Arene–Osmium Chemistry: Synthesis *via* Osmium Atoms of $[Os(\eta^6-C_6H_6)(\eta^4-C_6H_6)]$, $[\{Os(\eta^6-C_6H_3Me_3-1,3,5)\}_2(\mu-H)_2\{\mu-CH(C_6H_3Me_2-3,5)\}]$, $[\{Os(\eta^6-C_6H_3Me_3-1,3,5)\}_2(\mu-CHC_6H_3Me_2-3,5)]$, and $[\{Os(\eta^6-C_6H_6)\}_3\{\mu_3-(CH_2)_3CH\}(\mu-H)_3]$. *X*-Ray Crystal Structure of $[\{Os(\eta^6-C_6H_3Me_3-1,3,5)\}_2(\mu-CHC_6H_3Me_2-3,5)]$ *

Judith A. Bandy
Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD
Malcolm L. H. Green and Dermot O'Hare
Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

The new compounds $[Os(\eta^6-C_6H_6)(\eta^4-C_6H_6)]$, $[Os(\eta^6-C_6H_6)(\eta^5-C_6H_7)]BF_4$, $[Os(\eta^5-C_6H_7)_2]$, $[\{Os(\eta^6-C_6H_3Me_3-1,3,5)\}_2(\mu-H)_2\{\mu-CH(C_6H_3Me_2-3,5)\}]$, $[\{Os(\eta^6-C_6H_3Me_3-1,3,5)\}_2\{\mu-CH(C_6H_3Me_2-3,5)\}]$, and $[\{Os(\eta^6-C_6H_6)\}_3\{\mu_3-(CH_2)_3CH\}(\mu-H)_3]$ are described. The crystal structure of $[\{Os(\eta^6-C_6H_3Me_3-1,3,5)\}_2\{\mu-CH(C_6H_3Me_2-3,5)\}]$ has been determined. The intramolecular ring-exchange process of $[Os(\eta^6-C_6H_6)(\eta^4-C_6H_6)]$ has been analysed by two-dimensional ($^1H-^1H$) chemical exchange and magnetisation transfer experiments. The formation of $[\{Os(\eta^6-C_6H_6)\}_3\{\mu_3-(CH_2)_3CH\}(\mu-H)_3]$ from osmium atoms, benzene, and 2-methylpropane represents a remarkable alkane activation reaction.

When rhenium atoms are co-condensed with alkylbenzene derivatives such as toluene, binuclear μ-arylidene derivatives $[(\eta-arene)Re(\mu-arylidene)(\mu-H)_2Re(\eta-arene)]$ are formed.[1,2] Similarly, co-condensation of rhenium atoms with alkane–benzene mixtures gives related μ-alkylidene derivatives $[(\eta^6-C_6H_6)Re(\mu-alkylidene)(\mu-H)_2Re(\eta^6-C_6H_6)]$: these reactions require the activation of the alkanes.[3,4] The latter reaction between the rhenium atoms and the alkane–benzene mixture suggested that highly reactive intermediates were formed which could insert into C–H bonds of alkanes in a selective manner.

We are interested to examine the extent to which osmium atoms would show a chemistry analogous to that of rhenium atoms and this study is described below. A preliminary report of part of this work has been published.[5]

Results

Co-condensation of osmium atoms with pure benzene yields pale yellow crystals of $[Os(\eta^6-C_6H_6)(\eta^4-C_6H_6)]$ (**1**). The structure of (**1**) is clearly suggested by the analytical and ^{13}C and ^1H n.m.r. data given in Table 1. The data in Table 1 for compound (**1**), and for the other new compounds described below, will only be discussed further where required.

Magnetisation transfer and two-dimensional ($^1H-^1H$) chemical exchange n.m.r. spectra [Figure 1(*a*)] show that (**1**) undergoes degenerate haptotropic ring equilibria at room temperature. The two-dimensional ($^1H-^1H$) chemical exchange n.m.r. spectra also show that the rate of exchange between the $H_{a,a'}$, $H_{b,b'}$, and $H_{c,c'}$ hydrogens at temperatures less than 70 °C is much less than the exchange between the $\eta^6-C_6H_6$ and $\eta^4-C_6H_6$ rings. This enables the $\eta^4 \rightleftharpoons \eta^6$ exchange process to be modelled as a simple two-spin exchange system. The ^1H magnetisation transfer n.m.r. data provided values for the exchange rate and activation energy.

The $\eta^6-C_6H_6$ resonance was selectively inverted and the variation of intensity of the other three resonances was recorded as a function of time after the 180° inversion pulse. The variation of the peak intensity *versus* time for the three sites is given in Figure 1 (*b*). The data have been fitted to the generalised expression for a two-spin exchanging system.[6] Calculation of the rate of exchange at various temperatures leads to a value of $\Delta G^{\ddagger} = ca.\ 80 \pm 5$ kJ mol^{-1}.

The mechanism of this haptotropic rearrangement is likely to proceed either *via* a 16-electron bis($\eta^4-C_6H_6$) osmium moiety or *via* a 20-electron bis($\eta^6-C_6H_6$) osmium intermediate.

An analogous dynamic process has been observed previously for $[Ru(\eta^6-C_6H_6)(\eta^4-C_6H_6)]$[7] and $[Ru(\eta^6-C_6Me_6)(\eta^4-C_6Me_6)]$,[8] but thermal instability precluded a detailed analysis.

Warming (**1**) in C_6D_6 to 100 °C causes slow exchange of the η^6-benzene with solvent deuteriobenzene to give $[Os(\eta^6-C_6D_6)(\eta^4-C_6D_6)]$ (**1′**) together with formation of the compound $[Os(\eta^6-C_6D_6)(\eta^4-C_6D_8)]$ (**2′**) *via* some unknown hydrogen abstraction process. The compounds (**1′**) and (**2′**) were characterised by mass and ^2H n.m.r. spectroscopy. No intermediates could be detected but it seems likely that the ring-exchange reaction proceeds *via* a bis(η^2-arene) moiety. When a sample of (**1**) was heated in C_6D_{12} at 60 °C only decomposition was observed.

Treatment of (**1**) with dihydrogen at room temperature gives $[Os(\eta^6-C_6H_6)(\eta^4-C_6H_8)]$ (**2**),[9] in a rapid reaction. Treatment of (**1**) with trimethylphosphine gives yellow crystals of $[Os(\eta^6-C_6H_6)(PMe_3)(Ph)H]$ (**3**). The data (Table 1) suggest (**3**) to have the structure analogous to the ruthenium compound $[Ru(\eta^6-C_6H_6)(PMe_3)(Ph)H]$.[10] Compound (**3**) is also formed, in modest yield, by the reaction of osmium atoms with a mixture of benzene and trimethylphosphine.[10] A likely intermediate is $[Os(\eta^6-C_6H_6)(\eta^2-C_6H_6)(PMe_3)]$ which rearranges rapidly to (**3**). The rearrangement of η^2-benzene to a phenyl–hydride isomer has been observed previously for the isoelectronic $[Rh(\eta^5-C_5Me_5)(PMe_3)(Ph)H]$.[11]

Protonation of $[Os(\eta^6-C_6H_6)(\eta^4-C_6H_6)]$ (**1**) with tetrafluoroboric acid–diethyl ether at −78 °C gives the cationic derivative $[Os(\eta^6-C_6H_6)(\eta^5-C_6H_7)]BF_4$ (**4**). Presumably, this reaction proceeds by an initial protonation of the osmium followed by *endo*-hydrogen-to-ring migration. A similar protonation reaction has been observed for the ruthenium complex $[Ru(\eta^6-C_6Me_6)(\eta^4-C_6Me_6)]$.[12]

Treatment of (**4**) with lithium aluminium hydride gives the expected[13] neutral bis(η^5-cyclohexadienyl) compound $[Os(\eta^5-C_6H_7)_2]$ (**5**).

