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# FORMATION OF THE TRIOSMIUM $\mu$-CARBYNE COMPLEX IN THE REACTION OF $O{=}COs_3H(CO)_9\{\mu_3\text{-}\eta^2\text{-}C{=}C(Ph)C{=}C(Ph)Re(CO)_4\}$ WITH DIMETHYLPHENYLPHOSPHINE. X-RAY STRUCTURE OF $HOs_3(CO)_{10}\{\mu\text{-}CC(Ph){=}C{=}C(Ph)Re(CO)_4PMe_2Ph\}$

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## Summary

The $\mu$-acyl complex $O{=}COs_3H(CO)_9\{\mu_3\text{-}\eta^2\text{-}C{=}C(Ph)C{=}C(Ph)Re(CO)_4\}$ (I) reacts with $PMe_2Ph$ to yield the allenyl-substituted $\mu$-carbyne complex $HOs_3(CO)_{10}\{\mu\text{-}CC(Ph){=}C{=}C(Ph)Re(CO)_4PMe_2Ph\}$ (II). Complex II has been characterized by an X-ray structural study.

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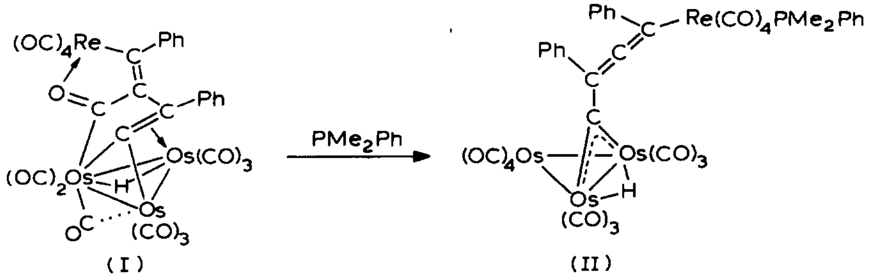
We have recently reported the reaction of complex I with dimethylphenylphosphine which proceeds with cleavage of the carbon–carbon and rhenium–oxygen bonds, and transformation of the $\mu$-acyl group into the terminal CO ligand (in the $^{13}C$ NMR spectrum of the product obtained from the $^{13}CO$-enriched complex $O{=}^{13}COs_3H(^{13}CO)_9\{\mu_3\text{-}\eta^2\text{-}C{=}C(Ph)C{=}C(Ph)Re(CO)_4\}$, ten signals of the terminal CO groups are observed] [1]. On the basis of $^1H$ and $^{31}P$ NMR data and elemental analysis, the zwitterionic structure $[PhMe_2P(OC)_4Re]^+[HOs_3(CO)_{10}\{\mu\text{-}C{=}C(Ph)\text{-}C{\equiv}CPh\}]^-$ has been assigned to the product of the reaction of I with $PMe_2Ph$. However, an X-ray structural study has proved that this product is an allenyl-substituted $\mu$-carbyne complex, $HOs_3(CO)_{10}\{\mu\text{-}CC(Ph){=}C{=}C(Ph)Re(CO)_4PMe_2Ph\}$ (II).



(I) (II)

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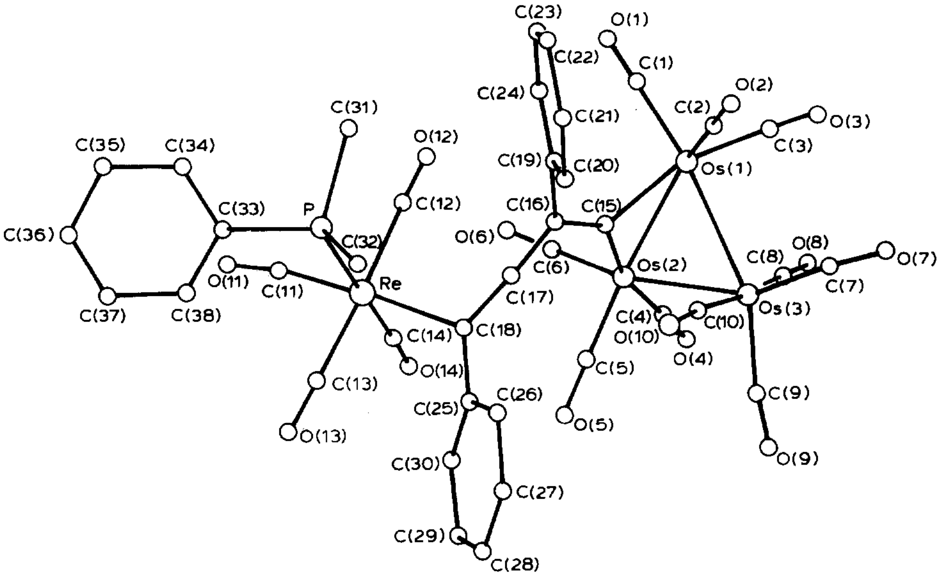

