# Synthesis, Reactivity, and *X*-Ray Crystal Structures of $[Os_6Pt_2H_2(CO)_{16}(\mu\text{-}C_8H_{10})(C_8H_{12})]\cdot CH_2Cl_2$ and $[Os_6H(CO)_{16}(\mu\text{-}C_8H_{11})]$.† Model Compounds for C–H Activation

**Christiane Couture and David H. Farrar***
*Lash Miller Chemical Laboratories, 80 St. George Street, University of Toronto, Toronto, Canada M5S 1A1*

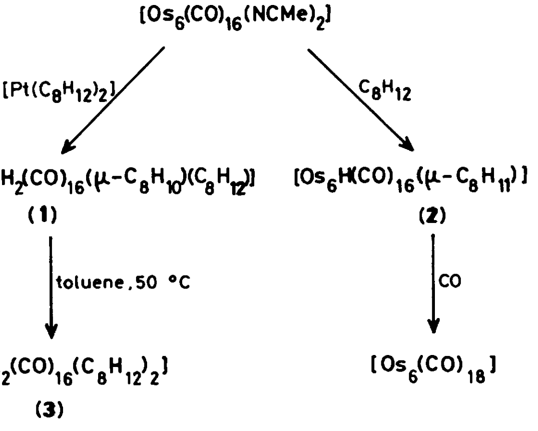
The reaction of $[Os_6(CO)_{16}(NCMe)_2]$ with $[Pt(C_8H_{12})_2]$ ($C_8H_{12}$ = cyclo-octa-1,5-diene) results in the formation of $[Os_6Pt_2H_2(CO)_{16}(\mu\text{-}C_8H_{10})(C_8H_{12})]$ (**1**). The geometry of (**1**) may be derived from that of $[Os_6(CO)_{18}]$ by bridging one edge of the central Os tetrahedron with one Pt atom of the dimer unit $Pt_2(\mu\text{-}C_8H_{10})(C_8H_{12})$. One $C_8H_{12}$ group has been dehydrogenated to $C_8H_{10}$ and the two resulting hydride ligands are terminally bound to different metals of the $Os_6$ core. The $C_8H_{10}$ ligand is bound in an $\eta^3$-allyl fashion to one Pt atom and by an $\eta^2$-olefinic bond and $\sigma$-alkyl bond to the second Pt atom. Upon heating in toluene, complex (**1**) rearranges to the known complex $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ (**3**). Complex (**3**) is without hydride ligands and possesses a geometry of two edge-fused Os tetrahedra, one of which is Pt-bicapped. The complex $[Os_6H(CO)_{16}(\mu\text{-}C_8H_{11})]$ (**2**) was isolated from the reaction of $[Os_6(CO)_{16}(NCMe)_2]$ with $C_8H_{12}$. Complex (**2**) has the bicapped tetrahedral geometry of $[Os_6(CO)_{18}]$ with the $\mu\text{-}C_8H_{11}$ group bridging two Os atoms of the central tetrahedron. The hydride ligand caps a triangulated Os face. This complex reacts with CO to afford the parent cluster $[Os_6(CO)_{18}]$.

Considerable attention has been devoted to the study of high-nuclearity transition metal clusters as they are attractive models[1] for surface intermediates in catalytic processes. Carbon–hydrogen bond activation has been the subject of extensive research most of which deals with mononuclear species.[2]

During our investigation[3,4] of the reaction of the activated clusters $[Os_6(CO)_{18-n}(NCMe)_n]$ ($n$ = 1 or 2) with $[Pt(C_8H_{12})_2]$ ($C_8H_{12}$ = cyclo-octa-1,5-diene), we have found that the hexaosmium cluster can assist in the C–H bond activation of cyclo-octa-1,5-diene by acting as a hydrogen acceptor.[2] We have thus isolated the hydride complexes $[Os_6Pt_2H_2(CO)_{16}(\mu\text{-}C_8H_{10})(C_8H_{12})]$ (**1**) and $[Os_6H(CO)_{16}(\mu\text{-}C_8H_{11})]$ (**2**). The reverse dehydrogenation reaction proceeds under mild conditions for both clusters. Upon heating in toluene at 50 °C, complex (**1**) rearranges to $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ (**3**), a cluster having the same empirical formula but with a different solid-state metallic skeleton. Complex (**2**) reacts with CO to generate $[Os_6(CO)_{18}]$. These clusters can serve as model compounds for multi-metal site dehydrogenation of alkenes.

## Results and Discussion

The reactions are summarized in the Scheme and the spectroscopic data are presented in Table 1. The red compound $[Os_6Pt_2H_2(CO)_{16}(\mu\text{-}C_8H_{10})(C_8H_{12})]$ (**1**) is the first product to be observed by thin-layer chromatography (t.l.c.) from the reaction of $[Os_6(CO)_{16}(NCMe)_2]$ with $[Pt(C_8H_{12})_2]$, being present in 20% yield after 1 h. The amount of (**1**) remains constant over the period (18 h) required for the formation of $[Os_6Pt_2(CO)_{17}(C_8H_{12})_2]$ and $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ (**3**).[3] The formula and molecular structure of compound (**1**) were established by a combination of $^1H$ n.m.r. and single-crystal *X*-ray crystallography.



**Scheme.** Summary of reactions; all were performed in $CH_2Cl_2$ except where indicated

The molecular structure of mixed-metal cluster (**1**) is shown in Figure 1 and selected intramolecular distances and angles are listed in Table 2. The six Os atoms form a bicapped tetrahedron characteristic of the parent cluster $[Os_6(CO)_{18}]$.[5] One edge of the central tetrahedron [Os(1)–Os(2)] is bridged by a dimeric Pt unit, $Pt_2(\mu\text{-}C_8H_{10})(C_8H_{12})$, through Pt(1). Also, the structure of (**1**) is reminiscent of that of $[Os_7H_2(CO)_{20}]$,[6] substituting the $Pt_2(\mu\text{-}C_8H_{10})(C_8H_{12})$ fragment for an $Os(CO)_4$ unit. The difference is that in the structure of (**1**) the bridging unit is almost capping a face; the separation between Os(3) and Pt(1) is 3.370(4) Å which is too large to be considered as a formal metal–metal bond.

A $Pt(C_8H_{12})$ fragment is bound to Pt(1) with a Pt–Pt separation of 2.859(3) Å and the co-ordination geometry about each Pt atom is distorted square pyramidal. A $C_8H_{10}$ group bridges the two Pt centres. Three C atoms of the $\mu\text{-}C_8H_{10}$ ligand [C(113), C(114), and C(115)] are bound to Pt(1) in an $\eta^3$-allyl fashion with an average Pt(1)–C distance of 2.15(2) Å, one C atom [C(116)] is $\sigma$ bound to Pt(2) with a bond length of 2.05(7) Å, and two C atoms [C(111) and C(112)] form a metal–olefin bond with Pt(2) [Pt(2)–C(111) 2.23(4) and Pt(2)–C(112)

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† Hexadecacarbonyl-μ-[($\eta^4$-cyclo-octa-1,5-diene)($\sigma,\eta^2$:$\eta^3$-cyclo-octa-3,5-diene-1,2-diyl)diplatinio]-dihydrido-*polyhedro*-hexaosmium(*Pt–Pt*)(2*Pt–Os*)(12*Os–Os*)–dichloromethane(1/1)andhexadecacarbonyl-μ-($\eta^3$-cyclo-octa-2,5-dien-1-yl)-$\mu_3$-hydrido-*polyhedro*-hexaosmium(12 *Os–Os*) respectively.