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* μ-3,5-Dimethylphenylmethylidene-bis[(η^6-1,3,5-trimethylbenzene)-osmium] (*Os–Os*).

Supplementary data available (No. SUP 56630, 2 pp.): anisotropic thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. units employed: atm ≈ 101 325 N m^{-2}, Torr ≈ 133 N m^{-2}.

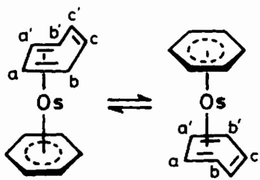
Table 1. Analytical and spectroscopic data[a]

Compound, colour, and analysis[b]	N.m.r. data[c]	
	^1H	^{31}P and ^{13}C
(1) $[Os(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)]$ Yellow C, 42.1 (41.6); H, 3.5 (3.5)[d]	6.23 [2 H, dd, $J(H_a-H_b)$ 4.0, $J(H_a-H_{b'})$ 1.5, $H_{a,a'}$], 5.62 [2 H, t, $J(H_b-H_{c'})$ 3, $J(H_b-H_c)$ 3, $H_{c,c'}$], 4.74 [6 H, s, η^6-C_6H_6], 3.63 [2 H, ddt, $J(H_b-H_{a'})$ 1.5, $J(H_b-H_a)$ 4.0, $J(H_b-H_c)$ 3.0, $J(H_b-H_{c'})$ 3.0, $H_{b,b'}$][e]	130.8 [d, J(C–H) 168, C_c], 72.1 [d, J(C–H) 171, η^6-C_6H_6], 68.7 [d, J(C–H) 170, C_a], 47.2 [d, J(C–H) 161, C_b][e]
(1′) $[Os(\eta^6\text{-}C_6D_6)(\eta^4\text{-}C_6D_6)]$ Yellow[f]	^2H-{^1H}: 6.2 (s, br, $D_{a,a'}$), 5.5 (s, br, η^6-C_6D_6), 4.6 (s, br, $D_{b,b'}$), 3.6 (s, br, $D_{c,c'}$)[e]	
(2) $[Os(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ Yellow[g]	5.2 [2 H, m (4 lines), $H_{a,a'}$], 4.8 (6 H, s, η^6-C_6H_6), 3.3 [2 H, m (13 lines), $H_{b,b'}$], 1.9 [2 H, m (10 lines), $H_{cc'}$ or $H_{dd'}$)], 1.7 [2 H, m (12 lines), $H_{dd'}$ or $H_{cc'}$][e]	71.1 [d, J(C–H) 171, η^6-C_6H_6], 69.4 [d, J(C–H) 169, $C_{a,a'}$], 44.5 [d, J(C–H) 159, $C_{b,b'}$], 29.8 [t, J(C–H) 129, $C_{c,d} + C_{c',d'}$][e]
(2′) $[Os(\eta^6\text{-}C_6D_6)(\eta^4\text{-}C_6D_8)]$ Yellow[h]	^2H-{^1H}: 5.2 (s, br, $D_{a,a'}$), 4.6 (s, br, η^6-C_6D_6), 3.3 (s, br, $D_{b,b'}$), 1.8 (s, br, $D_{cc'}$ or $D_{dd'}$), 1.6 (s, br, $D_{dd'}$ or $D_{cc'}$)[e]	
(3) $[Os(\eta^6\text{-}C_6H_6)(PMe_3)(Ph)H]$ Yellow C, 41.6 (42.6); H, 4.1 (5.0)[i]	7.97 [2 H, m, H_o (Ph)], 7.09 [3 H, m, H_m and H_p (Ph)], 4.64 (6 H, s, η^6-C_6H_6), 1.12 [9 H, d, J(P–H) 10, PMe_3], − 9.74 [1 H, d, J(P–H) 42.9, Os–H][e]	^{31}P-{^1H}: −44.5 (s, PMe_3)[e] ^{13}C: 147.4 [d, J(C–H) 154, C_o (Ph)], 126.8 [d, J(C–H) obscured, C_m (Ph)], 121 [d, J(C–H) 157, C_p (Ph)], 77.8 [dd, J(P–C) 25, J(C–H) 174, η^6-C_6H_6], 22.3 [dq, J(P–C) 37, J(C–H) 130, PMe_3][e]
(4) $[Os(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_6H_7)]BF_4$ Orange C, 32.9 (33.1); H, 2.9 (2.9)	6.78 [1 H, tt, $J(H_a-H_b)$, 5, $J(H_a-H_c)$, 1, H_a], 6.34 [6 H, s, η^6-C_6H_6], 5.41 [2 H, ddt, $J(H_b-H_a)$ 5, $J(H_b-H_c)$ 6, $J(H_b-H_{endo})$ 1, $J(H_b-H_{c'})$ 1, $H_{b,b'}$], 4.98 [2 H, tt, $J(H_c-H_{exo})$ 1, $J(H_c-H_b)$ 6, $J(H_c-H)_{endo}$ 6, $J(H_c-H_a)$ 1, $H_{c,c'}$], 3.83 [1 H, dt, $J(H_{exo}-H_{endo})$ 12, $J(H_{exo}-H_c)$ 1, H_{exo}], 2.71 [1 H, dtt, $J(H_{endo}-H_{exo})$ 12, $J(H_{endo}-H_c)$ 6, $J(H_{endo}-H_b)$ 1, H_{endo}][j]	84.8 [d, J(C–H) 172, C_a], 84.6 [d, J(C–H) 175, $C_{b,b'}$], 83.1 [d, J(C–H) 180, η^6-C_6H_6], 28.9 [t, J(C–H) 135, $C_{exo,endo}$], 26.2 [d, J(C–H) 168, $C_{c,c'}$][j]
(5) $[Os(\eta^5\text{-}C_6H_7)_2]$ Yellow[k]	5.50 [1 H, tt, $J(H_a-H_b)$ 5, $J(H_a-H_c)$ 1, H_a], 4.56 [1 H, dt, $J(H_{exo}-H_{endo})$ 10.5, $J(H_{exo}-H_c)$ 0.5, H_{exo}], 4.5 [2 H, ddd, $J(H_b-H_a)$ 5.0, $J(H_b-H_c)$ 6.0, $J(H_b-H_{endo})$ 1, $H_{b,b'}$], 3.28 [2 H, ddt, $J(H_c-H_b)$ 6, $J(H_c-H_{endo})$ 6, $J(H_c-H_{exo})$ 0.5, $H_{c,c'}$], 2.92 [1 H, dtt, $J(H_{endo}-H_{exo})$ 10.5, $J(H_{endo}-H_c)$ 6, $J(H_{endo}-H_b)$ 1, H_{endo}][e]	82.7 [d, J(C–H) 169, C_a], 71.0 [d, J(C–H) 175, $C_{b,b'}$], 32.6 [t, J(C–H) 131, $C_{exo,endo}$], 18.2 [d, J(C–H) 157, $C_{cc'}$][e]
(6) $[\{Os(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)\}_2(\mu\text{-}H)_2(\mu\text{-}CHC_6H_3Me_2\text{-}3,5)]$ Orange C, 43.3 (43.7); H, 5.0 (4.8)[l]	6.63 [1 H, s, H_p (μ-$CHC_6H_3Me_2$-3,5)], 6.61 [2 H, s, 2 × H_o (μ-$CHC_6H_3Me_2$-3,5)], 4.96 [1 H, dd, $J(C_a-H_c)$ 7.5, $J(H_a-H_b)$ 3, μ-CH_c], 4.72 (6 H, s, η^6-$C_6\mathit{H}_3Me_3$-1,3,5), 2.28 (6 H, s, 2 × Me_e), 2.22 (18 H, s, 6 × Me_d), −12.24 [1 H, dd, $J(H_b-H_a)$ 3, $J(H_b-H_c)$ 5, H_b], −14.77 [1 H, dd, $J(H_c-H_a)$ 7.5, $J(H_c-H_b)$ 5, H_a][c]	168.99 [s, C_{ipso} (μ-$CHC_6H_3Me_2$-3,5)], 133.5 [s, C_m (μ-$CHC_6H_3Me_2$-3,5)], 126.6 [d, br, J(C–H) 154, C_o (μ-$C_6H_3Me_2$-3,5)], 124.2 [d, J(C–H) 154, C_p (μ-$CHC_6H_3Me_2$-3,5)], 87.3 (s, η^6-$\mathit{C}_6H_3Me_3$-1,3,5), 71.4 [d, J(C–H) 171, η^6-$\mathit{C}_6H_3Me_3$-1,3,5], 59.1 [d, J(C–H) 135, μ-C_c], 22.0 [q, J(C–H) 127, 2 × Me_e], 21.9 [q, J(C–H) 127, 6 × Me_d][e]
	At −60 °C: 6.82 (1 H, s, H_o), 6.4 (1 H, s, H_o), 6.12 (1 H, s, H_p), 4.64 [1 H, dd, $J(H_a-H_c)$ 7.5, $J(H_a-H_b)$ 3, H_a], 4.39 (6 H, s, η^6-$C_6\mathit{H}_3Me_3$-1,3,5), 2.23 (3 H, s, Me_e), 2.18 (3 H, s, Me_e), 1.53 (18 H, s, 6 × Me_d), −12.54 [1 H, dd, $J(H_b-H_a)$ 3, $J(H_b-H_c)$ 5, H_b], −14.77 [1 H, dd, $J(H_c-H_a)$ 7.5, $J(H_c-H_b)$ 4, H_c][m]	^{13}C-{^1H} at −60 °C: 168.99 (s, C_{ipso}), 135.5 (s, C_o–H), 134.0 (s, C_m), 133.3 (s, C_m), 127.5 (s, C_p–H), 87.6 [s, C–Me (η^6-$C_6H_3Me_3$-1,3,5)], 71.0 [s, C–H (η^6-$C_6H_3Me_3$-1,3,5)], 59.1 (s, C_c), 22.8 (s, Me_c), 21.9 (s, 6 × Me_d), 21.0 (s, Me_e)[m]
(7) $[\{Os(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)\}_2(\mu\text{-}CHC_6H_3Me_2\text{-}3,5)]$ Red C, 43.3 (43.8); H, 5.0 (4.6)[n]	6.96 (2 H, s), 6.79 (1 H, s), 5.29 (6 H, s, η^6-$C_6\mathit{H}_3Me_3$-1,3,5), 2.39 (6 H, s, $CHC_6H_3\mathit{Me}_2$-3,5), 2.12 (18 H, s, η^6-$C_6H_3\mathit{Me}_3$], 0.19 (1 H, s, μ-CH)[e]	168.4 (s, C_{ipso}), 135.3 (s, $CHC_6H_3\mathit{Me}_2$-3,5), 127.8 [d, J(C–H), 155, μ-ring], 125.9 [d, J(C–H) 154, μ-ring], 83.0 [s, η^6-$C_6H_3Me_3$-1,3,5], 73.3 [d, J(C–H) 171, η^6-$C_6H_3Me_3$-1,3,5], 27.2 [q, J(C–H) obscured, μ-ring], 21.7 [q, J(C–H) 129, η^6-$C_6H_3Me_3$-1,3,5 and μ-$\mathit{C}H(C_6H_3Me_2$-3,5)][e]

