Benzene Migration in an Osmium Cluster: the Formation of $Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3:\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)$ from $Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$. The Crystal Structure of $Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3:\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)$

Dario Braga,[a] Fabrizia Grepioni,[a] Brian F. G. Johnson,[b] Jack Lewis,[b] Marcia Martinelli,[b] and Mark A. Gallop[c]

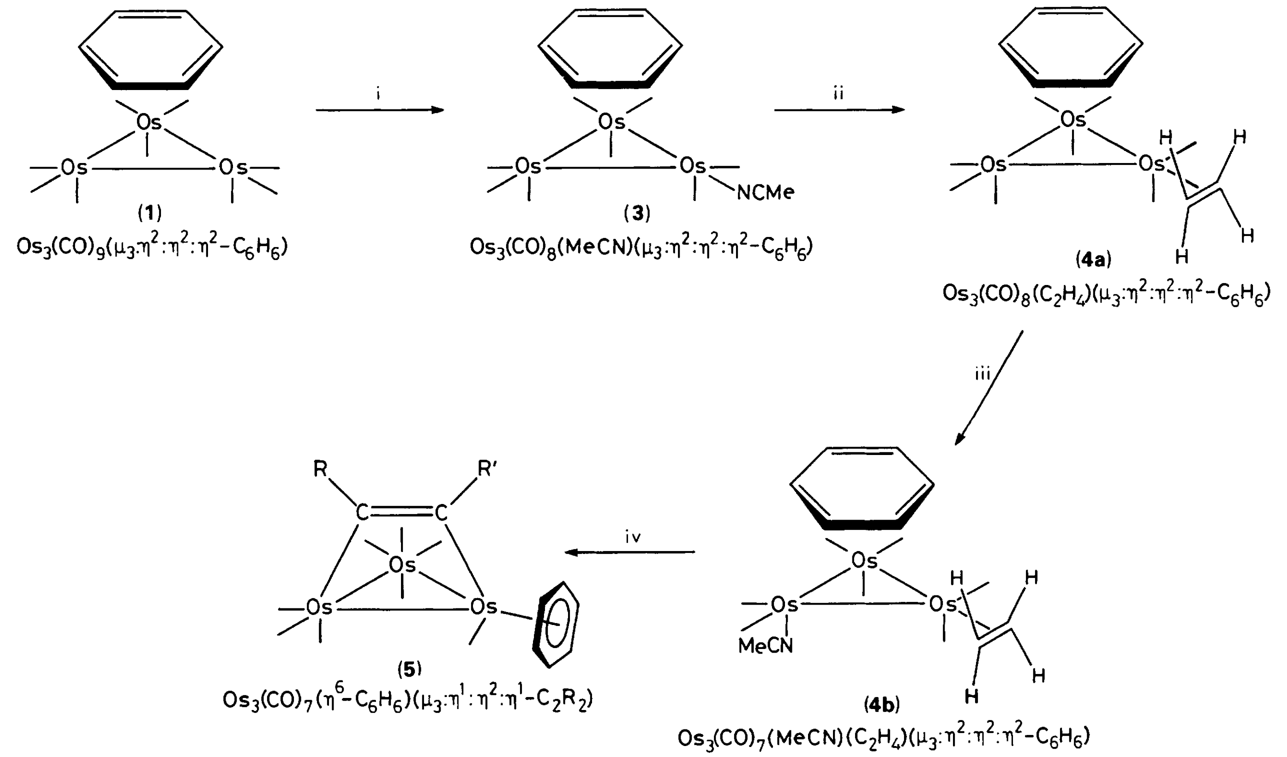
[a] *Dipartimento di Chimica 'G. Ciamician,' Universitá degli Studi di Bologna, Via Selmi 2, 40126 Bologna, Italy*
[b] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.*
[c] *Department of Chemistry, University of California, Berkeley, California 94720, U.S.A.*

The activated cluster $[Os_3(CO)_7(C_2H_4)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(MeCN)]$ reacts with alkynes RC_2R' (R = R' = H, Ph or Me; R = H, R' = Ph; R = Me, R' = Et), to produce the new clusters $[Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3:\eta^1:\eta^2:\eta^1\text{-}RC_2R')]$ in which the benzene is bonded to a single metal atom as shown by a single crystal *X*-ray structure determination of the C_2Me_2 derivative.

