(η^6-Arene)osmium Chemistry: Crystal Structure of [(η^6-$C_6H_3Me_3$)Os(μ-CHC_6H_3-Me_2-3,5)Os(η^6-$C_6H_3Me_3$)]

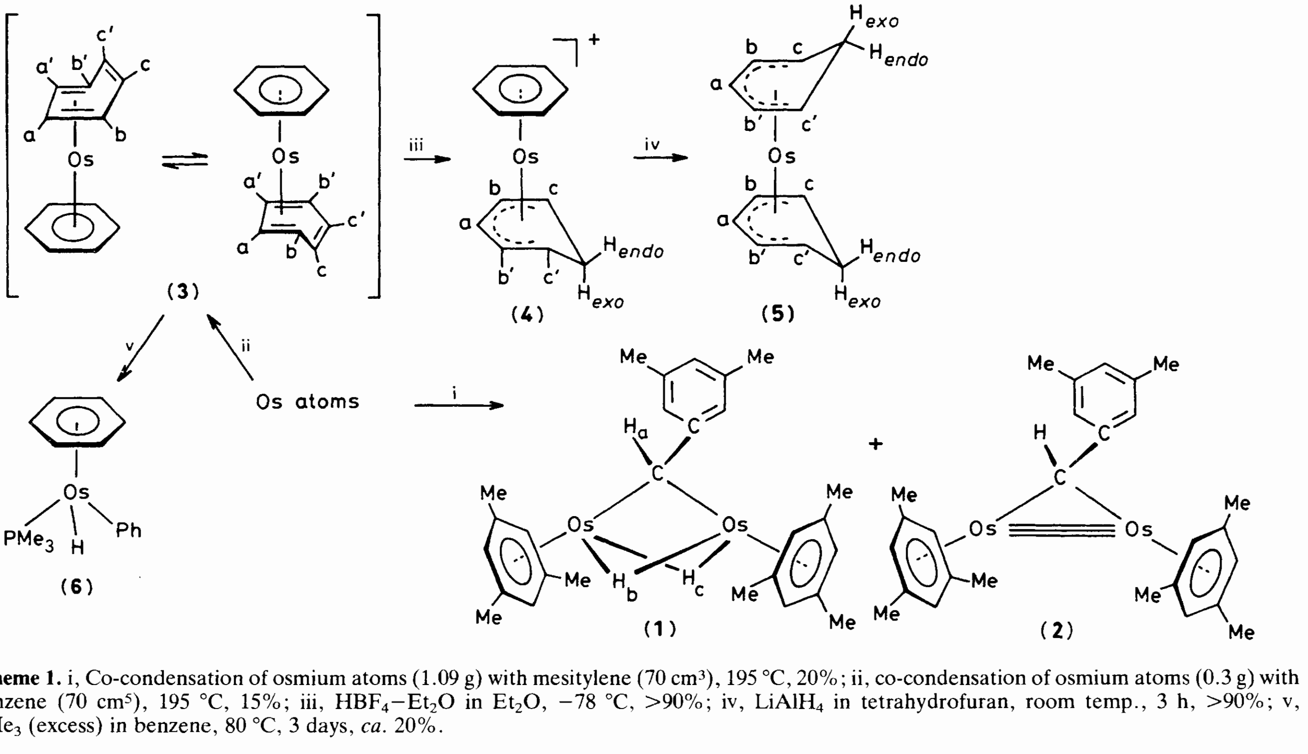
Judith A. Bandy,[b] Malcolm L. H. Green,[a] Dermot O'Hare,[a] and Keith Prout[b]

[a] *Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, U.K.*
[b] *Chemical Crystallography Laboratory, 9 Parks Road, Oxford, OX1 3PD, U.K.*

Co-condensation of osmium atoms with benzene gives stable Os(η^6-C_6H_6)(η^4-C_6H_6) whereas co-condensation of osmium atoms with mesitylene forms the dimers [(η^6-$C_6H_3Me_3$)Os(μ-H)$_2$(μ-$CHC_6H_3Me_2$-3,5)Os(η^6-$C_6H_3Me_3$)] and [(η^6-$C_6H_3Me_3$)Os(μ-$CHC_6H_3Me_2$-3,5)Os(η^6-$C_6H_3Me_3$)].

We have previously shown that rhenium atoms react with alkylbenzenes giving binuclear [(η-arene)Re(μ-H)$_2$(μ-arylidene)Re(η-arene)] derivatives[1] and these studies suggested that the 'Re(μ-H)$_2$(μ-alkylidene)Re' moiety was especially stable. We were interested to discover whether osmium showed a similar chemistry.

