# *X*-Ray Structure Analysis of the Salts $[N(PPh_3)_2][M_4H_3(CO)_{12}]$ (M = Ru or Os);† Confirmation of the Existence of Discrete Structural Isomers for a Hydrido–Carbonyl Cluster in the Solid State

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*X*-Ray analysis has shown that the salt $[N(PPh_3)_2][Ru_4H_3(CO)_{12}]$ crystallizes in two forms, (**1**) and (**2**), which correspond to two different structural isomers (tautomers) of the anion. These have overall geometries of virtual $C_2$ [(**1**)] and $C_{3v}$ [(**2**)] symmetry, and provide the first confirmation of the existence of such isomers in the solid state. Crystals of (**1**) and (**2**) are triclinic, space group $P\bar{1}$. For (**1**), $a$ = 17.361(4), $b$ = 11.735(2), $c$ = 12.321(2) Å, $\alpha$ = 94.61(2), $\beta$ = 98.44(2), $\gamma$ = 88.52(2)°, $Z$ = 2; refinement of atomic parameters using 7 210 data converged at $R$ = 0.0473. For (**2**), $a$ = 15.608(3), $b$ = 15.370(3), $c$ = 11.219(2) Å, $\alpha$ = 99.26(2), $\beta$ = 103.27(2), $\gamma$ = 105.72(2)°, $Z$ = 2; refinement of atomic parameters using 10 945 data converged at $R$ = 0.0432. Although three crystalline modifications, (**3**), (**4**), and (**5**), of the corresponding salt $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$ were isolated, *X*-ray analysis has shown that in all three the same isomer of the monoanion, of virtual $C_2$ symmetry, is present. Crystals of the osmium salt (**3**), which are isomorphous with those of the ruthenium salt (**1**), are triclinic, space group $P\bar{1}$, $a$ = 17.378(4), $b$ = 11.691(2), $c$ = 12.308(2) Å, $\alpha$ = 94.40(2), $\beta$ = 98.62(2), $\gamma$ = 88.41(2)°, $Z$ = 2. Modification (**4**) crystallizes as a $0.5CH_2Cl_2$ solvate, orthorhombic, space group $Pna2_1$, $a$ = 17.648(4), $b$ = 19.597(4), $c$ = 15.429(3) Å, $Z$ = 4. Modification (**5**) is monoclinic, space group $P2_1/c$, $a$ = 11.683(2), $b$ = 28.976(4), $c$ = 14.733(3) Å, $\beta$ = 100.13(2)°, $Z$ = 4. Complete structure analysis was carried out for modification (**4**) only, for which refinement of atomic parameters using 3 347 data converged at $R$ = 0.0426.

The structures of tetranuclear metal hydrido–carbonyls and their derivatives have been widely studied. Interest in them arises from the diversity of their reactions and the range of catalytic processes in which they are implicated. For example it is well established that solutions of $[Ru_4H_4(CO)_{12}]$ act as powerful catalysts for olefin hydrogenation.[1,2] Although the exact nature of the active catalytic species in these processes has not yet been established it appears that the tetranuclear metal cores provide the catalytic sites.[3] Early work indicated that the two neutral tetrahydrido species $[M_4H_4(CO)_{12}]$ (M = Ru or Os) may exist as more than one isomer in solution.[3,4] However, in the solid state, in each case only one isomeric form has been observed with four edge-bridging hydrogen ligands and $D_{2d}$ symmetry of the $M_4H_4$ core.[5,6] The $^1$H n.m.r. spectra of the related monoanions $[M_4H_3(CO)_{12}]^-$ show that two structural isomers, one having $C_2$ symmetry and the second $C_{3v}$ symmetry, are present in solution for both ruthenium[7] and osmium.[8] This work presents details of the *X*-ray analysis of two forms of $[N(PPh_3)_2][Ru_4H_3(CO)_{12}]$, which gave the first confirmation in the solid state of isomers in which two cluster species differ only in the distribution of the hydrogen ligands.[9] Examples of this type of isomerism in the solid state are still very rare, although there are several examples of cluster isomers which differ in the distributions of other types of ligands. The recent *X*-ray structure analysis of two isomeric forms of $[Os_3Pt(\mu\text{-}H)_2(\mu\text{-}CH_2)(CO)_{10}\{P(cyclo\text{-}C_6H_{11})_3\}]$ shows that they are isomers differing not only in the relative conformation of the organophosphine and carbonyl ligands but also in the distribution of the two hydrido ligands which bridge an Os–Os and an Os–Pt bond in one case and two Os–Os bonds in the other.[10]

Since the preliminary results in 1978 which characterized the $C_2$ and $C_{3v}$ isomers of $[Rh_4H_3(CO)_{12}]^-$ as their $[N(PPh_3)_2]^+$ salts,[9] many samples of crystals of the $[Os_4H_3(CO)_{12}]^-$ salt, obtained during studies of high-nuclearity species of osmium, have been examined crystallographically. In the course of this screening three different crystalline modifications of $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$, (**3**), (**4**), and (**5**), have been characterized. Remarkably, in all three modifications the same isomer of the monoanion $[Os_4H_3(CO)_{12}]^-$ is present, that of virtual $C_2$ symmetry. The details of the structure analyses of the $[N(PPh_3)_2]^+$ salts of the $C_2$ and $C_{3v}$ isomers of the monoanion $[Ru_4H_3(CO)_{12}]^-$, (**1**) and (**2**), and the $C_2$ isomer of $[Os_4H_3(CO)_{12}]^-$ present in (**4**) are reported here.

## Results and Discussion

The *X*-ray analysis of the $[N(PPh_3)_2][Ru_4H_3(CO)_{12}]$ salt shows that modification (**1**) has the monoanion of virtual $C_2$ symmetry shown in Figure 1(*a*) and (*b*), and modification (**2**) has the monoanion of virtual $C_{3v}$ symmetry shown in Figure 2(*a*) and (*b*). The first crystalline modification of the salt $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$, (**3**), is isomorphous with the ruthenium salt (**1**), as can be seen by comparison of the unit-cell dimensions given in Table 1. The monoanion in this osmium salt is therefore the isomer of $C_2$ symmetry, and as the structure of this isomer has already been reported[11] as its $[NMe_4]^+$ salt the crystal has not been studied further.

The second crystalline modification of the osmium salt (**4**) was originally identified in the same batch of crystals that gave

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† Bis(triphenylphosphine)iminium 1,1,1,2,2,2,3,3,3,4,4,4-dodecarbonyl-1,2;1,4;2,3-tri-μ-hydrido-*tetrahedro*-tetraruthenate (6 *Ru–Ru*) and -tetraosmate (6 *Os–Os*).

