Reactions of $[Os_3H_2(CO)_9(PR_3)]$, PR_3 = PPh_3, PPh_2Et, or $P(OMe)_3$, with Nucleophiles

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The vinyl complexes $[Os_3H(CO)_9L(CHCH_2)]$ [L = PPh_2Et, $P(OMe)_3$, and PPh_3] are formed by reacting the $[Os_3H_2(CO)_9L]$ species with acetylene, and exist in two isomeric forms. Vinyl complexes are also obtained by reacting $[Os_3H_2(CO)_9L]$ (L = PPh_2Et and PPh_3) with ethylene. Intermediate ethylene adducts were also observed. In these adducts, and also those of MeNC, the substrate is bound to the phosphine-substituted osmium atom, with the C_2H_4 and MeNC ligands in equatorial and axial sites respectively. Thermolysis of $[Os_3H(CO)_9(PPh_2Et)(CHCH_2)]$ affords $[Os_3H_2(CO)_8(PPh_2Et)(CCH_2)]$ in high yield. The latter complex reacts with hydrogen to form $[Os_3H_3(CO)_8(PPh_2Et)(CCH_3)]$. Nucleophilic addition to $[Os_3H(CO)_9L]$ appears to be orbitally controlled.

THE unsaturated cluster $[Os_3H_2(CO)_{10}]$ (1) catalyses olefin isomerisation and hydrogenation.[1-3] We were therefore interested in studying the chemistry of a particular phosphine-substituted derivative, $[Os_3H_2(CO)_9(PPh_2Et)]$ (2) since it is a close analogue of a species anchored to phosphinated silica gel (sil), namely $[Os_3H_2(CO)_9(PPh_2CH_2CH_2sil)]$ (3).[4] This work provided the necessary chemical and spectroscopic background for studying catalytic ethylene hydrogenation by complex (3).[5,6] However, it also demonstrates the effects of phosphine substitution on the reactivity and stereochemical non-rigidity of these trinuclear complexes. Some of this work has been reported in outline.[5]

EXPERIMENTAL

Mass spectra were recorded on an AEI MS12 spectrometer, i.r. spectra on a Perkin-Elmer 580B with a model 3500 Data Station and ^1H and ^{13}C n.m.r. spectra on a Varian XL-100 spectrometer.

All preparations were carried out under nitrogen, unless otherwise stated. Solvents were distilled from calcium hydride and stored over molecular sieves. Chromatography was on 20 × 20 × 0.1 cm silica t.l.c. plates. The compounds $[Os_3H_2(CO)_{10}]$ [7] and $[Os_3H_2(CO)_9(PR_3)]$ [8] were prepared by methods similar to those published.

$[Os_3H(CO)_9(PPh_2Et)(CHCH_2)]$ (4).—The complex $[Os_3H_2(CO)_9(PPh_2Et)]$ (2) (0.1088 g) was dissolved in n-hexane (100 cm^3) and acetylene, passed through a trap containing concentrated H_2SO_4 and a second at −78 °C, was bubbled gently through for 6 h. The solution became deep yellow in colour. After removing the solvent under reduced pressure, chromatography using hexane as solvent afforded a single band. The *product* (0.1104 g, 99%) was obtained from this band as an orange crystalline solid after recrystallisation from n-pentane (Found: C, 29.0; H, 1.60. Calc. for $C_{25}H_{19}O_9Os_3P$: C, 28.2; H, 1.60%). Mass spectrum: M = 1 066 based on Os_3 = 572. I.r. (cyclohexane): 2 091m, 2 059w, 2 046s, 2 031w, 2 011vs, 2 003vs, 1 985w, 1 969w, 1 967w, and 1 954w cm^{-1}. A similar method was used to prepare two other $[Os_3H(CO)_9L(CHCH_2)]$ species.

Complex (5), L = $P(OMe)_3$. Mass spectrum: M = 976 based on Os_3 = 572. I.r. (cyclohexane): 2 092.5m, 2 051m (sh), 2 047vs, 2 023w (sh), 2 018w (sh), 2 011vs, 2 002s, 1 987w, 1 980w, and 1 968.5m br cm^{-1}.

Complex (6), L = PPh_3. Mass spectrum: M = 1 114 based on Os_3 = 572. I.r. (cyclohexane): 2 091m, 2 060w, 2 046vs, 2 032.5mw, 2 011vs, 2 005vs, 2 001s (sh), 1 992w br, 1 986w, 1 970w, 1 959vw (sh), 1 956w cm^{-1}.

