# Addition of Dimethylphenylphosphine to μ- and $\mu_3$-Alkynyl and $\mu_3$-Allenyl Ligands in Triosmium Clusters: *X*-Ray Crystal Structures of Three Zwitterionic Adducts

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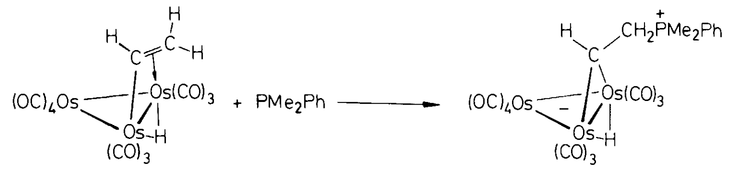
The $\mu_3$-alkynyl complexes [$Os_3H(CO)_9(C{\equiv}CR)$] (R = H, Me, Ph, or $CMe_2OH$), the μ-alkynyl complex [$Os_3H(CO)_{10}(C{\equiv}CPh)$], and the $\mu_3$-allenyl complex [$Os_3H(CO)_9(MeC{=}C{=}CH_2)$] all form 1:1 adducts with $PMe_2Ph$. The tertiary phosphine molecules add at carbon atoms to give zwitterionic complexes containing phosphonium centres and negative charges formally on the metal atoms. To confirm structures based on $^1H$ n.m.r. and i.r. data, single-crystal *X*-ray structures of three rather different adducts have been determined. Crystals of [$Os_3H(CO)_9(HC{=}CPMe_2Ph)$] are monoclinic, space group $P2_1/c$, with $a$ = 14.579(6), $b$ = 8.301(3), $c$ = 19.523(9) Å, β = 93.45(2)°, $Z$ = 4, and final $R$ = 0.053. Crystals of [$Os_3H(CO)_9(MeC{=}CCH_2PMe_2Ph)$] are monoclinic, space group $C_c$, with $a$ = 15.990(5), $b$ = 11.974(4), $c$ = 13.480(4) Å, β = 98.11(2)°, $Z$ = 4, and final $R$ = 0.037. Crystals of [$Os_3H(CO)_{10}(C{=}CPhPMe_2Ph)$] are triclinic, space group $P\bar{1}$, with $a$ = 14.075(3), $b$ = 12.210(3), $c$ = 8.724(2) Å, α = 100.86(3), β = 95.41(2), γ = 101.51(3)°, $Z$ = 2, and final $R$ = 0.040. The two nonacarbonyl complexes are structurally very similar, both containing $\mu_3$-alkyne ligands with phosphonium centres positioned β and γ respectively to the metal atoms. The different relative positions of the phosphonium centres have no detectable effect on structural parameters but lead to different carbonyl-stretching frequencies. The fluxional behaviour of the $\mu_3$-alkyne complexes is described. Whereas $PMe_2Ph$ attack is at the 1-position of the $\mu_3$-alkynyl ligands, it is at the 2-position of the μ-alkynyl ligand to give [$Os_3H(CO)_{10}(C{=}CPhPMe_2Ph)$] which is structurally characterised as containing a μ-alkylidene ligand with a phosphonium substituent.

TERTIARY phosphines add readily to unsaturated hydrocarbon ligands in cationic complexes such as the cyclohexadienyl complex [$Fe(CO)_3(C_6H_7)$][$BF_4$],[1] the alkene complex [$Fe(C_5H_5)(CO)_2(C_2H_4)$][$BF_4$],[2] and the arene complex [$Fe(C_6H_6)_2$][$PF_6$]$_2$ [3] to give adducts in which the positive charge becomes localised at a phosphonium substituent of the hydrocarbon ligand. The electron-withdrawing properties of the metal atoms in the cation render ligand carbon atoms electrophilic, reversing the normal reactivity of the free organic ligand. Such behaviour is rare in neutral complexes where metal-to-ligand π donation allows the carbon atoms to retain their nucleophilic character. For triosmium and other related clusters, electrophilic attack, such as protonation, normally gives a metal-bonded product,[4] although it is quite likely that attack at carbonyl oxygen precedes a transfer of the electrophile to the metal. Exceptionally, products of addition at carbonyl oxygen atoms have been isolated.[5,6] On the other hand, nucleophilic attack at neutral clusters may occur at a carbon atom of a carbonyl ligand [7,8] or at a hydrocarbon ligand.[9,10] Addition of $PMe_2Ph$ to [$Os_3H(CO)_{10}(\mu\text{-}CH{=}CH_2)$] gives the cluster [$Os_3H(CO)_{10}(\mu\text{-}CHCH_2PMe_2Ph)$], the structure of which in solution [9,10] and in the crystal [10] is consistent with a zwitterionic formulation with a substituted ethylidene ligand, equation (1). We noted that various other types of hydrocarbon ligand in triosmium clusters also undergo $PMe_2Ph$ attack as judged by the shift of ν(CO) absorptions to lower frequencies on forming zwitterionic adducts.[9] We now describe in detail $PMe_2Ph$ adducts of μ- and $\mu_3$-alkynyl and $\mu_3$-allenyl clusters and the *X*-ray crystal structures of three of these.



(1)

## RESULTS AND DISCUSSION

*Synthesis and Simple Characterisation of* $PMe_2Ph$ *Adducts.*—The clusters [$Os_3H(CO)_9(RC{=}CPMe_2Ph)$], (1) (R = H, Me, Ph, or $CMe_2OH$), are readily and rapidly formed on addition of $PMe_2Ph$ to the $\mu_3$-alkynyl complexes [$Os_3H(CO)_9(C{\equiv}CR)$], (4), in chloroform, toluene, or hexane solution at room temperature. The clusters [$Os_3H(CO)_9(MeC{=}CCH_2PMe_2Ph)$], (2), and [$Os_3H(CO)_{10}(C{=}CRPMe_2Ph)$], (3) (R = H or Ph), were prepared similarly from compounds (5)—(7) as shown in the Scheme. Spectroscopic data were used for characterisation of (1)—(3) (Table 1). Although the additions were carried out under nitrogen, this was hardly necessary since the clusters (1)—(7) are all thermally and air-stable and the adducts form more rapidly than $PMe_2Ph$ is oxidised in air.

Although compounds (3) were described earlier,[9] we did not know from n.m.r. spectra whether they contained the $RC{=}CPMe_2Ph$ or $C{=}CRPMe_2Ph$ arrangements of atoms,

TABLE 1

Spectroscopic data for compounds (1)—(3)

