Metal Cluster-induced Electrophilicity of Arenes

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Hydride or carbanion attack on the triosmium cluster complexes $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5R)]$, R = H or Me, proceeds highly regio- and stereo-selectively at the face-capping arene ligands. The *exo*-addition products are anionic, triply bridging cyclohexadienyl complexes $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_5RR')]^-$, R′ = H, Me, or Ph, that yield neutral compounds $[Os_3(CO)_9(\mu\text{-}E)(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_5RR')]$ on reaction with electrophiles E = H^+ or $Au(PEt_3)^+$.

The ability of certain transition-metal centres to activate normally unreactive π-hydrocarbons towards nucleophilic attack is well known.[1–4] In recent years this area has attracted considerable interest due to its potential applications in organic synthesis, and novel routes have been developed to organic molecules often inaccessible by conventional strategies. The $Cr(CO)_3$ group, for example, exerts a powerful electron-withdrawing influence on co-ordination with an arene (comparable to the effect of a nitro group), enhancing the acidity of the arene hydrogens and activating the ring towards nucleophilic addition.[5] *exo*-Attack of reactive carbanions on $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ affords anionic η^5-cyclohexadienyl complexes, which on oxidation or protonation generate the corresponding uncomplexed substituted arenes or cyclohexadienes respectively.[5,6] Electrophilicity of the arene is further enhanced in the cationic systems $[Mn(CO)_3(\eta^6\text{-arene})]^+$, which react with synthetically useful nucleophiles such as Grignard reagents and ketone enolates that do not add to the ring in $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$.[7] Attack on substituted arenes is often highly regioselective and correlations based on a balance of charge control and frontier orbital control have been made.[8,9]

A new bonding mode, $\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6R_6$, has recently been established for arenes in polynuclear transition-metal complexes, where the C_6 ligands are co-ordinated symmetrically over the face of a metal triangle.[10–13] In this paper we describe cluster-induced electrophilicity for benzene and toluene when co-ordinated in the face-capping bonding mode in triosmium complexes $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ (**1**) and $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5Me)]$ (**2**). Hydride and carbanion addition is characterised by a high degree of stereo- and regio-selectivity in these systems and stereodifferentiation is also apparent in hydride abstraction reactions. The addition products are anionic triply bridging cyclohexadienyl complexes which may be attacked regiospecifically by electrophiles H^+ and $Au(PEt_3)^+$ at the metal triangle.

Experimental

Materials and Methods.—All reactions were performed under N_2 atmospheres using standard Schlenk techniques. Tetrahydrofuran (thf) was dried over sodium diphenylketyl and CH_2Cl_2 over CaH_2. The compounds $Li(BHEt_3)$, $Li(BDEt_3)$, $HBF_4{\cdot}Et_2O$, LiPh and LiMe were used as received from Aldrich; $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5R)]$, R = H or Me, were prepared as previously described.[10,12] Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer using 0.1-mm solution cells, n.m.r. spectra in $CDCl_3$ solutions on a Bruker AM-400 or WM-250 spectrometer, chemical shifts being reported relative to $SiMe_4$. Nuclear Overhauser effect (n.O.e.) difference experiments were carried out using standard Bruker software. Resonance pre-saturation was typically achieved with 1.5—2 W irradiation on-resonance for *ca.* 10 s (*ca.* 5 T_1) and the spectra acquired with the decoupler gated off (acquisition time *ca.* 1 s); 32 transients were collected. Electron-impact (e.i.) mass spectra were recorded at 70 eV (*ca.* 1.12×10^{-17} J) on an AEI MS12 instrument. Neutral products were purified by thin-layer chromatography (t.l.c.) on 20 cm × 20 cm × 0.25 mm silica plates (Merck Kieselgel $60F_{254}$).

$[N(PPh_3)_2][Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_7)]$ (**3**). A solution of $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ (30 mg) in thf (5 cm^3) was cooled to −78 °C and $Li(BHEt_3)$ (40 μl of a 1.0 mol dm^{-3} solution in thf, 1.2 mol equiv.) added to give a yellow-orange solution. The salt $[N(PPh_3)_2]Cl$ (23 mg) in Pr^iOH (3 cm^3) was added and the solution warmed to room temperature. Concentration *in vacuo* gave bright yellow microcrystals of $[N(PPh_3)_2][Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_7)]$ (yield 42 mg, 88%) (Found: C, 43.15; H, 2.90; N, 1.00. Calc. for $C_{51}H_{37}NO_9Os_3P_2$: C, 42.55; H, 2.55; N, 0.95%). I.r.: $\nu_{CO}(CH_2Cl_2)$ at 2 038m, 1 991s, 1 976s, 1 954m, 1 926m, and 1 915 (sh) cm^{-1}.

