# Chemistry of the Metal Carbonyls. Part 78.[1] Synthesis and *X*-Ray Crystal Structures of $[NiOs_3(\mu\text{-}H)_2(\mu\text{-}CO)_2(CO)_8(PPh_3)_2]$ and $[Os_3Rh(\mu\text{-}H)_2(acac)(CO)_{10}]$ † (acac = acetylacetonate)

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The zerovalent nickel compound $[Ni(C_2H_4)(PPh_3)_2]$ reacts with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ to give the 60 valence electron cluster complex $[NiOs_3(\mu\text{-}H_2)(CO)_{10}(PPh_3)_2]$, the structure of which has been established by a single-crystal *X*-ray diffraction study. It crystallises in the monoclinic space group $P2_1/n$ with four molecules in a cell of dimensions $a$ = 15.579(6), $b$ = 17.205(4), $c$ = 18.976(5) Å, and $\beta$ = 99.97(3)°. The structure has been determined from 8 595 unique reflections ($2.9 \leqslant 2\theta \leqslant 55°$, Mo-$K_\alpha$ *X*-radiation) collected at 190 K, and refined to $R$ 0.038 ($R'$ 0.042). The metal atoms form a slightly distorted tetrahedron with two Ni–Os edges each bridged by a carbonyl group, and with the third Ni–Os edge and an Os–Os bond bridged by hydrido-ligands. Although the latter were not located by the diffraction study their assigned positions are argued on a variety of other evidence. The nickel atom carries one $PPh_3$ ligand, while the second $PPh_3$ group is bound to an osmium atom. The unsaturated triosmium compound $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ also reacts with $[Rh(acac)(C_2H_4)_2]$ (acac = acetylacetonate) affording in high yield the cluster complex $[Os_3Rh(\mu\text{-}H)_2(acac)(CO)_{10}]$. An *X*-ray diffraction study on a single crystal revealed that it was triclinic, space group $P\bar{1}$ (no. 2), $Z$ = 2, in a unit cell of dimensions $a$ = 8.759(3), $b$ = 9.463(2), $c$ = 13.680(4) Å, $\alpha$ = 100.59(2), $\beta$ = 93.86(2), and $\gamma$ = 107.84(2)°. The structure has been refined to $R$ 0.052 ($R'$ 0.059) for 4 240 independent reflections ($2.9 \leqslant 2\theta \leqslant 60°$, Mo-$K_\alpha$ *X*-radiation) collected at 200 K. The four metal atoms adopt a ' butterfly ' configuration. The pentane-2,4-dionato-ligand is chelated to the rhodium atom at one extremity but one of its oxygen atoms also bridges to an Os atom forming the other wing-tip of the ' butterfly,' so that this Os–Rh separation is 3.292(2) Å. The pentane-2,4-dionato-group thus functions as a five-electron donor, hence the cluster has 60 valence electrons. The rhodium atom also carries a carbonyl ligand, and this, and the remaining nine carbonyls on the osmium atoms, are all terminally bound. On the basis of $^1H$ n.m.r. studies, osmium–osmium distances, and other evidence the two hydrido-ligands bridge two of the Os–Os bonds. The compound is chemically unsaturated forming an adduct with triphenylphosphine; n.m.r. studies ($^1H$ and $^{31}P$) show that the $PPh_3$ group becomes attached to the rhodium atom of the cluster.

THE unsaturated 46-electron cluster $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ reacts with the zerovalent $d^{10}$ platinum complexes $[Pt(C_2H_4)_2(PPh_3)]$ and $[Pt(C_2H_4)(PPh_3)_2]$ to give the tetranuclear metal compounds $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)]$ (1) and $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$ (2), respectively. Structural studies revealed that complexes of the 58-electron type exemplified by (1) have a *closo* arrangement for the $Os_3Pt$ core, whereas those of which the 60-electron (2) is a prototype have a ' butterfly ' arrangement of the metal atoms.[1,2] Moreover, reaction of (1) with triphenylphosphine affords (2), and the latter when prepared from $[Pt(C_2H_4)(PPh_3)_2]$ has compound (1) as an intermediate. With these results in mind, we thought it worthwhile to investigate the reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with $[Ni(C_2H_4)(PPh_3)_2]$ and with $[Rh(acac)(C_2H_4)_2]$ (acac = acetylacetonate).[3] The reaction with the nickel compound was studied in order to compare the structure of any $NiOs_3$ species obtained with the structures of compounds (1) and (2). The structure of (2) did not accord with the predictions of the very useful skeletal bond pair approach, at least in its most simplistic form,[4] and it was of interest to establish whether nickel would follow the pattern set by platinum. The reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with $[Rh(acac)(C_2H_4)_2]$ was investigated in order to establish whether a $d^8$ metal species would add to the triosmium compound as readily as a $d^{10}$ species. The ethylene ligands in $[Rh(acac)(C_2H_4)_2]$ are readily displaced by a variety of reagents so that it effectively acts as a source of the Rh(acac) group.[5]

## RESULTS AND DISCUSSION

The complex $[Ni(C_2H_4)(PPh_3)_2]$[6,7] reacts with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$[8,9] quantitatively at room temperature over a period of several hours to give the orange crystalline compound $[NiOs_3(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$ (3). Examination of the i.r. spectrum of (3) in the carbonyl stretching region revealed immediately that (3) was not isostructural with the corresponding platinum-containing complex (2) since bands at 1 885 and 1 821 cm$^{-1}$ indicated the presence of bridging carbonyl ligands whereas the carbonyl ligands in (2) are all terminal. Seven other bands were observed between 2 073 and 1 973 cm$^{-1}$ due to terminal CO ligands. Further evidence for bridging carbonyls was provided by the $^{13}C$ n.m.r. spectrum measured at −60 °C. Two low-field resonances occurred at δ 220.1 and 214.5 p.p.m., while there were eight other signals in the region 170.2—183.6 p.p.m. The signals at 220.1 and 214.5 p.p.m. may be assigned to bridging carbonyl groups, and the other eight resonances to terminal carbonyl groups since bridging CO ligands have shifts to lower field than those which are terminally bound.[10] Complex (3) undergoes site exchange of its carbonyl groups since the $^{13}C$ n.m.r. spectrum at room

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† 1,3;1,4-Di-μ-carbonyl-1,2,2,2,3,3,4,4-octacarbonyl-1,2;2,3-di-μ-hydrido-1,3-bis(triphenylphosphine)-*cyclo*-nickeltriosmium(3-*Ni–Os*)(3*Os–Os*) and 1,2,2,2,3,3,3,4,4,4-decacarbonyl-2,3;2,4-di-μ-hydrido-[1,4;1-(pentane-2,4-dionato)-μ-*O,O′*]-*cyclo*-rhodiumtriosmium(2*Rh–Os*)(3*Os–Os*).

temperature showed only one broad singlet at low field (219.7 p.p.m.) and seven at higher field (170.2—182.8 p.p.m.).

The $^1H$ n.m.r. spectrum had two high-field signals at τ 23.64 and 30.20, as well as resonances due to the triphenylphosphine ligands. Both hydrido-ligand signals were doublets due to $^{31}P$ coupling, and the chemical shifts are suggestive of Os(μ-H)Ni and Os(μ-H)Os groups, respectively.[1,2] The $^{31}P$ ($^1H$-decoupled) n.m.r. spectrum showed two doublet resonances at δ −63.7 and −2.67 p.p.m. with *J*(PP) 7 Hz. The two $PPh_3$ ligands are therefore attached to different metal atoms in (3), and the chemical shifts indicate that the signal at −63.7 p.p.m. is due to a Ni*P*$Ph_3$ group and that at −2.67 p.p.m. to an Os*P*$Ph_3$ group.[2,11] A selectively $^1H$-decoupled $^{31}P$ n.m.r. spectrum afforded *J*(PH) constants which allowed correlation of the resonance at −63.7 p.p.m. with the $^1H$ n.m.r. peak at τ 23.64 [Os(μ-H)Ni] and the resonance at −2.67 p.p.m. with the $^1H$ n.m.r. peak at τ 30.20 [Os(μ-H)Os].

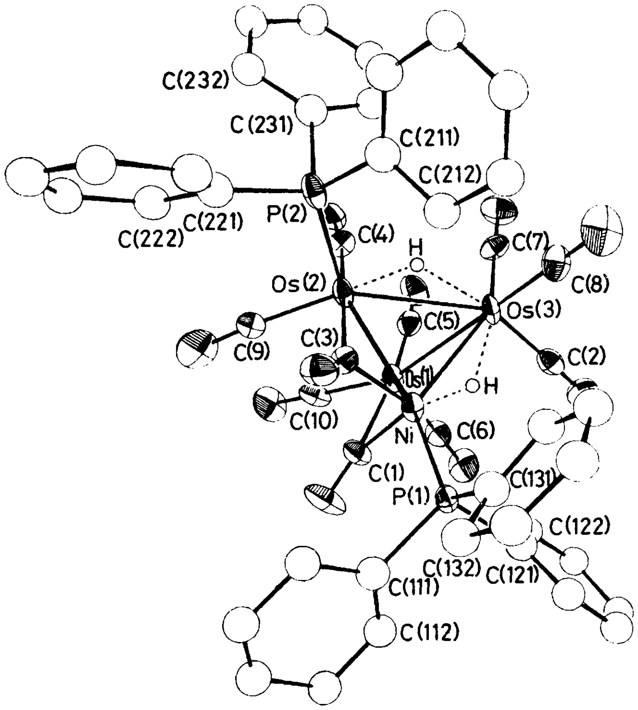


FIGURE 1 Molecular structure of (3), $[NiOs_3(\mu\text{-}H)_2(\mu\text{-}CO)_2(CO)_8(PPh_3)_2]$, showing the crystallographic numbering

In order to determine the configuration of the metal atoms and the arrangement of peripheral ligands in (3) a single-crystal *X*-ray diffraction study was made. The results are summarised in Tables 1 and 2; the molecular configuration, together with the atomic numbering scheme, is shown in Figure 1, and a stereoscopic view of the contents of the unit cell in Figure 2.