Recent studies[1] have shown that benzene readily forms complexes with a wide range of cluster systems. A remarkable feature of these complexes is the variety of bonding modes adopted by the benzene or its fragments (*e.g.* C_6H_4). One more recently observed structural type contains a benzene symmetrically bonded to three metal atoms of a triangulo-metal unit as in, for example, $Os_3(CO)_9(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$ (**1**) or $Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3:\eta^2:\eta^2:\eta^2\text{-}C_6H_6)$.[2a] In compounds of this type it is tempting to describe the bonding of the C_6H_6 molecule in terms of localised double bonds and related to the bonding exhibited by C_6H_6 to the Rh^{III} surface.[3] Very recently we demonstrated[4] that on irradiation, cluster (**1**) undergoes a double C–H activation to produce the benzyne complex $Os_3(H)_2(C_6H_4)(CO)_9$ (**2**). We have also observed that (**1**) readily undergoes reaction with $Me_3NO/MeCN$ to produce the activated species $Os_3(CO)_8(MeCN)(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}C_6H_6)$ (**3**) from which a range of derivatives of the type $Os_3(CO)_8L(\mu_3\text{-}\eta^2\eta^2\text{-}\eta^2\text{-}C_6H_6)$ (**4a**), (L = C_2H_4, R_3P *etc.*)[2b] and $Os_3(CO)_7(C_2H_4)(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}C_6H_6)(MeCN)$ (**4b**)† may be obtained (see Scheme 1). We report that (**4b**) reacts with alkynes ($RR'C_2$) to form the new complexes $Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3:\eta^1:\eta^2:\eta^1\text{-}RC_2R')$ (R = R' = H, Ph or Me; R = H, R' = Ph; R = Me, R' = Et) (**5**) in which the benzene is now bonded to a single osmium atom (Scheme 1). This unusual migration is the reverse of that previously observed[2] and clearly indicates the ease with which the C_6H_6 unit (or its relatives) may modify its co-ordination mode.

---

† *Spectroscopic data* for $[Os_3(CO)_7(C_2H_4)(\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}C_6H_6)\text{-}(MeCN)]$ (**4b**): IR ν_{CO}/cm^{-1} (MeCN) 2030m, 1992vs, 1973s, 1927sh; ^1H NMR (CD_3CN/CD_2Cl_2) δ 3.69 (vbr. s, 6H, C_6H_6), 2.15 (br. s, 4H, C_2H_4), co-ordinated MeCN resonance not observed. For $[Os_3(CO)_7\text{-}(\mu_3:\eta^1:\eta^2:\eta^1\text{-}C_2Me_2)(\eta^6\text{-}C_6H_6)]$ (**5a**): IR ν_{CO}/cm^{-1} (CH_2Cl_2) 2057m, 2019vs, 1969s, br., 1721w; ^1H NMR (CD_2Cl_2) δ 5.94 (s, 6H, C_6H_6), 2.69 (s, 3H, Me), 2.24 (s, 3H, Me); 904.



Scheme 1. *Reagents and conditions:* i, 1.1 mol equiv. of Me_3NO/CH_2Cl_2 added dropwise to a $CH_2Cl/MeCN$ solution, at −78 °C; ii, C_2H_4 passed in CH_2Cl_2 at room temp.; iii, 1.5 mol equiv. of Me_3NO in CH_2Cl_2 added dropwise to a $CH_2Cl_2/MeCN$ solution, at room temp.; iv, excess of C_2R_2 added at room temp.

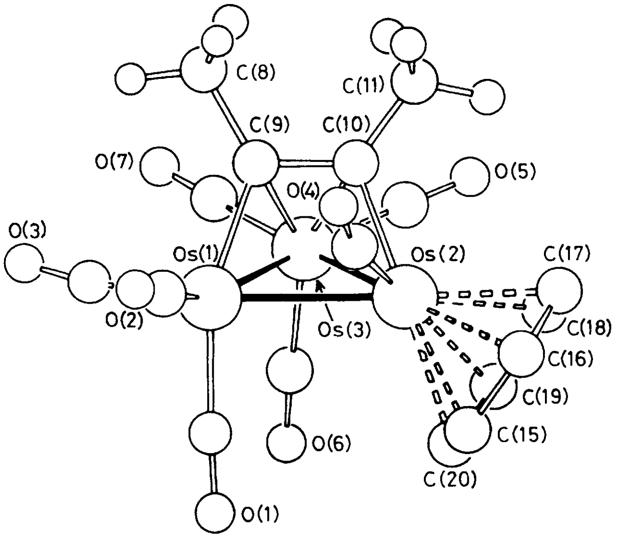


Figure 1. Molecular structure of (**5a**), showing labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. H atoms of the benzene group are omitted for clarity. Relevant bond distances (Å) and angles (°) include: Os(1)–Os(2) 2.832(1), Os(1)–Os(3) 2.708(1), Os(2)–Os(3) 2.791(1), Os(1)–C(9) 2.09(1), Os(3)–C(9) 2.27(1), Os(2)–C(10) 2.14(1), Os(3)–C(10) 2.18(1), C(9)–C(10) 1.44(2), C(8)–C(9)–C(10) 119(1), C(9)–C(10)–C(11) 127(1), mean Os–C(C_6H_6) 2.25(1), mean C(C_6H_6)–C(C_6H_6) 1.39(1), mean Os–C(CO) 1.90(2), mean C–O 1.13(2) Å.