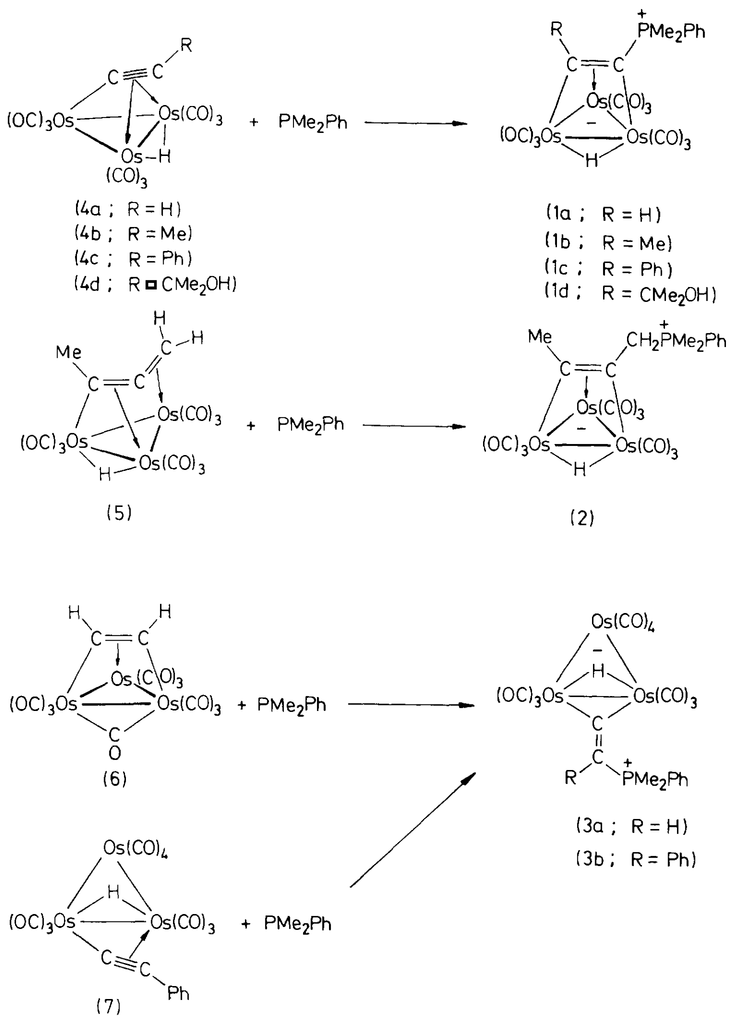
| Compound | $\tilde{\nu}$(CO)/cm$^{-1}$ | $^1$H N.m.r. | | |
|---|---|---|---|---|
| | | δ | | $J$/Hz |
| (1a) $[Os_3H^y(CO)_9(H^wC{=}CPMe^x{}_2Ph)]$ [a] | 2 081m, 2 052s, 2 023vs, 2 002s, 1 985m, 1 973s, 1 965 (sh), 1 941w | 9.28 (dd) | CH$^w$ | $J(H^wP)$ = 17.8 |
| | | 7.7 (m) | Ph | $J(H^wH^y)$ = 1.7 |
| | | 2.91 (d) | Me$^x$ | $J(Me^xP)$ = 12.5 |
| | | 2.76 (d) | Me$^x$ | $J(H^yP)$ = 1.7 |
| | | −19.49 (dd) | H$^y$ | |
| (1b) $[Os_3H^y(CO)_9(Me^wC{=}CPMe^x{}_2Ph)]$ [b] | 2 078m, 2 049s, 2 022vs, 2 000s, 1 983m, 1 970s, 1 962 (sh), 1 939w | 7.7 (m) | Ph | $J(Me^xP)$ = 12.9 |
| | | 2.05 (d) | Me$^x$ | $J(H^yP)$ = 3.8 |
| | | 1.92 (d) | Me$^x$ | |
| | | 2.48 (s) | Me$^w$ | |
| | | −18.84 (d) | H$^y$ | |
| (1c) $[Os_3H^y(CO)_9(PhC{=}CPMe^x{}_2Ph)]$ [c] | 2 080s, 2 053vs, 2 021vs, 2 003vs, 1 987m, 1 973s, 1 963 (sh), 1 939w | 7.37 (m) | Ph | $J(H^yP)$ = 2.6 |
| | | 6.95 (m) | Ph | $J(Me^xP)$ = 12.5 |
| | | 1.77 (d) | Me$^x$ | |
| | | 1.70 (d) | Me$^x$ | |
| | | −19.24 (d) | H$^y$ | |
| (1d) $[Os_3H^z(CO)_9(H^wOMe^x{}_2CC{=}CPMe^y{}_2Ph)]$ [d] | 2 077s, 2 047s, 2 019vs, 1 997s, 1 981m, 1 969s, 1 960 (sh), 1 936w | 7.7 (m) | Ph | $J(Me^yP)$ = 11.0, 11.7 |
| | | 1.82 (d) | Me$^y$ | $J(H^zP)$ = 3.4 |
| | | 2.20 (d) | Me$^y$ | |
| | | 0.99 (s) | Me$^x$ | |
| | | 1.35 (s) | Me$^x$ | |
| | | 1.24 (s) | OH | |
| | | −18.44 (s) | H$^z$ | |
| (2) $[Os_3H^z(CO)_9(Me^vC{=}CCH_2{}^{w,x}PMe^y{}_2Ph)]$ [e] | 2 066m, 2 036s, 2 010s, 1 982s, 1 967m, 1 942m (br), 1 922 (sh) | 7.7 (m) | Ph | $J(H^wH^x)$ = 14.5 |
| | | 3.96 (m) | H$^w$ | $J(H^wP)$ = 11.4 |
| | | 3.33 (m) | H$^x$ | $J(H^xP)$ = *ca.* 14 |
| | | 2.44 (s) | Me$^v$ | $J(Me^yP)$ = 13.5 |
| | | 2.22 (d) | Me$^y$ | |
| | | 2.11 (d) | Me$^y$ | |
| | | −19.89 (s) | H$^z$ | |
| (3a) $[Os_3H^z(CO)_{10}(C{=}CH^xPMe^y{}_2Ph)]$ [f] | 2 090m, 2 044vs, 2 037s, 2 007vs, 1 992s, 1 983m, 1 975m, 1 966m, 1 947w | 7.6 (m) | Ph | $J(H^xH^z)$ = 1.3 |
| | | 6.60 (dd) | H$^x$ | $J(H^xP)$ = 40.7 |
| | | 2.08 (d) | Me$^y$ | $J(Me^yP)$ = 13.5 |
| | | 1.95 (d) | Me$^y$ | $J(H^zP)$ = 2.5 |
| | | −16.04 (dd) | H$^z$ | |
| (3b) $[Os_3H^y(CO)_{10}(C{=}CPhPMe^x{}_2Ph)]$ [f] | 2 089m, 2 046vs, 2 037s, 2 008vs, 1 990 (sh), 1 986s, 1 979m, 1 973m, 1 967s, 1 949m | 7.8 (m) | Ph | $J(Me^xP)$ = 12.3, 12.5 |
| | | 7.3 (m) | Ph | $J(H^yP)$ = 3.2 |
| | | 2.49 (d) | Me$^x$ | |
| | | 1.76 (d) | Me$^x$ | |
| | | −16.35 (d) | H$^y$ | |

[a] I.r. in $C_6H_{12}$; n.m.r. in $CD_2Cl_2$ at −18 °C. [b] I.r. in n-hexane; n.m.r. in $CD_2Cl_2$ at −21 °C. [c] I.r. in n-hexane; n.m.r. in $CD_2Cl_2$ at 0 °C. [d] I.r. in n-hexane; n.m.r. in $CD_2Cl_2$ at 32 °C. [e] I.r. in $CHCl_3$; n.m.r. in $CD_2Cl_2$ at −18 °C. [f] I.r. in $C_6H_{12}$; n.m.r. in $CDCl_3$ at 27 °C.