Co-condensation of osmium atoms with mesitylene gives as the major product the yellow crystalline compound [(η^6-



Scheme 1. i, Co-condensation of osmium atoms (1.09 g) with mesitylene (70 cm^3), 195 °C, 20%; ii, co-condensation of osmium atoms (0.3 g) with benzene (70 cm^5), 195 °C, 15%; iii, HBF_4–Et_2O in Et_2O, −78 °C, >90%; iv, $LiAlH_4$ in tetrahydrofuran, room temp., 3 h, >90%; v, PMe_3 (excess) in benzene, 80 °C, 3 days, *ca.* 20%.

$C_6H_3Me_3)Os(\mu\text{-}H)_2(\mu\text{-}CHC_6H_3Me_2\text{-}3,5)Os(\eta^6\text{-}C_6H_3Me_3)]$, (**1**).† Typically, osmium atoms (1.0 g) were condensed with mesitylene (70 cm^3) giving (**1**) (0.3 g) in *ca.* 15% yield. Fractional crystallisation of the reaction mixture gave a second minor product (3%) as red crystals which the n.m.r. spectra† and a crystal structure determination‡ showed to be $[(\eta^6\text{-}C_6H_3Me_3)Os(\mu\text{-}CHC_6H_3Me_2\text{-}3,5)Os(\eta^6\text{-}C_6H_3Me_3)]$, (**2**).

Crystal data for (**2**): $Os_2C_{27}H_{34}$, $M = 738.97$, triclinic, space group $P\bar{1}$, $a = 11.507(4)$, $b = 12.005(6)$, $c = 11.507(6)$ Å, $\alpha = 111.50(5)$, $\beta = 119.13(3)$, $\gamma = 97.20(4)°$, $U = 1198.31$ Å^3, $D_c = 2.048$ Mg m^{-3}, $Z = 2$, $\mu = 112.34$ cm^{-1}, $F(000) = 696.00$, $R = 5.09\%$, $R_w = 6.60\%$ for 3849 unique absorption corrected reflections $[I > 3\sigma(I)]$, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å. Data were collected using an Enraf-Nonius CAD4F diffractometer ($2\theta_{max.} = 56°$). The structure was solved by using Patterson and Fourier syntheses and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions in all but the methyl groups, and were modified between cycles of refinement. Crystallographic calculations were carried out using the Oxford CRYSTALS system.[2]

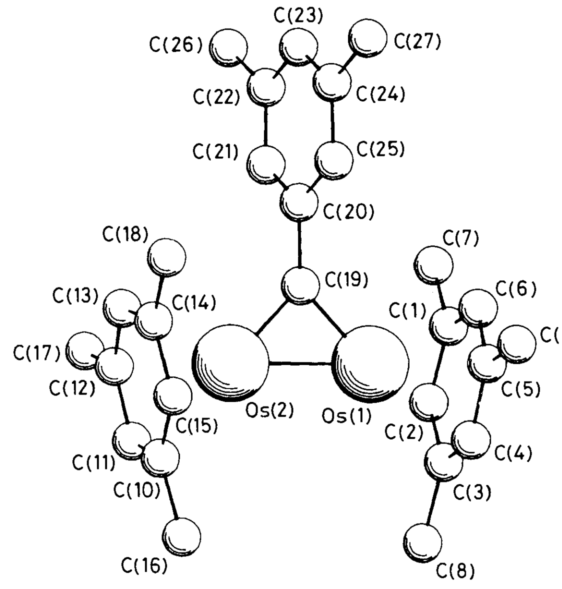


Figure 1. Crystal structure of (**2**): Important distances (Å) and angles (°): Os(1)–Os(2) 2.647(1), Os(1)–C(19) 1.91(2), Os(2)–C(19) 1.92(2), C(19)–C(20) 1.48(2), η^6-mesitylene–Os(1) 1.72, η^6-mesitylene–Os(2) 1.72; Os(1)–C(19)–Os(2) 87.4(7), Os(1)–C(19)–C(20) 136.4(11), Os(2)–C(19)–C(20) 136.1(12). Angle of normals of mesitylenes 163.63°.