$[N(PPh_3)_2][Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_6Me)]$ (**5***). A solution of $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5Me)]$ (15 mg) in thf (3 cm^3) was cooled to −78 °C and treated with $Li(BHEt_3)$ (20 μl of a 1.0 mol dm^{-3} solution in thf, 1.2 mol equiv.) to give a yellow-orange solution. The salt $[N(PPh_3)_2]Cl$ (12 mg) in Pr^iOH (2 cm^3) was added and the mixture warmed to room temperature. Concentration *in vacuo* gave bright yellow microcrystalline $[N(PPh_3)_2][Os_3(CO)_9(\mu_3{:}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_6Me)]$ (yield 16 mg, 72%). Analytically pure material was not obtained. I.r.: $\nu_{CO}(CH_2Cl_2)$ at 2 036m, 1 989s, 1 976s, 1 948m, and 1 922m cm^{-1}.

Reaction of $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ *with* $Li(BDEt_3)$ *and* $HBF_4{\cdot}Et_2O$. A solution of $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ (20 mg) in thf (5 cm^3) was cooled to −78 °C and treated with $Li(BDEt_3)$ (70 μl of a 1.0 mol dm^{-3} solution in thf, *ca.* 3 mol equiv.). The bright yellow solution was maintained at −78 °C for 10 min, $HBF_4{\cdot}Et_2O$ (20 μl, *ca.* 5 mol equiv.) added, and the solution warmed to room temperature. Separation of the reaction mixture by t.l.c., eluting with CH_2Cl_2 (30%)–hexane (70%), afforded the dienyl complex $[Os_3H(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_6D)]$ in 74% yield. The ^1H n.m.r. spectrum of the product indicated greater than 95% deuterium incorporation at the *exo*-methylene position, the resonances of H^2 and H^1 appearing as a broadened doublet and singlet respectively [*i.e.* $J(H^1H^2)$ not resolved], the hydride a singlet at δ −19.36 with essentially no ^1H resonance being observed at δ 5.36 {*i.e.* H^6 in $[Os_3H(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_7)]$}.

$[N(PPh_3)_2][Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_6Me)]$ (**5**). The compound $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ (90 mg) in thf (6 cm^3) was cooled to −78 °C and LiMe (250 μl of a 1.5 mol dm^{-3} solution in diethyl ether, *ca.* 4 mol equiv.) added dropwise to give an orange-yellow solution. Addition of $[N(PPh_3)_2]Cl$ (63 mg, 1.1 mol equiv.) in Pr^iOH (4 cm^3) and removal of the solvent *in vacuo* at room temperature afforded the product as a fine, bright yellow powder (yield 100 mg, 69%) (Found: C, 43.45; H, 3.10; N, 1.40. Calc. for $C_{52}H_{39}NO_9Os_3P_2$: C, 42.95; H, 2.70; N, 0.95%). I.r.: ν_{CO}(thf) at 2 038s, 1 992vs, 1 979vs, 1 954s, 1 928m, and 1 916m cm^{-1}.

$[N(PPh_3)_2][Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_6Ph)]$ (**6**). The compound $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$ (100 mg) was dissolved in thf (6 cm^3) and the solution cooled to −78 °C. Phenyllithium (120 μl of a 1.7 mol dm^{-3} solution in cyclohexane–diethyl ether) was added dropwise, followed by $[N(PPh_3)_2]Cl$ (70 mg, 1.1 mol equiv.) in Pr^{i}OH (4 cm^3) and the solution warmed to room temperature. Removal of the solvent *in vacuo* gave bright yellow microcrystals of the product which were filtered off and washed with cold Pr^{i}OH and hexane (yield 145 mg, 86%) (Found C, 47.1; H, 3.30; N, 1.40. Calc for $C_{57}H_{41}NO_9Os_3P_2$: C, 45.5; H, 2.70; N, 0.90%). I.r.: $\nu_{CO}(CH_2Cl_2)$ at 2 039m, 1 993vs, 1 980vs, 1 955s, 1 930s, and 1 916m cm^{-1}.

$[Os_3H(CO)_9(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_6Me)]$ (**7**). A solution of $[N(PPh_3)_2][Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_6Me)]$ (40 mg) in CH_2Cl_2 (5 cm^3) was treated at −78 °C with $HBF_4{\cdot}Et_2O$ (6 μl, 1.1 mol equiv.). After warming to room temperature, t.l.c. separation of the reaction mixture [eluting with CH_2Cl_2 (40%)–hexane (60%)] and crystallisation from CH_2Cl_2–hexane gave the product as pale yellow microcrystals (yield 14 mg, 55%) [Found: C, 20.45; H, 0.80%; $M^{\cdot +}$ 922 (as required). Calc. for $C_{16}H_{10}O_9Os_3$: C. 20.95; H, 1.10%]. I.r.: $\nu_{CO}(CH_2Cl_2)$ at 2 086m, 2 058s, 2 030vs, 2 007m, 1 992m, and 1 946m cm^{-1}.