TABLE 2

Summary of crystal data

| Compound | (1a) | (2) | (3b) |
|---|---|---|---|
| Formula | $C_{19}H_{13}O_9Os_3P$ | $C_{21}H_{17}O_9Os_3P$ | $C_{26}H_{17}O_{10}Os_3P$ |
| $M$ | 986.8 | 1 014.9 | 1 090.9 |
| Crystal system | Monoclinic | Monoclinic | Triclinic |
| $a$/Å | 14.579(6) | 15.990(5) | 14.075(3) |
| $b$/Å | 8.301(3) | 11.974(4) | 12.210(3) |
| $c$/Å | 19.523(9) | 13.480(4) | 8.724(2) |
| α/° | (90) | (90) | 100.86(3) |
| β/° | 93.45(2) | 98.11(2) | 95.41(2) |
| γ/° | (90) | (90) | 101.51(3) |
| Space group | $P2_1/c$ | $Cc$ | $P\bar{1}$ |
| $U$/Å$^3$ | 2 358.4 | 2 555.1 | 1 429.2 |
| $Z$ | 4 | 4 | 2 |
| $D_c$/g cm$^{-3}$ | 2.778 | 2.637 | 2.534 |
| $F$(000) | 1 744 | 1 832 | 932 |
| μ(Mo-$K_\alpha$)/cm$^{-1}$ | 155.93 | 143.95 | 128.71 |
| Crystal size/mm | 0.22 × 0.20 × 0.12 | 0.18 × 0.10 × 0.10 | 0.12 × 0.25 × 0.10 |
| Unique data, $F \geqslant 6\sigma(F)$ | 2 828 | 2 344 | 4 630 |
| No. of variables | 296 | 306 | 362 |
| Final $R$ | 0.053 | 0.037 | 0.040 |
| Final $R'$ [$w = 1/\sigma^2(F)$] | 0.052 | 0.038 | 0.041 |



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that is whether the $PMe_2Ph$ molecule had added at the α- or β-carbon atoms. Complexes (3a) and (3b) are isostructural, although formed from non-isostructural starting compounds, (6) and (7). We have now confirmed from a single-crystal *X*-ray study of compound (3b) that $PMe_2Ph$ attack is at the β-carbon atom.

Attack of $PMe_2Ph$ on compounds (4) gave the series of compounds (1) which are isostructural on the basis of their extremely similar ν(CO) spectra, around 2 000 $cm^{-1}$. Furthermore, it seemed from their $^1H$ n.m.r. spectra that attack had occurred at the α-carbon atoms in all cases. In particular there is no coupling observed between the $CH_3$ protons and the $^{31}P$ nucleus in (1b) as would be expected in the alternative arrangement $\mu_3$-C=CMePMe$_2$Ph. Compounds (1) and (2) are closely related except that the phosphonium centre is β to the metal in (1) but γ to the metal in (2). On forming the $PMe_2Ph$ adducts there is a lowering of the ν(CO) frequencies consistent with the zwitterionic formulation with negative charge accumulating at the metal atoms. In forming compounds (1) the ν(CO) frequencies are lowered by around 24—35 $cm^{-1}$ relative to the neutral parent compounds. However, in forming compound (2) the lowering is rather greater (37—50 $cm^{-1}$). Typically, deprotonation of a hydrido-triosmium cluster to give a full negative charge lowers the ν(CO) frequencies by a little more than 50 $cm^{-1}$. Thus in (1) there is roughly 0.5 of an electronic charge at the metal atoms but around 0.8 in (2). One view is that the extra $CH_2$ group in (2) insulates the charged centres of the zwitterion which makes the alkyne ligand a poorer π acceptor and allows the greater accumulation of negative charge at the metal atoms. The order of atoms within the organic ligands of (1) and (2) was clear from $^1H$ n.m.r. data (Table 1) but details of the mode of attachment at the metal cluster and the possible differences between (1) and (2) in this respect justified single-crystal *X*-ray studies. Furthermore, interpretation of the observed fluxionality of complexes (1) and (2) (see later) would be assisted by detailed knowledge of their structures. Compounds (1a) and (2) gave good quality crystals and were chosen for study.

TABLE 3

Fractional atomic co-ordinates for $[Os_3H(CO)_9$-$(HC=CPMe_2Ph)]$, (1a)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Os(1) | 0.184 92(5) | 0.088 17(10) | 0.108 73(4) |
| Os(2) | 0.321 01(5) | 0.316 89(9) | 0.132 81(4) |
| Os(3) | 0.383 75(5) | 0.003 64(10) | 0.111 64(4) |
| P | 0.210 6(3) | 0.322 8(6) | −0.035 1(3) |
| C(1) | 0.256 6(11) | 0.219 5(22) | 0.035 2(8) |
| C(2) | 0.350 3(12) | 0.175 8(23) | 0.038 0(8) |
| C(111) | 0.167 3(12) | 0.189 2(24) | −0.099 2(10) |
| C(112) | 0.097 0(15) | 0.230 8(33) | −0.148 3(12) |
| C(113) | 0.070 3(18) | 0.122 7(35) | −0.197 9(12) |
| C(114) | 0.112 4(19) | −0.024 1(36) | −0.202 3(15) |
| C(115) | 0.181 8(20) | −0.062 1(32) | −0.158 2(16) |
| C(116) | 0.211 3(14) | 0.041 6(28) | −0.103 6(13) |
| C(117) | 0.113 1(15) | 0.455 9(25) | −0.016 7(11) |
| C(118) | 0.289 9(15) | 0.461 6(36) | −0.072 8(13) |
| C(11) | 0.088 0(14) | 0.239 2(27) | 0.119 4(8) |
| O(11) | 0.028 9(10) | 0.326 2(20) | 0.129 4(9) |
| C(12) | 0.109 2(12) | −0.050 4(24) | 0.050 8(11) |
| O(12) | 0.064 8(11) | −0.143 8(19) | 0.021 2(9) |
| C(13) | 0.172 4(13) | −0.006 9(26) | 0.197 7(13) |
| O(13) | 0.163 0(12) | −0.053 6(22) | 0.250 4(9) |
| C(21) | 0.246 2(17) | 0.506 9(34) | 0.137 4(11) |
| O(21) | 0.200 1(13) | 0.616 1(19) | 0.147 6(11) |
| C(22) | 0.432 1(14) | 0.434 8(24) | 0.125 4(10) |
| O(22) | 0.501 0(12) | 0.503 2(21) | 0.126 4(10) |
| C(23) | 0.338 9(13) | 0.277 2(26) | 0.230 2(10) |
| O(23) | 0.346 7(13) | 0.247 5(26) | 0.285 6(8) |
| C(31) | 0.408 6(13) | −0.168 2(27) | 0.055 0(12) |
| O(31) | 0.426 0(14) | −0.270 4(22) | 0.014 9(11) |
| C(32) | 0.509 4(16) | 0.069 4(27) | 0.122 4(12) |
| O(32) | 0.584 1(11) | 0.106 3(25) | 0.128 4(11) |
| C(33) | 0.389 3(18) | −0.108 8(32) | 0.195 7(15) |
| O(33) | 0.385 9(17) | −0.176 3(28) | 0.249 7(12) |

X-*Ray Crystal Structures of Compounds* (1a), (2), *and* (3b).—Crystal data for these three compounds are given in Table 2 and the fractional atomic co-ordinates for (1a), (2), and (3b) in Tables 3, 4, and 5 respectively. Since compounds (1a) and (2) are closely related in structure, the atoms have been labelled correspondingly and selected interatomic distances (Table 6) and intramolecular angles (Table 7) tabulated together for easy comparison. The appropriate interatomic distances and angles for compound (3) are presented in Tables 8 and 9. The molecular structures of (1a) and (2) are shown in Figures 1 and 2 respectively.