$[Os_3H_2(CO)_9(PPh_3)(C_2H_4)]$ (7).—The complex $[Os_3H_2(CO)_9(PPh_3)]$ (0.0530 g) in hexane (40 cm^3) was charged in a 100-cm^3 autoclave with ethylene (6 bar).† A pressure drop to 2.5 bar occurred on agitation and the solution was stirred overnight (15 h) at room temperature. After venting, the solvent was removed from the solution under reduced pressure to leave a yellow residue. On extraction of a small amount of (6), the *product* was isolated as a yellow crystalline solid (0.0524 g, 96%) (Found: C, 31.8; H, 1.55. Calc. for $C_{29}H_{21}O_9Os_3P$: C, 31.2; H, 1.90%). Mass spectrum: 1 114 (M − 28) based on Os_3 = 572. I.r. (cyclohexane): 2 090w, 2 069m, 2 042m, 2 006vs, 1 999m (sh), 1 989w br (sh), 1 970w, and 1 964w cm^{-1}.

$[Os_3H_2(CO)_9(PPh_2Et)(C_2H_4)]$ (8) was prepared under similar conditions, but was not obtained pure.

$[Os_3H_2(CO)_9(PPh_2Et)(MeNC)]$ (9).—Methyl isocyanide (0.030 cm^3) was added to a solution of (2) (0.0466 g) in hexane (30 cm^3). An immediate colour change occurred, affording a light yellow precipitate after stirring for 15 min. The precipitate was filtered off, washed, and dried *in vacuo* to yield the *product* as a light yellow solid (0.0449 g, 93%) (Found: C, 30.1; H, 1.45; N, 1.30. Calc. for $C_{25}H_{20}NO_9Os_3P$: C, 27.8; H, 1.87; N, 1.30%). I.r. (cyclohexane): 2 212w br [ν(CN)], 2 081s, 2 046vs, 2 018s, 2 006s, 1 998mw (sh), 1 981m, 1 976m (sh), 1 970m, 1 961w, 1 943vw, and 1 917vw cm^{-1}.

$[Os_3H_2(CO)_9(PPh_3)(MeNC)]$ (10) was prepared similarly.

$[Os_3H_2(CO)_8(PPh_2Et)(CCH_2)]$ (11).—A solution of (4) in n-heptane (60 cm^3) was heated under reflux for 3 h, during which time the solution lightened to a pale yellow. The solvent was removed under reduced pressure and the residue chromatographed, using hexane–diethyl ether (5 : 1) as solvent to afford the *product* (R_f 0.55) (Found: C, 27.6; H, 1.5. Calc. for $C_{24}H_{19}O_8Os_3P$: C, 27.8; H, 1.85%). Mass spectrum: M 1 038 based on Os_3 = 572. I.r. (cyclohexane): 2 084m, 2 050vs, 2 036w, 2 030m, 2 021vw, 2 005s, 1 997m, 1 979m, 1 965w (sh) cm^{-1}.

$[Os_3H_3(CO)_8(PPh_2Et)(CCH_3)]$ (12).—Hydrogen was bubbled through a solution of (11) in n-octane (50 cm^3) and heated under reflux for 12 h. Infrared measurements indicated a quantitative reaction to give (12). Removal of the solvent and chromatography using hexane–diethyl ether (5 : 1) as solvent afforded the *product* as a colourless crystal-

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† Throughout this paper: 1 bar = 101 325 Pa.

line solid (Found: C, 27.9; H, 1.9. Calc. for $C_{24}H_{21}O_8Os_3P$: C, 27.7; H, 2.05%). Mass spectrum: M 1 040 based on $Os_3 = 572$. I.r. (cyclohexane): 2 091.5mw, 2 069vs, 2 026m, 2 022s, 2 006vs, 1 991w, 1 979vw, 1 966vw, and 1 954w cm^{-1}.