In the crystal structure of (**2**) (see Figure 1) the molecule possesses a pseudo C_2 symmetry axis bisecting the Os(1)–Os(2) vector. Interestingly the least squares plane containing the bridging mesitylene group lies at an angle of 99.8° to the Os(1),Os(2),C(19) plane. The observed Os(1)–Os(2) bond length of 2.647(1) Å is much shorter than the Os–Os bond distances in the trinuclear compounds $Os_3(CO)_{10}(\mu\text{-}H)_2(\mu\text{-}CH_2)$ [Os–Os, 2.824(3) Å],[3] $Os_3(CO)_{10}(\mu\text{-}CHCH_2PMe_2Ph)$ [Os–Os, 2,8002(6) Å],[4] and $Os_3(CO)_{10}(\mu\text{-}H)_2$ [Os–Os, 2.683(1) Å].[5]

The reaction between rhenium atoms and benzene does not give bis-η-benzenerhenium.[6] In contrast, co-condensation of osmium atoms with an excess of benzene gives orange crystals of $Os(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)$, (**3**). The structure of (**3**) is clearly suggested by microanalysis and especially the n.m.r. data.†

Magnetization transfer experiments show that (**3**) undergoes degenerate haptotropic ring equilibria (Scheme 1) for which k at 37 °C is 0.2 ± 0.03 s^{-1} and $\Delta G^\ddagger = 80 \pm 5$ kJmol^{-1}. The equilibria result in chemical exchange between all hydrogens of the compound.

Protonation of (**3**) gives the cationic η^5-cyclohexadienyl derivative $[Os(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)]BF_4$, (**4**).† Addition of the nucleophile H^- to (**4**) proceeds as predicted by charge control[7] giving the neutral bis-η^5-cyclohexadienyl compound $Os(\eta^5\text{-}C_6H_7)_2$, (**5**).† This observation contrasts with the addition of nucleophiles, *e.g.* H^-, to the iron analogue of (**4**) giving $Fe(\eta\text{-}C_6H_6)(\eta\text{-}C_6H_8)$.[8] Treatment of (**3**) with trimethylphosphine, somewhat surprisingly, gives orange crystals of $Os(\eta^6\text{-}C_6H_6)(PMe_3)HPh$, (**6**).† It was expected that the compound $Os(\eta\text{-}C_6H_6)(L)_2$, L = PMe_3, could be formed, since analogues where L = PPh_3 are known. It appears that the likely intermediate $Os(\eta\text{-}C_6H_6)(\eta^2\text{-}C_6H_6)(PMe_3)$ rearranges rapidly to (**6**). The rearrangement of an η^2-benzene complex to the phenyl-hydride has been shown previously for $Rh(\eta\text{-}C_5Me_5)(PMe_3)(Ph)H$.[9]

Added in proof. The H shown on the μ-C of (**2**) is not observed by X-ray diffraction. The presence of a hydrogen atom is indicated by the mass spectrum, ^{1}H n.m.r. at δ 0.19 [the n.m.r. spectrum of the X-ray single crystal showed it to be (**2**)], and implied from the diamagnetism. A nuclear Overhauser enhancement experiment showed the hydrogen atom at δ 0.19 to interact with xylyl hydrogen atoms. Symmetry locates the hydrogen atom in the plane of μ-C normal to the