The similar structures of (1a) and (2) may be represented simply as shown in the Scheme. Each molecule has an approximate isosceles triangle of metal atoms with the Os(1)–Os(3) bonds longer by around 0.2 Å than the other two Os–Os bonds in each compound. The nine carbonyl groups are distributed in two equatorial and one axial positions at each metal atom. The $\mu_3$ ligands are attached with $\sigma$-Os–C bonds, Os(1)–C(1) and Os(3)–C(2), with lengths in the range 2.064—2.132 Å for the two compounds with the third point of attachment of these ligands, a $\eta^2$-linkage to Os(2), with rather longer Os–C distances in the range 2.226—2.293 Å. For this description of (1a), a hydrogen atom, corresponding to the methyl group, C(3), in (2) must be bonded to C(2). This hydrogen atom was not located in the *X*-ray study, but a doublet of doublets in the $^1$H n.m.r. spectrum at $\delta$ 9.28 (coupled to the $^{31}$P and hydride nuclei) is consistent with the low-field signal expected for a $\mu_3$-terminal alkyne hydrogen atom.[11]

TABLE 4

Fractional atomic co-ordinates for $[Os_3H(CO)_9(MeC{=}CCH_2PMe_2Ph)]$, (2)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Os(1) | 0 | 0.130 41(17) | 0 |
| Os(2) | −0.105 67(7) | 0.139 13(7) | −0.180 42(7) |
| Os(3) | −0.183 52(7) | 0.073 46(6) | −0.020 72(9) |
| P | −0.032 4(4) | 0.480 3(5) | 0.020 5(5) |
| C(1) | −0.077 5(13) | 0.266 8(17) | −0.058 1(14) |
| C(2) | −0.165 0(13) | 0.241 3(16) | −0.064 5(14) |
| C(3) | −0.237 3(15) | 0.322 6(19) | −0.088 7(17) |
| C(111) | −0.114 8(14) | 0.473 1(16) | 0.097 8(16) |
| C(112) | −0.177 4(15) | 0.554 5(15) | 0.090 6(22) |
| C(113) | −0.243 2(17) | 0.542 0(26) | 0.144 3(22) |
| C(114) | −0.247 7(19) | 0.450 5(22) | 0.205 3(25) |
| C(115) | −0.187 9(19) | 0.370 4(25) | 0.216 1(18) |
| C(116) | −0.122 4(19) | 0.382 8(20) | 0.154 3(23) |
| C(117) | 0.068 5(16) | 0.454 0(21) | 0.094 4(21) |
| C(118) | −0.028 0(17) | 0.615 8(18) | −0.033 6(25) |
| C(119) | −0.048 2(16) | 0.382 8(14) | −0.079 9(19) |
| C(11) | 0.094 5(17) | 0.186 6(27) | −0.056 0(16) |
| O(11) | 0.152 1(12) | 0.210 8(20) | −0.090 4(16) |
| C(12) | 0.045 8(14) | 0.163 8(19) | 0.133 8(17) |
| O(12) | 0.076 9(11) | 0.186 0(18) | 0.214 6(13) |
| C(13) | 0.040 5(17) | −0.024 8(21) | 0.001 8(22) |
| O(13) | 0.057 7(18) | −0.114 4(16) | −0.005 7(22) |
| C(21) | −0.029 8(14) | 0.206 2(26) | −0.256 1(17) |
| O(21) | 0.016 6(15) | 0.249 6(25) | −0.306 3(14) |
| C(22) | −0.201 7(19) | 0.201 7(19) | −0.275 9(15) |
| O(22) | −0.263 1(11) | 0.177 5(16) | −0.333 9(13) |
| C(23) | −0.092 5(16) | −0.014 0(21) | −0.210 4(17) |
| O(23) | −0.082 7(14) | −0.110 4(16) | −0.216 2(7) |
| C(31) | −0.234 8(13) | 0.108 2(18) | 0.082 3(16) |
| O(31) | −0.260 4(16) | 0.115 6(14) | 0.157 5(25) |
| C(32) | −0.288 2(17) | 0.054 6(24) | −0.105 7(17) |
| O(32) | −0.352 5(12) | 0.044 4(18) | −0.154 0(16) |
| C(33) | −0.171 3(13) | −0.083 9(16) | −0.017 0(20) |
| O(33) | −0.151 1(14) | −0.176 5(17) | −0.015 0(16) |

The metal hydride atom in either structure was not located. The CO groups around the Os(1)–Os(3) bond in (1a) and (2) are clearly splayed out relative to those around the other metal–metal bonds consistent with a hydride ligand bridging the Os(1) and Os(3) atoms in both structures. For instance, in (1a) the Os–Os–C(equatorial) angles for CO groups adjacent to each Os–Os

TABLE 5

Fractional atomic co-ordinates for $[Os_3H(CO)_{10}(C{=}CPhPMe_2Ph)]$, (3b)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Os(1) | 0.159 67(3) | 0.259 02(3) | 0.176 64(5) |
| Os(2) | 0.306 43(3) | 0.200 24(4) | −0.011 28(5) |
| Os(3) | 0.169 20(3) | 0.325 78(3) | −0.112 73(5) |
| P | 0.270 7(2) | 0.593 3(2) | 0.390 0(3) |
| C(1) | 0.207 3(6) | 0.419 0(8) | 0.121 1(12) |
| C(2) | 0.242 8(7) | 0.532 3(9) | 0.181 6(11) |
| C(3) | 0.262 8(7) | 0.620 3(8) | 0.083 2(12) |
| C(4) | 0.356 6(8) | 0.657 9(10) | 0.049 0(15) |
| C(5) | 0.372 9(9) | 0.740 1(11) | −0.044 4(17) |
| C(6) | 0.299 7(10) | 0.790 3(11) | −0.091 3(16) |
| C(7) | 0.206 6(10) | 0.754 4(11) | −0.057 4(17) |
| C(8) | 0.188 7(9) | 0.668 6(10) | 0.031 2(16) |
| C(111) | 0.269 6(8) | 0.743 0(9) | 0.425 8(12) |
| C(112) | 0.177 9(8) | 0.774 8(9) | 0.424 8(15) |
| C(113) | 0.178 5(10) | 0.889 4(11) | 0.452 7(16) |
| C(114) | 0.261 6(11) | 0.970 4(11) | 0.473 6(18) |
| C(115) | 0.350 3(11) | 0.941 4(11) | 0.475 2(24) |
| C(116) | 0.354 6(9) | 0.826 6(10) | 0.449 5(17) |
| C(117) | 0.185 4(8) | 0.531 8(9) | 0.511 6(13) |
| C(118) | 0.393 1(8) | 0.582 8(11) | 0.469 6(14) |
| C(11) | 0.057 9(9) | 0.301 4(10) | 0.285 8(14) |
| O(11) | −0.004 8(6) | 0.322 7(9) | 0.353 1(12) |
| C(12) | 0.252 2(9) | 0.272 5(9) | 0.353 6(14) |
| O(12) | 0.310 8(7) | 0.278 7(8) | 0.456 7(10) |
| C(13) | 0.104 6(8) | 0.095 1(9) | 0.163 5(14) |
| O(13) | 0.073 2(7) | 0.002 2(7) | 0.158 6(13) |
| C(21) | 0.205 8(9) | 0.066 0(11) | −0.117 7(15) |
| O(21) | 0.147 9(7) | −0.012 3(7) | −0.173 9(12) |
| C(22) | 0.377 9(8) | 0.193 6(11) | −0.186 7(14) |
| O(22) | 0.426 2(6) | 0.196 6(9) | −0.283 7(10) |
| C(23) | 0.371 1(9) | 0.118 7(11) | 0.114 2(17) |
| O(23) | 0.415 0(8) | 0.075 0(10) | 0.190 3(15) |
| C(24) | 0.389 8(8) | 0.349 3(12) | 0.096 6(18) |
| O(24) | 0.440 5(6) | 0.431 7(8) | 0.158 3(13) |
| C(31) | 0.277 3(7) | 0.409 0(9) | −0.191 1(13) |
| O(31) | 0.341 5(6) | 0.454 5(8) | −0.238 8(10) |
| C(32) | 0.074 7(8) | 0.409 6(9) | −0.158 9(14) |
| O(32) | 0.019 1(6) | 0.458 9(7) | −0.202 4(12) |
| C(33) | 0.121 9(8) | 0.206 9(9) | −0.306 0(13) |
| O(33) | 0.092 8(7) | 0.144 0(8) | −0.419 0(10) |