The compound $Os_3(CO)_7(\eta^6\text{-}C_6H_6)(\mu_3{:}\eta^1{:}\eta^2{:}\eta^1\text{-}C_2Me_2)$ (**5a**)† is obtained by reacting (**4b**) with excess of Me_2C_2 in CH_2Cl_2 at room temperature and then separation by TLC on silica. Crystallisation of the compound (**5a**) from dichloromethane/hexane gave orange rhombic crystals which were subjected to single crystal *X*-ray analysis.‡

The molecular structure of (**5a**) is shown in Figure 1 together with some relevant structural parameters. Os–Os bond distances within the Os-triangle range from 2.708(1) to 2.832(1) Å [mean 2.777(1) Å] thus being substantially shorter than in (**1**) and (**4a**) [2.865(1) and 2.847(1) Å (L = C_2H_4), respectively] which bear a $\mu_3\text{-}\eta^2\text{-}\eta^2\text{-}\eta^2\text{-}C_6H_6$ ligand. In (**5a**) the C_6H_6-ligand is found η^6-interacting with a single Os-atom [Os(2)] while the C_2Me_2 ligand lies above the metal triangle. This latter ligand bonds to the metal atoms *via* two σ-interactions [Os(1)–C(9) and Os(2)–C(10), mean 2.12(1) Å] and one π-interaction [Os(3)–C(9), Os(3)–C(10), mean

---

‡ *Crystal data* for (**5a**) $C_{17}H_{12}O_7Os_3$: M = 899, triclinic, space group $P1$, 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, Z = 2, D_c = 3.12 g cm^{-3}, $F(000)$ = 796, μ(Mo-K_α) = 191.3 cm^{-1}, 2.5 < θ < 25°, final R value 0.056, R_W = 0.061 for 2938 out of 3252 independent reflections [$I_o > 2\sigma(I_o)$] collected by the ω/2θ scan method. Absorption correction was applied by azimuthal scan of 12 reflections [χ > 80°] (minimum transmission factor 46%) and subsequently by the Walker and Stuart method (correction range 0.89—1.31).[5] All non-H atoms allowed to vibrate anisotropically. The H atoms of the Me and benzene groups were added in calculated positions [C–H 1.08 Å] and refined 'riding' on their respective C atoms; two isotropic thermal parameters were also refined for the H(Me) and H(Bz) atoms [0.16 and 0.08 Å^2, respectively]. The structure was solved by direct methods and refined by full-matrix least-squares.[6] Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

2.23(1) Å], the atoms belonging to the Os(1)–Os(2)–MeCCMe system being almost coplanar [dihedral angle between the C(8)–C(9)–C(10)–C(11) and Os(1)–C(9)–C(10)–Os(2) planes 12°]. The C–C–C angles and C–C bond lengths within the C_2Me_2 fragment also agree with an sp^2 hybridization on the metal co-ordinated C-atoms.

Considering a 6-electron donation from the C_6H_6 fragment, the electron distribution over the three metal centres appears to be uneven: while Os(1) formally receives nine electrons, Os(2) receives eleven electrons, and Os(3) receives ten electrons from the ligands and metal atoms. The Os–C(C_6H_6) and C(C_6H_6)–C(C_6H_6) bond lengths are shorter in their mean values [2.25(1) and 1.39(1) Å, respectively] than the corresponding values in (**1**) and (**3**) [2.33(2), 1.44(3); 2.32(2), 1.46(3) Å, respectively] indicating that the C_6H_6 fragment establishes a substantially different bonding interaction when co-ordinated to one or three metal centres. The occurrence of rotational disorder of the C_6H_6 ligand which could be accommodated in large mean square vibrational motion of the ligand around its six-fold axis, may be taken as indicative that the fragment lies in a shallow potential energy well and may well show dynamic behaviour in the solid state as well as in solution. A more detailed discussion of this aspect will be given in the full report.

We thank the CNPq (Brazil) for a Ph.D. scholarship (M. M.) and Ministero Pubblica Istruzione (Italy) for financial support.

Received, 10th March 1989; Com. 9/01066A

References

1 See for example: S. A. R. Knox, B. R. Lloyd, A. G. Orpen, J. M. Vinas, and M. Weber, *J. Chem. Soc., Chem. Commun.*, 1987, 1498 and references cited therein.
2 (a) M. P. Gomez-Sal, B. F. G. Johnson, J. Lewis, P. R. Raithby, and A. H. Wright, *J. Chem. Soc., Chem. Commun.*, 1985, 1682; (b) M. A. Gallop, B. F. G. Johnson, J. Lewis, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1987, 1809.
3 R. F. Lin, G. S. Blackman, M. A. Van Hove, and G. A. Somorjai, *Acta Crystallogr., Sect. B*, 1987, **43**, 368; M. A. Van Howe, R. F. Lin, and G. A. Somorjai, *J. Am. Chem. Soc.*, 1986, **108**, 2532; F. P. Netzer, H. H. Graen, H. Kuhlenbeck, and M. Neumann, *Chem. Phys. Lett.*, 1987, **133**, 49; J. U. Mack, E. Bertl, and F. P. Netzer, *Surf. Sci.*, 1985, **159**, 265.
4 M. A. Gallop, B. F. G. Johnson, J. Lewis, A. McCamley, and R. N. Perutz, *J. Chem. Soc., Chem. Commun.*, 1988, 1071.
5 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
6 G. M. Sheldrick, SHELX76 system of computer programs, University of Cambridge, 1976.