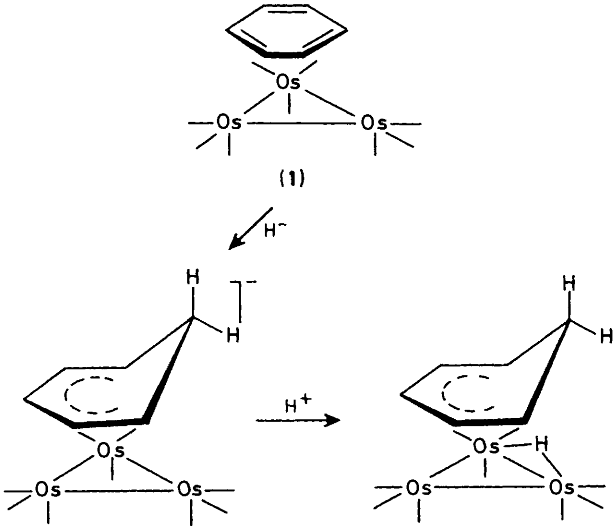
$[Os_3H(CO)_9(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_6Ph)]$ (**8**). The compound $[N(PPh_3)_2][Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_6Ph)]$ (40 mg) was dissolved in CH_2Cl_2 and the solution treated with $HBF_4{\cdot}Et_2O$ (10 μl, *ca.* 2 mol equiv.) at −78 °C. The reaction mixture was warmed to room temperature and separated by t.l.c., eluting with CH_2Cl_2 (40%)–hexane (60%). The product crystallised from CH_2Cl_2–hexane as pale yellow microcrystals (yield 20 mg, 77%) [Found: C, 25.85; H, 1.30%; $M^{\cdot +}$ 948 (as required). Calc. for $C_{21}H_{12}O_9Os_3$: C, 25.75; H, 1.25%]. I.r.: $\nu_{CO}(CH_2Cl_2)$ at 2 088m, 2 061s, 2 033s, 2 010m, 1 996m, and 1 950w cm^{-1}.

$[Os_3(CO)_9\{Au(PEt_3)\}(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_7)]$ (**9**). The compound $[N(PPh_3)_2][Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_7)]$ (30 mg) was dissolved in thf (5 cm^3) and the solution cooled to −78 °C. The salt $[Au(PEt_3)][SbF_6]$ (1.5 mol equiv.), prepared by treating $[Au(PEt_3)Cl]$ (11 mg) with $AgSbF_6$ (11 mg) in CH_2Cl_2 (4 cm^3), was added dropwise and the intense yellow solution warmed to room temperature. The product was isolated as bright orange crystals by t.l.c. separation of the reaction mixture, eluting with CH_2Cl_2 (50%)–hexane (50%), and crystallising from CH_2Cl_2–hexane (yield 19 mg, 76%) {Found: C, 21.15; H, 1.75; P. 2.20%; $M^{\cdot +}$ 1 222 (as required); 906 ['$AuH(PEt_3)$']. Calc. for $C_{21}H_{22}AuO_9Os_3P$: C, 20.75; H, 1.80; P, 2.55%}. I.r.: $\nu_{CO}(CH_2Cl_2)$ at 2 058m, 2 013s, 1 981m, 1 963w, and 1 935m cm^{-1}.

$[Os_3(CO)_9\{Au(PEt_3)\}(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_6Ph)]$ (**10**). A solution of $[N(PPh_3)_2][Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_6Ph)]$ (40 mg) in CH_2Cl_2 (5 cm^3) was cooled to −78 °C and treated with $[Au(PEt_3)Cl]$ (14 mg, 1.5 mol equiv.) in CH_2Cl_2 (2 cm^3). The bright orange solution was allowed to warm to room temperature and separated by t.l.c., eluting with CH_2Cl_2 (40%) – hexane (60%). Vermillion crystals of the product were obtained from CH_2Cl_2–MeOH solution on refrigeration (yield 22 mg, 64%) [Found: C, 25.30; H, 2.10; P, 2.20%; $M^{\cdot +}$ 1 298 (as required). Calc. for $C_{27}H_{26}AuO_9Os_3P$: C, 25.10; H, 2.00; P, 2.40%]. I.r.: $\nu_{CO}(CH_2Cl_2)$ at 2 059s, 2 015vs, 1 983m, 1 965w, and 1 936m cm^{-1}.

Results and Discussion

Characterisation of the $(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_7)$ *Ligand*.—Complex (**1**) reacts rapidly with good hydride donors {*e.g.* $Li(BHEt_3)$, $[NEt_4][BH_4]$} in thf at −78 °C to afford an anionic product, readily crystallised from Pr^{i}OH on metathesis to the $[N(PPh_3)_2]^+$ salt, that is formulated as $[N(PPh_3)_2][Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_7)]$ (**3**). The ^{1}H n.m.r. spectrum of (**3**) shows, in addition to phenyl resonances of the counter cation, five multiplets having integrated intensities 1:1:2:1:2 (see Table) consistent with hydride incorporation at the ring to give the triply bridging cyclohexadienyl moiety. There is a close correspondence between the ^{1}H n.m.r. spectra of (**3**) and the neutral hydrido dienyl complex $[Os_3H(CO)_9(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_7)]$ (**4**)[14] (see Table) and, indeed, anion (**3**) is cleanly converted into (**4**) on protonation with $HBF_4{\cdot}Et_2O$ in thf. Protonation at the ring would initially afford a co-ordinatively unsaturated η^4-cyclohexadiene complex that could undergo intramolecular activation to give (**4**) or alternatively decompose in some other fashion. We have no evidence for either of these processes.



