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Preliminary communication

THE SYNTHESIS AND CHARACTERISATION OF SOME MIXED-METAL CARBONYL HYDRIDES CONTAINING TUNGSTEN: THE X-RAY CRYSTAL STRUCTURE OF $[(Ph_3P)_2N][Os_3WH(CO)_{14}]$

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Summary

The mixed-metal cluster anion $[Os_3W(\mu\text{-}H)(\mu\text{-}CO)(CO)_{13}]^-$ has been prepared by the reaction of $[Os_3(\mu\text{-}H)(CO)_{11}]^-$ with $W(CO)_3(MeCN)_3$, and the dianion, $[Os_3W(CO)_{14}]^{2-}$, may be obtained by subsequent deprotonation. An X-ray analysis of the monoanion shows that the metals adopt a *closo*-tetrahedral geometry with the W atom coordinated to four terminal and one bridging carbonyl groups. The neutral clusters $[Os_3WH_2(CO)_{14}]$ and $[Os_3WH(CO)_{14}I]$ are formed upon treatment of the monoanion with sulphuric acid and iodine, respectively.

Mixed-metal clusters have been the subject of an increasing number of studies in recent years, partly because of their catalytic properties [1], and partly because of the wide variety of accessible cluster geometries which often lead to novel reaction chemistry. However, much of this work has concentrated on the later transition metals, and there are relatively few examples of mixed-metal clusters containing elements of the iron subgroup combined with Group VIA metals [2—4]. All the structural studies in the area have been on substituted complexes containing a wide variety of ligands, and there have been no reports of binary carbonyls or carbonyl hydrides. In this communication we report the preparation of the $[(Ph_3P)_2N]^+$ salt of the mixed-metal cluster anion $[Os_3W(\mu\text{-}H)(CO)_{14}]^-$ by the reaction of $[(Ph_3P)_2N][Os_3H(CO)_{11}]$ with an equimolar quantity of $W(CO)_3(MeCN)_3$ in tetrahydrofuran, under reflux. The salt was purified by thin layer chromatography using a 3/2 mixture of CH_2Cl_2/petroleum ether as eluant.

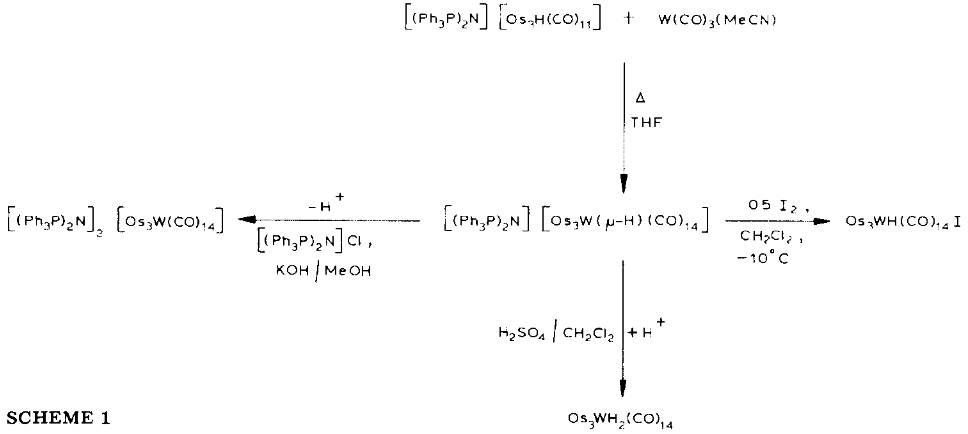
The $[Os_3W(\mu\text{-}H)(CO)_{14}]^-$ anion displays an IR spectrum in the carbonyl region which closely resembles that of $[(Ph_3P)_2N][Os_4H(CO)_{13}]$ [5], and this suggests that the two molecules have a similar geometry. In the mixed-metal anion the absorption bands occur at 2029s, 2017vs, 2000s, 1970m, and 1940sh cm^{-1}.

At all temperatures the ^{1}H NMR spectrum of $[Os_3W(\mu\text{-}H)(CO)_{14}]^-$ in CD_2Cl_2 exhibits a single hydride resonance at −14.3 ppm which shows two sets of Os satellites about the hydride signal [6]. The $J(^{187}Os—^1H)$ coupling is 20.5 Hz, and this data is consistent with the hydride bringing two Os atoms. At room temperature the ^{13}C NMR spectrum recorded in CD_2Cl_2 exhibits a singlet at 197.04 ppm, while at −70°C a singlet is observed at 188.94 and a doublet at 180.67—180.59 ppm; these peaks are in the ratio 12/2.

Deprotonation of $[Os_3W(\mu\text{-}H)(CO)_{14}]^-$ with an excess of KOH in dry methanol and subsequent addition of an equimolar quantity of $[(Ph_3P)_2N]Cl$ affords a red-orange microcrystalline precipitate of the $[(Ph_3P)_2N]^+$ salt of the $[Os_3W(CO)_{14}]^{2-}$ dianion. This complex displays signals in the carbonyl region of the IR spectrum at 2044w, 2004vs, 1961vs,br, 1937sh, 1926sh, 1892m, 1819w, and 1669vw cm^{-1} (CH_2Cl_2 solvent). The last band is consistent with the presence of a carbonyl capping three Os atoms similar to the arrangement observed in the analogous $[Fe_4(CO)_{13}]^{2-}$ dianion [7].

