

### Preliminary communication

## PREPARATION OF THE CLUSTERS $[\text{Os}_3(\text{CO})_{11}\text{CR}_2]$ ( $\text{R} = \text{H}, \text{CH}_2$ ); THE MOLECULAR STRUCTURE OF $[\text{Os}_3(\text{CO})_{11}\text{C}(\text{CH}_2)_2]$

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### Summary

The reaction of  $[\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)]$  (I) with diazomethane and with allene gives the clusters  $[\text{Os}_3(\text{CO})_{11}\text{CH}_2]$  (II) and  $[\text{Os}_3(\text{CO})_{11}\text{C}(\text{CH}_2)_2]$  (III), respectively, in high yields, the structure of the latter complex has been confirmed by a single crystal X-ray analysis.

It has recently been reported that the cluster  $[\text{Os}_3(\text{CO})_{11}\text{CH}_2]$  (II) may be prepared via the acidification of the formyl species  $[\text{Os}_3(\text{CO})_{11}(\text{CHO})]^-$  [1]. Because of the interest in the chemistry of (II) we now report an alternative, high yield preparation via the versatile complex  $[\text{Os}_3(\text{CO})_{11}(\text{NCCH}_3)]$  (I); replacement of the acetonitrile group occurs readily, and in the presence of the ligand, L, yields species  $[\text{Os}_3(\text{CO})_{11}\text{L}]$ . This method may be extended, by reaction with other ligands, to form complexes of the type  $[\text{Os}_3(\text{CO})_{11}\text{CR}_2]$ .

The room temperature reaction of (I) with an ether solution of  $\text{CH}_2\text{N}_2$  gave (II) in good yield\*, and that with allene ( $\text{C}_3\text{H}_4$ ) gave  $[\text{Os}_3(\text{CO})_{11}\text{C}(\text{CH}_2)_2]$  (III) in quantitative yield. The spectroscopic and analytical data for II are in agreement with the values reported previously [1]. The infrared spectrum of III exhibited  $\nu(\text{CO})$  resonances at 2122m, 2075vs, 2066w(sh), 2043vs, 2033vs, 2017s, 2008w, 1996s, 1990m, 1974s, 1943vw  $\text{cm}^{-1}$ . The mass spectrum showed a parent ion at  $m/e$  924. Yellow crystals were grown from  $\text{CH}_2\text{Cl}_2$ /benzene.

The molecular structure was confirmed by a single crystal X-ray analysis.

*Crystal data:*  $\text{C}_{14}\text{H}_4\text{O}_{11}\text{Os}_3$ ,  $M = 918.77$ , monoclinic, space group  $P2_1/c$ ,  $a$  12.650(5),  $b$  9.873(4),  $c$  30.299(15) Å,  $\beta$  91.76(3)°,  $U$  3782.4 Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 3.23 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 201.53 \text{ cm}^{-1}$ . 3964 intensities ( $2\theta_{\text{max}} = 55.0^\circ$ ) were recorded on a Stoe four-circle diffractometer using graphite-monochromated

\*This compound was prepared by this method by the same route [3].

Mo- $K_{\alpha}$  radiation and an  $\omega$ - $\theta$  scan technique. The data were corrected for absorption and averaged to give 3149 unique observed reflections [ $F > 3\sigma(F)$ ]. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked cascade least squares (Os anisotropic, C and O isotropic) to  $R = 0.048$  and  $R' = [\Sigma w^{\frac{1}{2}} \Delta / \Sigma w^{\frac{1}{2}} |F_0|] = 0.048$ .

The asymmetric unit of the unit cell contains two independent but structurally similar molecules, one of which is shown in Fig. 1 together with some bond parameters, averaged between the molecules.

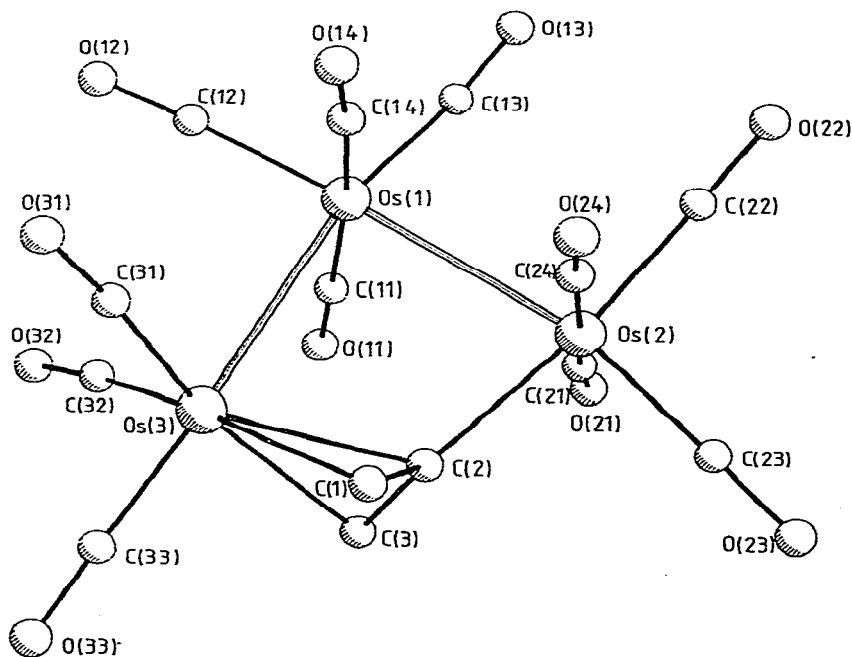
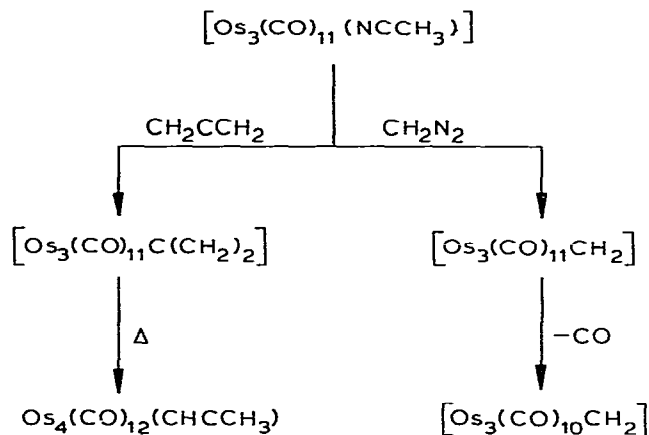