Table 1 (*continued*)

Compound, colour, and analysis[b]	N.m.r. data[c] ^1H	 ^{31}P and ^{13}C
(**8**) $[\{Os(\eta^6-C_6H_6)\}_3\{\mu_3-(CH_2)_3CH\}(\mu-H)_3]$ Yellow[o] C, 30.1 (30.6); H, 3.1 (3.2)	4.41 (18 H, s, 3 × $\eta^6-C_6H_6$), 4.2 [1 H, spt, J(H–H) 6.6, CH], 1.4 [6 H, d, J(H–H) 6.6, 3 × CH_2], −17.09 (3 H, s, 3 × Os–H)[m]	At 60 °C: 70.0 (d, 3 × $\eta^6-C_6H_6$), 59.9 (d, CH), 30.3 (t, 3 × CH_2)[m]
(**8'**) $[\{Os(\eta^6-C_6D_6)\}_3\{\mu_3-(CH_2)_3CH\}(\mu-H)_3]$ Yellow[p]	$^2H-\{^1H\}$: 4.46 (s, br, 3 × $\eta^6-C_6D_6$)[e]	

[a] For atom labelling see Scheme or Figure 3. [b] Found (required) %. Mass spectrum for ^{190}Os, P^+ represents the parent ion. Infrared spectra were determined in Nujol mulls on CsI plates (cm^{-1}). [c] Given as: chemical shift (δ) [relative intensity, multiplicity, coupling (J in Hz), assignment]. 300-MHz ^1H n.m.r. and 62.8-MHz ^{13}C n.m.r. unless stated otherwise. At r.t. unless stated otherwise. [d] M/e 346 [P^+]. [e] In C_6D_6. [f] M/e 258 [P^+]. [g] M/e 348 [P^+]. [h] M/e 362 [P^+]. [i] M/e 422 [P^+]. [j] In [$^2H_4$]methanol. [k] M/e 348 [P^+]. [l] M/e 740 [P^+]. Possibly ν(Os–H–Os) 1 580m cm^{-1}. [m] In [$^2H_8$]toluene. [n] M/e 738 [P^+]. [o] M/e 862 [P^+]. [p] M/e 880 [P^+].



(**1**)

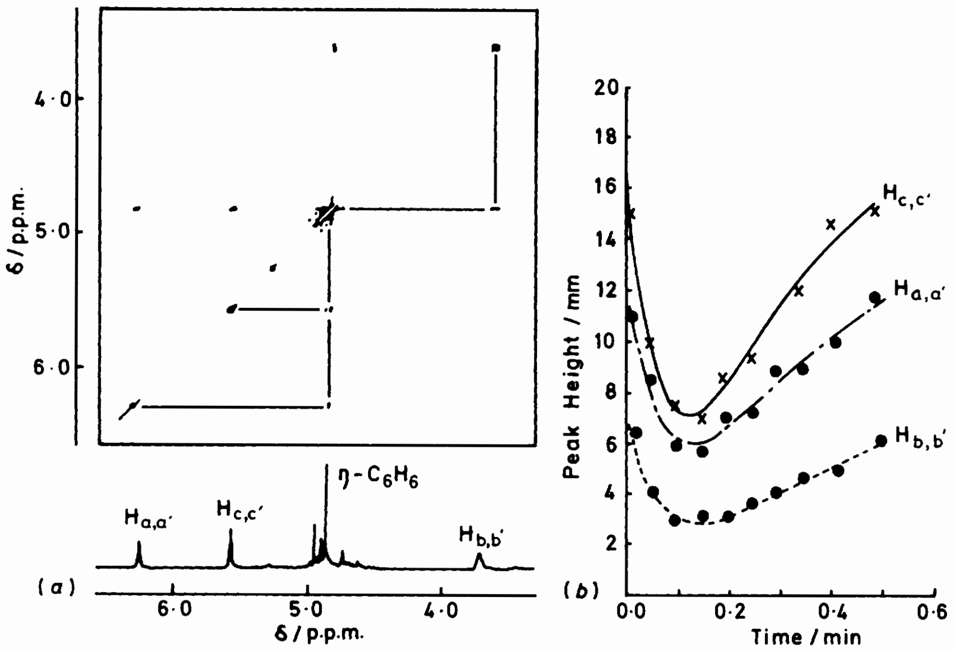


Figure 1. (*a*) 250-MHz Two-dimensional (^1H-^1H) chemical exchange spectrum of (**1**) in C_6D_6 at 60 °C. (*b*) Experimental points and fitted exponential curves for $H_{a,a'}$, $H_{b,b'}$, and $H_{c,c'}$ after inversion of the $\eta^6-C_6H_6$ protons at 60 °C in C_6D_6