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

2.22(5) Å]. The same type of linkage for the μ-$C_8H_{10}$ group was previously described[7] for a dinuclear iron complex, $[Fe_2(CO)_6(\mu\text{-}C_8H_{10})]$. This complex was obtained from the direct reaction of cyclo-octa-1,3,5-triene with $[Fe_2(CO)_9]$ or $[Fe_3(CO)_{12}]$, and not from the dehydrogenation of $C_8H_{12}$ as for cluster (**1**). One C–C distance in the μ-$C_8H_{10}$ group of (**1**) is abnormally long [C(112)–C(113) 1.73(8) Å], while the corresponding distance in $[Fe_2(CO)_6(\mu\text{-}C_8H_{10})]$ [1.45(2) Å] is a more typical C–C bond length. This long separation may arise from steric effects or it may simply be an artefact of the

**Table 1.** Spectroscopic data for the complexes

| Complex | ν(CO)$^a$/cm$^{-1}$ | $^1$H N.m.r. (δ)$^b$ | | |
|---|---|---|---|---|
| (**1**) $[Os_6Pt_2H_2(CO)_{16}(\mu\text{-}C_8H_{10})(C_8H_{12})]$ | 2 082m, 2 052s, 2 018vs, 2 001m, 1 981m | − 9.08 (s) | $J(^{195}Pt\text{-}H)$ | 7 Hz |
| | | − 9.40 (s) | $J(^{195}Pt\text{-}H)$ | 7 Hz |
| | | − 9.12 (s)$^c$ | $J(^{195}Pt\text{-}H)$ | 13 Hz |
| | | − 9.43 (s)$^c$ | $J(^{195}Pt\text{-}H)$ | 10 Hz |
| (**2**) $[Os_6H(CO)_{16}(\mu\text{-}C_8H_{11})]$ | 2 098m, 2 069vs, 2 047s, 2 033s, 2 025s, 2 001m, 1 942w | −21.09 (s) | $J(^{187}Os\text{-}H)$ | 27 and 24 Hz |
| (**3**) $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ | 2 075m, 2 057vs, 2 032m (sh), 2 017s, 2 009s, 1 988s, 1 960w | | | |

$^a$ In $CH_2Cl_2$. $^b$ In $CD_2Cl_2$; measured at 400 MHz at 20 °C unless otherwise stated. $^c$ In $CDCl_3$; measured at 200 and 400 MHz.