The protonation of $[(Ph_3P)_2N][Os_3W(\mu\text{-}H)(CO)_{14}]$ is achieved by treating a dry CH_2Cl_2 solution with two drops of concentrated sulphuric acid. The orange microcrystalline product exhibits a molecular ion at m/e^+ 1156 in the mass spectrum. The carbonyl IR spectrum in CH_2Cl_2 shows absorption bands at 2082w, 2050vs, 2022sh, 2012s, and 1932s,br cm^{-1} which are similar to those observed for $Os_4H_2(CO)_{13}$ [8] indicating a similar symmetry. The two hydrides appear as a single resonance, at −17.35 ppm (CD_2Cl_2), and this signal is not split as the temperature is lowered. The spectroscopic data is consistent with the formulation of the product as $Os_3WH_2(CO)_{14}$.

When a half molar proportion of iodine is added to a dichloromethane solution of $[(Ph_3P)_2N][Os_3W(\mu\text{-}H)(CO)_{14}]$ at −10°C the red solution turns orange-yellow, and after purification of the reaction mixture by thin layer chromatography, using a 7/3 ratio of CH_2Cl_2/petroleum ether as eluant, the product $Os_3WH(CO)_{14}I$ is obtained. The carbonyl IR spectrum has absorption bands at 2095m, 2070m,sh, 2057s, 2012vs, 2000sh, 1939vs, 1920sh, and 1867m cm^{-1} (CH_2Cl_2), and is similar to that observed for $Os_4H(CO)_{13}I$ [9], again suggesting a related structure. The mass spectrum exhibits a molecular ion at m/e^+ 1282.



SCHEME 1

The chemistry of the $[Os_3W(\mu\text{-}H)(CO)_{14}]^-$ anion is summarised in Scheme 1. The chromium and molybdenum analogues may also be prepared by the reaction of $[Os_3(\mu\text{-}H)(CO)_{11}]^-$ with $M(CO)_3(MeCN)_3$. The complexes $M(CO)_3(MeCN)_3$ (M = Cr, Mo, W) have previously been shown [10] to be useful reagents for introducing a heterometal into a cluster by reaction with a cluster anion.

In order to establish the molecular structure of the $[Os_3W(\mu\text{-}H)(CO)_{14}]^-$ anion, and to investigate the stereochemistry around the tungsten atom which requires the coordination of a larger number of carbonyl groups than would an osmium atom if the 18-electron rule is to be obeyed, an X-ray structure determination was undertaken. Dark-red platelets suitable for such an analysis were obtained by recrystallisation from CH_2Cl_2/ethanol.

Crystal data. $C_{50}H_{31}NO_{14}Os_3P_2W$, M 1686.15, monoclinic space group $P2_1/n$, a 18.560(6), b 15.923(2), c 18.502(3) Å, β 112.07(1)°, U 5067.3 Å^3, $Z = 4$, D_c 2.21 g cm^{-3}, $F(000) = 3128$, μ(Mo-K_α) 99.12 cm^{-1}. 18,493 Intensities ($2\theta_{max}$ 50.0°) were recorded on a Stoe four-circle diffractometer using graphite-monochromated Mo-K_α radiation and an ω/θ scan technique. The data were corrected for absorption and for Lp factors, and averaged to give 6504 observed reflections [$F > 5\sigma(F)$]. The structure was solved by a combination of direct methods (Os and W atom location) and Fourier difference techniques, and refined by blocked-cascade least-squares (Os, W, P, N, and O atoms anisotropic) to $R = 0.057$ and $R_w = [\Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|] = 0.055$. The phenyl rings were refined as a rigid body with the H atoms placed in idealised positions (C—H 1.08 Å; C—C—H 120.0°) and assigned a common isotropic temperature factor*.

The structure of the $[Os_3W(\mu\text{-}H)(CO)_{14}]^-$ anion is shown in Fig. 1 together with some important bond parameters. The four metal atoms adopt a distorted, *closo*-tetrahedral geometry consistent with the 60 electron count for the cluster. One of the longer Os—W edges [Os(2)—W(1)] is spanned by an asymmetrically bridging carbonyl group [C(41)—O(41)], while two other carbonyl groups ligated to W(1) show weak interactions with the other two Os atoms [Os(1)···C(42) 2.91(2) Å, W(1)—C(42)—O(42) 171(2)°; Os(3)···C(44) 2.92(2) Å, W(1)—C(44)—O(44) 165(2)°]. These two carbonyl groups may be considered to form incipient bridge bonds and help to redress the formal electron inbalance in the cluster if the anionic charge is delocalised over the metal framework; either Os(1) or Os(3) may be considered to be electron poor with 17 electrons. Similar incipient bridges from tungsten to osmium have been observed in the neutral cluster $Os_3W(\mu\text{-}H)_3(CO)_{11}(\eta^5\text{-}C_5H_5)$ [11]. The hydride was not located directly in the analysis but by applying the criteria proposed by Churchill [11,12] it is clear that it bridges the long Os(2)—Os(3) edge, a location consistent with the ^{1}H NMR data. The carbonyl groups adjacent to this edge bend away from it with an average *cis* Os—Os—C angle of 115(2)° compared to a value of 94(2)° for the other two Os—Os edges. The carbonyl groups which are not involved in bridge bonding are essentially linear with a maximum deviation from linearity of 3σ.