TABLE 1

Final atomic positional (fractional co-ordinates) parameters for $[NiOs_3(\mu\text{-}H)_2(\mu\text{-}CO)_2(CO)_8(PPh_3)_2]$ (3)

| Atom | *x*/*a* | *y*/*b* | *z*/*c* |
|---|---|---|---|
| Os(1) | 0.036 62(2) | 0.087 70(2) | 0.152 30(2) |
| Os(2) | 0.168 15(2) | 0.088 43(2) | 0.277 81(2) |
| Os(3) | 0.141 39(2) | −0.049 93(2) | 0.181 70(2) |
| Ni | 0.024 24(7) | 0.001 60(6) | 0.262 99(5) |
| μ-H(1) * | 0.213 4 | −0.003 8 | 0.256 0 |
| μ-H(2) * | 0.072 0 | −0.084 9 | 0.240 4 |
| O(1) | −0.109 4(5) | 0.115 8(4) | 0.244 1(4) |
| O(2) | 0.015 8(5) | −0.134 8(4) | 0.066 5(4) |
| O(3) | 0.092 4(4) | 0.029 4(4) | 0.410 4(3) |
| O(4) | 0.267 2(5) | 0.174 4(4) | 0.175 8(4) |
| O(5) | 0.151 4(5) | 0.124 2(4) | 0.041 9(4) |
| O(6) | −0.113 5(6) | 0.034 8(4) | 0.039 2(4) |
| O(7) | 0.275 7(5) | −0.011 9(5) | 0.086 1(4) |
| O(8) | 0.246 9(6) | −0.192 3(4) | 0.236 8(4) |
| O(9) | 0.097 1(6) | 0.237 0(4) | 0.331 6(4) |
| O(10) | −0.010 1(6) | 0.259 4(4) | 0.158 5(4) |
| C(1) | −0.049 8(7) | 0.081 5(5) | 0.230 5(5) |
| C(2) | 0.063 4(7) | −0.102 4(5) | 0.109 6(5) |
| C(3) | 0.096 8(6) | 0.034 1(5) | 0.350 5(4) |
| C(4) | 0.229 2(7) | 0.142 2(5) | 0.212 8(4) |
| C(5) | 0.109 6(7) | 0.107 5(5) | 0.083 7(5) |
| C(6) | −0.057 2(7) | 0.053 6(6) | 0.081 2(5) |
| C(7) | 0.222 7(7) | −0.024 2(5) | 0.120 3(5) |
| C(8) | 0.207 3(7) | −0.137 8(5) | 0.217 0(5) |
| C(9) | 0.126 7(7) | 0.182 7(6) | 0.311 5(5) |
| C(10) | 0.006 5(7) | 0.195 7(6) | 0.156 0(5) |
| P(1) | −0.069 5(2) | −0.067 6(1) | 0.310 8(1) |
| P(2) | 0.294 2(2) | 0.077 4(1) | 0.365 5(1) |
| C(111) | −0.148 0(4) | −0.009 5(3) | 0.348 9(3) |
| C(112) | −0.234 0(4) | −0.003 2(3) | 0.313 4(3) |
| C(113) | −0.292 4(4) | 0.044 9(3) | 0.340 7(3) |
| C(114) | −0.265 0(4) | 0.086 6(3) | 0.403 6(3) |
| C(115) | −0.179 0(4) | 0.080 4(3) | 0.439 1(3) |
| C(116) | −0.120 6(4) | 0.032 3(3) | 0.411 7(3) |
| H(112) | −0.255 3(4) | −0.035 5(3) | 0.264 7(3) |
| H(113) | −0.359 0(4) | 0.049 7(3) | 0.313 3(3) |
| H(114) | −0.310 2(4) | 0.123 8(3) | 0.424 8(3) |
| H(115) | −0.157 7(4) | 0.112 7(3) | 0.487 7(3) |
| H(116) | −0.054 0(4) | 0.027 4(3) | 0.439 2(3) |
| C(121) | −0.138 8(4) | −0.129 8(3) | 0.246 6(3) |
| C(122) | −0.150 1(4) | −0.110 8(3) | 0.174 1(3) |
| C(123) | −0.206 9(4) | −0.154 3(3) | 0.124 3(3) |
| C(124) | −0.252 4(4) | −0.216 7(3) | 0.147 0(3) |
| C(125) | −0.241 1(4) | −0.235 7(3) | 0.219 5(3) |
| C(126) | −0.184 3(4) | −0.192 2(3) | 0.269 3(3) |
| H(122) | −0.114 9(4) | −0.062 5(3) | 0.156 6(3) |
| H(123) | −0.215 6(4) | −0.139 6(3) | 0.068 2(3) |
| H(124) | −0.296 3(4) | −0.250 3(3) | 0.108 4(3) |
| H(125) | −0.276 3(4) | −0.284 0(3) | 0.237 0(3) |
| H(126) | −0.175 5(4) | −0.206 9(3) | 0.325 4(3) |
| C(131) | −0.024 5(4) | −0.137 7(3) | 0.380 1(3) |
| C(132) | −0.056 5(4) | −0.146 2(3) | 0.443 9(3) |
| C(133) | −0.024 4(4) | −0.205 1(3) | 0.491 8(3) |
| C(134) | 0.039 7(4) | −0.255 5(3) | 0.475 8(3) |
| C(135) | 0.071 8(4) | −0.247 0(3) | 0.412 0(3) |
| C(136) | 0.039 6(4) | −0.188 0(3) | 0.364 2(3) |
| H(132) | −0.106 2(4) | −0.107 2(3) | 0.456 3(3) |
| H(133) | −0.049 2(4) | −0.211 8(3) | 0.541 2(3) |
| H(134) | 0.064 6(4) | −0.301 1(3) | 0.512 9(3) |
| H(135) | 0.121 4(4) | −0.285 9(3) | 0.399 7(3) |
| H(136) | 0.064 4(4) | −0.181 4(3) | 0.314 7(3) |
| C(211) | 0.329 2(3) | −0.020 1(3) | 0.397 4(3) |
| C(212) | 0.269 5(3) | −0.081 0(3) | 0.394 4(3) |
| C(213) | 0.297 3(3) | −0.154 2(3) | 0.420 3(3) |
| C(214) | 0.384 7(3) | −0.166 7(3) | 0.449 4(3) |
| C(215) | 0.444 4(3) | −0.105 8(3) | 0.452 4(3) |
| C(216) | 0.416 7(3) | −0.032 5(3) | 0.426 4(3) |
| H(212) | 0.201 8(3) | −0.071 3(3) | 0.371 9(3) |
| H(213) | 0.251 0(3) | −0.201 3(3) | 0.418 0(3) |
| H(214) | 0.406 2(3) | −0.223 4(3) | 0.469 5(3) |
| H(215) | 0.512 1(3) | −0.115 4(3) | 0.474 9(3) |
| H(216) | 0.462 9(3) | 0.014 6(3) | 0.428 8(3) |
| C(221) | 0.292 8(4) | 0.135 5(3) | 0.445 7(2) |
| C(222) | 0.280 9(4) | 0.215 6(3) | 0.437 3(2) |
| C(223) | 0.282 2(4) | 0.262 9(3) | 0.497 1(2) |

The metal atoms adopt essentially a tetrahedral geometry with some slight asymmetry in the metal–metal bond lengths so that dihedral angles within the