**Table 2.** Selected internuclear distances (Å) and angles (°) for $[Os_6Pt_2H_2(CO)_{16}(\mu\text{-}C_8H_{10})(C_8H_{12})]$ (**1**)*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Os(2)–Os(1) | 2.741(3) | Os(3)–Os(1) | 2.879(3) | C(122)–Pt(2) | 2.41(7) | C(125)–Pt(2) | 2.11(5) |
| Os(4)–Os(1) | 2.665(3) | Os(6)–Os(1) | 2.828(3) | C(126)–Pt(2) | 2.12(3) | Os(1)–C(11) | 1.72(7) |
| Pt(1)–Os(1) | 2.669(2) | C(11)–Os(1) | 1.72(7) | Os(1)–C(12) | 1.76(6) | Os(2)–C(21) | 1.82(5) |
| C(12)–Os(1) | 1.76(6) | Os(3)–Os(2) | 2.867(3) | Os(2)–C(22) | 1.87(5) | Os(3)–C(31) | 1.84(7) |
| Os(5)–Os(2) | 2.788(3) | Os(6)–Os(2) | 2.865(3) | Os(3)–C(32) | 1.87(4) | Os(3)–C(33) | 1.90(5) |
| Pt(1)–Os(2) | 2.733(3) | C(21)–Os(2) | 1.82(5) | Os(4)–C(41) | 1.80(5) | Os(4)–C(42) | 1.79(10) |
| C(22)–Os(2) | 1.87(5) | Os(4)–Os(3) | 2.868(3) | Os(4)–C(43) | 2.05(9) | Os(5)–C(51) | 1.84(4) |
| Os(5)–Os(3) | 2.870(4) | Os(6)–Os(3) | 2.788(3) | Os(5)–C(52) | 1.87(6) | Os(5)–C(53) | 1.78(9) |
| C(31)–Os(3) | 1.84(7) | C(32)–Os(3) | 1.87(4) | Os(6)–C(61) | 1.85(7) | Os(6)–C(62) | 1.78(5) |
| C(33)–Os(3) | 1.90(5) | Os(6)–Os(4) | 2.856(4) | Os(6)–C(63) | 1.82(13) | C(112)–C(111) | 1.44(8) |
| C(41)–Os(4) | 1.80(5) | C(42)–Os(4) | 1.79(10) | C(118)–C(111) | 1.49(8) | C(113)–C(112) | 1.73(8) |
| C(43)–Os(4) | 2.05(9) | Os(6)–Os(5) | 2.836(3) | C(114)–C(113) | 1.38(10) | C(115)–C(114) | 1.46(6) |
| C(51)–Os(5) | 1.84(4) | C(52)–Os(5) | 1.87(6) | C(116)–C(115) | 1.52(7) | C(117)–C(116) | 1.45(8) |
| C(53)–Os(5) | 1.78(9) | C(61)–Os(6) | 1.85(7) | C(118)–C(117) | 1.49(7) | C(122)–C(121) | 1.38(7) |
| C(62)–Os(6) | 1.78(5) | C(63)–Os(6) | 1.82(13) | C(128)–C(121) | 1.47(8) | C(123)–C(122) | 1.51(8) |
| Pt(2)–Pt(1) | 2.859(3) | C(113)–Pt(1) | 2.17(5) | C(124)–C(123) | 1.59(10) | C(125)–C(124) | 1.39(8) |
| C(114)–Pt(1) | 2.13(6) | C(115)–Pt(1) | 2.16(6) | C(126)–C(125) | 1.38(7) | C(127)–C(126) | 1.57(8) |
| C(111)–Pt(2) | 2.23(4) | C(112)–Pt(2) | 2.22(5) | C(128)–C(127) | 1.51(11) | | |
| C(116)–Pt(2) | 2.05(7) | C(121)–Pt(2) | 2.28(6) | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Os(3)–Os(1)–Os(2) | 61.3(1) | Os(4)–Os(1)–Os(2) | 114.8(1) | Os(5)–Os(6)–Os(1) | 108.3(1) | Os(5)–Os(6)–Os(2) | 58.6(1) |
| Os(4)–Os(1)–Os(3) | 62.2(1) | Os(6)–Os(1)–Os(2) | 61.9(1) | Os(5)–Os(6)–Os(3) | 61.4(1) | Os(5)–Os(3)–Os(4) | 119.6(1) |
| Os(6)–Os(1)–Os(3) | 58.5(1) | Os(6)–Os(1)–Os(4) | 62.6(1) | C(62)–Os(6)–C(61) | 96(3) | C(63)–Os(6)–C(61) | 83(4) |
| Pt(1)–Os(1)–Os(2) | 60.7(1) | Pt(1)–Os(1)–Os(3) | 74.6(1) | C(63)–Os(6)–C(62) | 98(4) | Os(2)–Pt(1)–Os(1) | 60.9(1) |
| Pt(1)–Os(1)–Os(4) | 127.5(1) | Pt(1)–Os(1)–Os(6) | 117.9(1) | Pt(2)–Pt(1)–Os(1) | 110.7(1) | Pt(2)–Pt(1)–Os(2) | 118.7(1) |
| C(12)–Os(1)–C(11) | 87(3) | Os(3)–Os(2)–Os(1) | 61.7(1) | C(114)–Pt(1)–C(113) | 37(2) | C(115)–Pt(1)–C(113) | 70(2) |
| Os(5)–Os(2)–Os(1) | 112.2(1) | Os(5)–Os(2)–Os(3) | 61.0(1) | C(115)–Pt(1)–C(114) | 40(2) | C(112)–Pt(2)–C(111) | 38(2) |
| Os(6)–Os(2)–Os(1) | 60.6(1) | Os(6)–Os(2)–Os(3) | 58.2(1) | C(116)–Pt(2)–C(111) | 75(2) | C(116)–Pt(2)–C(112) | 95(2) |
| Os(6)–Os(2)–Os(5) | 60.2(1) | Pt(1)–Os(2)–Os(1) | 58.4(1) | C(121)–Pt(2)–C(111) | 116(2) | C(121)–Pt(2)–C(112) | 90(1) |
| Pt(1)–Os(2)–Os(3) | 73.9(1) | Pt(1)–Os(2)–Os(5) | 129.1(1) | C(121)–Pt(2)–C(116) | 166(2) | C(122)–Pt(2)–C(111) | 96(2) |
| Pt(1)–Os(2)–Os(6) | 114.6(1) | C(22)–Os(2)–C(21) | 91(2) | C(122)–Pt(2)–C(112) | 88(2) | C(122)–Pt(2)–C(116) | 160(2) |
| Os(4)–Os(3)–Os(1) | 55.3(1) | Os(4)–Os(3)–Os(2) | 105.2(1) | C(122)–Pt(2)–C(121) | 34(2) | C(125)–Pt(2)–C(111) | 112(2) |
| Os(5)–Os(3)–Os(1) | 106.0(1) | Os(5)–Os(3)–Os(2) | 58.2(1) | C(125)–Pt(2)–C(112) | 145(2) | C(125)–Pt(2)–C(116) | 89(2) |
| Os(5)–Os(3)–Os(4) | 118.1(1) | Os(6)–Os(3)–Os(1) | 59.9(1) | C(125)–Pt(2)–C(121) | 95(2) | C(125)–Pt(2)–C(122) | 77(2) |
| Os(6)–Os(3)–Os(2) | 60.9(1) | Os(6)–Os(3)–Os(4) | 60.6(1) | C(126)–Pt(2)–C(111) | 149(2) | C(126)–Pt(2)–C(112) | 171(2) |
| Os(6)–Os(3)–Os(5) | 60.1(1) | C(32)–Os(3)–C(31) | 88(2) | C(126)–Pt(2)–C(116) | 93(2) | C(126)–Pt(2)–C(121) | 81(2) |
| C(33)–Os(3)–C(31) | 94(3) | C(33)–Os(3)–C(32) | 96(2) | C(126)–Pt(2)–C(122) | 85(2) | C(126)–Pt(2)–C(125) | 38(2) |
| Os(3)–Os(4)–Os(1) | 62.6(1) | Os(6)–Os(4)–Os(1) | 61.5(1) | C(118)–C(111)–C(112) | 134(5) | C(113)–C(112)–C(111) | 110(5) |
| Os(6)–Os(4)–Os(3) | 58.3(1) | C(42)–Os(4)–C(41) | 102(3) | C(114)–C(113)–C(112) | 126(5) | C(115)–C(114)–C(113) | 122(5) |
| C(43)–Os(4)–C(41) | 93(3) | C(43)–Os(4)–C(42) | 89(4) | C(116)–C(115)–C(114) | 124(4) | C(117)–C(116)–C(115) | 114(4) |
| Os(3)–Os(5)–Os(2) | 60.9(1) | Os(6)–Os(5)–Os(2) | 61.3(1) | C(118)–C(117)–C(116) | 112(6) | C(117)–C(118)–C(111) | 106(4) |
| Os(6)–Os(5)–Os(2) | 58.5(1) | C(52)–Os(5)–C(51) | 93(2) | C(128)–C(121)–C(122) | 112(5) | C(123)–C(122)–C(121) | 130(4) |
| C(53)–Os(5)–C(51) | 91(3) | C(53)–Os(5)–C(52) | 90(3) | C(124)–C(123)–C(122) | 111(6) | C(125)–C(124)–C(123) | 114(5) |
| Os(2)–Os(6)–Os(1) | 57.5(1) | Os(3)–Os(6)–Os(1) | 61.7(1) | C(126)–C(125)–C(124) | 130(6) | C(127)–C(126)–C(125) | 118(5) |
| Os(3)–Os(6)–Os(2) | 60.9(1) | Os(4)–Os(6)–Os(1) | 55.9(1) | C(128)–C(127)–C(126) | 111(5) | C(127)–C(128)–C(121) | 119(7) |
| Os(4)–Os(6)–Os(2) | 105.5(1) | Os(4)–Os(6)–Os(3) | 61.1(1) | | | | |

* Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables.

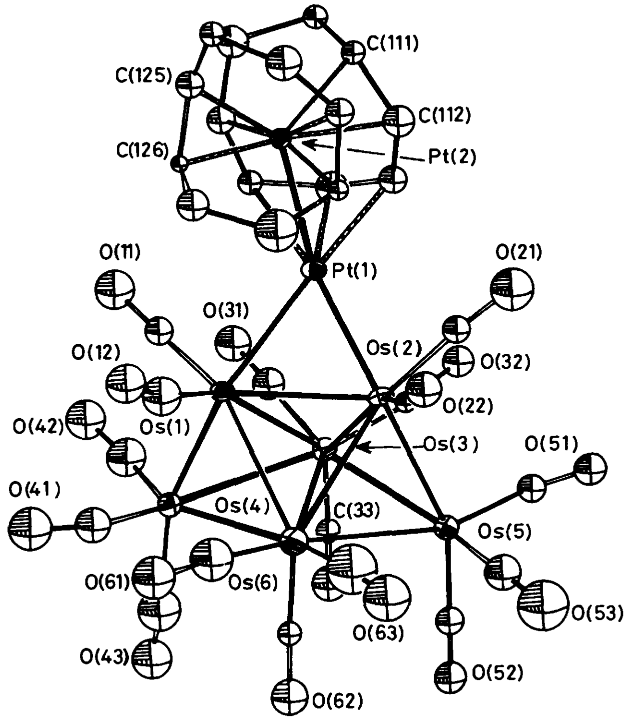

**Figure 1.** The molecular structure of $[Os_6Pt_2H_2(CO)_{16}(\mu\text{-}C_8H_{10})(C_8H_{12})]$ (**1**). The bonds of the μ-$C_8H_{10}$ and $C_8H_{12}$ ligands to the Pt atoms are hatched