Fig. 1. The molecular structure of  $[\text{Os}_3(\text{CO})_{11}\text{C}(\text{CH}_2)_3]$ . Bond lengths (Å) (distances in the second molecule are given in square brackets): Os(1)—Os(2), 2.917(1) [2.925(2)]; Os(1)—Os(3), 2.947(2) [2.935(2)]; Os(2)—C(2), 2.11(3) [2.13(3)]; Os(3)—C(1), 2.29(3) [2.27(3)]; Os(3)—C(2), 2.28(2) [2.26(3)]; Os(3)—C(3), 2.29(3) [2.24(3)]; C(1)—C(2), 1.43(4) [1.43(4)]; C(2)—C(3), 1.50(4) [1.43(4)] Å. Bond angles: Os(2)—Os(1)—Os(3), 81.7(1) [83.0(1)]; C(1)—C(2)—C(3), 116(2) [113(2)]°.

In III the allyl group, acting as a four electron donor,  $\pi$ -bonds to Os(3) and  $\sigma$ -bonds to Os(1) by means of its available  $p$  orbitals. The inclusion of this additional electron pair from the allene to give a 50 electron system has the effect of breaking the Os(2)—Os(3) bond [Os(2)  $\cdots$  Os(3) 3.860 Å]. The allyl group is orientated so that it is approximately perpendicular to the Os<sub>3</sub> triangle, with C(2) occupying the sixth coordination site of the octahedrally coordinated Os(2) atom and the C(1)C(2)C(3) unit occupying the last site of the six-coordinate Os(3) atom. The allyl C—C distances (average 1.45 Å) indicate a weakening of the C—C bonding upon the coordination of the molecule to the cluster [free ligand C—C distance is 1.36 Å]. This mode of bonding of the CR<sub>2</sub> group is not possible for II, and has not been previously observed in osmium cluster chemistry although it is common in binuclear systems. Recent work with  $[\text{M}_3(\text{CO})_{12}]$

(M = Fe, Ru, Os) and functionalised alkynes has produced allyl substituted clusters but these have the ligand  $\mu_3$ -substituted to the cluster [2].

It has been shown that mono- and bi-nuclear allyl complexes undergo fluxionality on the  $^1\text{H}$  NMR time scale [3]. In view of this the  $^1\text{H}$  NMR spectrum of III was recorded in the range  $-80$  to  $+80^\circ\text{C}$ . At room temperature a doublet of triplets is observed which collapses to a singlet at  $-50^\circ\text{C}$ . At temperatures higher than  $+20^\circ\text{C}$ , there is no change in the spectrum. At first it was considered that fluxionality of the allyl group was responsible, but it was realised that this would necessitate a multiplet at low temperatures and broadening at higher temperatures, the opposite of what is seen. Furthermore, the  $^{13}\text{C}$  NMR spectrum of III showed no fluxionality over the temperature range. Therefore it was concluded that III is not fluxional and that the phenomenon occurring in the  $^1\text{H}$  NMR is probably a solvent effect. This was confirmed by a computer analysis of the FID at  $-10^\circ\text{C}$ , which showed that under the two broad lines were in fact the expected doublet of triplets, indicating the variation of the line shape is in fact pseudo-fluxionality.



SCHEME 1

When  $[\text{Os}_3(\text{CO})_{11}\text{CH}_2]$  (II) is heated, decarbonylation to  $[\text{Os}_3(\text{CO})_{10}\text{CH}_2]$  occurs. This does not happen for  $[\text{Os}_3(\text{CO})_{11}\text{C}(\text{CH}_2)_2]$  (III), which is stable up to the reflux point of octane, whereupon cluster breakdown occurs and a new butterfly cluster  $[\text{Os}_4(\text{CO})_{12}\text{CHCCH}_3]$  can be isolated in 50% yield (Scheme 1).

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## References

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