TABLE 1 (*continued*)

| Atom | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| C(224) | 0.295 4(4) | 0.230 2(3) | 0.565 4(2) |
| C(225) | 0.307 3(4) | 0.150 1(3) | 0.573 8(2) |
| C(226) | 0.306 0(4) | 0.102 8(3) | 0.513 9(2) |
| H(222) | 0.270 8(4) | 0.240 9(3) | 0.384 4(2) |
| H(223) | 0.273 0(4) | 0.324 8(3) | 0.490 6(2) |
| H(224) | 0.296 4(4) | 0.266 8(3) | 0.611 7(2) |
| H(225) | 0.317 5(4) | 0.124 8(3) | 0.626 7(2) |
| H(226) | 0.315 2(4) | 0.040 8(3) | 0.520 5(2) |
| C(231) | 0.390 8(4) | 0.110 8(3) | 0.330 5(3) |
| C(232) | 0.441 5(4) | 0.174 3(3) | 0.357 9(3) |
| C(233) | 0.510 0(4) | 0.199 2(3) | 0.324 8(3) |
| C(234) | 0.527 6(4) | 0.160 6(3) | 0.264 3(3) |
| C(235) | 0.476 9(4) | 0.097 2(3) | 0.236 8(3) |
| C(236) | 0.408 4(4) | 0.072 3(3) | 0.269 9(3) |
| H(232) | 0.427 9(4) | 0.204 1(3) | 0.404 8(3) |
| H(233) | 0.549 3(4) | 0.248 3(3) | 0.346 1(3) |
| H(234) | 0.580 6(4) | 0.179 9(3) | 0.238 6(3) |
| H(235) | 0.490 5(4) | 0.067 3(3) | 0.189 9(3) |
| H(236) | 0.369 1(4) | 0.023 1(3) | 0.248 7(3) |
| Solvent molecule, diethyl ether | | | |
| O(11) | 0.604 0(7) | −0.015 0(6) | 0.153 8(6) |
| C(11) | 0.546 6(13) | −0.081 4(10) | 0.146 2(10) |
| H(1) | 0.482 0(13) | −0.064 1(10) | 0.120 9(10) |
| H(2) | 0.570 7(13) | −0.125 6(10) | 0.114 2(10) |
| C(12) | 0.614 7(16) | 0.019 5(13) | 0.090 6(12) |
| H(3) | 0.644 9(16) | −0.021 8(13) | 0.059 7(12) |
| H(4) | 0.551 6(16) | 0.035 8(13) | 0.061 2(12) |
| C(13) | 0.669 0(17) | 0.084 8(14) | 0.102 9(14) |
| H(5) | 0.658 8(17) | 0.099 5(14) | 0.046 7(14) |
| H(6) | 0.737 9(17) | 0.078 1(14) | 0.122 5(14) |
| H(7) | 0.643 3(17) | 0.130 5(14) | 0.132 2(14) |
| C(14) | 0.545 6(16) | −0.111 0(13) | 0.218 7(11) |
| H(8) | 0.505 1(16) | −0.162 3(13) | 0.212 3(11) |
| H(9) | 0.521 4(16) | −0.070 7(13) | 0.254 2(11) |
| H(10) | 0.611 7(16) | −0.127 2(13) | 0.241 0(11) |

* Positional parameters unrefined.

cluster vary from 67.1 to 74.8°, not far from the 70.5° required for a $T_d$ arrangement (see Table 2). Two of the Ni–Os edges are bridged by carbonyl ligands. Not surprisingly, in view of the differing atomic radii of osmium and nickel, the bridging is asymmetric with the mean for Os(1)–C(1) and Os(2)–C(3) being 2.15(1) Å, and the mean for Ni–C(1) and Ni–C(3) being 1.87(1) Å. The remaining eight carbonyl ligands are all terminal and close to linear, with Os–C distances [1.88(1)—1.92(3) Å] within the range generally observed in osmium cluster complexes.[12,13] In $[Os_3(CO)_{12}]$ axial Os–CO distances are consistently longer (0.03 Å) than equatorial and this has been rationalised as being due to the competition for back-donated electron density which is severe for mutually *trans* carbonyl ligands and minimal for carbonyl ligands *trans* to a metal–metal bond.[13] The effect is barely discernible in compound (3) where the mean axial and mean equatorial Os–CO distances differ by only 0.01 Å. In (3) there are no mutually *trans* terminal carbonyl ligands and the presence of $PPh_3$ groups on Os(2) and the Ni atom should result in overall high electron density on these metal atoms. This may account for the presence of bridging carbonyl ligands since these are considered better π acceptors than terminal carbonyl groups.[14] A similar situation exists with $[Ir_4(CO)_{12}]$ and $[Ir_4(CO)_{10}(PPh_3)_2]$ where the latter molecule has bridging CO ligands and the former does not.[15,16]

The *X*-ray diffraction study shows that in the reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ with $[Ni(C_2H_4)(PPh_3)_2]$ a $PPh_3$ group is transferred from nickel to osmium. In the synthesis of (2) from $[Pt(C_2H_4)(PPh_3)_2]$ a similar transfer occurs. In (3) the Ni–P(1) and Os–P(2) distances of 2.198(3) and 2.352(2) Å, respectively, are typical for such bonds. Thus in $[Os_3(H)(\mu\text{-}H)(CO)_{10}(PPh_3)]$ the Os–P distance is 2.370(2) Å[17] and in $[Ni(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ the Ni–P distance is 2.196(2) Å.[18]

The Ni–Os(3) and Os(2)–Os(3) edges of the tetrahedron are *ca.* 0.1 Å longer than the other corresponding Ni–Os and Os–Os distances, and as such suggest that it is these edges which are bridged by the two hydrido-ligands known to be present from the $^1H$ n.m.r. spectra. The formation of a three-centre two-electron M(μ-H)M bond results in an increase in the intermetallic distance, as compared with an unsupported M–M bond.[19,20] The lengthening of the Ni–Os(3) internuclear distance, as compared with the Ni–Os(1) and Ni–Os(2) separations is no doubt accentuated to some degree by these two edges being bridged by a carbonyl ligand, which is known to have the contrary effect of a hydrido-ligand and to shorten metal–metal bond lengths.[21,22] Nevertheless, calculations[23] indicate that the two lengthened edges Ni–Os(3) and Os(2)–Os(3) possess sites for hydrido-ligands which are of substantially lower potential energy than other edge-bridging positions, or terminal or face-bridging locations. Further evidence for the position of the hydrido-ligands is afforded by the widening observed in the *cis* angles Os(2)–Os(3)–C(8) [114.4(3)°] and Ni–Os(3)–C(8) [115.9(3)°]. These are significantly larger than the other *cis*-Os–Os–C and *cis*-Ni–Os–C angles which range from 80.2(3) to 104.0(3)°. This widening of *cis*-M–M–C angles is also observed where edges are bridged by carbonyl ligands, *viz.* Ni–Os(1)–C(10) 117.9(3)° and Ni–Os(2)–C(9) 100.7(3)°.

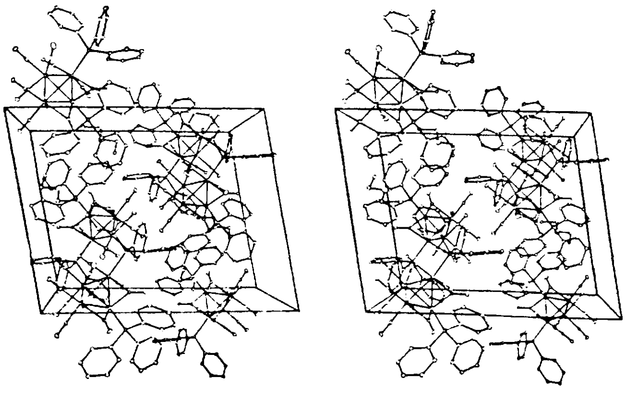


FIGURE 2 Stereoscopic view of complex (3)

The unbridged Os–Os internuclear distances of 2.861(1) and 2.878(1) Å are within the normal range observed[13] for such bonds and may be compared with a mean value of 2.843(1) Å found[2] in the 60-electron platinum analogue (2) which, however, has a ' butterfly ' structure rather than the *closo* structure of (3). In contrast, in the molecule $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$, which has a tetrahedral structure but only 58 electrons and is thus formally unsaturated, the unbridged Os–Os bonds [2.759(1) Å] are distinctly shorter.[2]

TABLE 2

Internuclear distances (Å) and bond angles (°), for $[NiOs_3(\mu\text{-}H)_2(\mu\text{-}CO)_2(CO)_8(PPh_3)_2]$ (3), with estimated standard deviations in parentheses

(*a*) Bonds [a]

| | | | |
|---|---|---|---|
| Os(1)–Os(2) | 2.861(1) | C(3)–O(3) | 1.15(1) |
| Os(1)–Os(3) | 2.876(1) | C(4)–O(4) | 1.14(1) |
| Os(2)–Os(3) | 2.984(1) | C(5)–O(5) | 1.15(1) |
| Os(1)–Ni | 2.605(1) | C(6)–O(6) | 1.13(1) |
| Os(2)–Ni | 2.668(1) | C(7)–O(7) | 1.15(1) |
| Os(3)–Ni | 2.733(1) | C(8)–O(8) | 1.15(1) |
| Os(1)–C(1) | 2.17(1) | C(9)–O(9) | 1.14(1) |
| Os(1)–C(5) | 1.90(1) | C(10)–O(10) | 1.13(1) |
| Os(1)–C(6) | 1.90(1) | O(11)–C(11) [b] | 1.44(2) |
| Os(1)–C(10) | 1.92(1) | O(11)–C(12) [b] | 1.38(3) |
| Os(2)–C(3) | 2.13(1) | C(11)–C(14) [b] | 1.47(3) |
| Os(2)–C(4) | 1.92(1) | C(12)–C(13) [b] | 1.40(3) |
| Os(2)–C(9) | 1.89(1) | P(1)–C(111) | 1.824(6) |
| Os(2)–P(2) | 2.352(2) | P(1)–C(121) | 1.827(6) |
| Os(3)–C(2) | 1.89(1) | P(1)–C(131) | 1.832(6) |
| Os(3)–C(7) | 1.92(1) | P(2)–C(211) | 1.835(6) |
| Os(3)–C(8) | 1.88(1) | P(2)–C(221) | 1.824(5) |
| Ni–C(1) | 1.83(1) | P(2)–C(231) | 1.839(7) |
| Ni–C(3) | 1.92(1) | μ-H(1)–Os(2) | 1.813 [c] |
| Ni–P(1) | 2.198(3) | μ-H(1)–Os(3) | 1.825 [c] |
| C(1)–O(1) | 1.16(1) | μ-H(2)–Os(3) | 1.786 [c] |
| C(2)–O(2) | 1.15(1) | μ-H(2)–Ni | 1.750 [c] |