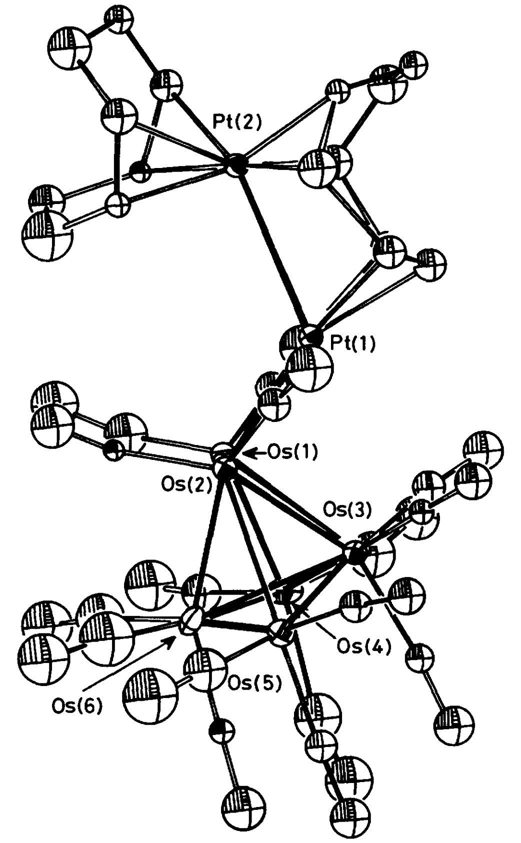

**Figure 2.** The cluster (**1**) viewed from a different angle to show the co-ordination sites available for two terminal hydride ligands, and the crowding between $C_8H_{12}$ and carbonyl groups

refinement. The remaining bond parameters in the μ-$C_8H_{10}$ bridge fall within the range observed in the complex $[Fe_2(CO)_6(\mu\text{-}C_8H_{10})]$.[7]

The $C_8H_{12}$ ligand is not symmetrically bound to Pt(2); the Pt(2)–C bond lengths vary from 2.11(5) to 2.41(7) Å, and the largest separations [Pt(2)–C(121) 2.28(6), Pt(2)–C(122) 2.41(7) Å] are *trans* to the Pt(2)–C σ bond. This trend was also observed in the mixed-metal cluster $[Os_6Pt(CO)_{17}(\mu_3\text{-}NCMe)(C_8H_{12})]$[4] in which the longest Pt–C (olefinic) carbon separations were also *trans* to a Pt–C σ bond. All of the bond parameters associated with the $C_8H_{12}$ unit appear normal.[3,4]

The 16 carbonyl ligands are terminal with Os–C–O angles in the range 164(6)—179(5)°. Os(1) and Os(2) each have two carbonyl ligands while the remaining Os atoms each have three carbonyl ligands, the mean Os–C and C–O bond lengths being 1.83(7) and 1.20(4) Å, respectively. The Os–Os separations vary from 2.665(3) to 2.879(3) Å. A large asymmetry is observed in the metallic core of cluster (**1**). The Os(1)–Os(4) and Os(1)–Pt(1) distances [2.665(3) and 2.669(2) Å] are significantly shorter than the corresponding opposite edges, Os(2)–Os(5) and Os(2)–Pt(1) [2.788(3) and 2.733(3) Å]. This imbalance also is shown by a network of incipient bridging carbonyl ligands between metal atoms with different formal electron counts.

Although the hydride ligands were not located in the *X*-ray analysis, information about their sites was obtained from the $^1H$ n.m.r. spectra (Table 1). Two distinct single resonances, measured at magnetic fields of both 200 and 400 MHz in $CDCl_3$, were found at δ −9.12 and −9.43, with satellite peaks due to $^{195}Pt\text{-}^1H$ coupling of 13 and 10 Hz respectively. These signals are attributed to two terminal hydrides,[8] located on two different Os atoms, Os(1) and Os(2), and *cis*-coupled to Pt(1). The $^1H\text{-}^1H$ coupling is not observed and must be less than 1 Hz while the peak width at half-height is *ca.* 2 Hz. This assignment is fully consistent with the solid-state structure of (**1**) and also implies that the $Pt_2(\mu\text{-}C_8H_{10})(C_8H_{12})$ moiety does not undergo chemical exchange at room temperature as does the related complex $[Fe_2(CO)_6(\mu\text{-}C_8H_{10})]$.[9] Figure 2 clearly shows the co-ordination sites available for two terminal hydrides on Os(1) and Os(2). The only other hydride sites which are consistent with the n.m.r. data are the edges Os(2)–Os(5) and Os(1)–Os(4); the short Os–Os distances, 2.788(3) and 2.665(3) Å respectively, preclude this choice.

Cluster (**1**) is a 112-electron system with the Pt centres having different electron counts. Pt(1) is best considered as a 16-electron system while Pt(2) has an 18-electron configuration if these Pt atoms are given a formal oxidation state of +1. Cluster (**1**) is another example[3,4] of a cluster where application of the current electron-counting procedures[10] is difficult.

The reaction of $[Os_6(CO)_{16}(NCMe)_2]$ with $C_8H_{12}$ in $CH_2Cl_2$ afforded the orange complex $[Os_6H(CO)_{16}(\mu\text{-}C_8H_{11})]$ (**2**) in 25% yield. Complex (**2**) is also observed in the reaction of $[Os_6(CO)_{16}(NCMe)_2]$ with $[Pt(C_8H_{12})_2]$ but in minute amounts. Crystals of (**2**) were obtained from the slow evaporation of an ethyl acetate solution and an *X*-ray diffraction analysis was undertaken.

The molecular structure of complex (**2**) is shown in Figure 3 while selected bond parameters are listed in Table 3. The overall geometry of the $Os_6$ bicapped tetrahedra resembles that in the parent binary carbonyl $[Os_6(CO)_{18}]$.[5] The $C_8H_{11}$ ligand bridges two Os atoms, Os(3) and Os(5), through C(1), C(2), and C(3) in an $\eta^3$-allyl fashion. This $\eta^3$-allyl segment is not co-ordinated symmetrically to the $Os_6$ metallic core. The dihedral angle between the plane defined by the bridged Os atoms and C(2) and the triangulated face Os(3)–Os(5)–Os(4) is *ca.* 133°. The distances between the Os and C atoms of the allyl fragments