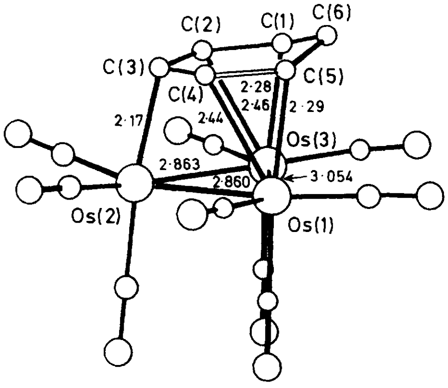
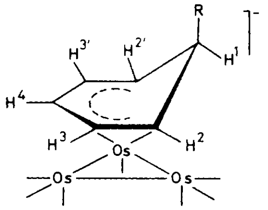


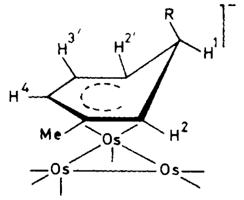
Figure 1. Molecular structure of $[Os_3H(CO)_9(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_7)]$ (**4**); distances in Å

Complex (**4**) is also formed in the reaction of $[Os_3H_2(CO)_{10}]$ with 1,3-cyclohexadiene and has been characterised by single-crystal *X*-ray diffraction:[14] the molecular structure is reproduced in Figure 1. The complex possesses non-crystallographically imposed C_s symmetry. In the cyclohexadienyl ligand, the five carbon atoms forming the pentadienyl fragment are planar to within 0.01 Å and C(6) lies 0.32 Å above this plane. The pentadienyl plane is tilted some 3.3° with respect to the osmium triangle so that the Os(2)–C(3) distance (2.17 Å) is significantly shorter than the other Os–C bond lengths (2.28, 2.45 Å). This former value falls in the range typically found for

Table. Proton n.m.r. data; *J* in Hz

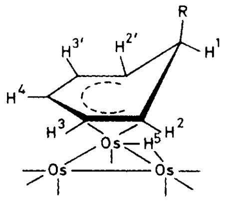


Complex	R	H^1	H^2	H^3	H^4	$[N(PPh_3)_2]^+$
(**3**) R = H^5	5.91 (br d) $J(H^1H^5)$ 14.7 $J(H^2H^5)$ not resolved	3.11 (dt) $J(H^1H^2)$ 2.5	2.14 (pdt) $J(H^2H^3)$ 8.2 $J(H^1H^2) \approx J(H^2H^5)$	3.98 (dd) $J(H^3H^4)$ 4.3	5.60 (t)	7.35—7.71 (m)
(**5**) R = Me	1.04 (d) J(1-Me) 6.7	3.14 (qt) $J(H^1H^2)$ 2.5	2.08 (dd) $J(H^2H^3)$ 8.4	3.96 (dd) $J(H^3H^4)$ 4.6	5.67 (t)	7.3—7.7 (m)
(**6**) R = Ph	7.1—7.8 (m)	4.34 (t) $J(H^1H^2)$ 2.4	2.29 (dd) $J(H^2H^3)$ 8.3	4.12 (dd) $J(H^3H^4)$ 4.6	5.92 (t)	7.1—7.8 (m)

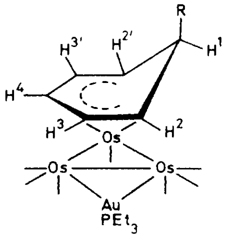


(**5***)

(**5***) R = H^5	5.75 (dt) $J(H^1H^5)$ 14.2 $J(H^2H^5)$ 1.6	2.94 (dt) $J(H^1H^2)$ 2.5	Obscured by impurity at *ca.* 2.2	4.08 (dd) $J(H^2H^3)$ 8.3 $J(H^3H^4)$ 4.8	5.43 (d)	Methyl 2.52 (s)