(*b*) Angles [d]

(*i*) About Os(1)

| | | | |
|---|---|---|---|
| Os(3)–Os(1)–Os(2) | 62.7(1) | C(6)–Os(1)–Os(3) | 102.9(3) |
| Os(2)–Os(1)–Ni | 58.2(1) | C(6)–Os(1)–Ni | 104.0(3) |
| Os(3)–Os(1)–Ni | 59.6(1) | C(6)–Os(1)–C(1) | 88.7(4) |
| C(1)–Os(1)–Os(2) | 82.6(2) | C(6)–Os(1)–C(5) | 92.7(4) |
| C(1)–Os(1)–Os(3) | 103.0(2) | C(10)–Os(1)–Os(2) | 96.3(3) |
| C(1)–Os(1)–Ni | 44.0(2) | C(10)–Os(1)–Os(3) | 157.5(3) |
| C(5)–Os(1)–Os(2) | 98.2(3) | C(10)–Os(1)–Ni | 117.9(3) |
| C(5)–Os(1)–Os(3) | 83.9(3) | C(10)–Os(1)–C(1) | 80.7(4) |
| C(5)–Os(1)–Ni | 142.2(3) | C(10)–Os(1)–C(5) | 91.7(4) |
| C(5)–Os(1)–C(1) | 172.4(4) | C(10)–Os(1)–C(6) | 99.3(4) |
| C(6)–Os(1)–Os(2) | 160.7(3) | | |

(*ii*) About Os(2)

| | | | |
|---|---|---|---|
| Os(3)–Os(2)–Os(1) | 58.9(1) | C(9)–Os(2)–Os(3) | 150.3(3) |
| Ni–Os(2)–Os(1) | 56.1(1) | C(9)–Os(2)–Ni | 100.7(3) |
| Ni–Os(2)–Os(3) | 57.5(1) | C(9)–Os(2)–C(3) | 84.9(4) |
| C(3)–Os(2)–Os(1) | 99.1(2) | C(9)–Os(2)–C(4) | 92.3(4) |
| C(3)–Os(2)–Os(3) | 90.7(2) | P(2)–Os(2)–Os(1) | 168.2(1) |
| C(3)–Os(2)–Ni | 45.6(2) | P(2)–Os(2)–Os(3) | 112.3(1) |
| C(4)–Os(2)–Os(1) | 80.2(3) | P(2)–Os(2)–Ni | 127.8(1) |
| C(4)–Os(2)–Os(3) | 91.4(2) | P(2)–Os(2)–C(3) | 88.4(2) |
| C(4)–Os(2)–Ni | 134.6(2) | P(2)–Os(2)–C(4) | 92.7(3) |
| C(4)–Os(2)–C(3) | 177.1(4) | P(2)–Os(2)–C(9) | 97.0(3) |
| C(9)–Os(2)–Os(1) | 92.7(3) | | |

(*iii*) About Os(3)

| | | | |
|---|---|---|---|
| Os(2)–Os(3)–Os(1) | 58.4(1) | C(7)–Os(3)–Ni | 147.6(3) |
| Ni–Os(3)–Os(1) | 55.3(1) | C(7)–Os(3)–C(2) | 94.6(4) |
| Ni–Os(3)–Os(2) | 55.4(1) | C(8)–Os(3)–Os(1) | 170.4(3) |
| C(2)–Os(3)–Os(1) | 88.9(3) | C(8)–Os(3)–Os(2) | 114.4(3) |
| C(2)–Os(3)–Os(2) | 145.7(3) | C(8)–Os(3)–Ni | 115.9(3) |
| C(2)–Os(3)–Ni | 98.9(3) | C(8)–Os(3)–C(2) | 96.7(4) |
| C(7)–Os(3)–Os(2) | 96.0(3) | C(8)–Os(3)–C(7) | 91.4(4) |
| C(7)–Os(3)–Os(2) | 98.6(3) | | |

(*iv*) About Ni

| | | | |
|---|---|---|---|
| Os(1)–Ni–Os(2) | 65.7(1) | Os(3)–Ni–C(3) | 103.4(3) |
| Os(1)–Ni–Os(3) | 65.1(1) | C(1)–Ni–C(3) | 108.3(4) |
| Os(2)–Ni–Os(3) | 67.1(1) | Os(1)–Ni–P(1) | 142.0(1) |
| Os(1)–Ni–C(1) | 55.4(3) | Os(2)–Ni–P(1) | 150.0(1) |
| Os(2)–Ni–C(1) | 94.8(3) | Os(3)–Ni–P(1) | 127.8(1) |
| Os(3)–Ni–C(1) | 119.8(3) | C(1)–Ni–P(1) | 96.9(3) |
| Os(1)–Ni–C(3) | 114.6(3) | C(3)–Ni–P(1) | 97.7(3) |
| Os(2)–Ni–C(3) | 52.3(3) | | |

TABLE 2 (*continued*)

(*v*) About carbonyl carbon atoms

| | | | |
|---|---|---|---|
| Ni–C(1)–Os(1) | 80.7(4) | Os(2)–C(4)–O(4) | 178.1(7) |
| Ni–C(1)–O(1) | 141.7(9) | Os(1)–C(5)–O(5) | 175.6(8) |
| Os(1)–C(1)–O(1) | 137.5(8) | Os(1)–C(6)–O(6) | 178.6(9) |
| Os(3)–C(2)–O(2) | 179.1(9) | Os(3)–C(7)–O(7) | 175.4(8) |
| Ni–C(3)–Os(2) | 82.1(3) | Os(3)–C(8)–O(8) | 178.3(8) |
| Ni–C(3)–O(3) | 134.8(8) | Os(2)–C(9)–O(9) | 175.8(9) |
| Os(2)–C(3)–O(3) | 142.6(7) | Os(1)–C(10)–O(10) | 179.1(9) |

(*vi*) About P(1)

| | | | |
|---|---|---|---|
| Ni–P(1)–C(111) | 113.9(2) | C(121)–P(1)–C(111) | 103.0(3) |
| Ni–P(1)–C(121) | 113.6(2) | C(131)–P(1)–C(111) | 106.0(3) |
| Ni–P(1)–C(131) | 117.0(2) | C(131)–P(1)–C(121) | 101.6(3) |

(*vii*) About P(2)

| | | | |
|---|---|---|---|
| Os(2)–P(2)–C(211) | 118.2(2) | C(211)–P(2)–C(221) | 105.8(3) |
| Os(2)–P(2)–C(221) | 114.7(2) | C(221)–P(2)–C(231) | 105.0(3) |
| Os(2)–P(2)–C(231) | 110.8(2) | C(211)–P(2)–C(231) | 101.0(3) |

(*viii*) About point-of-contact phenyl carbon atoms

| | | | |
|---|---|---|---|
| C(112)–C(111)–P(1) | 120.3(4) | C(212)–C(211)–P(2) | 121.0(4) |
| C(116)–C(111)–P(1) | 119.6(4) | C(216)–C(211)–P(2) | 119.0(4) |
| C(122)–C(121)–P(1) | 118.6(4) | C(222)–C(221)–P(2) | 117.8(3) |
| C(126)–C(121)–P(1) | 121.2(4) | C(226)–C(221)–P(2) | 122.2(4) |
| C(132)–C(131)–P(1) | 122.9(4) | C(232)–C(231)–P(2) | 123.8(5) |
| C(136)–C(131)–P(1) | 116.9(5) | C(236)–C(231)–P(2) | 116.0(5) |

(*ix*) In solvent molecule [e]

| | | | |
|---|---|---|---|
| C(12)–O(11)–C(11) | 115(1) | H(1)–C(11)–H(2) | 110(2) |
| C(13)–C(12)–O(11) | 111(2) | O(11)–C(12)–H(3) | 109(2) |
| C(14)–C(11)–O(11) | 107(2) | O(11)–C(12)–H(4) | 109(2) |
| O(11)–C(11)–H(1) | 110(2) | H(3)–C(12)–H(4) | 109(3) |
| O(11)–C(11)–H(2) | 110(2) | | |

(*x*) Dihedral angles between the metal atoms

| | | | |
|---|---|---|---|
| Ni–Os(1)–Os(2)–Os(3) | 69.5 | Ni–Os(2)–Os(3)–Os(1) | 67.1 |
| Os(2)–Os(1)–Os(3)–Ni | 67.4 | Os(1)–Os(2)–Ni–Os(3) | 71.9 |
| Os(3)–Os(1)–Ni–Os(2) | 74.8 | Os(2)–Os(3)–Ni–Os(1) | 72.8 |

[a] The phenyl rings were refined as rigid hexagons with C–C = 1.395 Å and C–H = 1.08 Å. The $CH_3$ and $CH_2$ groups in the solvent molecule of ether were refined as rigid groups with C–H = 1.08 Å. [b] Solvent molecule. [c] No estimated standard deviations given since positional parameters of hydrido-ligands are unrefined. [d] The phenyl rings were refined as rigid hexagons, all internal C–C–C angles 120° and C–C–H angles 120°. [e] The positions of the hydrogen atoms in the $CH_3$ groups in the solvent molecule ether were refined as rigid groups with tetrahedral geometry, *i.e.* H–C–H angles are 109.5°.