Nucleophilic attack on the $\eta^6-C_6H_6$ ring of (**4**) is presumed to occur *exo*, as observed in the reaction of $[Ru(\eta^6-C_6Me_6)(\eta^5-C_6Me_6H)]^+$ with H^-, but contrasts with the observation that H^- adds to the iron analogue of (**4**) to give $[Fe(\eta^6-C_6H_6)(\eta^4-C_6H_8)]$.[14]

Co-condensation of osmium atoms with mesitylene gives as the major product the orange crystalline compound $[\{Os(\eta^6-C_6H_3Me_3-1,3,5)\}_2(\mu-H)_2(\mu-CHC_6H_3Me_2-3,5)]$ (**6**) and, following fractional crystallisation of the reaction mixture, a second minor product (1%) (**7**) was isolated as red crystals.

The ^1H n.m.r. spectrum of (**6**) at room temperature shows the two methyl groups and the *ortho* hydrogens of the $CHC_6H_3Me_2$-3,5 group to be equivalent. This presumably arises from rotation about the C_c–C_{ipso} bond. At −60 °C the expected inequivalence of the two methyls and of the *ortho* hydrogens is observed indicating exchange at this temperature to be slow on the n.m.r. time-scale. The chemical shifts of both H_c and C_c at δ 4.96 and 59.1 p.p.m. in the ^1H and ^{13}C n.m.r. spectra are comparable with those for the $\mu-CH_2$ ligand [δ 5.12, 4.32 (^1H) and 25.8 p.p.m. (^{13}C)] in $[Os(CO)_{10}(\mu-H)_2(\mu-CH_2)]$.[15] The relatively high-field shift for the bridgehead carbon is reminiscent of the shifts observed in related metal–alkyl derivatives.[16]

The relative conformations of H_a, H_b, and H_c were determined by homonuclear ^1H nuclear Overhauser enhance-

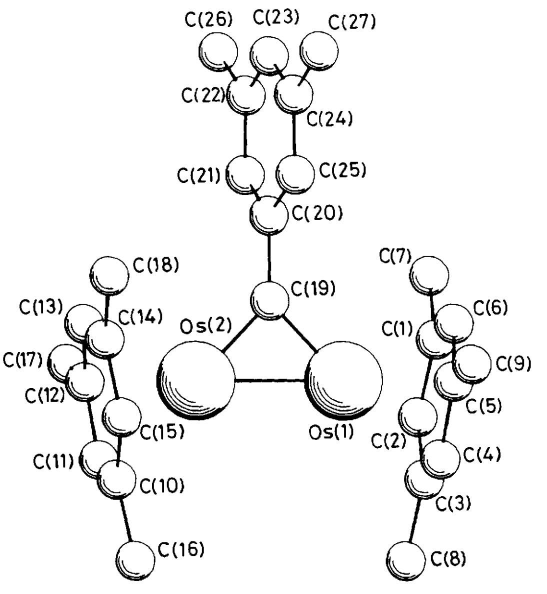


Figure 2. Molecular structure of (7), showing the atom-numbering scheme

ment (n.O.e.) experiments. The observation of a dipolar interaction between the osmium hydrides (H_a and H_b) establishes them in bridging positions.

The crystal structure of (7) has been determined and shows the compound to be of binuclear stoicheiometry [$\{Os(\eta^6-C_6H_3Me_3-1,3,5)\}_2(\mu-CHC_6H_3Me_2-3,5)$]. Compound (7) crystallises as red plates in the triclinic crystal system in space group $P\bar{1}$. The molecular structure of (7) is shown in Figure 2, and interatomic distances and angles are given in Table 2. The molecule possesses a non-crystallographic C_2 symmetry axis bisecting the Os(1)–Os(2) vector. The least-squares plane containing the μ-xylylmethylidene ligand lies at an angle of 99.8° to the plane defined by Os(1), Os(2), and C(19). Few simple diosmium compounds have been structurally characterised, which include [$Os_2(CO)_6(O_2CMe)_2$] [Os–Os 2.731(6) Å],[17] [$Os_2(\eta^5-C_5Me_5)_2(CO)(\mu-H)_2$] [Os–Os 2.677(6) Å],[18] and [$Os_2(CO)_6(C_8H_6)$] [Os–Os 2.754(2) Å].[19]

The observed Os(1)–Os(2) bond length of 2.647(1) Å in (7) can be best compared to the Os–Os distances in the trinuclear compounds containing μ-H and/or μ-alkylidene ligands, *e.g.* [$Os_3(CO)_{10}(\mu-H)_2(\mu-CH_2)$] [Os–Os 2.824(3) Å],[15] [$Os_3(CO)_{10}\{\mu-CH(CH_2PMe_2Ph)\}]^+$ [Os–Os 2.800(2) Å],[20] [$Os_3(CO)_{10}(\mu-H)_2$] [Os–Os 2.683(1) Å],[21] and [$Os_2(\eta^5-C_5Me_5)_2(CO)(\mu-H)_2$] [Os–Os 2.677(6) Å].[18] The metal–metal distance in (7) is shorter than these, which is consistent with the presence in (7) of an osmium–osmium triple bond. However, by analogy with the relatively short Re–Re distance in [$\{Re(\eta^6-C_6H_6)\}_2(\mu-H)_2(\mu-CHBu^t)$],[1,2] a lower bond order is also possible.

The presence of a hydrogen (H_c) involved in the Os–Os bridging system is indicated by the mass spectrum, ^1H n.m.r. spectroscopy, and the observed diamagnetism, but it is not observed by *X*-ray diffraction. The bridging carbon [C(19)] is only displaced by 0.3 Å out of the plane defined by Os(1), Os(2), and C(20); symmetry locates the hydrogen atom in the plane of μ-C(19) normal to the Os(1)–Os(2) vector. The near-planar environment of μ-C(19) indicates a strongly distorted μ-$CHC_6H_3Me_2$-3,5 system. The data do not allow distinction between the two structures shown in Figure 3. In structure (**A**) the μ-C–H system is shown to be interacting with the osmium–osmium orbitals, akin to an agostic system. Unfortunately the

Table 2. Bond distances (Å) and angles (°) for (7) with estimated standard deviations in parentheses