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† Satisfactory microanalysis has been obtained for the compounds (**1**)—(**6**). *N.m.r. spectroscopic data* (J in Hz): (**1**), ^{1}H (C_6D_6, room temp.) 6.61 (2H, s, xylyl), 6.63 (1H, s, xylyl), 4.96 [1H, dd, $J(H_a\text{–}H_c)$ 7.5, $J(H_a\text{–}H_b)$ 3, μ-CH_a], 4.72 (6H, s, η^6-mesitylene), 2.28 (6H, s, 2Me), 2.22 (18H, s, 6Me), −12.24 [1H, dd, $J(H_b\text{–}H_a)$ 3, $J(H_b\text{–}H_c)$ 5, H_b], −14.77 [1H, dd, $J(H_c\text{–}H_a)$ 7.5, $J(H_c\text{–}H_b)$ 5, H_c]; ^{13}C (C_6D_6, room temp.) 168.99 (s, C_{ipso}), 133.5 (s, 2 × C–Me), 128.6 [d, br., J(C–H) 154, C-2,-6(xylyl)], 124.2 [d, J(C–H) 154, C-4(xylyl)], 87.3 (s, η^6-mesitylene), 71.4 [d, J(C–H) 171, η^6-mesitylene], 59.1 [d, J(C–H) 135, μ-CH], 22.0 [q, J(C–H) 127, 2Me], 21.9 [q, J(C–H) 127, 6Me]. (**2**), ^{1}H (C_6D_6) 6.96 (2H, s, xylyl) 6.79 (1H, s, xylyl), 5.29 (6H, s, η^6-mesitylene), 2.39 (6H, s, 2Me), 2.12 (18H, s, 6Me), 0.19 (1H, s, μ-CH); ^{13}C (C_6D_6, 126 MHz) 168.48 (s, C_{ipso}), 135.3 (s, 2 × C–Me), 127.8 [d, C-4(xylyl)], 125.9 [d, C-2,-6(xylyl)], 83.0 (s, η^6-mesitylene), 75.3 (d, η^6-mesitylene), 27.27 (q, 2Me), 21.74 (q, 6Me). The sample was very dilute, C-19 was not observed. (**3**), ^{1}H (C_6D_6) 6.23 [2H, dd, $J(H_a\text{–}H_b)$ 4.0, $J(H_a\text{–}H_{b'})$ 1.5, $H_{a,a'}$], 5.62 [2H, t, $J(H_b\text{–}H_{c'})$ 3, $J(H_b\text{–}H_c)$ 3, $H_{c,c'}$], 4.74 (6H, s, $\eta^6\text{-}C_6H_6$), 3.63 [2H, ddt, $J(H_b\text{–}H_{a'})$ 1.5, $J(H_b\text{–}H_a)$ 4.0, $J(H_b\text{–}H_c)$ 3.0, $J(H_b\text{–}H_{c'})$ 3.0, H_b]; ^{13}C (C_6D_6) 130.8 [d, J(C–H) 168, 2C_c], 72.1 [d, J(C–H) 171, $\eta^6\text{-}C_6H_6$], 68.7 [d, J(C–H) 170, 2C_a], 47.2 [d, J(C–H) 161, 2C_b]. (**4**), ^{1}H (CD_3OD) 6.78 [1H, tt, $J(H_a\text{–}H_b)$ 5, $J(H_a\text{–}H_c)$ 1, H_a], 6.34 (6H, s, $\eta^6\text{-}C_6H_6$), 5.41 [2H, ddt, $J(H_b\text{–}H_a)$ 5, $J(H_b\text{–}H_c)$ 6, $J(H_b\text{–}H_{endo})$ 1, $J(H_b\text{–}H_c{}')$ 1, H_b], 4.98 [2H, tt, $J(H_c\text{–}H_{exo})$ 1, $J(H_c\text{–}H_b)$ 6, $J(H_c\text{–}H_{endo})$ 1, H_c], 3.83 [1H, dt, $J(H_{exo}\text{–}H_{endo})$ 12, $J(H_{exo}\text{–}H_c)$ 1, H_{exo}], 2.71 [1H, dtt, $J(H_{endo}\text{–}H_{exo})$ 12, $J(H_{endo}\text{–}H_c)$ 6, $J(H_{endo}\text{–}H_b)$ 1, H_{endo}]; ^{13}C (CD_3OD) 84.8 [d, J(C–H) 172, C_a], 84.6 [d, J(C–H) 175, 2 × C_b], 83.1 [d, J(C–H) 180, $\eta^6\text{-}C_6H_6$], 28.9 [t, J(C–H) 135, $C_{exo/endo}$], 26.2 [d, J(C–H) 168, 2 C]. (**5**), ^{1}H (C_6D_6) 5.5 [1H, tt, $J(H_a\text{–}H_b)$ 5, $J(H_a\text{–}H_c)$ 1, H_a], 4.56 [1H, dt, $J(H_{exo}\text{–}H_{endo})$ 10.5, $J(H_{exo}\text{–}H_c)$ 0.5, H_{exo}], 4.5 [2H, ddd, $J(H_b\text{–}H_a)$ 5, $J(H_b\text{–}H_c)$ 6, $J(H_b\text{–}H_{endo})$ 1, 2 × H_b], 3.28 [2H, ddt, $J(H_c\text{–}H_b)$ 6, $J(H_c\text{–}H_{endo})$ 6, $J(H_c\text{–}H_a)$ 1, $J(H_c\text{–}H_{exo})$ 0.5, 2 × H_c], 2.92 [1H, dtt, $J(H_{endo}\text{–}H_{exo})$ 10.5, $J(H_{endo}\text{–}H_c)$ 6, $J(H_{endo}\text{–}H_b)$ 1, H_{endo}]; ^{13}C (C_6D_6) 82.7 [d, J(C–H) 169, C_a], 71.0 [d, J(C–H) 75, 2 × C_b], 32.6 [t, J(C–H) 131, $C_{exo/endo}$], 18.2 [d, J(C–H) 157, 2×C_c]. (**6**) ^{1}H (C_6D_6) 7.97 [2H, m (6 lines), Ph], 7.10 [3H, m (4 lines), Ph], 4.63 (6H, s, $\eta^6\text{-}C_6H_6$), 1.1 [9H, d, J(P–H) 10, PMe_3], −9.7 [1H, d, J(P–H) 43, Os–H]; $^{31}P\{^1H\}$ (C_6D_6) −44.5 (s) p.p.m. rel. to $(MeO)_3P$ (ext.).

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallography Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Os–Os vector. The near-planar environment of μ-C indicates a strongly distorted μ-CH($C_6H_3Me_2$-3,5) system. It may be that there is a μ-C–H system which is interacting with the Os–Os orbitals, akin to an agostic C–H system.

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