RESULTS

$[Os_3H(CO)_9L(CHCH_2)]$.—Complex (2) reacts with acetylene to afford the vinyl complex (4) similarly to (1).[9] However the ^1H n.m.r. spectrum of (4) contains two doublets due to metal hydride environments, each coupled to phosphorus. The combined integration of the δ −19.20 and −19.42 resonances (relative intensity 4 : 1) against the phosphine signals is that of a single hydride, indicating two isomeric forms. No significant change in relative proportions was apparent in spectra recorded at temperature intervals between 31 and −60 °C. At 95 °C, in [$^2H_8$]-toluene, any evidence for line-broadening was inconclusive. At that temperature, two new doublets centred at δ −17.46 and −20.87 were evident, due to partial pyrolysis to $[Os_3H_2(CO)_8(PPh_2Et)(CCH_2)]$ (11). The observation of phosphorus coupling to the hydride resonances suggests that the phosphine might occupy sites on metal atoms on either end of the bridging groups [isomers (a) and (b) in Figure 1]. Pairs of

TABLE 1

Hydrogen-1 n.m.r. data[a]

Complex	δ/p.p.m.
(4) $[Os_3H(CO)_9(PPh_2Et)(CHCH_2)]$	7.5 (*ca.* 10 H, m, Ph), 2.74 [*ca.* 2 H, m, J(HH) 7.5, $PC\mathit{H}_2Me$], 1.01 [*ca.* 3 H, dt, J(PH) 7.5, $PCH_2C\mathit{H}_3$]
Isomer (a)	7.76 (m, H_C), 4.14 (d, H_B), 2.44 (m, H_A), −19.20 (d, H_D). $J(H_AP)$ *ca.* 13, $J(H_AH_C)$ *ca.* 13, $J(H_BH_C)$ 9, $J(H_DP)$ 5.9
Isomer (b)	5.34 [d, H_B, $J(H_BH_C)$ 10.5], −19.42 [d, H_D, $J(H_DP)$ 11.7]. H_A and H_C obscured
(5) $[Os_3H(CO)_9\{P(OMe)_3\}(CHCH_2)]$	3.74 [9 H, d, J(HP) 13]
Isomer (a)	7.5 (m, H_C), 4.34 (d, H_B), 2.83 (dd, H_A), −19.92 (d, H_D). $J(H_AH_C)$ 13, $J(H_AP)$ 13, $J(H_BH_C)$ 10, $J(H_DP)$ 6
Isomer (b)	7.5 [m, H_C (?)], 4.81 (d, H_B), 3.10 (d, H_A), −20.03 (d, H_D). $J(H_AH_C)$ 15, $J(H_BH_C)$ 10, $J(H_DP)$ 10
(6) $[Os_3H(CO)_9(PPh_3)(CHCH_2)]$	7.45 (15 H, m, Ph)
Isomer (a)	7.89 (tt, H_C), 4.37 (d, H_B), 2.32 (m, H_A), −18.87 (m, H_D). $J(H_AH_B)$ 2, $J(H_AH_C)$ 14, $J(H_AP)$ 13, $J(H_BH_C)$ 9.5, $J(H_BH_D)$ 2 or $J(H_BP)$ 2, $J(H_CH_D)$ 2, $J(H_CP)$ 2, $J(H_DP)$ 7
Isomer (b)	8.95 (tt, H_C), 5.30 (dd, H_B), 2.50 (dd, H_A), −19.02 (dd, H_D). $J(H_AH_B)$ 1.5, $J(H_AH_C)$ 14.5, $J(H_BH_C)$ 10.5, $J(H_CH_D)$ 1.5, $J(H_DP)$ 12
(7) $[Os_3H_2(CO)_9(PPh_3)(C_2H_4)]$	7.46 (15 H, m, Ph), 2.56 [4 H, d, J(PH) 7, C_2H_4], −14.20 (1 H, s, Os–*H*), −19.89 [1 H, d, J(PH) 12.5, μ–OsH]
(9) $[Os_3H_2(CO)_9(PPh_2Et)(MeNC)]$[b]	7.45 (10 H, m, Ph), 3.11 (3 H, d, J(PH) 2.5, $C\mathit{H}_3NC$], 2.82 [2 H, m, J(HH) 7, $PC\mathit{H}_2Me$], 1.05 [3 H, dt, J(HH) 7, J(PH) 19, $PCH_2C\mathit{H}_3$], −10.11 [1 H, d, J(HH) 3.5, Os–H], −20.01 [1 H, dd, J(HP) 11.4, J(HH) 3.5, μ–OsH]
(11) $[Os_3H_2(CO)_8(PPh_2Et)(CCH_2)]$	7.47 (10 H, m, Ph), 6.63 [1 H, d, J(PH) 5, $CC\mathit{H}_2$], 6.15 [1 H, d, J(PH) 9, $CC\mathit{H}_2$], 2.60 [2 H, m, J(HH) 7, PCH_2CH_3], 1.00 [3 H, dt, J(PH) 19, J(HH) 7, $PCH_2C\mathit{H}_3$], −17.46 [1 H, d, J(PH) 11, μ–OsH], −20.87 [1 H, d, J(PH) 8.3 Hz, μ–OsH]
(12) $[Os_3H_3(CO)_8(PPh_2Et)(CCH_3)]$	7.43 (10 H, m, Ph), 4.63 [3 H, d, J(PH) 4, μ_3–$C\mathit{H}_3$], 2.60 [2 H, m, J(HH) 7, $PC\mathit{H}_2CH_3$], 0.96 [3 H, dt, J(HH) 7, J(PH) 19, $PCH_2C\mathit{H}_3$], −18.03 [2 H, d, J(PH) 11.8, μ–OsH], −18.76 (1 H, s, μ–OsH)