Os(1)–Os(2)	2.647(1)		
Os(1)–C(1)	2.22(1)	C(10)–C(11)	1.40(1)
Os(1)–C(2)	2.20(2)	C(10)–C(15)	1.45(1)
Os(1)–C(3)	2.34(1)	C(10)–C(16)	1.50(2)
Os(1)–C(4)	2.27(1)	C(11)–C(12)	1.44(1)
Os(1)–C(5)	2.20(1)	C(12)–C(13)	1.44(1)
Os(1)–C(6)	2.18(1)	C(12)–C(17)	1.49(2)
Os(1)–C(19)	1.92(2)	C(13)–C(14)	1.43(1)
		C(14)–C(15)	1.43(1)
Os(2)–C(10)	2.33(1)	C(14)–C(18)	1.50(2)
Os(2)–C(11)	2.28(1)		
Os(2)–C(12)	2.21(1)		
Os(2)–C(13)	2.19(1)	C(19)–C(20)	1.48(2)
Os(2)–C(14)	2.20(1)	C(20)–C(21)	1.39(1)
Os(2)–C(15)	2.21(1)	C(20)–C(25)	1.38(1)
Os(2)–C(19)	1.91(2)	C(21)–C(22)	1.39(1)
		C(22)–C(23)	1.39(2)
C(1)–C(2)	1.42(1)	C(22)–C(26)	1.55(2)
C(1)–C(6)	1.42(1)	C(23)–C(24)	1.38(1)
C(1)–C(7)	1.52(2)	C(24)–C(25)	1.39(1)
C(2)–C(3)	1.44(1)	C(24)–C(27)	1.52(2)
C(3)–C(4)	1.41(1)		
C(3)–C(8)	1.51(2)		
C(4)–C(5)	1.43(1)		
C(5)–C(6)	1.44(1)		
C(5)–C(9)	1.47(2)		
C(19)–Os(1)–Os(2)	46.1(5)		
C(19)–Os(2)–Os(1)	46.5(5)		
Os(1)–C(19)–Os(2)	87.4(7)		
C(7)–C(1)–C(6)	121.4(10)	C(25)–C(20)–C(21)	118.6(4)
C(7)–C(1)–C(2)	121.5(10)	C(22)–C(21)–C(20)	121.4(2)
C(6)–C(1)–C(2)	116.7(4)	C(23)–C(22)–C(21)	118.3(4)
C(1)–C(2)–C(3)	123.2(4)	C(24)–C(23)–C(22)	121.4(2)
C(2)–C(3)–C(4)	116.7(4)	C(25)–C(24)–C(23)	118.6(4)
C(3)–C(4)–C(5)	123.0(4)	C(24)–C(25)–C(20)	121.4(2)
C(4)–C(5)–C(6)	116.7(4)	C(27)–C(24)–C(23)	121.1(13)
C(2)–C(3)–C(8)	121.5(11)	C(27)–C(24)–C(25)	120.3(14)
C(4)–C(3)–C(8)	121.4(11)	C(26)–C(22)–C(23)	121.6(13)
C(9)–C(5)–C(6)	122.6(10)	C(26)–C(22)–C(21)	120.0(13)
C(9)–C(5)–C(4)	120.5(10)		
C(5)–C(6)–C(1)	122.9(4)		
C(16)–C(10)–C(11)	121.1(6)	C(18)–C(14)–C(15)	121.6(6)
C(16)–C(10)–C(15)	121.7(6)	C(18)–C(14)–C(13)	121.5(6)
C(10)–C(11)–C(12)	123.0(4)	C(17)–C(12)–C(13)	121.7(6)
C(11)–C(12)–C(13)	117.0(4)	C(17)–C(12)–C(11)	121.2(6)
C(12)–C(13)–C(14)	122.7(4)	C(15)–C(10)–C(11)	117.1(4)
C(13)–C(14)–C(15)	116.8(4)		
C(14)–C(15)–C(10)	123.0(4)		

J(CH) for this μ-C_c carbon could not be measured since it has the same chemical shift as the methyl groups of the μ-$CHC_6H_3Me_2$-3,5 ligand, as determined by the selective ^1H-decoupled ^{13}C n.m.r. experiments. The alternative and more probable structure (**B**) has a μ-hydride and an μ-alkylidyne group, *i.e.* μ-$CC_6H_3Me_2$-3,5.

Co-condensation of osmium atoms with a mixture of benzene and 2-methylpropane (1:1 w/w) gives yellow crystals of [$\{Os(\eta^6-C_6H_6)\}_3\{\mu_3-(CH_2)_3CH\}(\mu-H)_3$] (**8**), in low yield. Compound (**8**) is thermally stable in solution up to 150 °C. Detailed ^1H and ^{13}C n.m.r. experiments show the adamantane-like structure for (**8**) given in Figure 3. In particular, the ^1H n.m.r. spectrum shows a binomial septet for the apical hydrogen due to coupling to the six equivalent Os–CH_2 hydrogens, the fully ^1H coupled ^{13}C n.m.r. spectrum exhibits two doublets and

Table 3. Crystal data for [{Os(η^6-$C_6H_3Me_3$-1,3,5)}$_2$(μ-$CHC_6H_3Me_2$-3,5)] (7)

Formula	$C_{27}H_{34}Os_2$
M	738.97
T/K	295
a/Å	11.507(4)
b/Å	12.005(6)
c/Å	11.507(6)
α/°	111.50(5)
β/°	119.13(3)
γ/°	97.20(4)
U/Å^3	1 198.31
Crystal system	Triclinic
Space group	$P\bar{1}$
Z	2
D_c/g cm^{-3}	2.05
μ/cm^{-1}	106.2
F(000)	696
Crystal size/mm	0.28 × 0.24 × 0.12
θ limits/°	1.0—28.0
Scan mode	ω–2θ
Scan angle/°	1.0 + 0.35tanθ
Total data collected	11 330
Merging R factor	0.0865
No. of observations	3 849
No. of parameters	264
No. of restraints	41
Ratio of observations/parameters	14.6
Weighting scheme coefficients	4-term Chebyshev 322.34, 470.26, 182.86, 31.41
Maximum shift/error at convergence	0.03
Maximum peak in final difference map/e Å^{-3}	3.02
Final residuals R(R')	0.0509 (0.066)
Extinction coefficient	0.20

a triplet resonance for the CH, η^6-C_6H_6, and CH_2 groups respectively. The observed osmium–hydride ligands are assumed to be in bridging positions to maintain overall C_3 symmetry since no band can be observed in the i.r. spectrum assignable to ν(Os–H).

Co-condensation of osium atoms with a C_6D_6–2-methylpropane mixture (1 : 1 w/w) gives [{Os(η^6-C_6D_6)}$_3${μ_3-$(CH_2)_3$-CH}(μ-H)$_3$] (8′), as confirmed by ^{2}H n.m.r. and mass spectroscopy. There was no evidence for deuterium in any of the other positions in the molecule, and no scrambling of deuterium had occurred. Therefore, the three μ-H groups in (**8**) must arise from 2-methylpropane.

Discussion

Compound [Os(η^6-C_6H_6)(η^4-C_6H_6)] (**1**) is readily available from osmium atoms. It is reactive, and, as shown in the Scheme, it is a useful precursor for osmium chemistry. It is somewhat comparable with the 20-electron complex [Fe(η^6-C_6Me_6)$_2$], which also reacts readily with benzene, dihydrogen, or cyclohexa-1,3-diene giving the η^4-cyclohexa-1,3-diene derivative [Fe(η^6-C_6Me_6)(η^4-$C_6Me_6H_2$)].[22] The formation of [Os(η^6-C_6H_6)(PMe_3)(Ph)H] (**3**) rather than the bis(phosphine) compound [Os(η^6-C_6H_6)$(PMe_3)_2$] reflects the tendency for third-row transition metals to favour higher oxidation states. We note that [Os(η^6-C_6H_6)(PMe_3)(Ph)H] is thermally more stable than the ruthenium analogue which undergoes ring-exchange reactions with alkylbenzene compounds at *ca.* 60 °C.[10]