*Supplementary data available* (No. SUP 56542, 19 pp.): cation atomic co-ordinates, thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

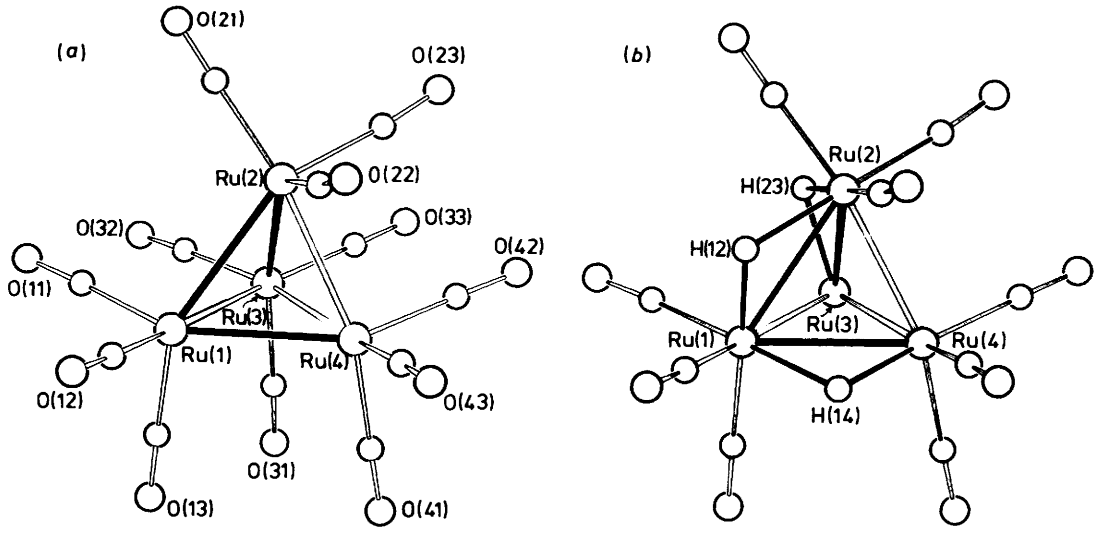

**Figure 1.** The isomer of $[Ru_4H_3(CO)_{12}]^-$ of virtual $C_2$ symmetry, (**1**): (*a*) overall molecular structure; (*b*) distribution of the hydrogen atoms which bridge the solid Ru–Ru bonds. Only the major component of disorder (A) is illustrated; in (*b*) the CO ligands attached to Ru(3) have been omitted for clarity. The carbonyl C atoms have the same numbering as the O atoms to which they are attached. The virtual $C_2$ axis passes through H(12) and the mid-points of Ru(2)–Ru(1) and of Ru(3)–Ru(4)

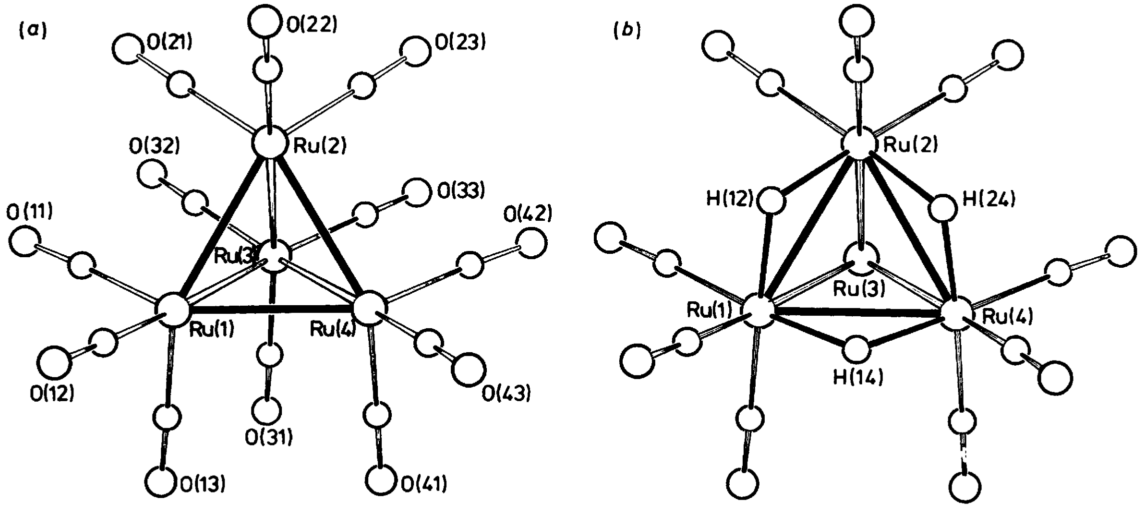

**Figure 2.** The isomer of $[Ru_4H_3(CO)_{12}]^-$ of virtual $C_{3v}$ symmetry, (**2**): (*a*) overall molecular structure; (*b*) distribution of hydrogen atoms which bridge the solid Ru–Ru bonds. The carbonyl C atoms have the same numbering as the O atoms to which they are attached; in (*b*) the CO ligands attached to Ru(3) have been omitted for clarity

the first modification (**3**). These crystals were orthorhombic, and it seemed probable from the results obtained with the ruthenium salt, that these would contain a second isomeric form of $[Os_4H_3(CO)_{12}]^-$. Full structure analysis of this modification once more revealed that the $[Os_4H_3(CO)_{12}]^-$ monoanion was present in (**4**) as the isomer of $C_2$ symmetry with the structure shown in Figure 3.

The third modification of $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$, (**5**), was obtained at a much later stage. This was monoclinic (Table 1) unlike the earlier crystals (**3**) and (**4**), but a partial structure analysis revealed the characteristic M–M bond pattern previously established for the monoanion isomer of $C_2$ symmetry, so no further work was done on this structure. This was particularly disappointing because although the isomers of $[Os_4H_3(CO)_{12}]^-$ in solution have the same symmetries ($C_2$ and $C_{3v}$) as the ruthenium monoanions, $^{187}Os$–$^{1}H$ n.m.r. studies have shown that the osmium isomer of $C_{3v}$ symmetry has a structure unlike the solid-state structure of the ruthenium isomer, the former having each H atom bonded to Os atoms in different environments.[12]

It can be seen in Figures 1—3 that in all the monoanions characterized each metal atom is co-ordinated to three terminal carbonyl ligands with the $M(CO)_3$ units adopting staggered conformations relative to the three adjacent M–M bonds. This arrangement is usually observed when edge-bridging hydrogen ligands are present. In contrast, in $[Re_4H_4(CO)_{12}]$ where the hydrides bridge the four faces of the $Re_4$ tetrahedron, the carbonyls adopt an eclipsed configuration.[13]