**Table 3.** Selected internuclear distances (Å) and angles (°) for $[Os_6H(CO)_{16}(\mu\text{-}C_8H_{11})]$ (**2**)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Os(2)–Os(1) | 2.890(4) | Os(3)–Os(1) | 2.974(4) | C(61)–Os(6) | 1.89(8) | C(62)–Os(6) | 1.85(8) |
| Os(4)–Os(1) | 2.787(4) | Os(5)–Os(1) | 2.998(4) | C(63)–Os(6) | 1.90(10) | Os(1)–C(11) | 1.80(8) |
| Os(6)–Os(1) | 2.891(4) | C(11)–Os(1) | 1.80(8) | Os(1)–C(12) | 1.92(8) | Os(1)–C(13) | 1.90(8) |
| C(12)–Os(1) | 1.92(8) | C(13)–Os(1) | 1.90(8) | Os(2)–C(21) | 1.89(11) | Os(2)–C(22) | 2.01(10) |
| Os(4)–Os(2) | 2.796(4) | Os(5)–Os(2) | 2.747(5) | Os(2)–C(23) | 1.87(7) | Os(3)–C(31) | 1.69(7) |
| C(21)–Os(2) | 1.89(11) | C(22)–Os(2) | 2.01(10) | Os(3)–C(32) | 1.84(11) | Os(4)–C(41) | 1.90(7) |
| C(23)–Os(2) | 1.87(7) | Os(4)–Os(3) | 2.841(5) | Os(4)–C(42) | 1.76(7) | Os(4)–C(43) | 1.88(7) |
| Os(5)–Os(3) | 2.716(4) | Os(6)–Os(3) | 2.752(4) | Os(5)–C(51) | 1.97(10) | Os(5)–C(52) | 1.88(7) |
| C(31)–Os(3) | 1.69(7) | C(32)–Os(3) | 1.84(12) | Os(6)–C(61) | 1.89(8) | Os(6)–C(62) | 1.85(8) |
| C(1)–Os(3) | 2.39(8) | Os(1)–Os(4) | 2.787(4) | Os(6)–C(63) | 1.90(10) | C(2)–C(1) | 1.32(11) |
| Os(2)–Os(4) | 2.796(4) | Os(3)–Os(4) | 2.841(5) | C(8)–C(1) | 1.39(11) | C(3)–C(2) | 1.47(13) |
| Os(5)–Os(4) | 2.835(4) | Os(6)–Os(4) | 2.810(4) | C(4)–C(3) | 1.56(12) | C(5)–C(4) | 1.50(14) |
| C(41)–Os(4) | 1.90(7) | C(42)–Os(4) | 1.76(7) | C(6)–C(5) | 1.67(17) | C(7)–C(6) | 1.54(16) |
| C(43)–Os(4) | 1.88(7) | C(51)–Os(5) | 1.97(10) | C(8)–C(7) | 1.53(14) | | |
| C(52)–Os(5) | 1.88(7) | C(3)–Os(5) | 2.21(10) | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Os(3)–Os(1)–Os(2) | 102.1(1) | Os(4)–Os(1)–Os(2) | 59.0(1) | Os(6)–Os(4)–Os(1) | 62.2(1) | Os(6)–Os(4)–Os(2) | 122.3(1) |
| Os(4)–Os(1)–Os(3) | 59.0(1) | Os(5)–Os(1)–Os(2) | 55.6(1) | Os(6)–Os(4)–Os(1) | 58.3(3) | Os(6)–Os(4)–Os(5) | 108.5(1) |
| Os(5)–Os(1)–Os(3) | 54.1(1) | Os(5)–Os(1)–Os(4) | 58.6(1) | C(41)–Os(4)–Os(1) | 101(2) | C(42)–Os(4)–C(41) | 97(3) |
| Os(6)–Os(1)–Os(2) | 116.3(1) | Os(6)–Os(1)–Os(3) | 56.0(1) | C(43)–Os(4)–C(41) | 97(3) | C(43)–Os(4)–C(42) | 89(3) |
| Os(6)–Os(1)–Os(4) | 59.3(1) | Os(6)–Os(1)–Os(5) | 102.1(1) | Os(2)–Os(5)–Os(1) | 60.2(1) | Os(3)–Os(5)–Os(1) | 62.5(1) |
| C(12)–Os(1)–C(11) | 90(3) | C(13)–Os(1)–C(11) | 94(4) | Os(3)–Os(5)–Os(2) | 113.2(1) | Os(4)–Os(5)–Os(1) | 57.0(1) |
| C(13)–Os(1)–C(12) | 94(3) | Os(4)–Os(2)–Os(1) | 58.7(1) | Os(4)–Os(5)–Os(2) | 60.1(1) | Os(4)–Os(5)–Os(3) | 61.5(1) |
| Os(5)–Os(2)–Os(1) | 64.2(1) | Os(5)–Os(2)–Os(4) | 61.5(1) | C(52)–Os(5)–C(51) | 92(3) | C(3)–Os(5)–Os(3) | 88(3) |
| C(22)–Os(2)–C(21) | 87(4) | C(23)–Os(2)–C(21) | 93(4) | Os(3)–Os(6)–Os(1) | 63.6(1) | Os(4)–Os(6)–Os(1) | 58.5(1) |
| C(23)–Os(2)–C(22) | 88(3) | Os(4)–Os(3)–Os(1) | 57.2(1) | Os(4)–Os(6)–Os(3) | 61.4(1) | C(62)–Os(6)–C(61) | 90(3) |
| Os(5)–Os(3)–Os(1) | 63.4(1) | Os(5)–Os(3)–Os(4) | 61.3(1) | C(63)–Os(6)–C(61) | 103(4) | C(63)–Os(6)–C(62) | 91(4) |
| Os(6)–Os(3)–Os(1) | 60.5(1) | Os(6)–Os(3)–Os(4) | 60.3(1) | C(2)–C(1)–Os(3) | 86(6) | C(8)–C(1)–Os(3) | 105(6) |
| Os(6)–Os(3)–Os(5) | 113.8(1) | C(32)–Os(3)–C(31) | 85(4) | C(8)–C(1)–C(2) | 131(8) | C(3)–C(2)–C(1) | 129(8) |
| C(1)–Os(3)–Os(5) | 87(2) | Os(2)–Os(4)–Os(1) | 62.3(1) | C(2)–C(3)–Os(5) | 94(6) | C(4)–C(3)–Os(5) | 116(6) |
| Os(3)–Os(4)–Os(1) | 63.8(1) | Os(3)–Os(4)–Os(1) | 63.8(1) | C(4)–C(3)–C(2) | 121(8) | C(5)–C(4)–C(3) | 118(8) |
| Os(3)–Os(4)–Os(2) | 108.0(1) | Os(5)–Os(4)–Os(1) | 64.4(1) | C(6)–C(5)–C(4) | 119(9) | C(7)–C(6)–C(5) | 112(10) |
| Os(5)–Os(4)–Os(2) | 58.4(1) | Os(5)–Os(4)–Os(3) | 57.2(1) | C(8)–C(7)–C(6) | 124(11) | C(7)–C(8)–C(1) | 97(8) |

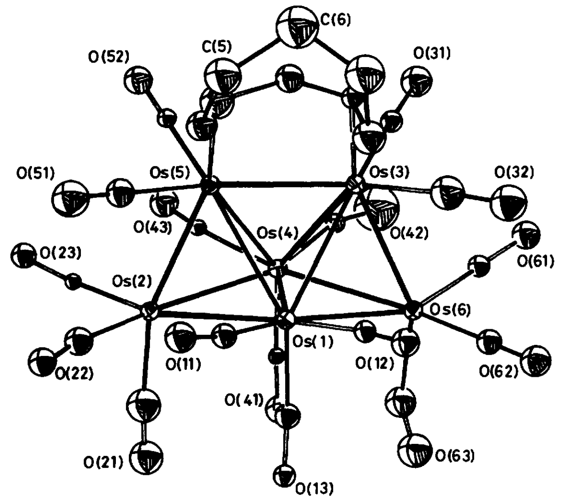

**Figure 3.** The molecular structure of $[Os_6H(CO)_{16}(\mu\text{-}C_8H_{11})]$ (**2**)

$Os(3)–C(1)$, $Os(3)–C(2)$, $Os(5)–C(2)$, and $Os(5)–C(3)$ are 2.39(8), 2.66(8), 2.73(8), and 2.21(10) Å respectively.

The position of the pendant C=C bond is not apparent as the C(5)–C(6) and C(6)–C(7) distances [1.67(17) and 1.54(16) Å] are statistically equivalent (0.5σ). The high estimated standard deviations on the bond parameters of the $\mu\text{-}C_8H_{11}$ ligand and the higher thermal parameters for C(5), C(6), and C(7) indicate some positional disorder, which we were unable to model.