Previously reported arene complexes of osmium are the cationic bis(η^6-arene) derivatives [Os(η^6-arene)$_2$]$^{2+}$ (arene = C_6H_6[23] or $C_6H_3Me_3$-1,3,5[24]), polymeric [{$OsCl_2$(η^6-C_6H_6)}$_n$],[25] which is a useful precursor to the mono(arene) derivatives [Os(η^6-C_6H_6)(PMe_3)(η^2-C_2H_3R)X]PF_6 (R = Me or H, X = Cl or I), and the zerovalent compounds [Os(η^6-C_6H_6)LL′] [L = L′ = PPh_3 or P(OMe)$_3$; L = C_2H_3R (R = H or Me), L′ = PMe_3].[26]

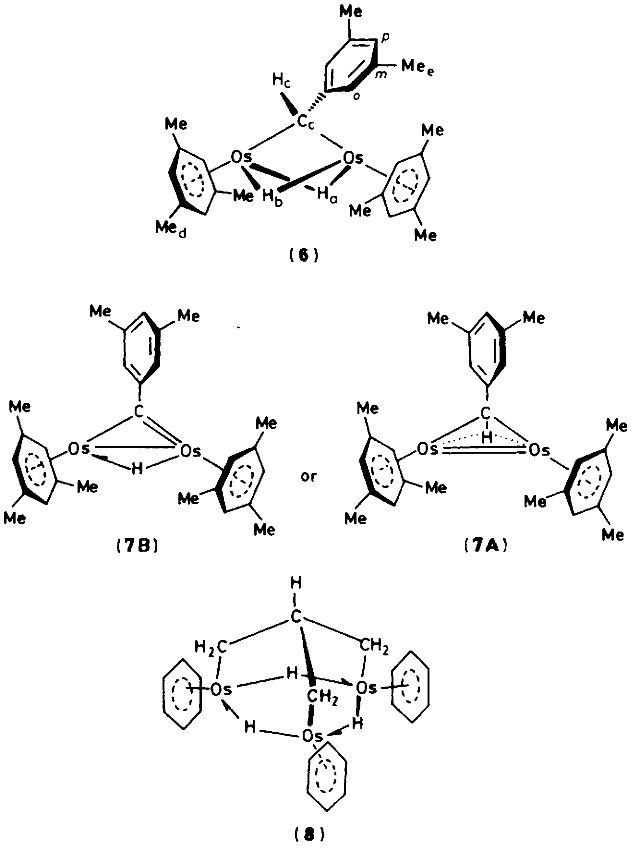


Figure 3. Structures proposed for (**6**), (**7A**) or (**7B**), and (**8**)

It seems that the ability of osmium atoms to form the binuclear μ-arylidene complexes (**6**) and (**7**) parallels the reactivity pattern first discovered for rhenium atoms.[1–4]

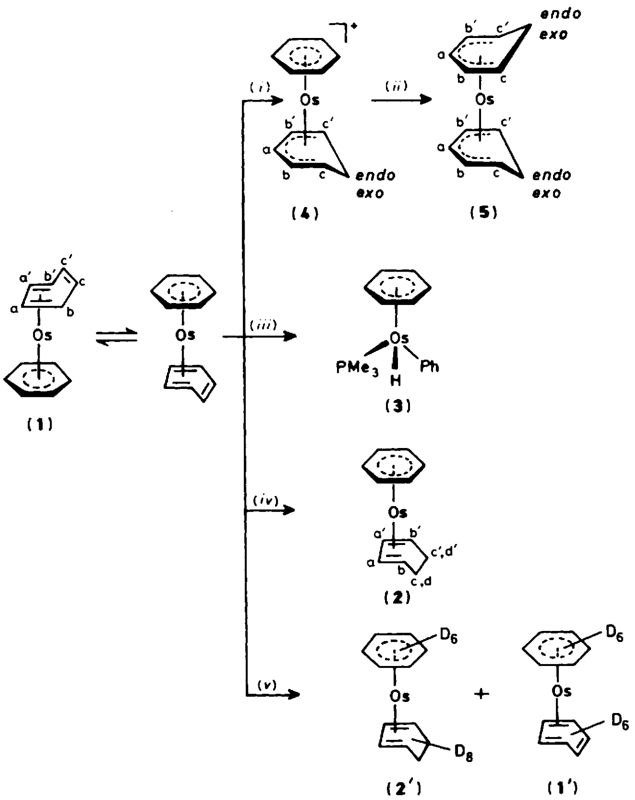
The formation of the triosmium compound (**8**) is quite unprecedented in metal atom chemistry. The synthesis of such an unusual compound requires three osmium atoms or three co-ordinatively unsaturated mono(η^6-arene)osmium moieties to combine to form a planar Os_3 species, which must then be 'capped' by the 2-methylpropane. It seems quite extraordinary that (**8**), whose formation requires the insertion of three osmium centres into the C–H bonds of 2-methylpropane, should take place in the presence of a large excess of benzene and that in this reaction there is less than 1% (n.m.r.) of (**1**) formed. This observation illustrates that the concept of an 'inert solvent' must be treated with judicious caution where metal atom reactions are concerned.

Finally, compound (**8**) provides a striking model for a surface adsorbed alkane.

Experimental

All preparations and reactions described were carried out under an atmosphere of nitrogen (< 10 p.p.m. oxygen or water) using standard Schlenk-tube and vacuum-line techniques or in a dry-box. Nitrogen was purified by passage through a gas drying column containing BASF catalyst and 5 Å molecular sieves.

All solvents were thoroughly deoxygenated before use by



Scheme. Reactions of [Os(η^6-C_6H_6)(η^4-C_6H_6)] (**1**). (*i*) HBF_4, −78 °C; (*ii*) $LiAlH_4$, r.t.; (*iii*) PMe_3 (excess), thf; (*iv*) H_2, 10 atm, r.t. or C_6H_6, 60 °C; (*v*) C_6D_6, 60 °C

repeated pumping followed by admission of nitrogen. Solvents were pre-dried over molecular sieves and then distilled from potassium [toluene, benzene, tetrahydrofuran (thf), cyclohexane], sodium–potassium alloy [pentane, light petroleum (b.p. 40—60 °C), diethyl ether], or phosphorus pentoxide (dichloromethane), under an inert atmosphere of nitrogen. Deuteriated solvents for n.m.r. were stored in Rotaflo ampoules over activated molecular sieves or a potassium film and transferred by vacuum distillation.

Liquid alkanes used in C–H activation studies were either of spectroscopic grade or were purified by treatment with a mixture of concentrated HNO_3–H_2SO_4 (3:1 v/v), followed by washing with an aqueous solution of $NaHCO_3$, and distillation from 4 Å molecular sieves. Liquid alkenes were passed through a column containing activated Al_2O_3. Gaseous reactants were used as supplied (research grade) without further purification. Elemental analyses were performed by the Analysis Department in this laboratory, or in the case of very air-sensitive materials, by Analytische Laboratorien, 5270 Gummersbach, 1 Elbach, West Germany.

Proton n.m.r. spectra were determined using a 300-MHz Bruker WH-300 spectrometer, ^{13}C n.m.r. using 62.8-MHz Bruker AM-250 or 125.6-MHz Bruker AM-500 instruments, and ^2H n.m.r. using a 38.4-MHz Bruker AM-250 spectrometer. Abbreviations used in multiplicities are s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet, sxt = sextet, spt = septet, m = multiplet, vt = virtual triplet, br = broad. Spectra were referenced internally using the solvent resonance (^1H, ^{13}C) relative to $SiMe_4$ (δ = 0 p.p.m.) or externally using trimethyl phosphate in D_2O (^{31}P). All chemical shifts (δ) are quoted in p.p.m. and coupling constants in Hz.