TABLE 6

Selected interatomic distances (Å) for (1a) and (2)

| | (1a) | (2) |
|---|---|---|
| (*a*) Metal–metal bonds | | |
| Os(1)–Os(2) | 2.766(1) | 2.761(1) |
| Os(1)–Os(3) | 2.980(1) | 2.987(1) |
| Os(2)–Os(3) | 2.795(1) | 2.749(1) |
| (*b*) Metal–carbon distances | | |
| Os(1)–C(1) | 2.127(18) | 2.132(19) |
| Os(2)–C(1) | 2.226(15) | 2.247(20) |
| Os(2)–C(2) | 2.252(16) | 2.293(19) |
| Os(3)–C(2) | 2.064(17) | 2.127(19) |
| Os(1) · · · C(2) | 2.941(19) | 2.973(20) |
| Os(3) · · · C(1) | 2.922(17) | 2.954(20) |
| (*c*) Os–C (carbonyl) | | |
| Range | 1.85—1.93(2) | 1.76—1.97(2) |
| Mean | 1.91 | 1.88 |
| (*d*) Ligand distances | | |
| C(1)–C(2) | 1.411(23) | 1.423(28) |
| C(2)–C(3) | | 1.511(29) |
| C(1)–C(119) | | 1.508(25) |
| P–C(1) | 1.763(17) | |
| P–C(111) | 1.814(21) | 1.793(23) |
| P–C(117) | 1.767(23) | 1.801(26) |
| P–C(118) | 1.804(20) | 1.784(25) |
| P–C(119) | | 1.779(22) |
| (*e*) C–O (carbonyl) | | |
| Range | 1.11—1.20(3) | 1.11—1.19(3) |
| Mean | 1.15 | 1.15 |

TABLE 7

Selected intramolecular angles (°) for (1a) and (2)

| | (1a) | (2) |
|---|---|---|
| (*a*) Angles at osmium | | |
| Os(2)–Os(1)–Os(3) | 58.1(1) | 57.0(1) |
| C(1)–Os(1)–Os(2) | 52.1(4) | 52.8(5) |
| C(1)–Os(1)–Os(3) | 67.4(4) | 68.1(6) |
| C(1)–Os(1)–C(11) | 97.7(7) | 92.1(11) |
| C(1)–Os(1)–C(12) | 101.4(8) | 108.4(9) |
| C(1)–Os(1)–C(13) | 153.6(8) | 154.4(11) |
| C(11)–Os(1)–Os(2) | 93.4(6) | 93.4(7) |
| C(11)–Os(1)–Os(3) | 151.4(6) | 150.2(7) |
| C(11)–Os(1)–C(12) | 93.1(8) | 94.6(9) |
| C(11)–Os(1)–C(13) | 93.4(8) | 93.5(12) |
| C(12)–Os(1)–Os(2) | 153.4(6) | 159.8(7) |
| C(12)–Os(1)–Os(3) | 113.3(6) | 112.4(7) |
| C(12)–Os(1)–C(13) | 101.8(9) | 96.0(12) |
| C(13)–Os(1)–Os(2) | 103.5(7) | 101.9(9) |
| C(13)–Os(1)–Os(3) | 91.8(6) | 95.9(8) |
| Os(1)–Os(2)–Os(3) | 64.8(1) | 65.7(1) |
| C(1)–Os(2)–Os(1) | 49.0(5) | 49.1(5) |
| C(1)–Os(2)–Os(3) | 70.1(4) | 71.7(5) |
| C(2)–Os(2)–Os(1) | 70.9(5) | 71.4(5) |
| C(2)–Os(2)–Os(3) | 46.8(4) | 48.9(5) |
| C(1)–Os(2)–C(2) | 36.7(6) | 36.5(7) |
| C(1)–Os(2)–C(21) | 97.3(8) | 91.7(10) |
| C(1)–Os(2)–C(22) | 116.0(8) | 117.1(8) |
| C(1)–Os(2)–C(23) | 143.7(8) | 142.9(8) |
| C(2)–Os(2)–C(21) | 126.9(8) | 120.3(11) |
| C(2)–Os(2)–C(22) | 90.1(8) | 90.4(8) |
| C(2)–Os(2)–C(23) | 134.3(7) | 136.9(9) |
| C(21)–Os(2)–Os(1) | 99.7(6) | 97.7(7) |
| C(21)–Os(2)–Os(3) | 164.0(6) | 161.6(8) |
| C(21)–Os(2)–C(22) | 94.0(9) | 95.1(11) |
| C(21)–Os(2)–C(23) | 97.9(9) | 101.5(12) |
| C(22)–Os(2)–Os(1) | 160.8(7) | 161.3(7) |
| C(22)–Os(2)–Os(3) | 100.3(7) | 99.5(8) |
| C(22)–Os(2)–C(23) | 95.5(9) | 96.3(10) |
| C(23)–Os(2)–Os(1) | 95.9(7) | 94.5(7) |
| C(23)–Os(2)–Os(3) | 87.8(6) | 88.1(7) |
| Os(1)–Os(3)–Os(2) | 57.1(1) | 57.4(1) |
| C(2)–Os(3)–Os(1) | 68.6(5) | 68.7(6) |
| C(2)–Os(3)–Os(2) | 52.6(5) | 54.3(5) |
| C(2)–Os(3)–C(31) | 99.4(8) | 95.4(7) |
| C(2)–Os(3)–C(32) | 93.7(9) | 95.2(10) |
| C(2)–Os(3)–C(33) | 160.8(8) | 158.4(8) |
| C(31)–Os(3)–Os(1) | 113.2(6) | 115.7(10) |
| C(31)–Os(3)–Os(2) | 151.8(7) | 149.7(11) |
| C(31)–Os(3)–C(32) | 93.7(9) | 92.0(11) |
| C(31)–Os(3)–C(33) | 98.0(10) | 105.8(12) |
| C(32)–Os(3)–Os(1) | 149.3(7) | 148.4(8) |
| C(32)–Os(3)–Os(2) | 92.2(7) | 91.1(8) |
| C(32)–Os(3)–C(33) | 93.2(11) | 88.6(11) |
| C(33)–Os(3)–Os(1) | 97.1(8) | 97.4(6) |
| C(33)–Os(3)–Os(2) | 109.2(7) | 104.4(7) |
| (*b*) Os–C–O | | |
| Range | 172—179(2) | 168—178(2) |
| Mean | 175 | 174 |
| (*c*) Angles within the organophosphine ligand | | |
| Os(1)–C(1)–Os(2) | 79(1) | 78(1) |
| C(2)–C(1)–Os(1) | 111(1) | 112(1) |
| C(2)–C(1)–Os(2) | 73(1) | 73(1) |
| C(119)–C(1)–Os(1) | | 127(1) |
| C(119)–C(1)–Os(2) | | 121(1) |
| C(119)–C(1)–C(2) | | 121(1) |
| P–C(1)–Os(1) | 128(1) | |
| P–C(1)–Os(2) | 126(1) | |
| P–C(1)–C(2) | 119(1) | |
| Os(2)–C(2)–Os(3) | 81(1) | 77(1) |
| C(1)–C(2)–Os(2) | 71(1) | 70(1) |
| C(1)–C(2)–Os(3) | 113(1) | 111(1) |
| C(3)–C(2)–Os(2) | | 125(1) |
| C(3)–C(2)–Os(3) | | 123(1) |
| C(3)–C(2)–C(1) | | 126(2) |
| C(111)–P–C(117) | 109(1) | 110(1) |
| C(111)–P–C(118) | 105(1) | 111(1) |
| C(117)–P–C(118) | 107(1) | 108(1) |
| C(119)–P–C(111) | | 112(1) |
| C(119)–P–C(117) | | 109(1) |
| C(119)–P–C(118) | | 107(1) |
| C(1)–P–C(111) | 107(1) | |
| C(1)–P–C(117) | 115(1) | |
| C(1)–P–C(118) | 115(1) | |
| C(1)–C(119)–P | | 118(2) |
| P–C(111)–C(112) | 121(2) | 120(2) |
| P–C(111)–C(116) | 119(2) | 120(2) |