All of the 16 carbonyl ligands are approximately linear and terminal although C(42)–O(42) and C(63)–O(63) both have an Os–C–O angle of 158°. These two carbonyls are slightly bent but do not semi-bridge any metallic edges. The Os–C distances vary from 1.76(7) to 2.01(10) Å and the C–O distances from 0.99(9) to 1.44(10) Å. These large variations are a consequence of low-quality data and are not assigned any chemical significance.

A significant variation is observed in the Os–Os distances of

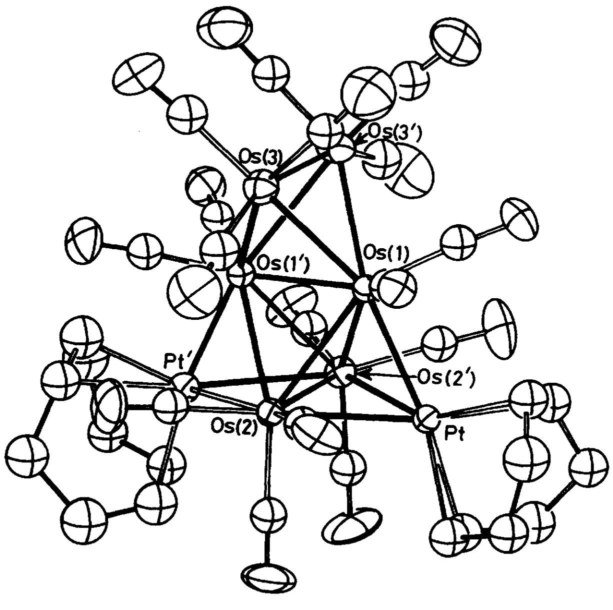

**Figure 4.** The structure of $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ (**3**) (ref. 3)

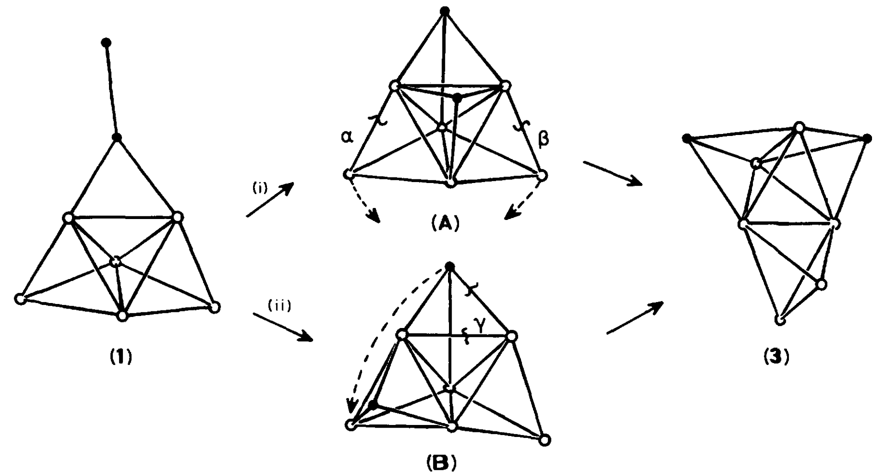

Figure 5. Two possible pathways for the transformation of cluster (1) to cluster (3). (●) Pt atoms, (○) Os atoms

cluster (2), 2.716(4)—2.998(4) Å. The shortest separation is Os(3)–Os(5) which is the edge-bridged by the μ-$C_8H_{11}$ group. The longest separations, Os(1)–Os(3) 2.974(4) and Os(1)–Os(5) 2.998(4) Å, are edges forming a triangulated face of the central tetrahedron of the $Os_6$ core. The hydride ligand was not located in the *X*-ray analysis; however, the distortion[11] in the metallic core of cluster (2) indicates that the hydride ligand triply bridges the face of the central tetrahedron with long Os–Os separations.

The $^1H$ n.m.r. spectrum of (2) is consistent with the solid-state structure and shows a single resonance at $\delta$ −21.09, with satellite peaks due to two $^{187}Os-^1H$ couplings, $^1J(^{187}Os-^1H)$ 27 and 24 Hz.

The dehydrogenation of cyclo-octa-1,5-diene is probably promoted by the proximity of two activated metallic centres and is likely to proceed *via* a mechanism similar to cyclometallation, *i.e.* co-ordination of a C=C bond and oxidative addition of a C–H bond to an adjacent Os atom.

The reverse dehydrogenation reaction occurs under relatively mild conditions for both clusters (1) and (2). A solution of cluster (1) in $CH_2Cl_2$ reacts with CO to yield the isoelectronic complex $[Os_6(CO)_{18}]$, with 35% yield after 4 d. Although $C_8H_{12}$ is not directly observed we believed that the hydrogen ligand has migrated back onto the μ-$C_8H_{11}$ group which is released as $C_8H_{12}$ as no new hydride complexes have appeared.

Upon heating in toluene at 50 °C for 1.5 h, complex (1) is converted to $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ (3) (35% yield), a cluster[3] having a different metallic framework and without hydride ligands (Figure 4). Thus the hydride ligands of cluster (1) have migrated back onto the μ-$C_8H_{10}$ group and this leads to a rearrangement of the metallic framework from a bicapped tetrahedral geometry of the six Os atoms to two edge-fused tetrahedra. The Pt atoms of (1) which were originally bridging and terminal are found to be capping two opposed faces in complex (3). It is interesting to note that compound (3) was also isolated from the original reaction mixture that yielded cluster (1) at room temperature.

Figure 5 illustrates two possible rearrangement pathways, both of which involve single-edge cleavage,[12] for the transformation of structure (1) to (3). The Pt 'spike' in both pathways is moved to a capping position as in postulated intermediate geometries (A) and (B). The two capping $Os(CO)_3$ units of intermediate (A), pathway (i), can be brought into interaction (breaking edges α and β) and thus producing the metallic framework of (3). In pathway (ii), one Pt cap migrates on the face opposite to the other capping $Pt(C_8H_{12})$ unit and by breaking the edge γ of intermediate (B) structure (3) is generated. Intermediate (A) has not been detected while the metal core of (B) has been observed in the cluster $[Os_6Pt_2(CO)_{16}(C_8H_{12})\{P(OMe)_3\}_2]$[3] in which one $C_8H_{12}$ of $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ (3) was substituted for two $P(OMe)_3$ groups. Furthermore, the core structure of inermediate (B) or $[Os_6Pt_2(CO)_{16}(C_8H_{12})\{P(OMe)_3\}_2]$ has been postulated[3] to be an alternative solution structure of cluster (3).

## Experimental

All reactions were performed under nitrogen using dry, freshly distilled solvents. Product separation was carried out, in air, using t.l.c. (plates 0.25 mm thick, Merck Kieselgel 60); $R_f$ values are not quoted as all the plates were continuously eluted until acceptable separation was achieved. Infrared spectra were recorded on a Nicolet 5DXFTIR spectrophotometer. $^1H$ N.m.r. spectra were obtained on Varian XL-200 and XL-400 spectrometers.