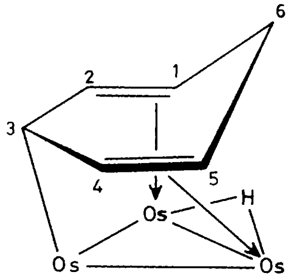


	R	H^1	H^2	H^3	H^4	H^5
(**4**) R = H^6	5.36 (ddt) $J(H^1H^6)$ 16.3 $J(H^5H^6)$ 4.0 $J(H^2H^6)$ 2.4	2.60 (dt) $J(H^1H^2)$ 2.1	2.82 (pdt) $J(H^1H^2) \approx J(H^2H^6)$ $J(H^2H^3)$ 8.4	4.64 (dd) $J(H^3H^4)$ 4.7	5.77 (t)	−19.35 (d)
(**7**) R = Me	1.10 (d) J(1-Me) 6.6	2.65 (m)	2.68 (br d) $J(H^2H^3)$ 8.3 $J(H^1H^2)$ not resolved	4.68 (dd) $J(H^3H^4)$ 4.8	5.88 (t)	−19.66 (s)
(**8**) R = Ph	7.20—7.36 (m)	3.82 (t) $J(H^1H^2)$ 1.3	2.90 (dd) $J(H^2H^3)$ 8.3	4.82 (dd) $J(H^3H^4)$ 4.8	6.14 (t)	−19.63 (s)



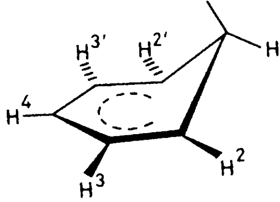
	R	H^1	H^2	H^3	H^4	PEt_3
(**9**) R = H^5	5.73 (d) $J(H^1H^5)$ 16.8	3.46 (dt) $J(H^1H^2)$ 2.0	2.82 and 2.59 (dd) $J(H^2H^3)$ 7.8 $J(H^2H^5)$ not resolved	4.47 and 4.25 (dd) $J(H^3H^4)$ 4.3	5.59 (t)	1.93 (dq) J(PH) 9.2 1.19 (dt) J(PH) 18.7 J(HH) 7.7
(**10**) R = Ph	7.1—7.3 (m)	4.63 (t) $J(H^1H^2)$ 2.2	2.97 and 2.73 (dt) $J(H^1H^2) \approx J(H^2H^2)$ $J(H^2H^3)$ 8.2	4.65 and 4.44 (dd) $J(H^3H^4)$ 4.1	5.94 (t)	1.94 (dq) J(PH) 9.3 1.19 (dt) J(PH) 18.7 J(HH) 7.6

Os–C σ bond lengths, and the angles around C(3) are also consistent with considerable σ character in the Os(2)–C(3) bond. In mononuclear η^5-cyclohexadienyl complexes the metal atom is situated roughly equidistant from the pentadienyl carbons,[5,15] while the bonding requirements of the *triangulo*-cluster apparently favour more hexa-1,4-diene character in the C_6 ligand.



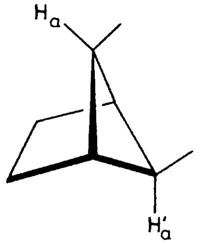
The dihedral angle between the pentadienyl plane and the plane containing carbons 1, 6, and 5 is the focus of a further structural difference between the trinuclear and mononuclear systems. Angles of *ca.* 40° are characteristically found in $[M(CO)_3(\eta^5\text{-}C_6H_6R)]$, M = Fe^+, Mn, or Cr,[6,16,17] whereas (**4**) shows a smaller out-of-plane distortion of 15°. Hoffmann and Hofmann[18] have identified a secondary antibonding interaction between the metal and *endo*-hydrogen (*i.e.* proximal to the metal) in the mononuclear complexes and propose an electronic basis for out-of-plane bending of the saturated carbon. This destabilising interaction is presumably less important in the cluster (**4**) and a smaller deviation from planarity is accommodated.

The variation in geometry between the two cyclohexadienyl bonding modes η^5-C_6H_7 and μ_3-η^2:σ:η^2-C_6H_7 is dramatically reflected in the ^1H n.m.r. spectra of their complexes. Thus in the η^5 mode multiplet resonances for the pentadienyl protons are successively deshielded on going from H^2 to H^4 (note renumbering below) with no significant variations in vicinal couplings [J(HH) *ca.* 6 Hz] being observed.[6] The methylene protons (H, H^1) appear upfield with the *exo*-hydrogen H frequently showing the more highly shielded resonance, possibly a consequence of ring current effects.[19,20] The coupling constant between H^1 and H^2, *ca.* 6 Hz, is appropriate for a dihedral angle of *ca.* 40° (see below).[6]



The chemical shifts for the pentadienyl resonances of the μ_3-η^2:σ:η^2-C_6H_7 moiety in (**4**) show a similar trend (Table) but the significant difference between $J(H^2H^3)$ (8.4 Hz) and $J(H^3H^4)$ (4.7 Hz) emphasises the 1,4-diene character of the triply bridging ligand. One remarkable feature of the ^1H n.m.r. spectrum of (**4**) is the apparent long range coupling [^4J(HH) = 4 Hz] between a highly deshielded methylene proton (δ 5.36) and the bridging hydride ligand; the location of the second methylene resonance (δ 2.60) is unexceptional. A combination of decoupling and n.O.e. difference experiments provides a complete assignment of this spectrum. Thus irradiation of the hydride signal produces a small but significant n.O.e. at the upfield (δ 2.60) methylene resonance reflecting the spatial proximity of the hydride and *endo*-hydrogen atoms. A more substantial enhancement is observed in the reverse experiment while no n.O.e. is found between the hydride and deshielded methylene proton (Figure 2). Evidently it is the *exo*-proton that couples to the hydride and an interesting comparison with the so-called long-range 'W' coupling ($J_{aa'}$ *ca.* 7 Hz) typically found in bicyclo[2.1.1]hexanes seems appropriate.[21]

