. 3 The molecular structure of compound **11b**, showing the atomic labelling scheme; other details as in Fig. 2

Table 5 Relevant structural parameters (distances in Å, angles in °) for compounds **8c** and **11b**

8c		**11b**	
Os(1)–Os(2)	2.832(1)	Ru(1)–Ru(2)	2.802(1)
Os(1)–Os(3)	2.708(1)	Ru(1)–Ru(3)	2.700(1)
Os(2)–Os(3)	2.791(1)	Ru(2)–Ru(3)	2.808(1)
Os(1)–C(9)	2.09(1)	Ru(2)–C(8)	2.060(3)
Os(2)–C(10)	2.14(1)	Ru(3)–C(9)	2.102(3)
Os(3)–C(9)	2.27(1)	Ru(1)–C(9)	2.274(3)
Os(3)–C(10)	2.18(1)	Ru(1)–C(10)	2.296(3)
Os(2)–C(12)	2.25(1)	Ru(2)–C(24)	2.364(3)
Os(2)–C(13)	2.32(1)	Ru(2)–C(25)	2.323(4)
Os(2)–C(14)	2.25(1)	Ru(2)–C(26)	2.270(4)
Os(2)–C(15)	2.26(1)	Ru(2)–C(27)	2.266(4)
Os(2)–C(16)	2.22(1)	Ru(2)–C(28)	2.274(3)
Os(2)–C(17)	2.22(1)	Ru(2)–C(23)	2.338(4)
Os(2)–C(4)	1.86(1)	Ru(2)–C(4)	1.877(3)
Os(1) · · · C(4)	2.75(2)	Ru(3) · · · C(4)	2.601(3)
C(4)–O(4)	1.15(2)	C(4)–O(4)	1.142(4)
C(9)–C(10)	1.44(2)	C(9)–C(10)	1.411(4)
C(8)–C(9)	1.53(2)	C(10)–C(8)	1.499(4)
C(10)–C(11)	1.46(2)	C(9)–C(11)	1.498(4)
		C(10)–C(17)	1.504(4)
		C(8)–O(8)	1.214(4)
C(12)–C(13)	1.38(1)	C(23)–C(24)	1.407(6)
C(13)–C(14)	1.39(1)	C(24)–C(25)	1.373(5)
C(14)–C(15)	1.39(1)	C(25)–C(26)	1.382(5)
C(15)–C(16)	1.39(1)	C(26)–C(27)	1.371(6)
C(16)–C(17)	1.38(1)	C(27)–C(28)	1.396(6)
C(12)–C(17)	1.38(1)	C(23)–C(28)	1.418(6)
Os(2)–C(4)–O(4)	168(2)	Ru(2)–C(4)–O(4)	161.6(3)
C(8)–C(9)–C(10)	119(1)	Ru(2)–C(8)–O(8)	120.1(2)
C(9)–C(10)–C(11)	127(1)	O(8)–C(8)–C(10)	121.6(3)
		C(8)–C(10)–C(9)	122.1(2)
		C(17)–C(10)–C(9)	121.4(2)
		C(10)–C(9)–C(11)	116.9(2)

for cluster **8b**, an upfield shift occurs particularly for the resonance associated with the R group.

Carbonyl insertion is a very common feature of alkyl-metal complexes and has been observed in a wide range of cluster carbonyl reactions with alkynes. It would not appear unreasonable to assume that the mechanism for the formation of this product involves the initial formation of [Ru$_3$(CO)$_7$(η^6-C$_6$H$_6$)(C$_2$Ph$_2$)] **10**, although further discussion is not warranted in view of the paucity of data available.

The Molecular Structures of Compounds **8c** *and* **11b** *in the Solid State.*—The molecular structures of compounds **8c** and **11b** are closely related and will be discussed together. They are depicted in Figs. 2 and 3, respectively. Relevant structural parameters are listed in Table 5.