The reaction of $[Os_6(CO)_{16}(NCMe)_2]$ with $[Pt(C_8H_{12})_2]$ and the product separation have been previously described.[3] Compound (1), obtained in 20% yield, is the lowest red band on the t.l.c. plate. Compound (2) is observed as a trace amount and is the orange first band (from the top) on the t.l.c. plate. The yield of (2) is increased to 25% by direct reaction of $[Os_6(CO)_{16}(NCMe)_2]$ with cyclo-octa-1,5-diene {under the same conditions as with $[Pt(C_8H_{12})_2]$} and after t.l.c. of the reaction mixture (2) is the second band; three other major products are yet to be characterized. *X*-Ray quality crystals of the clusters were obtained by recrystallization from $CH_2Cl_2$–cyclohexane at 0 °C for (1) and from the slow evaporation of an ethyl acetate solution of (2) at 23 °C.

*Reaction of* $[Os_6H(CO)_{16}(\mu\text{-}C_8H_{11})]$ (2) *with* CO.—A solution of (2) (2 mg) in $CH_2Cl_2$ (10 $cm^3$) was stirred under CO at room temperature for 4 d. T.l.c. of the solution using hexane–$CH_2Cl_2$ (5:1) as eluant gave four bands (decreasing $R_f$ order): yellow, $[Os_3(CO)_{12}]$ (trace); brown, $[Os_6(CO)_{18}]$ (30% yield); blue, $[Os_6(CO)_{21}]$ (trace); unreacted (2) (70%). The complexes $[Os_3(CO)_{12}]$[13] and $[Os_6(CO)_{21}]$[14] were identified according to their characteristic colours (no i.r. spectra) and their relative $R_f$ values on the t.l.c. plate.

*Conversion of* $[Os_6Pt_2H_2(CO)_{16}(\mu\text{-}C_8H_{10})(C_8H_{12})]$ (1) *into* $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ (3).—Complex (1) (3 mg) was heated in toluene (5 $cm^3$) at 50 °C. The heating was stopped after 1.5 h when some decomposition was observed by spot t.l.c. The

**Table 4.** Positional parameters ( × 10$^4$) for the non-H atoms of $[Os_6Pt_2H_2(CO)_{16}(\mu\text{-}C_8H_{10})(C_8H_{12})]$ (**1**)

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Os(1) | 9 473(3) | 1 588(1) | 7 853(1) | C(51) | 5 860(63) | 850(17) | 4 301(34) |
| Os(2) | 8 737(2) | 1 558(1) | 6 070(1) | O(51) | 4 683(49) | 888(13) | 3 609(27) |
| Os(3) | 6 812(2) | 1 051(1) | 6 698(1) | C(52) | 7 158(66) | 149(19) | 5 338(35) |
| Os(4) | 8 927(3) | 852(1) | 8 522(1) | O(52) | 6 782(48) | −218(14) | 5 358(26) |
| Os(5) | 7 683(3) | 737(1) | 5 338(1) | C(53) | 8 821(85) | 609(23) | 4 727(46) |
| Os(6) | 10 000(3) | 798(1) | 7 147(1) | O(53) | 9 627(78) | 520(21) | 4 311(42) |
| Pt(1) | 7 273(2) | 2 137(1) | 6 734(1) | C(61) | 12 008(99) | 835(27) | 8 122(54) |
| Pt(2) | 8 456(2) | 3 010(1) | 7 067(1) | O(61) | 13 225(68) | 811(18) | 8 828(37) |
| C(11) | 8 866(67) | 1 858(19) | 8 563(38) | C(62) | 9 727(53) | 231(15) | 7 236(29) |
| O(11) | 8 497(54) | 2 036(15) | 9 088(30) | O(62) | 9 488(51) | −163(15) | 7 268(28) |
| C(12) | 11 475(86) | 1 713(23) | 8 616(46) | C(63) | 11 242(116) | 772(33) | 6 536(63) |
| O(12) | 12 803(59) | 1 889(16) | 9 065(32) | O(63) | 12 182(69) | 714(19) | 6 176(39) |
| C(21) | 7 347(67) | 1 872(19) | 5 122(37) | C(111) | 6 160(53) | 3 343(15) | 6 173(29) |
| O(21) | 6 365(62) | 2 044(17) | 4 451(34) | C(112) | 6 440(71) | 2 986(20) | 5 697(39) |
| C(22) | 10 488(53) | 1 713(14) | 5 832(28) | C(113) | 5 362(65) | 2 536(18) | 5 762(36) |
| O(22) | 11 398(54) | 1 880(15) | 5 622(30) | C(114) | 5 001(65) | 2 432(18) | 6 463(36) |
| C(31) | 5 709(69) | 1 315(19) | 7 268(37) | C(115) | 6 133(54) | 2 524(15) | 7 390(30) |
| O(31) | 4 887(50) | 1 458(14) | 7 621(27) | C(116) | 6 982(65) | 2 957(18) | 7 704(35) |
| C(32) | 5 160(56) | 1 245(15) | 5 621(30) | C(117) | 5 882(72) | 3 323(20) | 7 530(39) |
| O(32) | 3 983(47) | 1 382(13) | 5 054(25) | C(118) | 4 990(55) | 3 422(15) | 6 560(29) |
| C(33) | 5 885(59) | 495(17) | 6 679(32) | C(121) | 10 294(52) | 2 900(14) | 6 496(28) |
| O(33) | 5 413(49) | 145(14) | 6 692(26) | C(122) | 10 104(68) | 3 345(19) | 6 436(37) |
| C(41) | 10 843(79) | 867(22) | 9 494(43) | C(123) | 11 114(82) | 3 699(23) | 7 064(43) |
| O(41) | 12 021(69) | 915(18) | 10 240(37) | C(124) | 10 561(55) | 3 787(16) | 7 835(30) |
| C(42) | 7 542(90) | 974(25) | 8 989(49) | C(125) | 9 988(65) | 3 421(18) | 8 103(34) |
| O(42) | 6 915(57) | 1 117(16) | 9 453(31) | C(126) | 10 614(46) | 3 005(13) | 8 276(26) |
| C(43) | 8 607(96) | 202(29) | 8 679(52) | C(127) | 12 214(68) | 2 911(18) | 8 171(37) |
| O(43) | 8 240(62) | −127(18) | 8 796(34) | C(128) | 11 846(99) | 2 774(28) | 7 231(53) |