The Ni–Os separations in (3) range from 2.605(1) to 2.733(1) Å. Comparisons with similar distances in other heteronuclear clusters of these metals are not possible since none has been prepared. However, a Ni–Os distance of 2.62 Å can be estimated from a mean Os radius of 1.44 Å deduced from a number of Os–Os single bonds[13] and a mean Ni radius of 1.18 Å inferred from average nickel–nickel distances found in $[\{Ni(CO)(\eta\text{-}C_5H_5)\}_2]$,[24] $[M_2Ni_3(CO)_{16}]^{2-}$ (M = Cr, Mo, or W) (ref. 25), and $[Ni_3(CO)_2(\eta\text{-}C_5H_5)_3]$.[26]

These results, and those reported earlier,[2] show that whereas both $[Ni(C_2H_4)(PPh_3)_2]$ and $[Pt(C_2H_4)(PPh_3)_2]$ react with $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ to give 60 valence electron clusters, the nickel compound (3) has a tetrahedral structure and the platinum complex (2) a $C_{2v}$ butterfly geometry. The latter customarily involves 62 cluster valence electrons,[27] as found in the anions $[Fe_4H(CO)_{13}]^-$ (ref. 28) and $[Re_4(CO)_{16}]^{2-}$ (ref. 29) which have $C_{2v}$ and $D_{2h}$ butterfly structures, respectively. Introduction of one platinum atom into the metal aggregate gives a total of 30 cluster valence molecular orbitals (c.v.m.o.) and six high-energy antibonding orbitals, thus requiring a 60-electron count, rather than the 62 needed for the 31 c.v.m.o. and five antibonding orbitals of the iron and rhenium species.[27] The conventional behaviour of the nickel complex (3) in adopting a $T_d$ structure can be correlated with the greater tendency of this metal in its mononuclear complexes to attain an 18-electron filled shell as contrasted with the 16-electron configuration of platinum in many of its compounds.

It was of interest to attempt the synthesis of a nickel analogue of the 58-electron platinum complex (1). Accordingly, the reaction between $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and $[Ni(cdt)(PPh_3)]$ (cdt = *trans*,*trans*,*trans*-cyclododeca-1,5,9-triene) [30] was investigated. However, the only product isolated was complex (3). Evidently any ' unsaturated ' nickeltriosmium cluster formed extracts a $PPh_3$ ligand so as to attain the more stable 60-electron configuration.

TABLE 3

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for $[Os_3Rh(\mu\text{-}H)_2(acac)(CO)_{10}]$ (4)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Os(1) | 0.235 65(5) | 0.433 36(4) | 0.798 86(3) |
| Os(2) | 0.414 46(5) | 0.232 90(4) | 0.813 88(3) |
| Os(3) | 0.084 32(5) | 0.123 51(4) | 0.834 05(3) |
| Rh | 0.250 8(1) | 0.220 69(8) | 0.637 28(6) |
| H(1) | 0.385 2 | 0.404 3 | 0.888 8 |
| H(2) | 0.040 1 | 0.294 4 | 0.810 7 |
| C(1) | 0.261 0(19) | −0.191 0(17) | 0.425 9(13) |
| C(2) | 0.197 0(10) | −0.088 6(12) | 0.501 1(9) |
| O(2) | 0.283 4(10) | 0.049 0(8) | 0.525 9(6) |
| C(02) | 0.052 0(18) | −0.158 3(13) | 0.539 0(8) |
| C(3) | −0.012 5(16) | −0.093 4(12) | 0.619 4(9) |
| O(3) | 0.056 3(10) | 0.048 6(8) | 0.671 9(6) |
| C(4) | −0.159 0(15) | −0.182 1(14) | 0.656 2(9) |
| C(01) | 0.416 4(14) | 0.367 5(13) | 0.611 9(9) |
| O(01) | 0.533 4(12) | 0.456 7(10) | 0.596 7(7) |
| C(11) | 0.098 5(16) | 0.486 7(13) | 0.707 1(9) |
| O(11) | 0.029 2(12) | 0.522 6(10) | 0.627 4(8) |
| C(12) | 0.418 4(13) | 0.597 5(12) | 0.784 0(9) |
| O(12) | 0.527 0(11) | 0.692 6(9) | 0.776 6(7) |
| C(13) | 0.184 8(17) | 0.550 4(11) | 0.918 2(9) |
| O(13) | 0.147 5(11) | 0.612 1(9) | 0.984 8(7) |
| C(21) | 0.476 1(13) | 0.194 4(12) | 0.937 8(8) |
| O(21) | 0.509 6(11) | 0.168 8(10) | 1.013 7(7) |
| C(22) | 0.424 3(12) | 0.041 1(13) | 0.742 1(9) |
| O(22) | 0.427 6(13) | −0.070 1(10) | 0.698 7(8) |
| C(23) | 0.633 0(18) | 0.353 9(13) | 0.801 8(9) |
| O(23) | 0.762 1(11) | 0.421 3(10) | 0.793 7(7) |
| C(31) | −0.146 4(13) | 0.069 3(13) | 0.850 6(9) |
| O(31) | −0.276 0(12) | 0.033 7(11) | 0.869 7(8) |
| C(32) | 0.130 5(12) | −0.057 2(12) | 0.852 0(9) |
| O(32) | 0.158 6(11) | −0.163 2(9) | 0.857 9(7) |
| C(33) | 0.136 8(12) | 0.209 2(12) | 0.971 0(8) |
| O(33) | 0.174 8(12) | 0.261 1(10) | 1.052 9(6) |
| Hydrogen atoms of the acac ligand | | | |
| H(11) | 0.371 1 | −0.123 2 | 0.403 8 |
| H(12) | 0.285 5 | −0.276 9 | 0.460 6 |
| H(13) | 0.171 5 | −0.245 0 | 0.360 7 |
| H(02) | 0.013 1 | −0.278 9 | 0.494 7 |
| H(41) | −0.187 2 | −0.110 3 | 0.718 5 |
| H(42) | −0.259 2 | −0.222 8 | 0.596 5 |
| H(43) | −0.137 7 | −0.277 5 | 0.680 5 |

Addition of a hexane solution of $[Rh(C_2H_4)_2(acac)]$ to $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ at room temperature affords the complex $[Os_3Rh(\mu\text{-}H)_2(acac)(CO)_{10}]$ (4) in high yield. The black crystals of (4) are reasonably stable in air but solutions in organic solvents are unstable. The spectroscopic properties of (4) were not especially informative in the context of assigning a molecular structure. The i.r. spectrum showed eight bands in the terminal carbonyl stretching region and a band at 1 597 $cm^{-1}$ assigned to C=O of the pentane-2,4-dionato-ligand. In the $^{13}C$ n.m.r. spectrum the appearance of 12 resonances in the low-field region (CO groups on Rh and Os, and in the acac) indicated that the molecule had little symmetry but since in the $^1H$ n.m.r. the two methyl groups gave one singlet resonance this suggested that these groups were equivalent. Two high-field signals ($\tau$ 20.10 and 25.55), broad at room temperature but sharp at −50 °C, indicated some fluxional behaviour but the absence of any $^{103}Rh$ coupling indicated strongly that the resonances are due to Os(μ-*H*)Os groups. The instability of (4) prevented measurement of n.m.r. spectra above ambient temperatures.

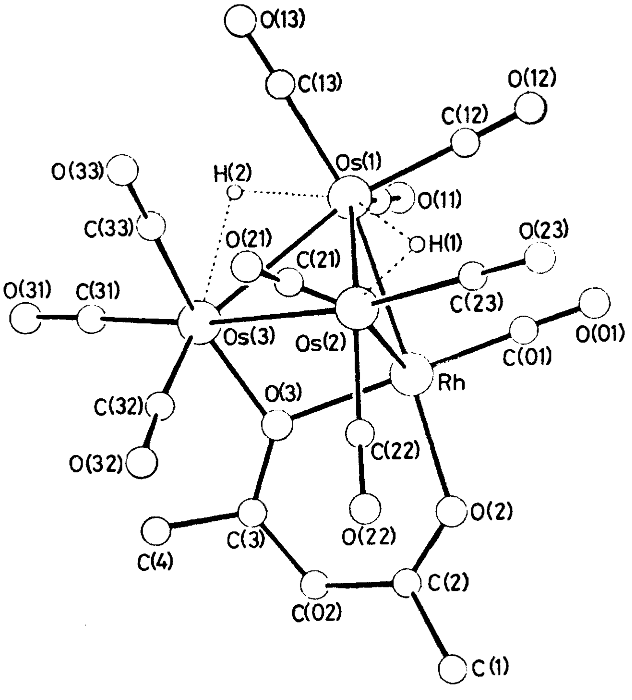


FIGURE 3 Molecular structure of (4), $[Os_3Rh(\mu\text{-}H)_2(acac)(CO)_{10}]$, showing the crystallographic numbering

An *X*-ray diffraction study was carried out on (4) with results summarised in Tables 3 and 4; the molecule is shown in Figure 3 with the atomic numbering scheme. The most striking feature is the bridging nature of the pentane-2,4-dionato-ligand which is thus functioning as a five-electron donor, for which there is precedent in such complexes as $[Co_4(acac)_8]$,[31] $[Ni_3(acac)_6]$,[32] and $[Ni_2(acac)_4(OAsPh_3)]$.[33]

With the bridging pentane-2,4-dionato-ligand donating five electrons, compound (4) is a 60 valence electron cluster. Notwithstanding this, the metal framework has a butterfly configuration with the dihedral angle between the planes Os(3)Os(1)Os(2) and RhOs(1)Os(2) being 85.7°, a 15° distortion from regular tetrahedral geometry. The separation of the Rh atom from Os(3) [3.292(2) Å] is very significantly larger than the other two Rh–Os distances [mean 2.717(2) Å]. This Os(3)–Rh separation, taken in conjunction with the approximate octahedral geometry about Os(3), suggests no direct Os(3)–Rh bond.