In the isomers of the monoanion $[M_4H_3(CO)_{12}]^-$ (M = Ru or Os) with $C_2$ symmetry (Figures 1 and 3) three tetrahedral edges, M(1)–M(2), M(1)–M(4), and M(2)–M(3), are significantly longer [mean Ru–Ru 2.922(1), mean Os–Os 2.944(1) Å] than the others [mean Ru–Ru 2.802(1), mean Os–Os 2.816(1) Å], which is consistent with these longer edges being bridged by μ-H ligands. This was confirmed for the Ru monoanions, where the hydrogen atoms bridging these edges were located directly from

**Table 1.** Crystal data for the salts $[N(PPh_3)_2][M_4H_3(CO)_{12}]$ (M = Ru or Os)

| Compound | (1)<br>$C_{48}H_{33}NO_{12}P_2Ru_4$ | (2)<br>$C_{48}H_{33}NO_{12}P_2Ru_4$ | (3)<br>$C_{48}H_{33}NO_{12}Os_4P_2$ | (4)<br>$C_{48}H_{33}NO_{12}Os_4P_2\cdot0.5CH_2Cl_2$ | (5)<br>$C_{48}H_{33}NO_{12}Os_4P_2$ |
|---|---|---|---|---|---|
| *M* | 1 282.0 | 1 282.0 | 1 638.5 | 1 681.0 | 1 638.5 |
| Crystal system | Triclinic | Triclinic | Triclinic | Orthorhombic | Monoclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $Pna2_1$ | $P2_1/c$ |
| $a$/Å | 17.361(4) | 15.608(3) | 17.378(4) | 17.648(4) | 11.683(2) |
| $b$/Å | 11.735(2) | 15.370(3) | 11.691(2) | 19.597(4) | 28.976(4) |
| $c$/Å | 12.321(2) | 11.219(2) | 12.308(2) | 15.429(3) | 14.733(3) |
| $\alpha$/° | 94.61(2) | 99.26(2) | 94.40(2) | 90 | 90 |
| $\beta$/° | 98.44(2) | 103.27(2) | 98.62(2) | 90 | 100.13(2) |
| $\gamma$/° | 88.52(2) | 105.72(2) | 88.41(2) | 90 | 90 |
| $U$/Å$^3$ | 2 474.7 | 2 449.0 | 2 491.4 | 5 336.1 | 4 909.8 |
| $F(000)$ | 1 260 | 1 260 | 1 516 | 3 116 | 3 032 |
| $Z$ | 2 | 2 | 2 | 4 | 4 |
| $D_c$/g cm$^{-3}$ | 1.72 | 1.74 | 2.18 | 2.09 | 2.21 |
| $\mu$(Mo-$K_\alpha$)/cm$^{-1}$ | 11.9 | 12.0 |  | 92.7 |  |

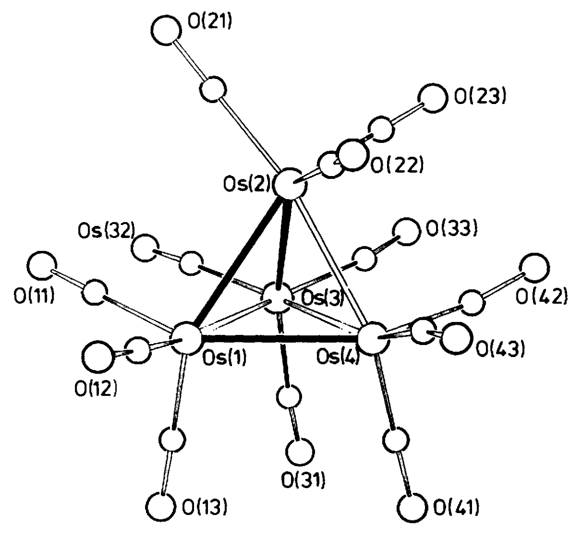

**Figure 3.** The structure of the anion in $[N(PPh_3)_2][Os_4H_3(CO)_{12}]\cdot0.5CH_2Cl_2$, (4). The anion has virtual $C_2$ symmetry, the $C_2$ axis passing through the mid-points of Os(1)–Os(2) and of Os(3)–Os(4). Solid Os–Os bonds are bridged by the hydrogen atoms; the carbonyl C atoms have the same numbering as the O atoms to which they are attached

the *X*-ray analysis and are shown in Figure 1(*b*). Although direct hydrogen location was not possible in the *X*-ray analysis of the osmium monoanion, the carbonyl ligands *cis* to the three long Os–Os bonds have very much larger Os–Os–C angles [mean 105(1)°] than those *cis* to the other Os–Os bonds [mean 93(1)°]; the widening of these angles supports the conclusion that the longer edges are bridged by the hydrogen atoms.

Comparison of Figures 1(*a*) and 3 show that the overall structures of the ruthenium and osmium monoanions of $C_2$ symmetry are very similar, and distinctly different from that of the ruthenium isomer of $C_{3v}$ symmetry shown in Figure 2(*a*). In this isomer (**2**) there are also three very long Ru–Ru bonds, in this case forming one triangular face Ru(1),Ru(2),Ru(4). These Ru–Ru distances are significantly longer [mean 2.937(1) Å] than the other Ru–Ru bonds in (**2**) [mean 2.787(1) Å]. The hydrogen atoms were located directly from the *X*-ray analysis, again bridging the long Ru–Ru bonds [Figure 2(*b*)].

In the isomer of $C_{3v}$ symmetry, (**2**), the Ru(μ-H)Ru bridges are symmetrical with Ru–H bond lengths in the range 1.80(4)—1.88(5) Å and are similar in that respect to those found, for example, in $[Ru_4H_4(CO)_{10}L]$[14] and $[Ru_4H_4(CO)_{10}(\mu\text{-}L)]$[15] [L = 1,2-bis(diphenylphosphino)ethane]. In the ruthenium isomer of $C_{3v}$ symmetry, (**2**), the hydride ligands H(12), H(14), and H(24) are coplanar to within 0.26 Å with the Ru(1),Ru(2),Ru(3); Ru(1),Ru(4),Ru(3); and Ru(2),Ru(4),Ru(3) faces respectively, and lie *ca.* 1 Å above the Ru(1),Ru(2),Ru(4) face. As might be expected the carbonyl distribution in this isomer of the $[Ru_4H_3(CO)_{12}]^-$ anion closely resembles that found for the neutral cluster $[CoOs_3H_3(CO)_{12}]$ where the three hydrogen atoms are also thought to bridge the edges of one triangular face.[16] There is a slight disorder of the cluster anion of $C_2$ symmetry (see Experimental section) which precludes detailed discussion of the Ru–H bonding, but the μ-bridging mode is clearly established.