All multiple-pulse and two-dimensional n.m.r. experiments were acquired using standard Bruker software, and processed using either ASPECT 2000 or ASPECT 3000 computers.

Metal-vapour synthesis experiments were carried out using both the 10-kW bell-jar reactor[27] and the twin-hearth bell-jar reactor.[10] Both machines were operated in the positive hearth mode. Metal-vapour synthesis reactions were carried out using a pre-melted ingot of the appropriate metal. A pre-melted ingot is required to minimise outgassing during the reaction which would lead to deterioration of the vacuum. In a typical reaction, the electron gun furnace is turned on when a vacuum better than 10^{-5} Torr is achieved. Ligand (*ca.* 10 cm^3) is condensed onto the walls of the vessel (maintained at liquid nitrogen temperature) prior to evaporation of the metal sample. The metal is evaporated using the appropriate power and the rate of ligand entry adjusted so that a vacuum better than 10^{-4} Torr is maintained. Over the period of the co-condensation (typically 3—4 h) a matrix forms on the wall of the vessel which varies in appearance from pale yellow to dark red, depending upon the metal and ligand. At the end of the reaction the apparatus is isolated from the cryopump and the cooling shroud of liquid nitrogen emptied. The apparatus is filled with nitrogen and allowed to warm to room temperature (r.t.). As the matrix melts the product collects in the gutter and is washed out by the appropriate solvent under a positive pressure of nitrogen to a collection vessel.

Low-resolution mass spectra were recorded on an AEI M.S. 902 mass spectrometer, updated by a data handling system supplied by Mass Spectroscopy Services Ltd.

(η^6-*Benzene*)(η^4-*benzene*)*osmium*, (**1**).—Osmium atoms (0.8 g, 4.2 mmol), generated from a molten ingot (*ca.* 4.9 g), were co-condensed with pure benzene (80 cm^3) over 4 h using the 3.5-kW twin-hearth reactor and the small glass reaction vessel. The input power was maintained at 6 kV and 300 mA throughout. After warming to room temperature the orange-red matrix was extracted from the walls of the reaction vessel with thf (500 cm^3), filtered through a bed of Celite, and the volatile components were removed under reduced pressure at 40 °C, leaving a red-orange solid. The solid was extracted with light petroleum (b.p. 40—60 °C, 2 × 100 cm^3), filtered through Celite, and the solvent removed under reduced pressure at 40 °C. Sublimation at 80 °C, 10^{-4} Torr using a liquid-nitrogen cooled probe gave a yellow solid. The yellow sublimate was washed from the probe with pentane (2 × 50 cm^3), giving a pale orange-yellow solution which was filtered and concentrated to *ca.* 10 cm^3 under reduced pressure. Cooling to −20 °C initially, and then to −80 °C, gave very pale yellow microcrystals, which were collected and dried *in vacuo*. Yield: 200 mg, 14%.

(η^6-*Benzene*)(η^4-*cyclohexa*-1,3-*diene*)*osmium*, (**2**).—[Os(η^6-C_6H_6)(η^4-C_6H_6)] (**1**) (100 mg, 0.28 mmol) was dissolved in C_6H_6 (15 cm^3) and exposed to hydrogen (100 atm) in an autoclave. The orange solution was stirred at r.t. for 24 h. Removal of the solvent, followed by crystallization from pentane (10 cm^3) afforded a yellow microcrystalline solid. Yield: 80 mg, 80%.

Reaction of [Os(η^6-C_6H_6)(η^4-C_6H_6)] (**1**) *with* C_6D_6; *Synthesis of* (**1'**) *and* (**2'**).—[Os(η^6-C_6H_6)(η^4-C_6H_6)] (20 mg, 0.05 mmol) in perdeuteriobenzene (1.0 cm^3) was sealed in a 5-mm n.m.r. tube. The n.m.r. tube was heated to 100 °C for 3 d. The tube was cracked open in an inert atmosphere and the solvent removed under reduced pressure. The red residue was sublimed at 100 °C, 10^{-4} Torr onto a liquid-nitrogen cooled probe yielding a very pale yellow sublimate. The sublimate was washed from the probe with light petroleum (b.p. 40—60 °C, 2 × 20 cm^3) and the solvent removed, leaving a pale yellow microcrystalline solid, which was shown to be a mixture of

Table 4. Fractional atomic atomic co-ordinates (× 10^4) for (**7**), with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Os(1)	−514.2(5)	1 324.9(4)	2 310.5(5)
Os(2)	986.1(5)	3 674.3(4)	3 160.2(5)
C(1)	−646(12)	−693(12)	1 652(13)
C(2)	−1 547(12)	−617(11)	315(12)
C(3)	−2 723(12)	−188(13)	59(11)
C(4)	−2 850(11)	316(12)	1 292(13)
C(5)	−1 916(13)	359(12)	2 718(12)
C(6)	−860(13)	−209(12)	2 826(12)
C(7)	567(17)	−1 168(14)	1 865(20)
C(8)	−3 667(18)	−141(19)	−1 385(19)
C(9)	−2 120(17)	871(17)	3 949(19)
C(10)	232(11)	5 169(12)	2 454(11)
C(11)	966(11)	4 694(11)	1 832(10)
C(12)	2 357(11)	4 659(12)	2 726(10)
C(13)	3 038(10)	5 225(13)	4 344(12)
C(14)	2 329(11)	5 673(11)	5 041(10)
C(15)	923(12)	5 619(12)	4 069(12)
C(16)	−1 248(17)	5 116(17)	1 461(17)
C(17)	3 091(16)	4 131(16)	2 011(16)
C(18)	3 024(16)	6 164(16)	6 718(17)
C(19)	1 415(17)	2 525(16)	3 957(18)
C(20)	2 693(11)	2 522(13)	5 208(13)
C(21)	3 767(14)	2 245(14)	5 062(12)
C(22)	4 953(13)	2 214(14)	6 224(17)
C(23)	5 070(11)	2 508(14)	7 575(14)
C(24)	4 018(15)	2 781(14)	7 749(12)
C(25)	2 811(12)	2 745(14)	6 531(15)
C(26)	6 136(22)	1 906(21)	6 024(33)
C(27)	4 154(28)	3 099(23)	9 224(22)

[Os(η^6-C_6D_6)(η^4-C_6D_6)] (**1′**) and [Os(η^6-C_6D_6)(η^4-C_6D_8)] (**2′**) in a 2:100 molar ratio. Yield: 10 mg, 50%.

(η^6-Benzene)hydrido(phenyl)(trimethylphosphine)osmium, (**3**).—[Os(η^6-C_6H_6)(η^4-C_6H_6)] (**1**) (100 mg, 0.28 mmol) was dissolved in thf (30 cm^3) and treated with trimethylphosphine (1 cm^3). The orange reaction mixture was heated to 60 °C for 3 d. No precipitate or colour change was observed. The solvent and excess unreacted trimethylphosphine were removed under reduced pressure affording an orange oily solid. The oily solid was sublimed at 100 °C, 10^{-4} Torr onto a water-cooled sublimation probe giving a pale yellow solid. The sublimate was extracted from the probe with pentane (2 × 50 cm^3), filtered, and the filtrate concentrated to *ca.* 10 cm^3. Cooling the solution initially to −20 °C, and then to −80 °C, yielded a yellow microcrystalline solid, which was collected and dried *in vacuo*. Yield: 70 mg, 61%.