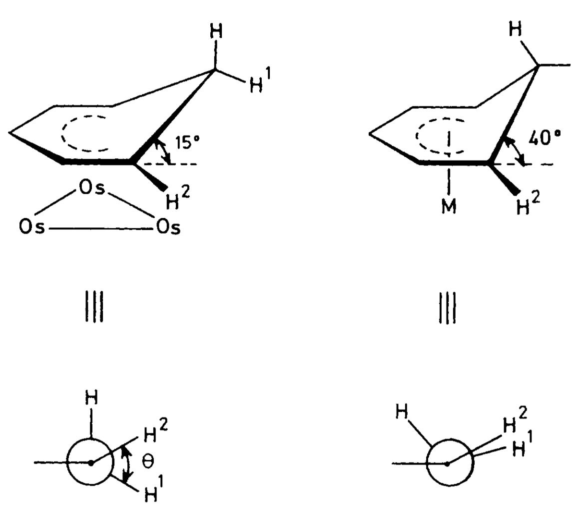
Figure 2. N.O.e. difference experiments for $[Os_3H(CO)_9(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_7)]$ (**4**)



The coupling between H^1 and H^2 is significantly smaller in (**4**), 2.1 Hz, than for the η^5-C_6H_7 ligand in monometal complexes. This is in accord with the Karplus relationship[22,23] since the reduced out-of-plane distortion in (**4**) increases the dihedral angle θ between the H^1–C^1 and H^2–C^2 bonds (*cf.* the Newman projections along the C^2–C^1 bond).

The substantial downfield shift suffered by the *exo*-proton H in (**4**) may well reflect significant magnetic anisotropy (or ring current effects) of the cyclohexadienyl ligand, with this proton located in a region of deshielding in the flatter ring.[24]

A large chemical shift difference is again observed between the *exo* and *endo* protons of the anionic face-capping cyclohexadienyl complex $[N(PPh_3)_2][Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\sigma\text{:}\eta^2\text{-}C_6H_7)]$ (**3**). From the close correspondence with the n.m.r. data for (**4**), a completely analogous bonding mode may be inferred for the C_6H_7 ligand in complex (**3**).

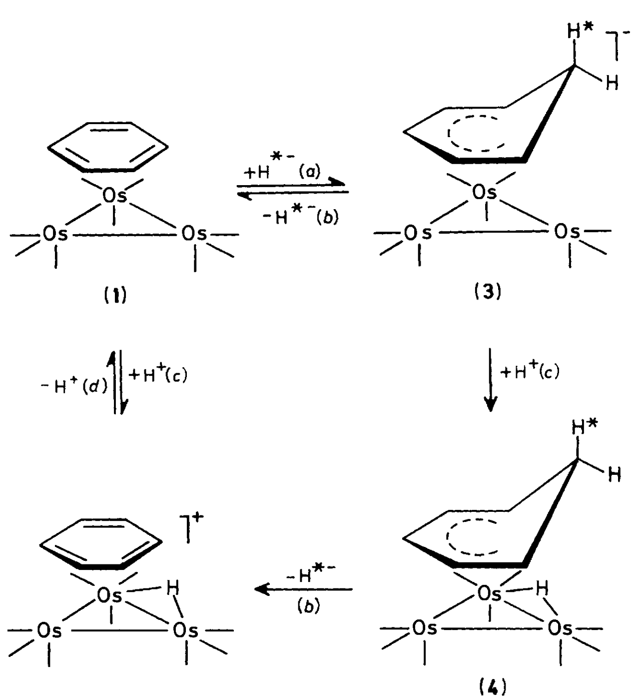


Exo-*Hydride Addition and Abstraction Reactions.*—While products of *exo*-attack are exclusively obtained in the vast majority of nucleophilic additions to co-ordinated π-hydrocarbons[2] some exceptions are known.[25–28] In these cases it is probable that the initial site of attack is the metal or a carbonyl ligand with subsequent migration to the carbocycle furnishing the observed *endo*-substituted products(s). Intramolecular metal-to-ring migrations have been substantiated for hydride and alkyl ligands in several instances.[29–33] Stereospecifically *exo*-attack of hydride on (**1**) is established here from the deuteride addition experiment. The product (**3D**) of the reaction of (**1**) with Li(BDEt$_3$) in thf at −78 °C shows essentially no resonance at δ 5.91 consistent with >95% incorporation of deuterium at the *exo*-position. Protonation with HBF$_4$·Et$_2$O affords [Os$_3$H(CO)$_9$(μ$_3$-η^2:σ:η^2-C$_6$H$_6$D)] (**4D**) with retention of configuration at the saturated carbon, the hydride ligand exhibiting a *singlet* resonance at δ −19.35 as anticipated. These are clearly kinetically formed products since at equilibrium the *exo*:*endo* distribution of deuteride should be close to 1:1.