[a] In $CDCl_3$ at 31 °C, unless otherwise stated; J values in Hz. [b] Recorded at −60 °C.

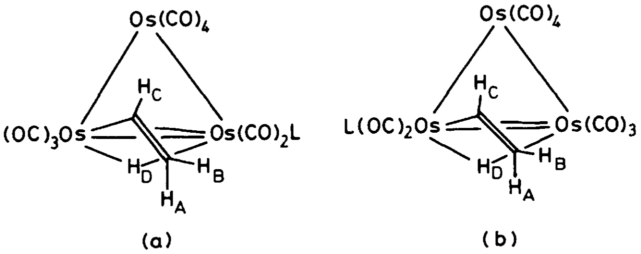

FIGURE 1 Isomeric forms of $[Os_3H(CO)_9L(CHCH_2)]$ (4; L = PPh_2Et), [5; L = $P(OMe)_3$], and (6; L = PPh_3): (a) major isomer and (b) minor isomer

vinyl resonances due to the two isomers were apparent, but partly masked by those of the phosphine. The $P(OMe)_3$ and PPh_3 derivatives (5) and (6) were prepared to circumvent this problem and showed two differences. Firstly, the reaction of $[Os_3H_2(CO)_9(PPh_3)]$ with acetylene was appreciably slower than the other derivatives, taking *ca.* 32 h to reach completion. Secondly, the isomeric ratios of (5) markedly favoured the major form, while for (6) the ratio was closer to unity. Specific proton–proton double irradiation experiments were carried out on (6) giving rise to the assignments in Table 1. The major isomer has a large (13 Hz) coupling between one of the methylene protons (H_A) and the ^{31}P nucleus. This suggests the major isomer is of type (a) with the methylene group and the phosphine co-ordinated to a common osmium atom. Assignments for (4) and (5) were made by comparison to (6).

TABLE 2

Carbonyl ^{13}C n.m.r. spectral data[a]

Complex	δ/p.p.m.
(4) $[Os_3H(CO)_9(PPh_2Et)(CHCH_2)]$	187.0, 185.8 [d, *J*(PC) 6.2], 183.7, 181.1, 175.9, 175.3, 174.4, 173.4, 167.8
(7) $[Os_3H_2(CO)_9(PPh_3)(C_2H_4)]$[b]	187.3 [d, *J*(PC) 5.1], 182.5 [d, *J*(PC) 4.5], 181.0 [d, *J*(CH) 4.9], 178.8, 177.7, 174.7 [dd, *J*(CH^1) 9, *J*(CH^2) 2.5], 173.2, 172.7, 167.7 [d, *J*(CH) 5.6]
(11) $[Os_3H_2(CO)_8(PPh_2Et)(CCH_2)]$	178.4 [d, *J*(CH) 3.6], 176.3 [d, *J*(CH) 5.1], 175.1 [d, *J*(CH) 3.4], 172.3 [d, *J*(CH) 9.4), 169.7, 169.1
(12) $[Os_3H_3(CO)_8(PPh_2Et)(CCH_3)]$	176.0 [d, *J*(CH) 5.0], 169.0 [d, *J*(CH) 7.0], 168.7 [d, *J*(CH) 8.0], 168.4

[a] In $CDCl_3$ at 31 °C, unless otherwise stated; *J* values in Hz.
[b] Recorded at 0 °C.