The metal—metal bond lengths within the tetrahedral framework in the $[Os_3W(\mu\text{-}H)(CO)_{14}]^-$ anion displays similar trends to those observed in a

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*Final atomic coordinates and bond parameters have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

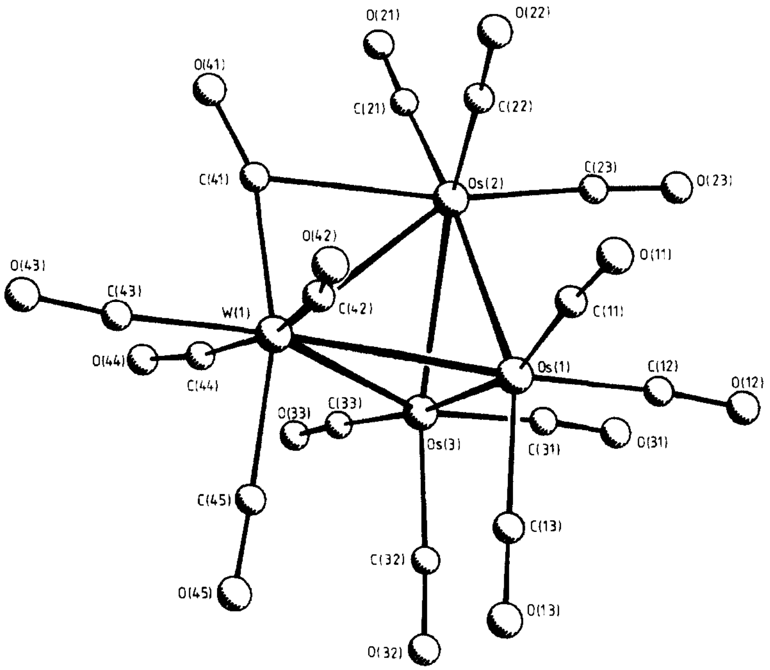

Fig. 1. The structure of the $[Os_3W(\mu\text{-}H)(CO)_{14}]^-$ anion. Bond lengths: W(1)—Os(1) 2.932(1); W(1)—Os(2) 2.973(1); W(1)—Os(3) 2.970(1); Os(1)—Os(2) 2.779(1); Os(1)—Os(3) 2.790(1); Os(2)—Os(3) 2.903(1); W(1)—C(41) 2.00(2); Os(2)—C(41) 2.52(2) Å. Bond angles: W(1)—C(41)—O(41) 160(2); Os(2)—C(41)—O(41) 119(1)°.

number of other tungsten—osmium clusters [3,11,12]. In particular the two unbridged Os—Os distances in the anion [Os(1)—Os(2) and Os(1)—Os(3)] are similar in length to the average value of 2.792(4) Å for the equivalent bonds in $Os_3W(\mu\text{-}H)(CO)_{12}(\eta^5\text{-}C_5H_5)$ [12]. The bond length of the hydride bridged Os—Os edge (2.932(2) Å) in the latter complex is only ca. 0.03 Å longer than that in the $[Os_3W(\mu\text{-}H)(CO)_{14}]^-$ anion. The W—Os edges in the anion are all somewhat longer than the non-hydride bridged W—Os edges in either $Os_3W(\mu\text{-}H)_3(CO)_{12}$-$(\eta^5\text{-}C_5H_5)$ [11] and $Os_3W(\mu\text{-}H)(CO)_{12}(\eta^5\text{-}C_5H_5)$ [12], the W(1)—Os(2) and W(1)—Os(3) distances by ca. 0.06 Å.

It is interesting to note that in $[Os_3W(\mu\text{-}H)(CO)_{14}]^-$ the tungsten atom can accommodate five carbonyl groups around it, all be it that one of these groups is involved in a bridge to an Os atom and two others are in incipient bridge bonding situations. The steric crowding around this tungsten atom may, in fact, be slightly less than that for the tungsten atom in $Os_3W(\mu\text{-}H)_3(CO)_{12}(\eta^5\text{-}C_5H_5)$ [11], where the metal is ligated to two terminal carbonyls, two bridging hydrides, and a cyclopentadienyl group which is considered to occupy a similar volume to two and a half carbonyl groups. The geometry of the anion may be stabilised by the negative charge which donates electron density to the cluster without exerting any steric influence.

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