Conclusions derived from n.m.r. data indicate that in solution the hydride ligands in several carbonyl clusters such as $[Ru_4H_4(CO)_{12-n}\{P(OMe)_3\}_n]$ ($n$ = 1—4),[17] $[Ru_4H_4(CO)_{10}L]$,[14] $[Ru_4H_4(CO)_{10}(\mu\text{-}L)]$,[15] and $[Os_3WH_3(CO)_{11}(\eta^5\text{-}C_5H_5)]$,[18] are scrambled over the metal framework implying a low energy barrier to rearrangement. In the solid the tetrahydrides $[Ru_4H_4(CO)_{11}\{P(OMe)_3\}]$,[19] $[Ru_4H_4(CO)_{10}(PPh_3)_2]$,[7,20] and $[Ru_4H_4(CO)_{12}]$[5] all have metal–hydrogen geometries approximating to $D_{2d}$ symmetry, but in $[Ru_4H_4(CO)_{10}L]$[14] and $[Ru_4H_4(CO)_{10}(\mu\text{-}L)]$[15] the $Ru_4H_4$ core possesses only $C_s$ symmetry. This is further evidence that the alternative metal–hydrogen arrangements differ little in energy. Theoretical calculations by Hoffmann *et al.*[21] on the staggered and eclipsed conformations of $[M_4H_n(CO)_{12}]$ clusters also lead to the same conclusion. It might be anticipated that as cluster size (and hence the number of possible metal polyhedra) increases,[22] the likelihood of isolating such discrete structural isomers in the solid state will also increase. Clearly the methods of cluster preparation, isolation, and crystallization will each play a role in determining which isomer is isolated in the solid state. In this connection it has recently been found that protonation of the dianion $[Os_6(CO)_{18}]^{2-}$ in $CH_2Cl_2$ using HCl(g) gives an isomer of $[Os_6H_2(CO)_{18}]$ with an octahedral metal core;[23] on standing in solution this converts to the previously characterized isomer with a capped square pyramidal $Os_6$ skeleton,[24] prepared by acidifying the dianion in MeCN using concentrated sulphuric acid.

## Experimental

The crude samples of $[N(PPh_3)_2][M_4H_3(CO)_{12}]$ (M = Os or Ru) were obtained by methods which have already been described.[10,25] Crystals of the salts $[N(PPh_3)_2][Ru_4H_3(CO)_{12}]$ and $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$ suitable for *X*-ray analysis were grown from $CH_2Cl_2$–MeOH using the slow evaporation

**Table 2.** Selected interatomic distances (Å) and angles (°) for the $[N(PPh_3)_2][M_4H_3(CO)_{12}]$ salts. Estimated standard deviations are given in parentheses[a]

(*a*) Bond lengths

Metal–metal bonds[b]

| | **(1A)** | **(1B)** | **(2)** | **(4)** |
|---|---|---|---|---|
| M(1)–M(2) | 2.959(1) | 2.90(2) | 2.935(1) | 2.968(1) |
| M(1)–M(3) | 2.799(1) | 2.87(2) | 2.799(1) | 2.826(1) |
| M(1)–M(4) | 2.892(1) | 2.89(2) | 2.941(1) | 2.951(1) |
| M(2)–M(3) | 2.916(1) | 2.94(2) | 2.777(1) | 2.912(2) |
| M(2)–M(4) | 2.803(1) | 2.80(2) | 2.936(1) | 2.821(1) |
| M(3)–M(4) | 2.805(1) | 2.81(2) | 2.786(1) | 2.800(2) |
| Mean M–M (long) | 2.922(1) | 2.91(2) | 2.937(1) | 2.944(1) |
| Mean M–M (short) | 2.802(1) | 2.83(2) | 2.787(1) | 2.816(1) |

| Ru–H bonds | **(1A)** | (2) |
|---|---|---|
| Ru(1)–H(12) | 1.71(7) | 1.83(4) |
| Ru(2)–H(12) | 1.91(7) | 1.87(5) |
| Ru(1)–H(14) | 2.10(8) | 1.83(4) |
| Ru(4)–H(14) | 1.98(8) | 1.86(4) |
| Ru(2)–H(23) | 1.80(8) | |
| Ru(3)–H(23) | 2.07(8) | |
| Ru(2)–H(24) | | 1.88(5) |
| Ru(4)–H(24) | | 1.80(4) |
| Mean Ru–H | 1.93(15) | 1.85(3) |

Carbonyl ligands

| | **(1A)** | **(2)** | **(4)** |
|---|---|---|---|
| M(1)–C(11) | 1.891(7) | 1.882(5) | 1.882(30) |
| M(1)–C(12) | 1.929(8) | 1.910(5) | 1.904(27) |
| M(1)–C(13) | 1.878(7) | 1.898(4) | 1.909(28) |
| M(2)–C(21) | 1.916(6) | 1.885(5) | 1.920(24) |
| M(2)–C(22) | 1.894(8) | 1.911(4) | 1.926(38) |
| M(2)–C(23) | 1.889(7) | 1.891(5) | 1.905(27) |
| M(3)–C(31) | 1.901(7) | 1.893(4) | 1.895(30) |
| M(3)–C(32) | 1.899(8) | 1.880(5) | 1.929(28) |
| M(3)–C(33) | 1.890(9) | 1.893(7) | 1.884(23) |
| M(4)–C(41) | 1.893(7) | 1.909(4) | 1.790(28) |
| M(4)–C(42) | 1.867(8) | 1.904(6) | 1.895(32) |
| M(4)–C(43) | 1.895(10) | 1.936(5) | 1.811(33) |
| Mean M–C | 1.895(16) | 1.899(16) | 1.888(44) |
| Mean C–O | 1.137(15) | 1.135(9) | 1.163(47) |

$[N(PPh_3)_2]^+$ cations

| | **(1A)** | **(2)** | **(4)** |
|---|---|---|---|
| P(1)–N | 1.565(5) | 1.571(3) | 1.604(18) |
| P(2)–N | 1.549(5) | 1.575(3) | 1.579(18) |

(*b*) Interbond angles (°)

Metal–carbon–oxygen angles

| | **(1A)** | **(2)** | **(4)** |
|---|---|---|---|
| M(1)–C(11)–O(11) | 176.2(6) | 175.7(5) | 174.8(26) |
| M(1)–C(12)–O(12) | 176.5(8) | 175.5(5) | 176.3(25) |
| M(1)–C(13)–O(13) | 178.3(6) | 175.8(6) | 178.6(27) |
| M(2)–C(21)–O(21) | 175.7(7) | 176.9(4) | 175.5(27) |
| M(2)–C(22)–O(22) | 172.6(7) | 175.2(4) | 174.6(29) |
| M(2)–C(23)–O(23) | 174.8(7) | 175.8(4) | 173.9(23) |
| M(3)–C(31)–O(31) | 175.6(7) | 177.1(6) | 174.6(27) |
| M(3)–C(32)–O(32) | 175.3(7) | 177.4(5) | 176.9(24) |
| M(3)–C(33)–O(33) | 178.7(9) | 175.7(5) | 174.8(20) |
| M(4)–C(41)–O(41) | 178.5(7) | 175.7(5) | 176.9(24) |
| M(4)–C(42)–O(42) | 178.8(7) | 177.1(5) | 176.6(29) |
| M(4)–C(43)–O(43) | 174.7(8) | 177.3(5) | 171.9(29) |
| Mean M–C–O | 176.3(19) | 176.3(8) | 175.5(17) |