A $^{13}C-\{^1H\}$ n.m.r. spectrum was recorded on a ^{13}CO enriched sample of (4), prepared from $[Os_3H_2(C^*O)_9(PPh_2Et)]$. From the isomer ratio, the observed features can be attributed to the major isomer, with the minor one contributing only weak resonances or shoulders. Nine terminal carbonyl resonances were observed (Table 2) and in a coupled spectrum, only small *J*(CH) couplings (< 2 Hz) were evident. The spectrum was invariant between −70 and 31 °C. Partial assignment is possible by comparison with published data on $[Os_3H(CO)_{10}(CHCH_2)]$ (13)[10] and $[Os_3H(CO)_{10}(COR)]$.[11] The ten carbonyl sites in (13) are shown in Figure 2 and the phosphine is in site 8, 9, or 10 in (4a). The two axial $Os(CO)_4$ sites 1 and 2 can be ascribed to two of the low-field singlets (δ 187.0 and 183.7); these occur at δ 184.5 and 181.0 in (13). In (13), the two equatorial resonances of that group were accidentally degenerate at δ 173.9 and thus two of the three resonances between δ 174 and δ 176 are assigned to sites 3 and 4 in (4a). In (13), carbonyls 5 and 8 resonate at δ 172.6 and 165.6. The Os–CO bond lengths in that complex suggest that the metal centre with the vinyl σ bond is more electron deficient than the other $Os(CO)_3$ group.[12] In general, this yields relatively upfield shifts [13] so that signal at δ 165.6 in (13) is assigned to site 5; so accordingly is the resonance at δ 167.8 in (4a). Comparisons between (1) and (2) indicate that carbonyl groups on a phosphine-substituted osmium suffer a *ca.* 7 p.p.m. downfield shift.[14] Carbonyl 8 would be anticipated to be near δ 180 and is therefore ascribed to the resonance at δ 181.1. The phosphine site is therefore either 9 or 10 and the observed *J*(PH) hydride coupling constant (5.9 Hz) is consistent with it retaining its original position in (2),[8] *viz.* site 9; the phosphorus-split doublet at δ 185.8 is therefore assigned to site 10.

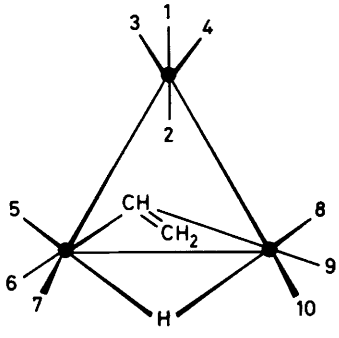

FIGURE 2 Carbonyl (and ligand L) sites in $[Os_3H(CO)_9L(CHCH_2)]$

The methine and methylene ^{13}C resonances in $[Os_3H(CO)_{10}(CHCH_2)]$ have been observed at δ 101.3 and 68.7 respectively.[15] Analogous signals for the major isomers of both $[Os_3H(CO)_9(PPh_2Et)(CHCH_2)]$ (δ 98.5 and 62.2) and $[Os_3H(CO)_9(PPh_3)(CHCH_2)]$ (6) (δ 100.0 and 64.9) were observed. However, only a tentative assignment of one weak peak at δ 56.5 could be made for the minor isomer of (6). The absence of ^{31}P coupling to the vinyl protons and the size of $J(H_DP)$ in the minor isomer indicate that the phosphine is *cis* to both the vinyl and hydride ligands, *i.e.* sites 7 or 10 in Figure 2. The unusual chemical shift of the methine proton H_C in the minor isomer of (6) suggests substitution may be at 7 but this is inconclusive.

Reaction of $[Os_3H_2(CO)_9L]$ *with Ethylene.*—Synthesis of the vinyl complex (13) has also been effected by the reaction of $[Os_3H_2(CO)_{10}]$ (1) with *ca.* 3 bar of ethylene after 40 h at 25 °C.[16] However, after interacting (2) with 2.5 bar of ethylene overnight, the i.r. spectrum of the recovered solution showed a new complex, identified as $[Os_3H_2(CO)_9(PPh_2Et)(C_2H_4)]$ (8), with weak peaks due to residual (2). In addition to the phosphine resonances, the ^1H n.m.r. spectrum of (8) exhibited two hydride resonances [δ −14.31, s, and −20.33, d, *J*(PH) 11.2 Hz] and a doublet [*J*(PH) 7 Hz] at δ 2.50 due to co-ordinated ethylene; the alkene protons in $[Os_3H(CO)_9(SMe)(C_2H_4)]$ resonate at δ 2.49.[17] The ethylene could be liberated by heating or pumping *in vacuo*. After 5 d under this ethylene pressure, conversion to the vinyl complex (4) and formation of some ethane was effected.