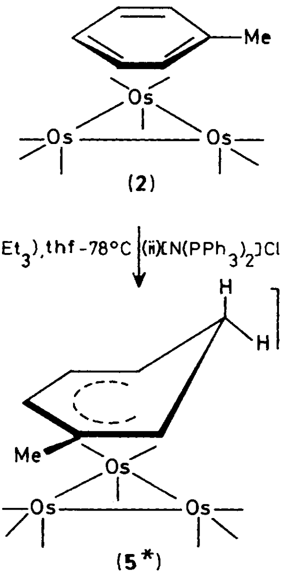
Abstraction of hydride from the anion (**3**) by reaction with the triphenylmethyl (trityl) cation at −78 °C in CH$_2$Cl$_2$ returns cleanly the benzene complex (**1**). The reaction with (**3D**) yields a product whose ^{2}H n.m.r. spectrum is silent, consistent with stereospecific abstraction of the *exo*-hydrogen. *Exo*-specific abstraction from the neutral complex (**4D**) is similarly found, and previous workers have also noted the marked propensity of the trityl cation to remove *exo*-substituent groups.[6,34] In the Scheme we summarise the interconversion of complexes (**1**) and (**4**) through the addition and removal of hydrogen atoms.

Regioselective Hydride Addition to [Os$_3$(CO)$_9$(μ$_3$-η^2:η^2:η^2-C$_6$H$_5$Me)] (**2**).—Experimental and theoretical studies have addressed the question of regioselectivity in the addition of nucleophiles to mononuclear π complexes of substituted arenes.[2,3,5,8] Steric effects generally mitigate against attack at ring positions *ortho* to a bulky substituent group, and in charge-controlled additions, nucleophilic attack at the site of least electron density (*e.g. meta* to strong resonance donors like RO and R$_2$N) is favoured. Frontier orbital effects become dominant for highly reactive nucleophiles and interaction between the highest occupied molecular orbital of the nucleophile and the lowest unoccupied arene-centred molecular orbital favours *ortho* and *meta* additions.

Hydride addition to the toluene complex [Os$_3$(CO)$_9$(μ$_3$-η^2:η^2:η^2-C$_6$H$_5$Me)] (**2**) affords a mixture of isomeric anionic dienyl complexes [N(PPh$_3$)$_2$][Os$_3$(CO)$_9$(μ$_3$-η^2:σ:η^2-C$_6$H$_6$Me)]. Although the ^{1}H n.m.r. spectrum of this mixture has not been completely deconvoluted, it is clear that the major component, (**5***) (predominating to the extent of *ca.* 65%), is formed through hydride attack at the ring carbon *meta* to the inductively electron-releasing methyl group (Table).

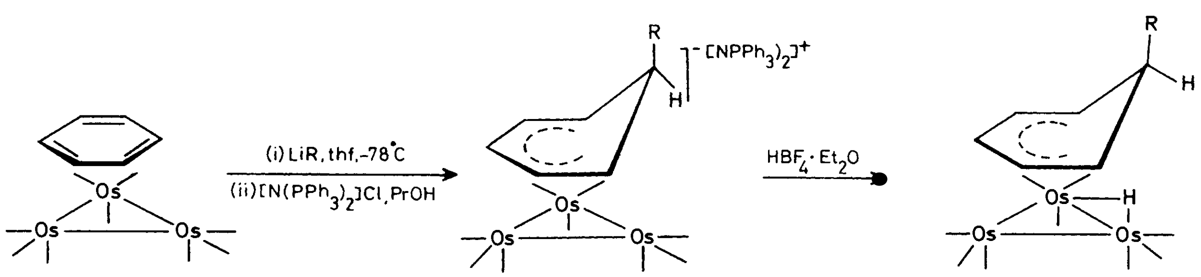


Scheme. Hydrogen-atom addition and abstraction reactions of complex (**1**). (*a*) LiBH*Et$_3$; (*b*) [CPh$_3$][BF$_4$]; (*c*) HBF$_4$·Et$_2$O; (*d*) 1,8-diazabicyclo[5.4.0]undec-7-ene



Carbanion Addition to [Os$_3$(CO)$_9$(μ$_3$:η^2:η^2:η^2-C$_6$H$_6$)] (**1**).—Treatment of compound (**1**) with methyl- or phenyl-lithium in thf solution at −78 °C affords functionalised cyclohexadienyl complexes, isolated as their [N(PPh$_3$)$_2$]$^+$ salts, [N(PPh$_3$)$_2$]-[Os$_3$(CO)$_9$(μ$_3$-η^2:σ:η^2-C$_6$H$_6$R)], R = Me (**5**) or Ph (**6**).