Bridging hydride angles

| | **(1A)** | **(2)** |
|---|---|---|
| Ru(1)–H(12)–Ru(2) | 110(3) | 105(2) |
| Ru(1)–H(14)–Ru(4) | 90(3) | 106(2) |
| Ru(2)–H(23)–Ru(3) | 99(3) | |
| Ru(2)–H(24)–Ru(4) | | 106(2) |

Carbon–metal–metal angles

| | **(1A)** | **(2)** | **(4)** |
|---|---|---|---|
| C(11)–M(1)–M(2) | 99.4(2) | 93.5(1) | 96.8(10) |
| C(11)–M(1)–M(3) | 86.2(2) | 86.4(2) | 87.2(9) |
| C(11)–M(1)–M(4) | 144.0(2) | 142.8(2) | 143.0(9) |
| C(12)–M(1)–M(2) | 110.9(3) | 116.8(1) | 110.1(9) |
| C(12)–M(1)–M(3) | 170.8(3) | 174.0(1) | 169.8(9) |
| C(12)–M(1)–M(4) | 113.8(3) | 117.5(2) | 114.8(9) |
| C(13)–M(1)–M(2) | 146.2(2) | 144.6(2) | 148.2(9) |
| C(13)–M(1)–M(3) | 89.7(2) | 87.9(2) | 90.6(8) |
| C(13)–M(1)–M(4) | 94.6(2) | 95.9(2) | 97.9(9) |
| C(21)–M(2)–M(1) | 110.5(2) | 95.0(1) | 107.6(8) |
| C(21)–M(2)–M(3) | 116.9(2) | 87.4(1) | 112.7(9) |
| C(21)–M(2)–M(4) | 170.7(2) | 144.2(1) | 168.0(9) |
| C(22)–M(2)–M(1) | 99.9(2) | 118.8(1) | 99.5(10) |
| C(22)–M(2)–M(3) | 140.0(2) | 175.1(1) | 143.9(9) |
| C(22)–M(2)–M(4) | 81.8(2) | 116.9(1) | 86.7(10) |
| C(23)–M(2)–M(1) | 148.6(2) | 140.7(1) | 147.8(8) |
| C(23)–M(2)–M(3) | 96.0(2) | 83.3(1) | 93.7(8) |
| C(23)–M(2)–M(4) | 93.4(2) | 93.4(1) | 92.7(8) |
| C(31)–M(3)–M(1) | 95.9(2) | 97.9(2) | 95.6(9) |
| C(31)–M(3)–M(2) | 147.5(2) | 159.9(2) | 147.3(9) |
| C(31)–M(3)–M(4) | 90.5(2) | 102.1(2) | 90.1(9) |
| C(32)–M(3)–M(1) | 99.9(2) | 101.0(2) | 100.0(9) |
| C(32)–M(3)–M(2) | 112.9(2) | 97.5(1) | 109.7(8) |
| C(32)–M(3)–M(4) | 161.9(2) | 159.2(2) | 162.5(9) |
| C(33)–M(3)–M(1) | 159.4(3) | 161.0(2) | 158.4(7) |
| C(33)–M(3)–M(2) | 100.6(3) | 103.1(1) | 100.2(7) |
| C(33)–M(3)–M(4) | 99.8(3) | 98.9(2) | 97.4(7) |
| C(41)–M(4)–M(1) | 100.8(2) | 93.5(2) | 100.7(9) |
| C(41)–M(4)–M(2) | 156.9(2) | 141.7(2) | 157.9(9) |
| C(41)–M(4)–M(3) | 95.4(2) | 85.2(2) | 97.6(9) |
| C(42)–M(4)–M(1) | 148.2(2) | 144.1(2) | 147.3(9) |
| C(42)–M(4)–M(2) | 92.9(2) | 94.6(1) | 94.0(9) |
| C(42)–M(4)–M(3) | 92.8(3) | 87.2(2) | 91.3(9) |
| C(43)–M(4)–M(1) | 110.0(3) | 116.4(2) | 110.4(10) |
| C(43)–M(4)–M(2) | 104.7(3) | 117.1(1) | 98.4(11) |
| C(43)–M(4)–M(3) | 165.5(3) | 173.8(1) | 160.4(10) |

$[N(PPh_3)_2]^+$ cation

| | **(1A)** | **(2)** | **(4)** |
|---|---|---|---|
| P(1)–N–P(2) | 169.9(4) | 147.6(3) | 134.8(12) |

[a] E.s.d.s on mean bond lengths and angles are calculated from the equation $\sigma = \{[\sum_{1}^{n}(x_i - \bar{x})^2]/(n - 1)\}^{\frac{1}{2}}$ where $x_i$ is the *i*th measurement and $\bar{x}$ is the mean of *n* equivalent measurements. [b] The e.s.d.s on the mean M–M lengths are the means of the individual e.s.d.s.

technique. For the ruthenium salt the habit of all the crystals grown from the first crystallization appeared to be the same, *i.e.* parallelpipeds with diamond-shaped faces, (**1**). From a later recrystallization, as well as the diamond-shaped crystals, (**1**), many were present which possessed rectangular faces, (**2**). A triclinic unit cell was also obtained for (**2**) but Delaunay reduction showed it was unrelated to the triclinic cell found for the diamond-shaped crystal (**1**) from the first recrystallization, and furthermore the unit-cell volume for (**2**) was *ca.* 26 Å$^3$ smaller. Data collection was carried out with a crystal of (**2**). Careful examination showed that for $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$ two different crystalline forms were also present. The first, (**3**), had characteristic diamond-shaped faces and was found to be isomorphous with one form of the ruthenium salt, (**1**). Data were therefore not collected. The second form, (**4**), had rectangular faces and these crystals were found to be orthorhombic. It seemed likely that this orthorhombic modification would correspond to a different isomer of the $[Os_4H_3(CO)_{12}]^-$ anion, so data were collected. Attempts to obtain the $C_{3v}$ isomer in the solid state by varying the concentrations of MeOH and $CH_2Cl_2$ were unsuccessful. However, much later[26] during studies of the reactions of $[Os_3(CO)_{12}]$ with KOH–Bu$^t$OH good crystals of $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$ were obtained which proved to be a monoclinic modification (**5**) unlike the earlier triclinic, (**3**), and orthorhombic, (**4**), crystals of the $C_2$ isomer. To explore the possibility that the illusive isomer of $C_{3v}$ symmetry was present a partial data set was collected with the crystals of (**5**).