However, a pure adduct, (7), of $[Os_3H_2(CO)_9(PPh_3)]$ was obtained. It is evidently more stable than (8) but will revert to the precursor after prolonged pumping *in vacuo*. After 5 d under 2.5 bar of ethylene, conversion to (6) was incomplete. The ^1H n.m.r. spectrum of (7) in $CDCl_3$ at 31 °C contained two hydride resonances, with the more upfield one coupled to phosphorus (Table 1). This, and the observation of phosphorus coupling to the ethylene resonance, suggests a similar structure to that of $[Os_3H_2(CO)_{10}(PPh_3)]$ (14) [18] with an ethylene substituent on the phosphine-bearing metal. Six isomers are plausible (Figure

3, L = C_2H_4), which might be distinguished by ^{13}C n.m.r. ^{13}C-{^{1}H} N.m.r. spectra of a ^{13}CO enriched sample of (7) between −80 and 0 °C indicated a rigid carbonyl frame (Table 2). Nine resonances were identified with one pair accidentally isochronous at −60 °C. The two lowest field resonances, at δ 187.3 and 182.5, show coupling to a *cis* phosphorus and compare more closely with the axial groups of the phosphine-substituted metal in (14) (δ 183.5). (The equatorial group resonates at δ 170.4.[19]) This suggests that the ethylene is equatorial and (7) is either isomer A or B in Figure 3. Equatorial sites are favoured for alkenes on trinuclear clusters, as evidenced by crystallographic studies on $[Os_3H(CO)_9(SMe)(C_2H_4)]$,[20] $[N(PPh_3)_2][Os_3(CO)_{10}(CF_3HC{=}CHCF_3)Br]$, and $[Os_3(CO)_{10}(CF_3HC{=}CHCF_3)(PEt_3)]$ [21] and ^{13}C n.m.r. work on $[Os_3(CO)_{11}(C_2H_4)]$.[15] The observations of C–H couplings and the shift precedents give the assignments for the three resonances of the $Os(CO)_3H$ group: δ 174.7, *trans* to terminal H; δ 181.0, equatorial; δ 167.7, equatorial, *trans* to bridging H. The remaining four resonances are due to the two axial (δ 178.8 and 177.7) and equatorial (δ 173.2 and 172.7) carbonyls of the $Os(CO)_4$ group. Although this does not differentiate between isomeric structures A and B, the magnitude of the hydride *J*(HP) value (12.5 Hz) is consistent with the *cis* relationship in A and the phosphine retaining its equatorial site in $[Os_3H_2(CO)_9(PPh_3)]$. Unfortunately, (7) exhibits gross crystallographic disorder.[22]

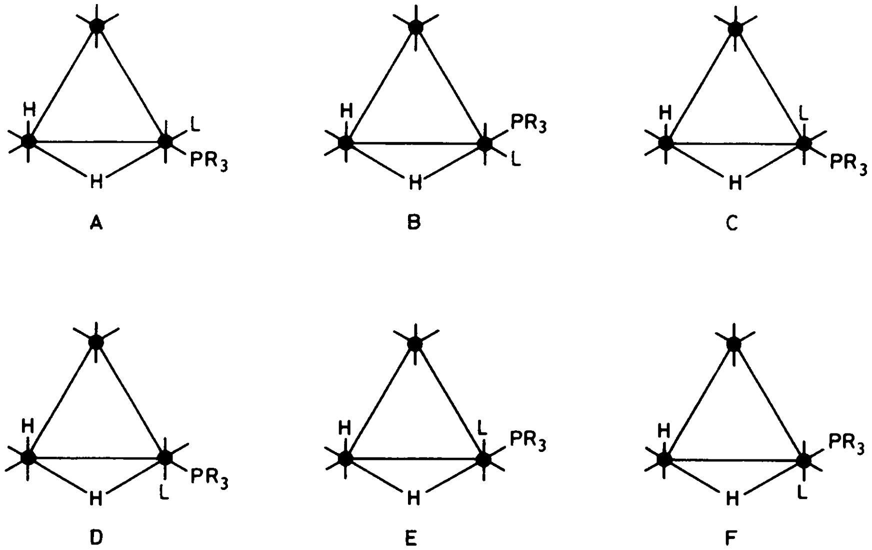

FIGURE 3 Possible structures of $[Os_3H_2(CO)_9(PR_3)L]$, L = MeNC and C_2H_4

In the static structure, all four ethylene protons are chemically distinct. Rotation about the metal olefin axis should generate two average environments of *trans* protons. However, at 31 °C, the ^{1}H n.m.r. signal of this group is a sharp doublet. Either a second intramolecular process, *e.g.* rotation about the C–C axis, causes a second averaging or the chemical shift difference between the end or, more likely, the sides of the ethylene ligand is negligible. Only some broadening of the ethylene resonance was apparent at −80 °C.