TABLE 8

Selected interatomic distances (Å) for (3b)

| | | | |
|---|---|---|---|
| (*a*) Metal–metal bonds | | | |
| Os(1)–Os(2) | 2.873(1) | Os(1)–Os(3) | 2.802(1) |
| Os(2)–Os(3) | 2.870(1) | | |
| (*b*) Metal–carbon distances | | | |
| Os(1)–C(1) | 2.096(10) | Os(3)–C(1) | 2.103(10) |
| (*c*) Os–C (carbonyl) | | | |
| Range 1.884—1.974(11) | | Mean 1.925 | |
| (*d*) Ligand distances | | | |
| C(1)–C(2) | 1.356(13) | C(2)–C(3) | 1.498(13) |
| P–C(2) | 1.804(10) | P–C(111) | 1.799(11) |
| P–C(117) | 1.820(10) | P–C(118) | 1.834(11) |
| (*e*) C–O (carbonyl) | | | |
| Range 1.115—1.157(12) | | Mean 1.132 | |

TABLE 9

Selected intramolecular angles (°) for (3b)

| | | | |
|---|---|---|---|
| (*a*) Angles at osmium | | | |
| Os(2)–Os(1)–Os(3) | 60.7(1) | C(1)–Os(1)–Os(2) | 82.3(2) |
| C(1)–Os(1)–Os(3) | 48.2(3) | C(1)–Os(1)–C(11) | 95.1(4) |
| C(1)–Os(1)–C(12) | 99.8(4) | C(1)–Os(1)–C(13) | 163.7(4) |
| C(11)–Os(1)–Os(2) | 175.2(4) | C(11)–Os(1)–Os(3) | 114.6(3) |
| C(11)–Os(1)–C(12) | 97.8(5) | C(11)–Os(1)–C(13) | 91.6(5) |
| C(12)–Os(1)–Os(2) | 86.6(3) | C(12)–Os(1)–Os(3) | 134.1(3) |
| C(12)–Os(1)–C(13) | 94.0(5) | C(13)–Os(1)–Os(2) | 89.9(3) |
| C(13)–Os(1)–Os(3) | 115.5(3) | Os(1)–Os(2)–Os(3) | 58.4(1) |
| C(21)–Os(2)–Os(1) | 85.6(3) | C(21)–Os(2)–Os(3) | 84.3(3) |
| C(21)–Os(2)–C(22) | 92.6(5) | C(21)–Os(2)–C(23) | 94.2(5) |
| C(21)–Os(2)–C(24) | 170.3(4) | C(22)–Os(2)–Os(1) | 157.0(4) |
| C(22)–Os(2)–Os(3) | 98.6(4) | C(22)–Os(2)–C(23) | 101.3(5) |
| C(22)–Os(2)–C(24) | 92.1(5) | C(23)–Os(2)–Os(1) | 101.7(4) |
| C(23)–Os(2)–Os(3) | 160.1(4) | C(23)–Os(2)–C(24) | 93.2(5) |
| C(24)–Os(2)–Os(1) | 86.8(3) | C(24)–Os(2)–Os(3) | 86.6(3) |
| Os(1)–Os(3)–Os(2) | 60.9(1) | C(1)–Os(3)–Os(1) | 48.0(3) |
| C(1)–Os(3)–Os(2) | 82.3(3) | C(1)–Os(3)–C(31) | 95.4(4) |
| C(1)–Os(3)–C(32) | 93.0(4) | C(1)–Os(3)–C(33) | 165.7(4) |
| C(31)–Os(3)–Os(1) | 130.0(3) | C(31)–Os(3)–Os(2) | 85.0(3) |
| C(31)–Os(3)–C(32) | 99.0(4) | C(31)–Os(3)–C(33) | 96.5(5) |
| C(32)–Os(3)–Os(1) | 113.3(3) | C(32)–Os(3)–Os(2) | 174.1(4) |
| C(32)–Os(3)–C(33) | 93.0(5) | C(33)–Os(3)–Os(1) | 117.7(3) |
| C(33)–Os(3)–Os(2) | 90.8(3) | | |
| (*b*) Os–C–O | | | |
| Range 173—179(1) | | Mean 177 | |
| (*c*) Angles within the organophosphine ligand | | | |
| C(2)–P–C(111) | 109.9(5) | C(2)–P–C(117) | 115.4(5) |
| C(2)–P–C(118) | 111.7(5) | C(111)–P–C(117) | 105.4(5) |
| C(111)–P–C(118) | 106.9(5) | C(117)–P–C(118) | 107.1(6) |
| Os(1)–C(1)–Os(3) | 83.7(4) | C(2)–C(1)–Os(1) | 144.7(8) |
| C(2)–C(1)–Os(3) | 131.5(7) | C(1)–C(2)–P | 123.5(8) |
| C(1)–C(2)–C(3) | 123.9(9) | P–C(2)–C(3) | 112.6(7) |
| P–C(111)–C(112) | 119(1) | P–C(111)–C(116) | 122(1) |

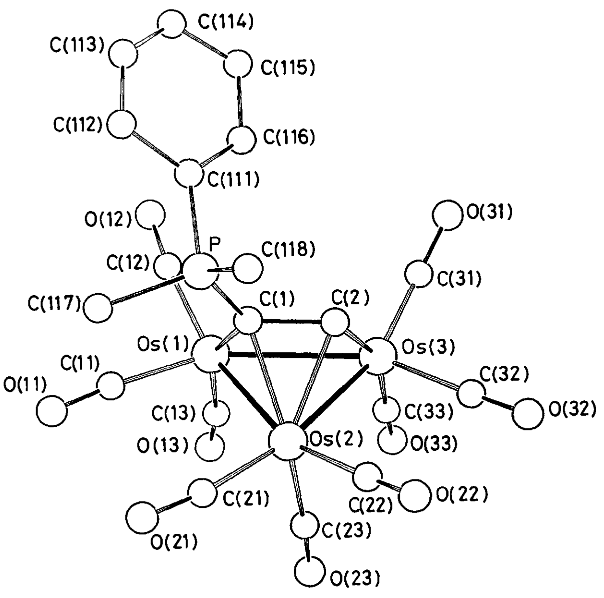

FIGURE 1 Molecular structure of $[Os_3H(CO)_9(HC{=}CPMe_2Ph)]$, (1a)

bond are 113.3 and 113.2° for Os(1)–Os(3); 93.4 and 99.7° for Os(1)–Os(2); and 92.2 and 100.3° for Os(2)–Os(3). The greater length of the Os(1)–Os(3) bond in both compounds is also consistent with a hydride bridge.

Tables 6 and 7 show that compounds (1a) and (2) are remarkably similar structurally. Within each structure, atoms C(1) and C(2) of the $\mu_3$-alkyne ligands are almost equivalent in their positions with respect to the metal triangles, such that the geometries of the $Os_3(CO)_9C_2$ units are nearly identical. There is no discernable distortion of the bonding of the $\mu_3$ ligands which could be ascribed to the presence of an α-phosphonium centre of C(1) in (1a) or a β-phosphonium centre in (2).