(η^6-Benzene)(η^5-cyclohexadienyl)osmium Tetrafluoroborate, (**4**).—[Os(η^6-C_6H_6)(η^4-C_6H_6)] (**1**) (150 mg, 0.43 mmol) was dissolved in diethyl ether (30 cm^3) and cooled to −78 °C with stirring. Dropwise addition of tetrafluoroboric acid in diethyl ether (5 drops) to the orange solution afforded a dark orange precipitate. The reaction mixture was allowed to warm to room temperature. The orange solid was washed with diethyl ether (3 × 30 cm^3) and dried *in vacuo*.

The orange solid was extracted with thf (2 × 50 cm^3), filtered, and the thf removed under reduced pressure yielding a dark orange solid. Recrystallization of the orange solid from methanol (20 cm^3) at −80 °C afforded a red microcrystalline solid. Yield: 130 mg, 70%.

Bis(η^5-cyclohexadienyl)osmium, (**5**).—[Os(η^6-C_6H_6)(η^5-C_6H_7)]BF_4 (**4**) (100 mg, 0.28 mmol) was dissolved in thf (30 cm^3) and an excess lithium aluminium hydride suspension (*ca.* 100 mg) in thf was added with stirring. An immediate reaction was observed and the orange solution became pale yellow, containing excess lithium aluminium hydride. Removal of solvent and extraction with light petroleum (b.p. 40—60 °C, 2 × 30 cm^3) yielded a yellow solution. Removal of the light petroleum and sublimation of the residue at 90 °C, 10^{-4} Torr onto a liquid-nitrogen cooled probe afforded a yellow microcrystalline sample of [Os(η^5-C_6H_7)$_2$]. Yield: 48 mg, 51%.

μ-3,5-Dimethylphenylmethylidene-di-μ-hydrido-bis[(η^6-1,3,5-trimethylbenzene)osmium], (**6**), *and* [{Os(η^6-$C_6H_5Me_3$-1,3,5)}$_2$-(μ-$CHC_6H_3Me_2$-3,5)] (**7**).—Osmium atoms (1.4 g, 7.3 mmol) were evaporated from a molten ingot (*ca.* 5.3 g) and co-condensed with pure mesitylene (100 cm^3). The input power was maintained at 6 kV × 300 mA throughout. After warming to r.t. the orange matrix was washed out of the reactor with toluene (500 cm^3), filtered through a bed of Celite, and the solvent and excess ligand removed under reduced pressure at 70 °C. The resulting red-orange oil was extracted with light petroleum (b.p. 40—60 °C, 2 × 100 cm^3), filtered through Celite, and the solvent removed from the filtrate under reduced pressure. Sublimation of the residue at 150 °C, 10^{-4} Torr, using a liquid-nitrogen cooled probe, gave a dark orange waxy solid. The sublimate was washed from the probe with pentane (2 × 50 cm^3), giving a bright red solution which was filtered and the filtrate concentrated to *ca.* 20 cm^3 under reduced pressure. Cooling to −20 °C gave bright red crystals of [{Os(η^6-$C_6H_3Me_3$-1,3,5)}$_2$(μ-$CHC_6H_3Me_2$-3,5)] (**7**). Yield: 20 mg, 1.0%.

Cooling the mother-liquor to −80 °C gave orange microcrystals of [{Os(η^6-$C_6H_3Me_3$-1,3,5)}$_2$(μ-H)$_2$(μ-$CHC_6H_3Me_3$-3,5)] (**6**). Yield: 200 mg, 10%. Crystals of (**7**) suitable for a single-crystal *X*-ray structure determination were grown by slow cooling of a saturated pentane solution.

1,2;1,3;2,3-Tri-μ-hydrido-μ$_3$-trimethylenemethane-tris[(η^6-benzene)osmium], (**8**).—Osmium atoms (0.8 g, 4.2 mmol), generated from a molten ingot (*ca.* 6.1 g), were co-condensed with a mixture of benzene and 2-methylpropane (90 cm^3, 50% w/w). After warming to r.t. the orange matrix was extracted with thf (500 cm^3), filtered through a bed of Celite, and the solvent and excess ligands were removed from the filtrate under reduced pressure at 60 °C. The resulting red-orange oily solid was extracted with light petroleum (b.p. 60—80 °C, 3 × 100 cm^3), filtered and the filtrate was concentrated to *ca.* 20 cm^3. Cooling to −20 °C and then to −80 °C overnight afforded an orange powder, which was collected and dried *in vacuo*. The orange powder was extracted with hot cyclohexane (2 × 50 cm^3) and concentrated to *ca.* 10 cm^3. Cooling gave bright yellow crystals of [{Os(η^6-C_6H_6)}$_3${μ$_3$-(CH_2)$_3$CH}(μ-H)$_3$] (**8**). Yield: 110 mg, 11%.

1,2;1,3;2,3-Tri-μ-hydrido-μ$_3$-trimethylenemethane-tris[(η^6-perdeuteriobenzene)osmium], (**8′**).—Osmium atoms (0.9 g, 4.7 mmol), evaporated from a molten ingot (*ca.* 3.1 g), were co-condensed with a mixture of C_6D_6 and 2-methylpropane (90 cm^3, 50% w/w). The subsequent work-up and recrystallization was identical to that described for the synthesis of (**8**). Yield: 110 mg, 9%.

Crystal Structure Determination.—Crystals of compound (**7**) were sealed under nitrogen in Lindemann glass capillaries and mounted on an Enraf-Nonius CAD4F diffractometer. Cell dimensions were obtained by least-squares methods from the positions of 25 carefully centred reflections. During data collection three intensity control reflections were measured every hour and four orientation controls checked after each 200 measurements. There was no significant variation in the magnitude of the intensity controls throughout data collection.

Lorentz and polarization corrections were applied, together with an empirical absorption correction.[28] Equivalent reflections were merged and only those for which $I > 3\sigma(I)$ were included in the refinement [where $\sigma(I)$ is the standard deviation based on counting statistics].

The osmium atomic co-ordinates were determined using Patterson methods; subsequent electron-density difference syntheses revealed the location of all the non-hydrogen atoms. The osmium atoms and the non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least squares. Hydrogen atoms of the CH groups belonging to the η^6-$C_6H_3Me_3$-1,3,5 or μ-$CHC_6H_3Me_2$-3,5 ligands were located, and included in calculated positions (C–H, 1.0 Å) which were modified between successive cycles of refinement. Refinement converged at $R = 0.0509$ ($R' = 0.066$) and the final electron-density difference synthesis showed no peaks > 3.02 e Å^{-3}, the largest peaks lying in close proximity to the osmium atom positions.

Corrections for anomalous dispersion and isotropic extinction[29] were made in the final cycles of refinement, a Chebyshev weighting scheme[30] was used with parameters as in Table 3. The final positional parameters are recorded in Table 4. All calculations were performed on the VAX 11/750 computer in the Chemical Crystallography Laboratory using the Oxford CRYSTALS system[31] and plotted using the CHEMGRAF package.[32] Atomic scattering factors and anomalous dispersion coefficients were taken from International Tables.[33]

Two-dimensional Experiments.—The (^{1}H–^{1}H) two-dimensional exchange spectra were acquired using the NOESY sequence,[34] wherein the intramolecular correlation is established by cross-relaxation leading to n.O.e. correctivities, or by magnetization transfer and slow chemical exchange. The pulse sequence for the NOESY experiment is (t_r–$\pi/2$–t_e–$\pi/2$–t_m–$\pi/2$–acquire) where $\pi/2$ is the non-selective ^{1}H pulse, and the times t_r, t_e, and t_m are respectively a relaxation delay, the incremented evolution period, and the mixing period during which exchange occurs. The values used in our experiment were $t_r = 10$ s and $t_m = 1.5$ s. 256 t_e Increments were measured giving a 512 K matrix after zero filling Fourier transformation in the f_1 and f_2 dimensions and symmetrization.

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