Reaction of (2) *with* MeNC.—Adducts of $[Os_3H_2(CO)_9L]$ (9; L = PPh_2Et) and (10; L = PPh_3) with MeNC were readily formed at room temperature. Their i.r. ν(CO) patterns were substantially different from those of the ethylene adducts, suggesting a different site for the added ligand. Indeed, the isonitrile in $[Os_3H_2(CO)_{10}(CNBu^t)]$ is in an axial site in the crystal.[23] The ^{1}H n.m.r. data obtained for (9) (Table 1) are similar to those reported for $[Os_3H_2(CO)_{10}(MeNC)]$,[24] with the additions of the phosphine resonances and the detection of only one isomer. Phosphorus coupling was again observed to the bridging hydride resonance (δ −20.01) and the protons of the added ligand. This evidence favours structure D in Figure 3 for (9). The hydride resonances are temperature dependent, broadening being apparent at −20 °C and the hydride site-exchange process causes coalescence near 31 °C. When (2) was refluxed with excess PPh_2Et for 5 h in n-hexane, a yellow product resulted which possessed a similar ν(CO) i.r. region to that of (9); this complex is suggested to be $[Os_3H_2(CO)_9(PPh_2Et)_2]$, with the same substituent sites as (9).

Pyrolysis of $[Os_3H(CO)_9(PPh_2Et)(CHCH_2)]$.—Refluxing (4) in n-heptane for 4 h affords $[Os_3H_2(CO)_8(PPh_2Et)(CCH_2)]$ (11) in high yield. Its ^{1}H n.m.r. spectrum (Table 1) contains hydride and vinylidene proton resonances slightly downfield from those of $[Os_3H_2(CO)_9(CCH_2)]$.[25] The phosphorus coupling constants suggest the structure shown in Figure 4, with the phosphine *cis* to both hydrides. The related complex $[Os_3H_2(CO)_8(o\text{-}PPh_2C_6H_4C_2H)]$ is constrained to have the phosphorus *trans* to one hydride and this gives a larger *J*(PH) value (25.4 Hz). This structure was confirmed by a ^{13}C n.m.r. study on a ^{13}CO enriched sample of (11). Six carbonyl resonances were observed (Table 2), with two sets of accidentally degenerate pairs at δ 175.1 and 169.1. Four resonances exhibit coupling to hydrogen, presumably due to the four carbonyl groups *trans* to the bridging hydrides.

Hydrogenation of $[Os_3H_2(CO)_8(PPh_2Et)(CCH_2)]$.—Complex (11) reacted with hydrogen in refluxing n-octane to afford $[Os_3H_3(CO)_8(PPh_2Et)(CCH_3)]$ (12) quantitatively after 12 h. The structure in Figure 4 is proposed on the basis of the ^{1}H and ^{13}C n.m.r. (Tables 1 and 2). Complex (12) appears to possess a plane of symmetry with the phosphine *cis* to the bridging hydrides. As in (11), coupling was observed to the protons of the hydrocarbon ligand and the phosphine site is *trans* to an osmium–carbon bond. Four ^{13}CO resonances were observed for an enriched sample,

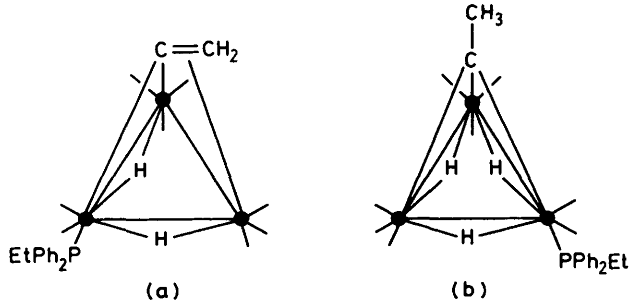

FIGURE 4 Proposed structures for (a) [Os$_3$H$_2$(CO)$_8$(PPh$_2$Et)(CCH$_2$)] and (b) [Os$_3$H$_3$(CO)$_8$(PPh$_2$Et)(CCH$_3$)]

with the lowest field signal (δ 176.0) assigned to the two carbonyl groups on the phosphine-substituted metal centre. The resonances at δ 169.0 and 168.7 exhibit coupling to protons and are presumably carbonyls in the Os(CO)$_3$ groups *trans* to the bridging hydrides. The remaining singlet at δ 168.4 is therefore assigned to the carbonyl groups *trans* to the Os-C(Me) bonds.