**Table 5.** Positional parameters ( × 10$^4$) for the non-H atoms of $[Os_6H(CO)_{16}(\mu\text{-}C_8H_{11})]$ (**2**)

| Atom | *x* | *y* | *z* | Atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Os(1) | −74(3) | 1 231(1) | −2 024(3) | O(41) | 664(61) | 2 397(17) | −203(57) |
| Os(2) | 1 611(4) | 1 247(1) | 620(3) | C(42) | 3 751(79) | 2 056(21) | −1 821(72) |
| Os(3) | 2 623(3) | 1 301(1) | −3 309(3) | O(42) | 4 469(104) | 2 416(27) | −2 133(98) |
| Os(4) | 2 504(3) | 1 753(1) | −1 141(3) | C(43) | 4 255(74) | 1 700(20) | 300(68) |
| Os(5) | 3 350(3) | 942(1) | −1 010(3) | O(43) | 5 402(68) | 1 763(18) | 1 047(61) |
| Os(6) | 393(4) | 1 903(1) | −3 526(3) | C(51) | 3 070(101) | 504(28) | 107(97) |
| C(11) | −836(86) | 793(24) | −1 444(77) | O(51) | 3 018(76) | 303(22) | 781(74) |
| O(11) | −1 249(68) | 445(19) | −1 106(64) | C(52) | 5 542(80) | 1 006(22) | −130(73) |
| C(12) | −1 466(86) | 1 133(22) | −3 682(80) | O(52) | 6 844(61) | 1 027(15) | 430(54) |
| O(12) | −2 355(64) | 1 055(17) | −4 560(60) | C(61) | 1 576(82) | 2 257(22) | −4 305(75) |
| C(13) | −1 580(91) | 1 571(24) | −1 526(81) | O(61) | 2 217(62) | 2 422(17) | −4 995(60) |
| O(13) | −2 526(53) | 1 771(14) | −1 159(49) | C(62) | −1 261(91) | 1 881(24) | −5 001(83) |
| C(21) | 291(117) | 1 591(32) | 1 244(102) | O(62) | −2 318(66) | 1 848(17) | −5 935(60) |
| O(21) | −375(71) | 1 848(19) | 1 599(63) | C(63) | −872(107) | 2 245(29) | −2 774(94) |
| C(22) | 660(98) | 803(27) | 1 380(87) | O(63) | −1 594(74) | 2 503(20) | −2 666(70) |
| O(22) | 89(64) | 610(17) | 1 794(56) | C(1) | 3 229(84) | 683(22) | −4 150(76) |
| C(23) | 3 295(72) | 1 267(20) | 2 130(66) | C(2) | 4 244(97) | 623(26) | −3 038(88) |
| O(23) | 4 387(59) | 1 249(16) | 3 022(53) | C(3) | 3 982(111) | 406(30) | −1 936(102) |
| C(31) | 4 240(83) | 1 501(22) | −3 735(76) | C(4) | 2 731(102) | 62(28) | −2 115(95) |
| O(31) | 5 417(6) | 1 712(18) | −3 943(59) | C(5) | 2 874(116) | −265(32) | −3 012(109) |
| C(32) | 1 554(120) | 1 366(31) | −4 986(111) | C(6) | 3 512(146) | −156(40) | −4 305(139) |
| O(32) | 789(82) | 1 421(22) | −6 060(77) | C(7) | 2 348(122) | 135(35) | −5 171(114) |
| C(41) | 1 425(74) | 2 165(20) | −499(67) | C(8) | 1 717(110) | 516(29) | −4 702(100) |

solvent was then removed under vacuum and t.l.c. of the solid using hexane–$CH_2Cl_2$ (4:1) as eluant gave two bands: complex (**3**) (35% yield), identified according to its i.r. spectrum, followed by unconverted (**1**) (60%). About 5% of the solid did not move on the t.l.c. plate.

*Crystal Data for* (**1**)·$CH_2Cl_2$.—$C_{33}H_{26}Cl_2O_{16}Os_6Pt_2$, $M$ = 2 280.83, monoclinic, $a$ = 9.143(1), $b$ = 30.778(6), $c$ = 16.618(3) Å, $\beta$ = 115.68(1)°, $U$ = 4 214.4 Å$^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda$ = 0.710 69 Å), space group $P2_1/c$, $Z$ = 4, $D_c$ = 3.59 g cm$^{-3}$, $F(000)$ = 3 992; dark red blocks, crystal dimensions 0.067 × 0.083 × 0.150 mm; crystal faces (10 − 2), (−100), {010}, {011}; $\mu$(Mo-$K_\alpha$) = 238.6 cm$^{-1}$.

*Crystal Data for* (**2**).—$C_{24}H_{12}O_{16}Os_6$, $M$ = 1 697.53, monoclinic, $a$ = 8.478(1), $b$ = 33.938(6), $c$ = 10.921(1) Å, $\beta$ = 104.516(9)°, $U$ = 3 041.8 Å$^3$ (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda$ = 0.710 69 Å), space group $P2_1/n$, $Z$ = 4, $D_c$ = 3.71 g cm$^{-3}$,

$F(000) = 2\,960$; red long blocks, crystal dimensions $0.04 \times 0.05 \times 0.12$ mm; crystal faces {010}, {011}, {110}; $\mu(\text{Mo-}K_\alpha) = 250.8$ cm$^{-1}$.

*Data Collection and Processing.*[15]—Enraf-Nonius CAD4 diffractometer, graphite-monochromated Mo-$K_\alpha$ radiation. For (**1**), $\theta/2\theta$ mode with scan width $0.75 + 0.35 \tan\theta$, scan speed 0.5—10.0° min$^{-1}$. 6 087 Unique reflections measured ($2 \leqslant 2\theta \leqslant 50°$; $+h$, $+k$, $\pm l$). Gaussian absorption correction with a grid of $12 \times 6 \times 6$ (transmission coefficients from 0.248 to 0.338), giving 3 070 with $I > 3\sigma(I)$. Crystal decay, *ca.* −2.8%, not corrected during processing. For (**2**), $\theta/2\theta$ mode with scan width $0.90 + 0.35 \tan\theta$, scan speed 0.4—10.0° min$^{-1}$. 3 148 Unique reflections measured ($2 \leqslant 2\theta \leqslant 44°$, $+h$, $+k$, $\pm l$). Gaussian absorption correction with a grid of $14 \times 6 \times 6$ (transmission coefficients from 0.202 to 0.468), giving 1 841 with $I > 3\sigma(I)$. Crystal decay, *ca.* 0.4%, not corrected during processing. The two data sets were corrected for Lorentz and polarization factors.

*Structure Analysis and Refinement.*—Structures were solved by automatic direct methods using SHELX,[16] followed by difference-Fourier syntheses. Structure (**1**) was first refined by blocked-cascade least-squares methods, with Os and Pt atoms assigned anisotropic thermal parameters and C and O atoms individual isotropic thermal parameters. The structure solution then revealed the existence of one independent solvated $CH_2Cl_2$ molecule. Consequently the Cl and C atoms of the solvent $CH_2Cl_2$ molecule were refined with anisotropic thermal parameters. Hydrogen atoms were not located. The refinement converged at $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.067$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}} = 0.067$, with the weighting $w = [\sigma^2(F) + p(F^2)]^{-1}$, where $p = 0.003$ (3 070 observations and 294 variables). In the final cycle no shift exceeded 0.06 of its standard deviation for the cluster and 0.135 for the solvent molecule. A total difference-Fourier synthesis calculated from the final structure factors contained no features of chemical significance with the highest peak, of electron density 4.3 e Å$^{-3}$, at fractional co-ordinates (0.973, 0.161, 0.600), associated with Os(2).

Structure (**2**) was refined by least-squares methods with Os atoms assigned anisotropic thermal parameters and C and O atoms individual isotropic thermal parameters. Hydrogen atoms were not located. The refinement converged at $R = 0.067$ and $R' = 0.065$, with the weighting $w = [\sigma^2(F) + p(F^2)]^{-1}$, where $p = 0.002$ (1 841 observations and 215 variables). In the final cycle no shift exceeded 0.012 of its standard deviation. A total difference-Fourier synthesis calculated from the final structure factors contained no features of chemical significance with the highest peak, of electron density 2.8 e Å$^{-3}$, at fractional co-ordinates (0.512, 0.238, −0.352), associated with O(42).

Complex neutral-atom scattering factors[17] were employed in both structure solutions and refinements. All computations were performed on a Gould S.E.L. computer at the University of Toronto. The molecular plots were drawn using the program ORTEP.[18] Final positional parameters of the atoms of complexes (**1**) and (**2**) are given in Table 4 and 5.

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