TABLE 10

Metal–carbon bond lengths (Å) in selected $\mu_3$-alkyne complexes (8)—(10) with related lengths in compounds (1a) and (2) [a]

| Compound | a | b | c | d | Ref. |
|---|---|---|---|---|---|
| (8) $[Os_3(CO)_{10}(Ph_2C_2)]$ | 2.182(8) | 2.070(9) | 2.188(8) | 2.293(9) | *b* |
| (9) $[Os_3(CO)_7(Ph_4C_4)(Ph_2C_2)]$ | 2.16(2) | 2.08(2) | 2.22(2) | 2.28(2) | *c* |
| (10) $[Ru_3H(CO)_9(C_8H_{12})]$ | 2.13 | 2.08 | 2.23 | 2.28 | *d* |
| (1a) | 2.127(18) | 2.064(17) | 2.226(15) | 2.252(16) | This work |
| (2) | 2.132(19) | 2.127(19) | 2.247(20) | 2.293(19) | This work |

[a] a and b are σ-Os–C bond lengths while c and d are the Os–C lengths in the $\eta^2$-linkage. [b] M. Tachikawa, J. R. Shapley, and C. G. Pierpont, *J. Am. Chem. Soc.*, 1975, **97**, 7172. [c] G. Ferraris and G. Gervasio, *J. Chem. Soc., Dalton Trans.*, 1973, 1933. [d] R. Mason and K. M. Thomas, *Ann. N.Y. Acad. Sci.*, 1974, **239**, 225.

In (1a) and (2) the asymmetry of the unsymmetrically substituted alkynes does not produce a pronounced asymmetry in the alkyne to cluster bonding. In certain related complexes with symmetrically substituted $\mu_3$-alkyne ligands, there is a significant twist of the alkyne out of a symmetrical arrangement. For example, in the clusters (8)—(10) (Table 10) one σ-M–C bond is longer than the other (a > b) and the shorter is associated with a longer M–C bond in the $\eta^2$-linkage (d > c). The data given in Table 10 suggest that the distortion present in (8)—(10) may be barely significant in (1a).

Compound (3b) (Figure 3) is a member of the large class of compounds of type $[Os_3H(CO)_{10}(\mu\text{-}X)]$ and belongs to the same sub-class as the $PMe_2Ph$ adduct shown in equation (1), having a formally two-electron donating group X with a negative charge at the cluster and positive charge at the phosphonium centre of the ligand. The bridged Os(1)–Os(3) distance (2.802 Å) is less than the non-bridged ones (2.873 and 2.870 Å) by approximately the same amount as found with related clusters where the metal atoms are bridged by a single N, O, or C atom.[12] The C(1)–C(2) distance of 1.356(13) Å indicates a double bond and the planarity of these two atoms with the substituents at them [P, C(3), Os(1), and Os(3)] is consistent with these atoms being $sp^2$ hybridised. The Os(1)–C(1)–Os(3) angle of 83.7°, however, is small for a simple substituted ethene but this is dictated by the Os–Os bond length.

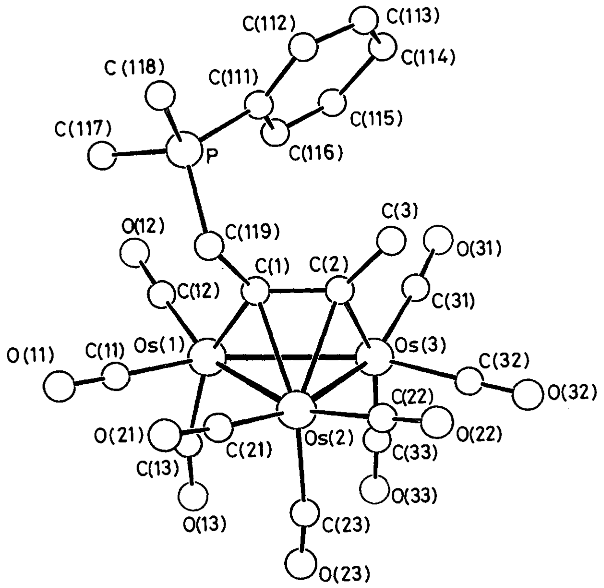

FIGURE 2 Molecular structure of $[Os_3H(CO)_9(MeC{=}CCH_2PMe_2Ph)]$, (2)

*Dynamic Behaviour of Compounds* (1)—(3).—Compounds (3) are asymmetric and consequently the two methyl groups are diastereotopic and give sharp doublets at room temperature in their $^1H$ n.m.r. spectra. Therefore there is no rotation about the C(1)–C(2) bond which would interconvert enantiomers, or at least such rotation is too slow to give any n.m.r. line broadening at room temperature. The methyl groups in the $PMe_2Ph$ groups of compounds (1) and (2) are similarly diastereotopic but here two sharp methyl doublets for each compound are found only below room temperature. For example, Figure 4 shows that the two methyl doublets for the PMe$_2$Ph group in compound (1b) (overlapping to give a triplet) are only sharp at 0 °C but broaden and coalesce at higher temperatures. The same effect is observed for other compounds (1) and (2). To interchange the methyl groups, the co-ordination of the $\mu_3$-alkyne to the Os$_3$ triangle cannot be rigid. Flipping of the alkyne ligand as it rotates from one configuration to the next is presumably occurring as proposed for other $\mu_3$-alkyne [13,14] and $\mu_3$-aryne [15,16] ligands.

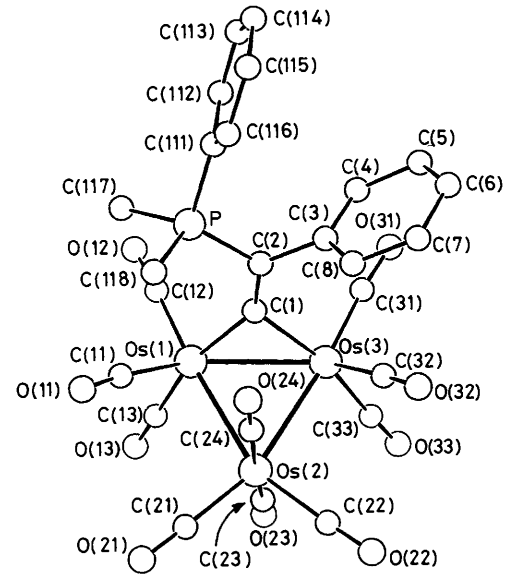

FIGURE 3 Molecular structure of $[Os_3H(CO)_{10}(C{=}CPhPMe_2Ph)]$, (3b)

EXPERIMENTAL

*Synthesis of Compounds.*—Compounds $[Os_3H(CO)_9(C\equiv CH)]$,[17] $[Os_3H(CO)_9(C\equiv CMe)]$,[17] $[Os_3H(CO)_9(C\equiv CCMe_2OH)]$,[14] $[Os_3H(CO)_9(MeC{=}C{=}CH_2)]$,[17] $[Os_3(CO)_{10}(C_2H_2)]$,[17] and $[Os_3H(CO)_{10}(C\equiv CPh)]$ [17] were prepared as described previously.

$[Os_3H(CO)_9(HC{=}CPMe_2Ph)]$, (1a). Dimethylphenylphosphine (3 mol per Os$_3$) was added to a solution of $[Os_3H(CO)_9(C\equiv CH)]$ (0.030 g) in chloroform (5 cm$^3$) under nitrogen. The solvent and excess of phosphine were removed under vacuum and the solid residue was washed with pentane to give compound (1a) quantitatively as an off-white solid. Recrystallisation by dissolving in CHCl$_3$ and precipitating by adding pentane gave white crystals in good yield (Found: C, 24.05; H, 1.60; P, 3.30. $C_{19}H_{13}O_9Os_3P$ requires C, 23.1; H, 1.35; P, 3.15%).