DISCUSSION

Phosphine substitution evidently does not drastically effect the chemistry of [Os$_3$H$_2$(CO)$_{10}$]. Thus [Os$_3$H$_2$(CO)$_9$(PPh$_2$R)] derivatives react similarly to (1) with acetylene,[9] ethylene,[16] and isonitriles.[25] Subsequent pyrolysis of [Os$_3$H(CO)$_9$(PPh$_2$Et)(CHCH$_2$)] and hydrogenation of [Os$_3$H$_2$(CO)$_8$(PPh$_2$Et)(CCH$_2$)] also follow the expected pathways,[9,26] although substitution does accelerate and retard these processes respectively. The major departure is the retarding of the reaction with ethylene to allow observation of the ethylene adducts (7) and (8). Acetylene insertion into a hydride bond was also slowed, particularly for [Os$_3$H$_2$(CO)$_9$(PPh$_3$)], but in this case no intermediate could be detected.

One feature of interest is that the added ligands in [Os$_3$H$_2$(CO)$_9$(PPh$_2$R)L] (L = MeNC and C$_2$H$_4$) were attached to the phosphine-substituted metal centres, which might not be intuitively expected. There is little evidence within the structure of [Os$_3$H$_2$(CO)$_9$(PPh$_3$)] in the crystal for any steric congestion or relief on phosphine substitution.[27] However, the Os–C bond lengths are consistent with the expected increase in electron density on the substituted metal atom, allowing greater metal to CO π* retrodative bonding. So any charge effects would favour the unsubstituted osmium atom at the end of the dihydride-bridged edge as the site of nucleophilic attack. But orbital control of nucleophilic addition, as expected for ' soft ' nucleophiles like MeNC and C$_2$H$_4$, will favour the site of attack being that with the largest-amplitude l.u.m.o. (lowest occupied molecular orbital).[28] A qualitative molecular orbital diagram for the metal–metal and metal–hydrogen bonding in [Os$_3$H$_2$(CO)$_{10}$] is given in Figure 5. The fragment orbitals of the C_{3v} M(CO)$_3$ and C_{2v} M(CO)$_4$ units are used [29] and the scheme, before inclusion of the hydrides, is analogous to the isolobal cyclopropene.[30] The probable l.u.m.o. is an Os–Os $\pi_{\perp}$* orbital along the bridged edge (a_2). The increased electron density at the phosphine-substituted metal should raise the energy of its fragment orbital and, accordingly, the l.u.m.o. will have a greater amplitude at that metal atom. Hence, under orbital control, addition to the substituted centre is indeed favoured.

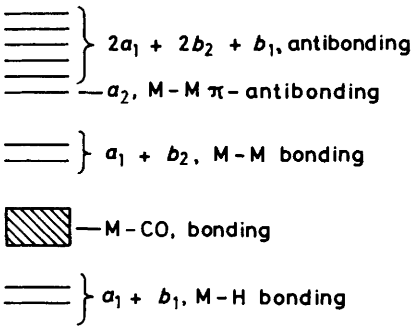

FIGURE 5 Qualitative molecular orbital diagram for the metal–metal and metal–hydrogen bonding in [Os$_3$H$_2$(CO)$_{10}$]

It is also evident that the substitution can markedly effect rates of fluxional processes. The barrier to vinyl group flipping, observed for [Os$_3$H(CO)$_{10}$(CHCH$_2$)],[10] is evidently increased in (4), (5), and (6). However, with the phosphine in site 9, Figure 2, neither of the two possible sites for the minor isomer, 7 or 10, allows the vinyl flip to be degenerate or to interconvert the two isomers. Ethylene substitution into [Os$_3$H$_2$(CO)$_{10}$-(PPh$_3$)] [8,31] increases the barrier to hydride exchange. Other derivatives, including [Os$_3$H$_2$(CO)$_9$(PPh$_2$Et)(MeNC)], do not exhibit this marked effect, which may be due to the *trans* relationship between the bridging hydride and the ethylene ligand. All other known derivatives have a carbonyl in that site, so this particular substitution may stabilise the ground state geometry.

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