TABLE 4

Important interatomic distances (Å) and bond angles (°) for the complex [$Os_3Rh(\mu$-$H)_2(acac)(CO)_{10}$] (4) with estimated standard deviations in parentheses

(*a*) Distances

| | | | |
|---|---|---|---|
| Rh–Os(1) | 2.743(2) | C(1)–C(2) | 1.53(2) |
| Rh–Os(2) | 2.690(2) | C(2)–O(2) | 1.26(1) |
| Rh–Os(3) | 3.292(2) | C(2)–C(02) | 1.43(2) |
| Os(1)–Os(2) | 2.831(1) | C(02)–C(3) | 1.39(2) |
| Os(1)–Os(3) | 2.968(1) | C(3)–O(3) | 1.33(1) |
| Os(2)–Os(3) | 2.809(1) | C(3)–C(4) | 1.48(2) |
| Os(3)–O(3) | 2.173(8) | C(01)–O(01) | 1.17(1) |
| Rh–O(2) | 2.115(8) | C(11)–O(11) | 1.15(2) |
| Rh–O(3) | 2.115(7) | C(12)–O(12) | 1.12(1) |
| Rh–C(01) | 1.78(1) | C(13)–O(13) | 1.11(1) |
| Os(1)–C(11) | 1.92(1) | C(21)–O(21) | 1.15(2) |
| Os(1)–C(12) | 1.91(2) | C(22)–O(22) | 1.12(2) |
| Os(1)–C(13) | 1.96(1) | C(23)–O(23) | 1.14(2) |
| Os(2)–C(21) | 1.88(1) | C(31)–O(31) | 1.15(2) |
| Os(2)–C(22) | 1.93(1) | C(32)–O(32) | 1.13(2) |
| Os(2)–C(23) | 1.94(1) | C(33)–O(33) | 1.12(1) |
| Os(3)–C(31) | 1.96(1) | | |
| Os(3)–C(32) | 1.92(1) | | |
| Os(3)–C(33) | 1.86(1) | | |

(*b*) Angles

| | | | |
|---|---|---|---|
| Os(1)–Rh–Os(2) | 62.81(3) | O(2)–C(2)–C(1) | 116(1) |
| Os(1)–Rh–Os(3) | 58.08(2) | O(2)–C(2)–C(02) | 126(1) |
| Os(2)–Rh–Os(3) | 54.90(3) | C(2)–C(02)–C(3) | 127(1) |
| Rh–Os(1)–Os(2) | 57.68(3) | O(3)–C(3)–C(02) | 124(1) |
| Rh–Os(1)–Os(3) | 70.27(2) | O(3)–C(3)–C(4) | 115(1) |
| Rh–Os(2)–Os(3) | 73.52(3) | | |
| Os(1)–Os(2)–Os(3) | 63.51(2) | Rh–Os(1)–C(11) | 85.5(4) |
| Rh–Os(2)–Os(1) | 59.51(2) | Rh–Os(1)–C(12) | 98.2(4) |
| Rh–Os(3)–Os(1) | 51.66(2) | Os(1)–Rh–C(01) | 86.0(4) |
| Rh–Os(3)–Os(2) | 51.58(2) | Os(1)–Os(2)–C(23) | 103.1(4) |
| Os(2)–Os(1)–Os(3) | 57.88(2) | Os(1)–Os(2)–C(21) | 121.7(4) |
| Os(1)–Os(3)–Os(2) | 58.61(2) | Os(1)–Os(3)–C(31) | 115.7(4) |
| | | Os(1)–Os(3)–C(33) | 87.4(3) |
| Os(3)–O(3)–Rh | 100.3(3) | Os(2)–Os(1)–C(12) | 94.5(4) |
| Rh–O(3)–C(3) | 127.2(8) | Os(2)–Os(1)–C(13) | 121.5(4) |
| Os(3)–O(3)–C(3) | 126.5(7) | Os(2)–Os(3)–C(32) | 84.3(4) |
| Rh–O(2)–C(2) | 127.8(8) | Os(2)–Os(3)–C(33) | 88.6(4) |
| Os(3)–Os(1)–C(11) | 112.3(3) | Os(2)–C(21)–O(21) | 178.2(9) |
| Os(3)–Os(1)–C(13) | 98.7(3) | Os(2)–C(22)–O(22) | 179(1) |
| Os(3)–Os(2)–C(21) | 92.3(3) | Os(2)–C(23)–O(23) | 178(1) |
| Os(3)–Os(2)–C(22) | 95.2(4) | Os(3)–C(31)–O(31) | 173(3) |
| Os(2)–Rh–C(01) | 90.9(4) | Os(3)–C(32)–O(32) | 177(1) |
| Rh–Os(2)–C(22) | 81.5(4) | Os(3)–C(33)–O(33) | 177(1) |
| Rh–Os(2)–C(23) | 102.2(4) | | |
| Rh–C(01)–O(01) | 174(1) | | |
| Os(1)–C(11)–O(11) | 173(1) | | |
| Os(1)–C(12)–O(12) | 179(1) | | |
| Os(1)–C(13)–O(13) | 176(1) | | |

(*c*) Dihedral angles

| | | | |
|---|---|---|---|
| Os(3)–Os(1)–Os(2)–Rh | 85.7 | Os(1)–Os(2)–Os(3)–Rh | 63.7 |
| Rh–Os(1)–Os(3)–Os(2) | 63.6 | Os(3)–Os(2)–Rh–Os(1) | 68.6 |
| Os(2)–Os(1)–Rh–Os(3) | 63.8 | Os(1)–Os(3)–Rh–Os(2) | 77.3 |

There is evidence that the two hydrido-ligands bridge the edges Os(1)–Os(2) and Os(1)–Os(3). Although these ligands could not be located from electron-density difference syntheses, the corresponding osmium–osmium distances are longer than Os(2)–Os(3). Moreover, the hydrido-ligand positions are consistent with wider *cis*-Os–Os–CO angles (Table 4) associated with the bridged bonds Os(1)–Os(2) and Os(1)–Os(3), which have a mean value of 107° compared with a mean for the unbridged Os(2)–Os(3) bond of 90°.[19,20] Furthermore, when the molecule is viewed normal to the Os(2)–Os(3)–Rh plane with the Os(1) apex uppermost, it is seen that the Os(1)(CO)$_3$ group adopts a staggered configuration with respect to the edges of the tetrahedron which meet at Os(1). Such geometry is frequently indicative of the presence of edge-bridging hydrides.[19] Additionally, the hydrido-positions shown accord with calculations based on minima of potential energy,[23] and with the absence of any $^{1}$H–$^{103}$Rh coupling in the low-temperature $^{1}$H n.m.r. spectrum.

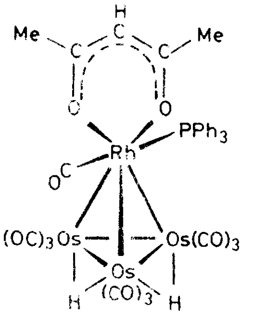
The bond lengthening of $\mu$-hydrido-ligands is generally *ca.* 0.1 Å.[19,34] The Os(1)–Os(3) distance of 2.968(1) Å in (4) compares well with that found for the Os($\mu$-H)Os linkage in [$Os_3H(\mu$-$H)(CO)_{11}$].[13,34] However, the Os(1)–Os(2) separation in (4) is only *ca.* 0.02 Å longer than the non-bridged distance Os(2)–Os(3). We suggest that the Os(1)–Os(2) bond has some multiple character, the inherent shortness being masked by the bridging hydrido-ligand. Complex (4) is formally unsaturated since a 62 valence electron configuration would be expected for a tetrametal species with a butterfly configuration.[27] In this context it is tempting to attribute the $^{1}$H n.m.r. resonance at $\tau$ 20.10 to the Os(1)($\mu$-H)Os(2) group because anomalously low shifts for $\mu$-hydrido-ligands in unsaturated complexes have been noted.[11,35] We have discussed [2] this phenomenon in relation to the complex [$Os_3Pt(\mu$-$H)_2(CO)_{10}\{P(cyclo$-$C_6H_{11})_3\}$]. In this unsaturated 58-electron tetrahedral complex the resonance for the Os($\mu$-H)Os group occurs at the relatively low value of $\tau$ 16.93 and the Os–Os internuclear distance [2.789(1) Å] is even shorter than the Os(1)–Os(2) distance in compound (4).