*X-Ray Data Collection.*—The methods of data collection, data processing, and absorption correction where appropriate have been described previously;[27] Mo-$K_\alpha$ radiation ($\lambda$ = 0.710 69 Å) was used for data collection. The crystals used for data collection had dimensions 0.29 × 0.25 × 0.13 for (**1**), 0.35 × 0.20 × 0.20 for (**2**), and 0.26 × 0.20 × 0.14 mm for (**4**). The scan widths were 0.90 for (**1**), 0.80 for (**2**), and 0.74° for (**4**).

Crystal data for (**1**)—(**5**) are given in Table 1. During each data collection the intensities of three reference reflections were monitored at intervals of 3 h, and for (**4**) they dropped progressively to final values *ca.* 8% lower than their initial values. No correction was made for this slight crystal decomposition. For the two independent crystals of $[N(PPh_3)_2]^+[Ru_4H_3(CO)_{12}]^-$, (**1**) and (**2**), several relatively intense reflections were measured after data collection at intervals of 20° around their diffraction vector $\psi$. The variation in intensity was, in each case, not significant ($<3\sigma$). This and the small values of the linear absorption coefficients, $\mu$(Mo-$K_\alpha$) *ca.* 12 cm$^{-1}$, indicated that absorption corrections could be reasonably neglected. Empirical absorption corrections were applied to the data set of the osmium salt (**4**) which gave relative transmission coefficients which ranged from 0.71 to 1.00 for the full data set. Equivalent reflections were averaged to give 7 210, 10 945, and 3 347 unique data [$I \geqslant 3\sigma(I)$] for (**1**), (**2**), and (**4**) respectively.

*Structure Solution and Refinement.*[28]—For the two independent crystals of $[N(PPh_3)_2][Ru_4H_3(CO)_{12}]$, (**1**) and (**2**), the centrosymmetric triclinic space group $P\bar{1}$ was assumed and confirmed by the satisfactory solution and refinement of the structures. The Ru atom positions in (**1**) and (**2**) were deduced from Patterson maps, the remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses. For the orthorhombic modification of $[N(PPh_3)_2][Os_4H_3(CO)_{12}]$, (**4**), systematic absences [$0kl$ for $k + l = 2n + 1$ ($00l$ for $l = 2n + 1$) and $h0l$ for $h = 2n + 1$] were consistent with either the non-centrosymmetric space group $Pna2_1$, or the centrosymmetric alternative $Pnam$ (a non-standard setting of $Pnma$). Direct methods failed to solve the structure in the centrosymmetric space group, but a suitable solution for the osmium atom positions was obtained in the non-centrosymmetric space group $Pna2_1$ from a Patterson map, and the remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses. The phenyl rings of the cation in (**1**), (**2**), and (**4**) were treated as rigid groups [$d$(C–C) = 1.395 Å] and the phenyl hydrogens were included in geometrically calculated positions [$d$(C–H) = 1.08 Å].

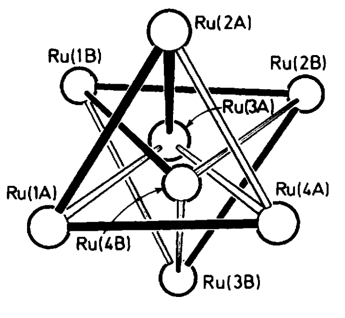

**Figure 4.** Configuration of the metal core in the $C_2$ isomer of $[Ru_4H_3(CO)_{12}]^-$, showing the disordering of the molecules. The solid Ru–Ru bonds are bridged by the hydrogen atoms

After several cycles of refinement a difference-Fourier map calculated for (**1**) showed four pronounced peaks in positions capping the faces of the metal tetrahedron. These features, which were *ca.* 3 e Å$^{-3}$ in height, were interpreted in terms of a second orientation of the cluster of low occupancy (Figure 4). Similar cluster disorder had been found in the neutral tetrahydride $[Ru_4H_4(CO)_{12}]$.[5] Therefore the original four ruthenium atoms were designated Ru(1A), Ru(2A), Ru(3A), and Ru(4A) and their occupancies were coupled in the least-squares refinement to a free variable $p_A$, which refined to 0.94. The common occupation factor of the ruthenium sites of minor occupancy, Ru(1B), Ru(2B), Ru(3B), and Ru(4B), was set to $1 - p_A$. No allowance was made in the structure factor calculations for the CO ligands associated with the second orientation of the cluster; the carbonyl ligands of the first orientation were assigned occupancies of C 0.94 and O 1.00. Initial blocked full-matrix refinement converged at $R$ = 0.0480 and $R'$ = 0.0519 with anisotropic thermal parameters for all atoms of the anion, except the Ru($n$B) atoms, and for the N and P atoms of the $[N(PPh_3)_2]^+$ cation. At this stage a difference-Fourier synthesis calculated using only those data for which ($\sin \theta)/\lambda < 0.3$ revealed the positions of the three hydride ligands associated with the Ru($n$A) atoms, the peaks having an average height of 0.3 e Å$^{-3}$. The occupation factors of these atoms were tied to that of the Ru($n$A) atoms ($p_A$), and their positional and thermal parameters were successfully optimized *via* least-squares refinement.

For (**2**), the second crystalline form of $[N(PPh_3)_2][Ru_4H_3(CO)_{12}]$, the initial blocked full-matrix refinement converged at $R$ = 0.0446 and $R'$ = 0.0509 using anisotropic thermal parameters for all atoms of the anion, and the N and P atoms of the cation. A difference-Fourier synthesis calculated at this stage using all the data revealed the positions of the three hydride ligands, the peaks having an average height of 0.4 e Å$^{-3}$. These atoms were included in the final cycles of refinement with isotropic thermal parameters.

For (**4**) initial blocked full-matrix refinement gave $R$ = 0.0528 and $R'$ = 0.0547 using anisotropic thermal parameters for the Os, N, and P atoms. A difference-Fourier synthesis calculated at this stage revealed two prominent peaks, approximately 3 e Å$^{-3}$ in height, that were well separated from the anion and cation and were *ca.* 2.8 Å apart. These were interpreted as Cl atoms of partial occupancy associated with a $CH_2Cl_2$ solvent molecule. Refinement of their occupation factors yielded values of 0.5; these were fixed at exactly 0.5 for the final cycles of