Both species are characterised by the presence of a benzene fragment η^6-bound to one corner of the triangular metal framework, with the additional organo-ligand interacting with the three metal atoms of the cluster. The main difference between **8c** and **11b** arises from the nature of this latter ligand: the C$_2$Me$_2$ ligand in **8c** is replaced by the more sophisticated PhC=C(Ph)CO fragment in **11b**. This latter fragment can be seen as derived from the insertion of a CO group on one of the two Os–C σ interactions present in the structure of **8c**, or by addition at the C atom of one terminally bound CO group of the diphenylacetylene reactant. In both cases the ligands formally contribute a total of four electrons to the cluster framework *via* two σ interactions [Os(1)–C(9) and Os(2)–C(10) in **8c**, mean 2.12(1) Å; Ru(2)–C(8), Ru(3)–C(9) in **11b**, mean 2.081(3) Å] and one π interaction [Os(3)–C(9), Os(3)–C(10), mean 2.23(1); Ru(1)–C(9), Ru(1)–C(10), mean 2.285(3) Å]. The two fragments show a clear sp^2-like pattern in the C–C–C angles and C–C distances (see Table 5). In particular, the bond distances C(8)–C(10) and C(9)–C(10) within the PhC$_2$(Ph)CO system in **11b** [1.499(4), 1.411(4) Å], as well as C(8)–O(8) [1.214(4) Å] and the angles at the three metal-co-ordinated carbon centres [O(8)–C(8)–C(10) 121.6(3), C(8)–C(10)–C(9) 122.1(2), C(10)–C(9)–C(11) 116.9(2)°], indicate extensive electron delocalisation over the whole OC–C–C system. In both **8c** and **11b** the benzene-co-ordinated metal atoms bear a slightly bent terminal CO ligand [Os(2)–C(4)–O(4) 168(2), Ru(2)–C(4)–O(4) 161.6(3)°]. This ligand is 'pushed' towards a semi-bridging position [Os(1) · · · C(4) 2.75(2), Ru(3) · · · C(4) 2.601(3) Å] by the steric pressure of the flat benzene fragment. This is also reflected in the off-centring of the benzene fragment with respect to the co-ordinated metal atoms, Os–C(benzene) and Ru–C(benzene) distances falling in the ranges 2.22(1)–2.32(1) and 2.274(3)–2.364(3) Å in **8c** and **11b**, respectively. These interactions are in their mean values [2.25(1) and 2.306(3) Å] shorter than the corresponding values in the face-capped species [Os$_3$(CO)$_9$(μ_3-η^2:η^2:η^2-C$_6$H$_6$)] and [Ru$_3$(CO)$_9$(μ_3-η^2:η^2:η^2-C$_6$H$_6$)] [2.33(1) and 2.331(4) Å] indicating that the η^6 co-ordination mode allows a somewhat more efficient orbital overlap between the arene and the metal atom than the μ_3 co-ordination (perhaps simply because of less intramolecular steric strain with the surrounding ligands).

Considering a six-electron donation from the C$_6$H$_6$ fragment, the electron distribution over the three metal centres in both species appears to be uneven with one atom formally receiving seven [Os(1) and Ru(3)], one nine [Os(2) and Ru(2)], and one eight electrons from the ligands [Os(3) and Ru(1)].

Metal–metal bonds in compound **8c** [range 2.708(1)–2.832(1), mean 2.777(1) Å] and in **11b** [range 2.700(1)–2.808(1), mean 2.770(1) Å] are longer, in both cases, than in the corresponding isoelectronic binary carbonyls [M = Os, 2.877(1); Ru, 2.855(1) Å].

It is probable that compounds **11** are formed from the ruthenium analogue **10** of the osmium compound **8**. Carbonyl insertion is expected to be more facile for ruthenium than osmium; however, attempts to carbonylate **8** under moderate temperature and pressures of CO have failed to date, and although very small amounts of other materials have been observed in the preparation of **11** there is no spectroscopic evidence to indicate that **10** is formed as an intermediate compound.

Acknowledgements

We thank CNPq (Brazil) for a Ph.D Scholarship (to M. M.) and Ministero dell'Universita' e della Ricerca Scientifica e Tecnologica (Italy) and the SERC (UK) for financial support. B. F. G. J., D. B. and F. G. acknowledge a collaborative research NATO grant.

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Received 4th October 1991; *Paper* 1/05059A