The carbonyl ligands in (4) are all terminal as expected from the spectroscopic evidence, and there are no notable deviations from linearity. As in related reactions [1,2] with [$Os_3(\mu$-$H)_2(CO)_{10}$], a CO group has been transferred from the triosmium compound to the attacking nucleophilic metal centre, in this case rhodium. The Rh(acac) fragment is close to planar; the Rh atom lies 0.08 Å from the plane, opposite to Os(3), which is 1.42 Å from the plane defined by the ligand ring atoms. The atom O(3) is not far (*ca.* 0.06 Å) from being equidistant from Os(3) and the rhodium atom. The C(2)–O(2) bond [1.26(1) Å] is distinctly shorter than C(3)–O(3) [1.33(1) Å], the latter distance being the same as the corresponding bond length in [$Ni_3(acac)_6$].[32]

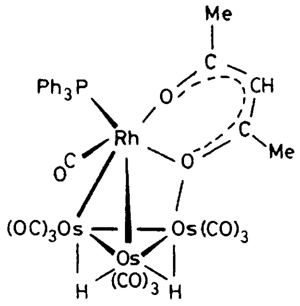
The lack of any symmetry element in compound (4) indicates that the apparent equivalence of the $^{1}$H signals for the Me groups is fortuitous. The assignment of the $^{13}$C n.m.r. spectrum of (4) on the basis of the observed structure is difficult. The structure would predict nine resonances for CO ligands bonded to osmium, two signals for the CO groups of the acac ligand, and one resonance for the RhCO group which should appear as a doublet with $J(^{103}$Rh–$^{13}$C) in the range 40—80 Hz.[36] In the spectrum of [Rh(acac)$(CO)_2$] resonances occur at $\delta$ 187.1 and 183.5 p.p.m. [$J(^{103}Rh-^{13}C)$ 73 Hz]; the former signal can thus be assigned to the keto-groups of the pentane-2,4-dionato-ligand and the latter to the rhodium-bound carbonyl ligands. The spectrum of (4), as mentioned above, has 12 low-field resonances. Although two of these signals at 191.7 and 188.7 p.p.m. are indeed separated by 76 Hz the variable intensities of all the bands as well as the similarity of chemical shifts between OsCO and RhCO groups precludes definitive assignments.

The formally ' unsaturated ' nature of (4) as revealed by the *X*-ray crystallographic study suggested that it would react readily with electron-pair donor molecules as do the unsaturated cluster complexes [$Os_3Pt(\mu-H)_2(CO)_{10}(PR_3)$].[2] Carbon monoxide gas reacted instantly with (4). However, the products proved to be [Rh(acac)$(CO)_2$][5] and [$Os_3H(\mu-H)(CO)_{11}$].[37,38] A similar degradation with CO occurs with the 56-electron cluster [$Re_4(\mu-H)_4(CO)_{12}$] which produces mononuclear [$ReH(CO)_5$] and trinuclear [$Re_3(\mu-H)_3(CO)_{12}$] as the main products.[39]

The reaction of (4) with triphenylphosphine was next investigated and found to afford an unstable complex [$Os_3Rh(\mu-H)_2$(acac)$(CO)_{10}(PPh_3)$] (5). Unfortunately it was impossible to prepare samples of this compound for n.m.r. studies which did not show signals due to the presence of impurities. Spectroscopic studies were carried out at low temperatures to minimise decomposition. The $^1H$ n.m.r. spectrum showed methyl group signals at $\tau$ 8.34 and 8.60. Two high-field doublets were also observed at $\tau$ 21.61 [$J$(PH) 3 Hz] and 26.01 [$J$(PH) 7 Hz], the absence of $^{103}Rh$ coupling indicating that the Os($\mu$-H)Os groups are preserved. Confirmation that these small couplings were due to a $^{31}P$ nucleus rather than $^{103}Rh$ was obtained by a $^1H$ selectively-decoupled $^{31}P$ n.m.r. spectrum (−70 °C) which revealed a doublet of doublets of doublets at $\delta$ −0.6 p.p.m. [$J$(PH) 6 and 2, $J$(RhP) 104 Hz], the hydrido-ligand couplings being poorly resolved. A broad band decoupled $^{31}P$ spectrum showed only the $^{103}Rh$ coupling. The magnitude of this coupling indicates that the $PPh_3$ group is bonded to the rhodium. This result is rather surprising since, as mentioned above, it was thought that the unsaturation of (4) was associated with Os(1)–Os(2). Structural analysis of the phosphine adducts of the 58-electron complexes [$Os_3Pt(\mu-H)_2(CO)_{10}(PR_3)$] revealed[1] that in the products [$Os_3Pt(\mu-H)_2(CO)_{10}(PR_3)_2$] the second phosphine ligand was co-ordinated to one of the osmium atoms. In the monophosphine triosmiumplatinum species some multiplicity of one of the osmium–osmium bonds was suspected.



(5a)



(5b)

The spectral data for (5) cannot fully characterise the complex structurally. Either a 60-electron tetrahedral cluster with a non-bridging pentane-2,4-dionato-ligand (5a), or a 62-electron butterfly complex with a bridging ligand (5b) seems likely. We consider (5b) the more probable in view of the established structure for (4).

## EXPERIMENTAL

The instrumentation and synthetic methods used have been described earlier.[2] Infrared measurements were made on cyclohexane solutions, and [$^2H_1$]chloroform was used as solvent for n.m.r. studies.

*Synthesis of the Compound* [$NiOs_3(\mu-H)_2(CO)_{10}(PPh_3)_2$].—To a stirred solution of [$Os_3(\mu-H)_2(CO)_{10}$] (0.85 g, 1 mmol) in diethyl ether (80 cm$^3$) was added a filtered solution of [$Ni(C_2H_4)(PPh_3)_2$] (0.64 g, 1 mmol). Stirring was continued overnight and concentration *in vacuo* gave bright orange *microcrystals* of [$NiOs_3(\mu-H)_2(CO)_{10}(PPh_3)_2$] (3) (1.3 g, 93%) (Found: C, 38.3; H, 2.4. $C_{46}H_{32}NiO_{10}Os_3P_2$ requires C, 38.4; H, 2.5%), m.p. 135—140 °C (decomp.), $\nu_{max.}$ at 2 073s, 2 065m(sh), 2 037vs, 2 015s, 1 999m(sh), 1 985m(sh), 1 973m, 1 855w, and 1 821w cm$^{-1}$. N.m.r.: $^1H$, $\tau$ 2.62 (m, 30 H, Ph), 23.64 [s, 1 H, Ni($\mu$-H)Os, $J$(PH) 16] and 30.20 [d, 1 H, Os($\mu$-H)Os, $J$(PH) 12 Hz]; $^{31}P$ ($^1H$ decoupled), $\delta$ −63.7 [d, PNi, $J$(PP) 7] and −2.6 p.p.m. [d, POs, $J$(PP) 6 Hz]; $^{31}P$ ($^1H$ selectively decoupled), $\delta$ −63.7 [d of d, PNi, $J$(PH) 15, $J$(PP) 7] and −2.7 p.p.m. [d of d, POs, $J$(PH) 10, $J$(PP) 7 Hz]; $^{13}C$ {in presence of [$Cr(acac)_3$]}, $\delta$ 219.7 [s,br, Ni($\mu$-*C*O)Os], 182.8, 181.8, 179.3, 178.4, 175.4, 171.7 and 170.2 (Os*C*O), 135.0, 134.1, 133.6, 133.4, 133.1, 131.4, 130.4, 128.7 and 128.3 p.p.m. (Ph); $^{13}C$ {−60 °C, in presence of [$Cr(acac)_3$]}, $\delta$ 220.1, 214.5 [s, Ni($\mu$-*C*O)Os], 183.6, 181.6, 180.0, 177.5, 175.4, 174.7, 170.9, 170.2 (s, Os*C*O), 128—133 p.p.m. (Ph).

*Synthesis of the Compound* [$Os_3Rh(\mu-H)_2$(acac)$(CO)_{10}$].—To a solution of [$Os_3(\mu-H)_2(CO)_{10}$] (0.5 g, 0.6 mmol) in hexane (50 cm$^3$) was added a previously filtered solution of [Rh(acac)$(C_2H_4)_2$] (0.15 g, 0.6 mmol) in hexane (10 cm$^3$). The mixture was allowed to stand at room temperature (0.5 h) depositing black *crystals* of [$Os_3Rh(\mu-H)_2$(acac)$(CO)_{10}$] (4) (0.46 g, 75%), washed with light petroleum (3 × 5 cm$^3$) and dried *in vacuo* (Found: C, 17.0; H, 0.9. $C_{15}H_9O_{12}Os_3Rh$ requires C, 17.0; H, 0.9%), m.p. 130—134 °C (decomp.), $\nu_{max.}$ at 2 091w, 2 072s, 2 045s, 1 997s, 1 987m(sh), 1 979w, 1 973w, 1 969m, and 1 597w(br) cm$^{-1}$. N.m.r.: $^1H$, $\tau$ 4.50 (s, 1 H, CH), 7.96 (s, 6 H, Me), 20.10 [s, 1 H, Os($\mu$-H)Os], and 25.55 [s, 1 H, Os($\mu$-H)Os]; $^{13}C$ {$^1H$ decoupled, in presence of [$Cr(acac)_3$]}, $\delta$ 191.7, 188.7, 187.1, 183.1, 179.3, 177.9, 176.3, 175.0, 172.9, 171.3, 170.7, 167.4 (CO groups on Os, Rh and in acac), 103.5 (CH), and 28.6 p.p.m. (Me).