**Table 3.** Fractional atomic co-ordinates* of the monoanions $[M_4H_3(CO)_{12}]^-$. E.s.d.s are in parentheses

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| (*a*) Ruthenium monoanion in (**1**) | | | | | | | |
| Ru(1A) | 0.175 94(3) | 0.386.22(4) | 0.286 42(5) | O(21) | 0.400 3(3) | 0.172 3(4) | 0.162 5(5) |
| Ru(2A) | 0.316 49(3) | 0.401 64(4) | 0.178 73(4) | C(22) | 0.269 4(4) | 0.407 1(6) | 0.030 4(7) |
| Ru(3A) | 0.303 47(3) | 0.510 28(4) | 0.396 72(5) | O(22) | 0.248 5(3) | 0.406 0(5) | −0.062 2(5) |
| Ru(4A) | 0.221 53(3) | 0.595 55(4) | 0.206 07(5) | C(23) | 0.401 9(4) | 0.488 0(6) | 0.154 6(7) |
| Ru(1B) | 0.303 8(7) | 0.377 2(9) | 0.343 7(10) | O(23) | 0.454 7(3) | 0.531 7(5) | 0.137 5(6) |
| Ru(2B) | 0.336 1(6) | 0.591 8(9) | 0.258 8(9) | C(31) | 0.245 2(4) | 0.608 2(6) | 0.485 8(7) |
| Ru(3B) | 0.198 2(6) | 0.566 8(9) | 0.368 1(9) | O(31) | 0.214 0(3) | 0.664 4(5) | 0.544 2(5) |
| Ru(4B) | 0.207 7(7) | 0.465 5(10) | 0.155 9(10) | C(32) | 0.337 3(4) | 0.413 6(6) | 0.511 3(7) |
| H(12) | 0.227 9(36) | 0.314 2(54) | 0.194 6(54) | O(32) | 0.358 1(4) | 0.361 8(6) | 0.585 6(6) |
| H(14) | 0.129 7(44) | 0.495 9(66) | 0.166 1(66) | C(33) | 0.390 9(5) | 0.606 5(8) | 0.418 8(6) |
| H(23) | 0.358 7(45) | 0.376 6(66) | 0.317 0(66) | O(33) | 0.443 8(4) | 0.666 8(6) | 0.433 7(7) |
| C(11) | 0.209 6(4) | 0.270 0(5) | 0.381 0(6) | C(41) | 0.162 1(4) | 0.704 6(5) | 0.281 4(6) |
| O(11) | 0.225 9(3) | 0.197 3(4) | 0.436 3(5) | O(41) | 0.126 1(3) | 0.771 0(4) | 0.324 3(5) |
| C(12) | 0.094 2(4) | 0.360 2(7) | 0.189 0(7) | C(42) | 0.301 1(5) | 0.695 5(6) | 0.193 1(8) |
| O(12) | 0.045 3(4) | 0.256 9(6) | 0.136 3(6) | O(42) | 0.347 9(5) | 0.757 0(5) | 0.185 2(8) |
| C(13) | 0.112 3(4) | 0.459 8(6) | 0.382 1(6) | C(43) | 0.166 3(6) | 0.613 8(8) | 0.063 9(8) |
| O(13) | 0.072 0(3) | 0.505 0(5) | 0.438 3(5) | O(43) | 0.134 0(5) | 0.633 8(7) | −0.022 2(6) |
| C(21) | 0.370 1(4) | 0.257 0(5) | 0.172 8(6) | | | | |
| (*b*) Ruthenium monoanion in (**2**) | | | | | | | |
| Ru(1) | 0.343 92(2) | 0.957 01(2) | 0.695 92(3) | O(22) | 0.095 2(3) | 0.646 1(2) | 0.427 3(4) |
| Ru(2) | 0.148 46(2) | 0.839 68(2) | 0.595 99(30) | C(23) | 0.032 1(3) | 0.826 8(3) | 0.627 0(5) |
| Ru(3) | 0.201 19(2) | 1.0115 7(2) | 0.763 80(3) | O(23) | −0.040 2(2) | 0.814 2(3) | 0.640 0(4) |
| Ru(4) | 0.246 66(2) | 0.869 73(2) | 0.863 33(3) | C(31) | 0.276 4(4) | 1.118 9(3) | 0.892 2(5) |
| H(12) | 0.266 9(28) | 0.851 2(29) | 0.579 2(41) | O(31) | 0.319 3(4) | 1.185 4(3) | 0.976 2(4) |
| H(14) | 0.348 7(25) | 0.878 1(25) | 0.801 5(37) | C(32) | 0.173 6(3) | 1.080 4(3) | 0.644 5(4) |
| H(24) | 0.181 7(27) | 0.779 1(28) | 0.723 4(39) | O(32) | 0.155 2(3) | 1.124 0(2) | 0.574 8(4) |
| C(11) | 0.333 7(3) | 1.028 6(3) | 0.575 4(5) | C(33) | 0.094 1(4) | 1.008 1(4) | 0.817 6(6) |
| O(11) | 0.328 5(3) | 1.067 6(3) | 0.497 6(4) | O(33) | 0.031 3(4) | 1.011 8(4) | 0.851 0(5) |
| C(12) | 0.433 3(3) | 0.906 6(3) | 0.647 1(5) | C(41) | 0.320 6(4) | 0.966 4(3) | 1.009 5(4) |
| O(12) | 0.488 2(3) | 0.881 1(3) | 0.614 2(4) | O(41) | 0.367 1(3) | 1.019 4(3) | 1.097 0(3) |
| C(13) | 0.429 9(3) | 1.060 2(4) | 0.823 8(5) | C(42) | 0.137 2(4) | 0.850 8(4) | 0.916 9(4) |
| O(13) | 0.485 3(3) | 1.121 6(3) | 0.896 4(5) | O(42) | 0.072 2(3) | 0.835 9(3) | 0.949 3(4) |
| C(21) | 0.119 9(3) | 0.899 8(3) | 0.465 5(4) | C(43) | 0.281 1(3) | 0.766 9(3) | 0.915 7(4) |
| O(21) | 0.101 5(3) | 0.932 4(3) | 0.382 6(3) | O(43) | 0.299 6(5) | 0.708 2(2) | 0.949 7(3) |
| C(22) | 0.119 0(3) | 0.718 4(3) | 0.491 2(4) | | | | |
| (*c*) Osmium monoanion in (**4**) | | | | | | | |
| Os(1) | −0.102 33(5) | −0.140 17(5) | 0 | C(23) | 0.015 9(17) | 0.022 8(13) | −0.176 8(17) |
| Os(2) | −0.059 18(5) | −0.037 82(4) | −0.132 87(8) | O(23) | 0.059 3(13) | 0.062 2(11) | −0.196 6(14) |
| Os(3) | 0.002 42(6) | −0.036 32(4) | 0.042 21(8) | C(31) | 0.051 2(17) | −0.085 7(16) | 0.131 9(19) |
| Os(4) | 0.049 94(6) | −0.133 92(5) | −0.078 64(8) | O(31) | 0.083 7(11) | −0.114 5(9) | 0.179 3(14) |
| C(11) | −0.176 6(15) | −0.086 9(17) | 0.055 5(21) | C(32) | −0.060 0(18) | 0.020 1(14) | 0.115 6(16) |
| O(11) | −0.219 3(12) | −0.051 4(12) | 0.095 2(17) | O(32) | −0.094 9(12) | 0.052 6(10) | 0.161 9(14) |
| C(12) | −0.168 1(15) | −0.206 7(13) | −0.049 2(20) | C(33) | 0.083 4(14) | 0.025 3(11) | 0.027 4(14) |
| O(12) | −0.211 3(13) | −0.245 4(11) | −0.076 9(16) | O(33) | 0.130 8(12) | 0.065 0(9) | 0.024 1(13) |
| C(13) | −0.075 7(18) | −0.189 3(12) | 0.102 4(19) | C(41) | 0.102 2(16) | −0.187 0(13) | −0.005 6(19) |
| O(13) | −0.060 8(14) | −0.218 7(9) | 0.165 5(13) | O(41) | 0.142 0(13) | −0.222 7(10) | 0.044 3(15) |
| C(21) | −0.143 2(14) | 0.023 5(12) | −0.146 7(20) | C(42) | 0.133 3(19) | −0.078 8(13) | −0.111 7(21) |
| O(21) | −0.193 2(13) | 0.057 4(10) | −0.159 9(18) | O(42) | 0.184 2(14) | −0.045 8(11) | −0.136 5(19) |
| C(22) | −0.070 5(19) | −0.092 6(13) | −0.235 7(27) | C(43) | 0.053 2(18) | −0.185 2(19) | −0.176 2(20) |
| O(22) | −0.072 3(16) | −0.123 2(11) | −0.300 2(14) | O(43) | 0.060 3(17) | −0.226 3(13) | −0.236 6(14) |