By similar routes the following PMe$_2$Ph adducts of $\mu_3$-alkynyl complexes were prepared: $[Os_3H(CO)_9(MeC{=}CPMe_2Ph)]$ (1b) (Found: C, 24.0; H, 1.45; P, 2.95. $C_{20}H_{15}O_9Os_3P$ requires C, 24.0; H, 1.50; P, 3.10%); $[Os_3H(CO)_9(PhC{=}CPMe_2Ph)]$ (1c) (Found: C, 28.25; H, 1.70; P, 2.75. $C_{25}H_{17}O_9Os_3P$ requires C, 28.25; H, 1.60; P, 2.90%); $[Os_3H(CO)_9(HOCMe_2C{=}CPMe_2Ph)]$ (1d) (Found: C, 25.95; H, 2.00; P, 3.00. $C_{22}H_{19}O_{10}Os_3P$ requires C, 25.3; H, 1.85; P, 2.95%).

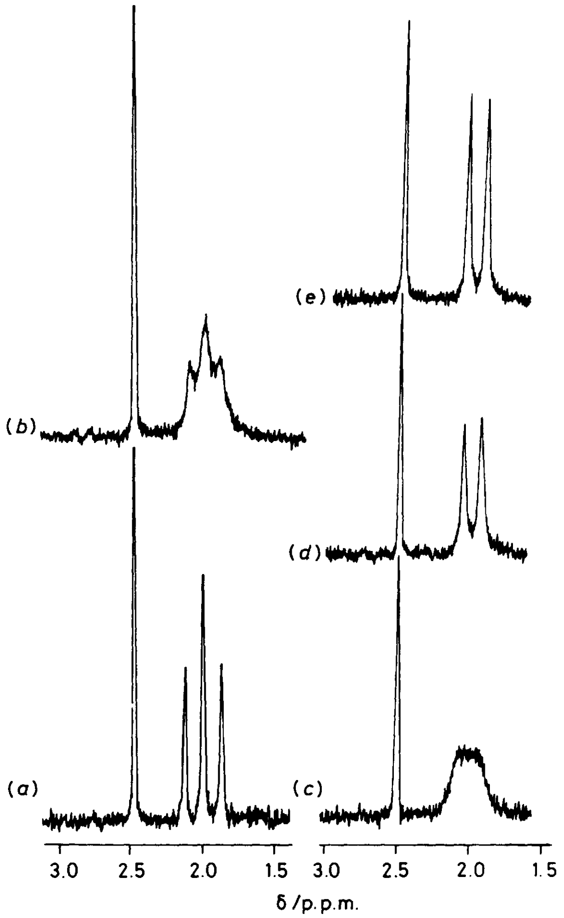

FIGURE 4 Proton n.m.r. spectra of the methyl groups of compound (1b), $[Os_3H(CO)_9(MeC{=}CPMe_2Ph)]$, in CD$_2$Cl$_2$ solution at 0 (*a*), 28 (*b*), 37 (*c*), 41 (*d*), and 52 °C (*e*)

$[Os_3H(CO)_9(MeC{=}CCH_2PMe_2Ph)]$, (2). The addition of stoicheiometric quantities of PMe$_2$Ph to a solution of $[Os_3H(CO)_9(MeC{=}C{=}CH_2)]$ in n-hexane gave a colourless precipitate of compound (2) in good yield (Found: C, 25.3; H, 1.90; P, 3.00. $C_{21}H_{17}O_9Os_3P$ requires C, 24.85; H, 1.70; P, 3.05%).

$[Os_3H(CO)_{10}(C{=}CHPMe_2Ph)]$, (3a). A slight excess of PMe$_2$Ph (0.013 cm$^3$, $9.5 \times 10^{-5}$ mol) was added to a solution of $[Os_3(CO)_{10}(C_2H_2)]$ (0.068 g, $7.8 \times 10^{-5}$ mol) in CDCl$_3$ (0.5 cm$^3$) and the solution allowed to stand at room temperature for 16 h. Removal of solvent and chromatography of the residue on silica (t.l.c.) gave some starting cluster (0.001 g) eluting with pentane, while elution with a chloroform–pentane mixture (1 : 2 v/v) gave a band which gave compound (3a) as yellow crystals (0.047 g, 60%) (Found: C, 24.9; H, 1.65; P, 3.00. $C_{20}H_{13}O_{10}Os_3P$ requires C, 23.65; H, 1.30; P, 3.05%).

$[Os_3H(CO)_{10}(C{=}CPhPMe_2Ph)]$, (3b). A solution of $[Os_3H(CO)_{10}(C\equiv CPh)]$ (0.048 g, $5 \times 10^{-5}$ mol) in CDCl$_3$ (0.5 cm$^3$) was treated with PMe$_2$Ph (0.007 cm$^3$, $5 \times 10^{-5}$ mol). Bright yellow crystals of compound (3b) were slowly deposited (0.049 g, 91%) (Found: C, 28.9; H, 1.70; P, 3.05. $C_{26}H_{17}O_{10}Os_3P$ requires C, 28.6; H, 1.55; P, 2.85%).

*X-Ray Crystallographic Determinations.*—Data for each compound were collected using a Philips PW1100 four-circle diffractometer and graphite-monochromatized Mo-$K_\alpha$ radiation ($\lambda$ 0.710 69 Å) in the range $3 < \theta < 25°$. The method of data collection was similar to that described previously.[18] Intensities $I$ and $\sigma(I)$ were corrected for Lorentz and polarisation factors and semi-empirical absorption corrections based on a pseudo-ellipsoid mode [19] were applied. Totals of 415, 472, and 486 azimuthal scan data from 14, 12, and 14 independent reflections were used for (1a), (2), and (3b) respectively; relative transmission factors for the full data ranged from 1.0 to 0.311 for (1a), 1.0 to 0.444 for (2), and 1.0 to 0.594 for (3b). The crystal data for each sample are summarised in Table 2.

*Structure solution and refinement.* The Os atoms in each case were located from a Patterson map. For each complex a subsequent difference-Fourier synthesis revealed the positions of all the non-hydrogen atoms. All three structures were refined by full-matrix least squares. The $sp^2$ C–H phenyl H atoms and the $sp^3$ C–H methylene H atoms were included at calculated positions in the refinement, riding on the respective C atoms with C–H of 1.08 Å. The methyl H, hydridic H, and the vinylic H in (1a) were not located. Complex neutral-atom [20] scattering factors and weights $w = 1/\sigma^2(F)$ were used with $R' = \Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|$. The refined parameters in each case included anisotropic thermal parameters for all the non-hydrogen atoms and a common hydrogen isotropic thermal parameter fixed at 0.10 Å$^2$, and an empirical extinction parameter, $x$, which refined to 0.000 18(5) (1a), 0.000 15(2) (2), 0.000 91(5) (3b); $F_c$ is multiplied by $(1 - 0.0001\ xF_c{}^2/\sin\theta)$.

The SHELX [21] and ORTEP [22] programs were used for calculations. The refined atomic positional parameters and principal bond lengths and angles for (1a), (2), and (3b) are presented in Tables 3—8. Hydrogen-atom co-ordinates, additional bond lengths and angles, thermal parameters, equations of least-squares planes, and observed and calculated structure factors are deposited in Supplementary Publication No. SUP 23240 (71 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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