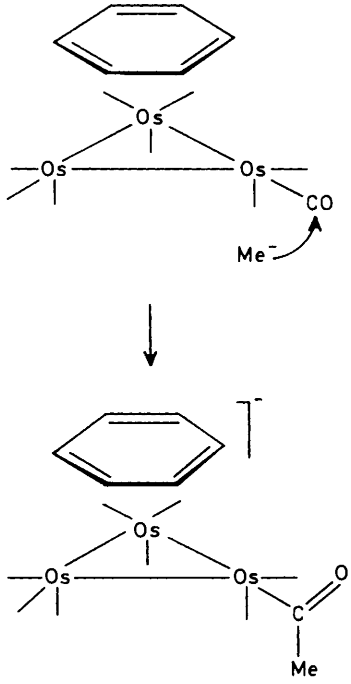
The ^{1}H n.m.r. spectra of (**5**) and (**6**) are wholly consistent with their formulation as *exo*-addition products and may be compared with the data for the parent compound (**3**) (Table). Additional singlet resonances at δ 4.02 and 2.51 with relative intensities 2:1 in the ^{1}H n.m.r. spectrum of (**5**) are attributed to a secondary product (accounting for *ca.* 10% of the total material



(5)
(6)

(7)
(8)

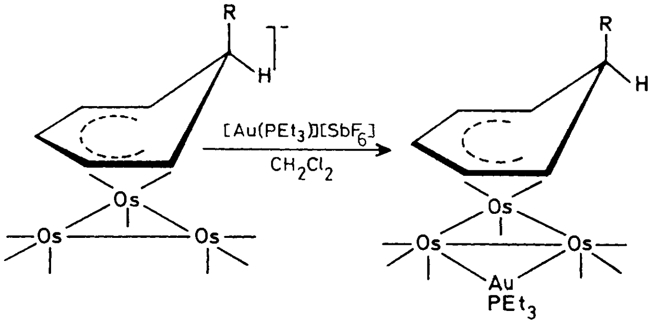
isolated). It is plausible that, when the nucleophile is Me^-, attack at carbonyl carbon to give an acyl or acyl-derived complex is competitive with addition to the ring, though rigorous characterisation of this material has not been possible.



Nucleophilic additions to co-ordinated CO are very well established reactions in mononuclear metal carbonyl chemistry,[3] and several reports of hydride or carbanion attack at carbonyls providing well characterised polynuclear formyl or acyl complexes have appeared.[35,36]

Protonation of the substituted cyclohexadienyl anions (**5**) and (**6**) gives the neutral, edge-bridging hydrido complexes $[Os_3H(CO)_9(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_6R)]$, R = Me (**7**) or Ph (**8**), in high yield. The hydride resonances of (**7**) and (**8**) are singlets (Table), consistent with *exo* substitution of Me and Ph respectively at the saturated carbon atom. N.O.e. difference experiments on (**8**) reveal a substantial positive n.O.e. between the hydride ligand and the methylene proton H^1, confirming the proposed stereochemistry of the cyclohexadienyl moiety.

Electrophilic attack of the gold phosphine cation $[Au(PEt_3)]^+$ at the metal triangles of the dienyl complex (**5**) and its phenyl analogue (**6**) afford bright orange clusters $[Os_3(CO)_9\{Au(PEt_3)\}(\mu_3\text{-}\eta^2{:}\sigma{:}\eta^2\text{-}C_6H_6R)]$, R = H (**9**) or Ph (**10**). In contrast to addition of the isolobal proton, ^1H n.m.r. spectroscopy (Table) indicates that these conditions do not occur at the unique Os–Os edge of the anions and the resulting products contain no plane of symmetry.



R = Me (**5**)
R = Ph (**6**)

(**9**)
(**10**)

Structural variation amongst formally analogous μ-hydride and gold cluster compounds has been noted previously.[37]

Conclusions

It is evident that there are remarkable similarities between the chemistry of nucleophilic addition to the face-capping arene ligands in cluster compounds (**1**) and (**2**) and at η^6-arene ligands in mononuclear complexes. Enhanced arene electrophilicity is anticipated in cationic species like $[Os_3H(CO)_8(PR_3)(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]^+$ [12] {compare, for example, the chemistry of $[Mn(CO)_3(\eta^6\text{-arene})]^+$ and $[Cr(CO)_3(\eta^6\text{-arene})]$} and additions of less reactive O-, N-, and S-based nucleophiles have very recently been observed in this system.[38] A possible synthetic route to substituted face-capping arene clusters, $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_5R)]$, based on *endo*-hydride abstraction from anionic μ_3-cyclohexadienyl complexes, is also under investigation. Preliminary experiments using trityl cation suggest that electron-transfer pathways may be competitive with removal of H^-, and that the abstraction products contain non-planar 'arene' residues.

Acknowledgements

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