* The atomic co-ordinates for the $[N(PPh_3)_2]^+$ cations have been deposited.

refinement. Attempts to locate the hydrogen ligands and the carbon atom of the solvent molecule from difference-Fourier syntheses were unsuccessful.

For the three refinements weights were assigned to the reflections as $w = 1/\sigma^2F$ and the final discrepancy indices were: (**1**), $R = 0.0473$ and $R' = 0.0508$; (**2**), $R = 0.0432$ and $R' = 0.0489$; (**4**), $R = 0.0426$ and $R' = 0.0435$. The final difference-Fourier syntheses for all three structures revealed a few residual maxima in the region of the metal atoms which had maximum heights of 1.0 for (**1**), 0.9 for (**2**), and 1.4 e Å$^{-3}$ for (**4**).

For the third modification of the osmium salt, (**5**), a Patterson synthesis was calculated after data to a θ value of 18° had been measured. Solution gave a tetrahedron of metal atoms which on partial refinement proved to have the $C_2$ pattern of Os–Os bond lengths found in the orthorhombic modification (**4**) showing that it was once more the isomer of that symmetry which had been obtained. No further work was done on this structure analysis.

Selected bond lengths and angles for (**1**), (**2**), and (**4**) are given in Table 2. The final atomic co-ordinates for the anions are given in Table 3.

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## References

1 See, for example, P. Frediano, U. Matteoli, M. Bianchi, F. Piacenti, and G. Menchi, *J. Organomet. Chem.*, 1978, **150**, 273; J. L. Graff and M. S. Wrighton, *J. Am. Chem. Soc.*, 1980, **102**, 213.
2 Y. Doi, K. Koshizuka, and T. Keii, *Inorg. Chem.*, 1982, **21**, 2732.
3 B. F. G. Johnson, R. D. Johnston, J. Lewis, B. H. Robinson, and G. Wilkinson, *J. Chem. Soc. A*, 1968, 2856.
4 J. R. Moss and W. A. G. Graham, *J. Organomet. Chem.*, 1970, **23**, C47.
5 R. D. Wilson, S. M. Wu, R. A. Love, and R. Bau, *Inorg. Chem.*, 1978, **17**, 1271.
6 B. F. G. Johnson, J. Lewis, P. R. Raithby, and C. Zuccaro, *Acta Crystallogr., Sect. B*, 1981, **37**, 1728.
7 J. W. Koepke, J. R. Johnson, S. A. R. Knox, and H. D. Kaesz, *J. Am. Chem. Soc.*, 1975, **97**, 3947.
8 B. F. G. Johnson, J. Lewis, P. R. Raithby, G. M. Sheldrick, K. Wong, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1978, 673.
9 P. F. Jackson, B. F. G. Johnson, J. Lewis, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Chem. Commun.*, 1978, 920.
10 L. J. Farrugia, M. Green, D. H. Hankey, M. Murray, A. G. Orpen, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 177.
11 B. F. G. Johnson, J. Lewis, P. R. Raithby, and C. Zuccaro, *Acta Crystallogr., Sect. B*, 1978, **34**, 3765.
12 E. C. Constable, B. F. G. Johnson, J. Lewis, G. N. Pain, and M. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 1982, 754.
13 R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, 1976, **98**, 4687.
14 M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, 1978, **17**, 1950.
15 M. R. Churchill, R. A. Lashewycz, J. R. Shapley, and S. I. Richter, *Inorg. Chem.*, 1980, **19**, 1277.
16 S. Bhaduri, B. F. G. Johnson, J. Lewis, P. R. Raithby, and D. J. Watson, *J. Chem. Soc., Chem. Commun.*, 1978, 343.
17 S. A. R. Knox and H. D. Kaesz, *J. Am. Chem. Soc.*, 1971, **93**, 4594.
18 M. R. Churchill and F. J. Hollander, *Inorg. Chem.*, 1979, **18**, 161.
19 R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, 1976, **98**, 4687.
20 K. Sasvari, P. Main, F. H. Cano, M. Martinez-Ripoll, and P. Frediani, *Acta Crystallogr., Sect. B*, 1979, **35**, 87.
21 R. Hoffmann, B. E. R. Schilling, R. Bau, H. D. Kaesz, and D. M. P. Mingos, *J. Am. Chem. Soc.*, 1978, **100**, 6088.
22 M. McPartlin and M. Mingos, *Polyhedron*, 1984, **3**, 1321.
23 J. Lewis and B. F. G. Johnson, *Pure Appl. Chem.*, 1982, **54**, 97.
24 M. McPartlin, C. R. Eady, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Chem. Commun.*, 1976, 883.
25 C. R. Eady, P. F. Jackson, B. F. G. Johnson, J. Lewis, M-C. Malatesta, M. McPartlin, and W. J. H. Nelson, *J. Chem. Soc., Dalton Trans.*, 1980, 383.
26 B. F. G. Johnson, J. Lewis, W. J. H. Nelson, M. D. Vargas, D. Braga, K. Henrick, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1984, 2151.
27 M. K. Cooper, P. A. Duckworth, K. Henrick, and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 1981, 2357.
28 G. M. Sheldrick, SHELX 76, Crystal Structure Solving Package, University of Cambridge, 1976.

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