*Preparation of* [$Os_3Rh(\mu-H)_2$(acac)$(CO)_{10}(PPh_3)$].—To a stirred solution of (4) (0.52 g, 0.5 mmol) in diethyl ether (30 cm$^3$) at −20 °C was added $PPh_3$ (0.13 g, 0.5 mmol).

The red solution was filtered immediately and the volume reduced *in vacuo* to *ca.* 10 cm$^3$. Cooling slowly to −70 °C gave red *crystals* of [$Os_3Rh(\mu$-$H)_2(acac)(CO)_{10}(PPh_3)$] (5) (0.35 g, 52% yield) (Found: C, 29.7; H, 2.3. $C_{33}H_{24}O_{12}Os_3PRh$ requires C, 30.1; H, 2.3%), m.p. 68—72 °C, $\nu_{max.}$ at 2 085m, 2 061s, 1 997s, 1 989w(sh), 1 981w, 1 969m, 1 961w, and 1 621w(br) cm$^{-1}$. N.m.r.: $^1H$ (−30 °C), $\tau$ 2.68 (m, 15 H, Ph), 5.66 (s, 1 H, CH), 8.34 and 8.60 (s, 3 H, Me), 21.61 [d, 1 H, Os($\mu$-H)Os, *J*(PH) 3], and 26.01 [d, 1 H, Os($\mu$-H)Os, *J*(PH) 7 Hz]; $^{31}P$ ($^1H$ decoupled, at −70 °C in [$^2H_8$]toluene), $\delta$ −0.6 p.p.m. [d, PRh, *J*(RhP) 104 Hz] {impurity peak, $\delta$ 6.5 p.p.m. [d, PRh, *J*(RhP) 100 Hz]}; $^{31}P$ (selectively $^1H$ decoupled, −70 °C), $\delta$ −0.6 p.p.m. [d of d of d, PRh, *J*(RhP) 104, *J*(PH) 2 and 6 Hz] {impurity peak, $\delta$ 6.5 p.p.m. [d of d, PRh, *J*(RhP) 100, *J*(PH) 3 Hz]}.

*Crystal Structure Determinations*.—(*a*) [$NiOs_3(\mu$-$H)_2(CO)_{10}(PPh_3)_2$] (3). Crystals of (3) grow as clear orange parallelepipeds from solution in diethyl ether. Diffracted intensities were collected at low temperature (*ca.* 190 K) from a crystal of dimensions 0.40 × 0.35 × 0.15 mm on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[40,41] Of the total 8 595 independent reflections measured for $2.9 \leqslant 2\theta \leqslant 55.0°$, 6 941 satisfied the criterion $F \geqslant 6.0\sigma(F)$, equivalent to $I \geqslant 2.78\sigma(I)$, and only these were used in the solution and refinement of the structure. Two reflections (3 $\bar{3}$ 5 and 0 0 4) were remeasured every 50 observations and indicated crystal decay of *ca.* 1% during the 259 h of exposure to *X*-rays. The intensities were corrected for Lorentz, polarisation, crystal decay, and *X*-ray absorption effects, and all computations were carried out on the South Western Universities' Computer Network with the 'SHELX' system of programs.[42]

*Crystal data for* (3). $C_{46}H_{32}NiO_{10}Os_3P_2 \cdot C_4H_{10}O$, $M$ = 1 451.3, Monoclinic, $a$ = 15.579(6), $b$ = 17.205(4), $c$ = 18.976(5) Å, $\beta$ = 99.97(3)°, $D_m$ not measured, $Z$ = 4, $D_c$ = 1.93 g cm$^{-3}$, $U$ = 5 010.1 Å$^3$, $F(000)$ = 2 863, space group $P2_1/n$, Mo-$K_\alpha$ $X$ radiation (graphite monochromator), $\lambda$ = 0.710 69 Å, $\mu$(Mo-$K_\alpha$) = 85.5 cm$^{-1}$.

*Structure solution and refinement for* (3). The structure was solved by heavy-atom methods, but after location of all expected non-hydrogen atoms for (3) there remained on the electron-density difference maps peaks which could be attributed to the presence in the crystal of a molecule of solvent (diethyl ether). The hydrogen atoms, with the exception of the two bridging hydrido-ligands, were incorporated into rigid-group refinement: for the aryl groups of the phosphine ligands, with C–C = 1.395 and C–H = 1.08 Å; for the $CH_3$ and $CH_2$ groups of the solvent molecule, with C–H = 1.08 Å. Individual isotropic thermal parameters were ascribed to the carbon atoms of the aryl groups and of the solvent molecule; one common isotropic thermal parameter was used for the hydrogen atoms of all the aryl groups, another common parameter for those of the solvent, and individual parameters for the bridging hydrides. All other atoms were allowed anisotropic motion. Refinement was by blocked-matrix least squares, with an optimised weighting scheme of the form: $w = 0.924\,7[\sigma^2(F) + 0.000\,17|F|^2]^{-1}$, where $\sigma(F)$ is the estimated error in $|F_{obs.}|$ based on counting statistics only. Convergence was reached at $R$ 0.038 ($R'$ 0.042) and the final electron-density difference synthesis showed no peaks >0.4 or < −0.5 e Å$^{-3}$ except for one peak of 0.8 e Å$^{-3}$ in the vicinity of one of the osmium atoms. The hydrido-ligands were located by means of potential-energy calculations[23] and the positions so derived were kept invariant during refinement. The high thermal parameters of the atoms of the solvent molecule (despite low-temperature data collection) are not unusual, and can be ascribed to the weakness of the van der Waals forces which hold such molecules in a crystal. Atomic scattering factors were those of ref. 43 for hydrogen and ref. 44 for all other atoms. Corrections for the real and imaginary parts of anomalous scattering were applied for the metal atoms only.[45]

(*b*) [$Os_3Rh(\mu$-$H)_2(acac)(CO)_{10}$] (4). Crystals of (4) grow readily as large black prisms. Because of very high *X*-ray absorption [$\mu$(Mo-$K_\alpha$) = 199.5 cm$^{-1}$] a small fragment cut from a larger crystal was used for collection of intensity data, *ca.* 0.20 × 0.15 × 0.20 mm. Conditions were the same as for (3) except the following: total number of independent reflections measured, 5 361; number with $I \geqslant 2.5\sigma(I)$, 4 240, and only these were used for refinement; there was no significant crystal decay during the 142 h of exposure to *X*-rays; a numerical correction for *X*-ray absorption was applied,[46] using conjectural crystal 'faces', and this gave transmission factors $A^*$ in the range 13.8—42.6. Computations were carried out at the University of London Computer Centre with the '*X*-Ray' system of programs.[46]

*Crystal data for* (4). $C_{15}H_9O_{12}Os_3Rh$, $M$ = 1 054.7, Triclinic, $a$ = 8.759(3), $b$ = 9.463(2), $c$ = 13.680(4) Å, $\alpha$ = 100.59(2), $\beta$ = 93.86(2), $\gamma$ = 107.84(2)°, $D_m$ not measured, $Z$ = 2, $D_c$ = 3.34 g cm$^{-3}$, $U$ = 1 052(1) Å$^3$, $F(000)$ = 934, space group $P\bar{1}$ (no. 2), Mo-$K_\alpha$ $X$-radiation, $\lambda$ = 0.710 69 Å, $\mu$(Mo-$K_\alpha$) = 199.5 cm$^{-1}$.

*Structure solution and refinement for* (4). A Patterson synthesis showed three strong Os–Os and three medium Os–Rh vectors which could be rationalised to give an irregular tetrahedron. Successive electron-density difference syntheses served to locate the remainder of the molecule including most of the hydrogen atoms. The two bridging hydrido-ligands, however, were located by potential-energy calculations[23] with restrictions of the metal–hydrogen distance to 1.85 Å; the positional co-ordinates so derived have been included in Table 3. Anisotropic thermal parameters were ascribed to all non-hydrogen atoms, but, for reasons which are not wholly clear, the thermal parameters of some of the lighter (mainly carbon) atoms tended to become non-positive definite, and were therefore held fixed. Otherwise refinement proceeded by blocked-matrix least squares, with weights $w = 1/\sigma^2(F_o)$; convergence was reached at $R$ 0.052 ($R'$ 0.059). All other conditions were as for (3). For both structures, observed and calculated structure factors, and all thermal parameters are listed in Supplementary Publication No. SUP 22900 (43 pp).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

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