Fig. 1. Molecular structure of II. Bond lengths: Os(1)–Os(2) 2.818, Os(1)–Os(3) 2.870, Os(2)–Os(3) 2.873, Os(1)–C(15) 2.07, Os(2)–C(15) 1.99, C(15)–C(16) 1.44, C(16)–C(17) 1.36, C(17)–C(18) 1.26, C(18)–Re 2.31, Re–P 2.463, Os–C(CO) 1.85–1.96, Re–C(CO) 1.90–2.03, e.s.d.s Os–Os 0.001, Re–P 0.005, Os, Re–C 0.01–0.02, C–C 0.02–0.04 Å.

*Crystal data.* $C_{38}H_{22}O_{14}Os_3PRe$, $M = 1490.4$, triclinic, $a$ 11.914(3), $b$ 12.844(2), $c$ 14.170(3) Å, $\alpha$ 85.18(2), $\beta$ 86.48(2), $\gamma$ 76.50(2)°, space group $P\bar{1}$, $Z = 2$. The intensities of 4780 reflections with $F^2 \geqslant 4\sigma$ were measured with a Syntex $P2_1$ diffractometer at 20°C (Mo-$K_\alpha$ radiation, $\theta/2\theta$ scan, $2\theta \leqslant 50°$; an empirical absorption correction ($\mu$ 127.3 $cm^{-1}$), following the DIFABS method [2], was applied). The structure was solved by the heavy atom method (the coordinates of the Os and Re atoms were determined from Patterson synthesis) and refined in the anisotropic approximation. Hydrogen atoms were not located. The final discrepancy factors were $R = 0.031$ and $R_w = 0.037$. All calculations were carried out using the modified [3] EXTL program package. The atomic coordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 IEW, U.K.

The structure of II is shown in in Fig. 1, which includes some of the important bond parameters. The carbyne atom C(15) is almost symmetrically bonded to Os(1) and Os(2) atoms (Os–C distances are 1.99(2) and 2.07(2) Å, respectively). The hydride ligand was not located by the X-ray study, but according to the $^{13}C$ NMR data * it also bridges the Os(1)–Os(2) bond. The increase of the Os(1)Os(2)C(6) and Os(2)Os(1)C(1) angles up to 108.2(5) and 108.7(7)°, in comparison with other OsOsC angles involving equatorial carbonyls (89.6–99.5°), is also indicative of this. The central part, C(15)C(19)C(16)C(17)C(18)C(25)Re, of the bridging organic ligand

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* At −40°C the Os–$^{13}$CO signals observed were: $\delta$ 180.1(s), 178.7(s), 178.6(s), 178.4(s,br), 176.1(s), 174.9(s), 173.5(d, $^2J$(CH) 11.3 Hz), 172.2(d, $^2J$(CH) 10.1 Hz), 171.5(s, br) and 170.8(s, br). The signals at $\delta$ 180.1, 178.7, 176.1 and 174.9 ppm of the $Os(CO)_4$ moiety are temperature-dependent.

(including the Re atom) has geometry which is typical for allene systems. The double bond lengths (C(16)=C(17) 1.36(2) and C(17)=C(18) 1.26(2) Å) are unexceptional, and the C(16)C(17)C(18) bond angle of 175(2)°, within experimental accuracy, does not differ from 180°; the mean planes C(15)C(19)C(16)C(17) and C(17)C(18)C(25)Re are almost perpendicular to each other (the dihedral angle is 82.9(6)°).

It is interesting to mention that the geometry of complex II reveals some substantial differences in comparison with the structures of related triosmium $\mu$-carbyne complexes [4–6]. The dihedral angle between the Os(1)C(15)Os(2) and $Os_3$ triangle planes is 99.1(1)°, whereas in the complexes $HOs_3(CO)_{10}(CH)$ (III) [4], $HOs_3(CO)_{10}(\mu\text{-CPh})$ (IV) [5] and $HOs_3(CO)_{10}(\mu\text{-CCCH}_2\text{CHMe}_2)$ (V) [6] the corresponding planes form the acute angles 69.7, 78.17 and 82.1°, respectively. As a result, the Os(3) $\cdots$ C(15) distance, 3.09(2) Å, in II is too long for any bonding interaction, in contrast to the other triosmium $\mu$-carbyne complexes [4–6], in which a distinct donor–acceptor interaction between the $Os(CO)_4$ moiety and the carbyne atom is observed. Another peculiar feature of the geometry of complex II is bridging by the $\mu$-hydride ligand of the shortest edge of the $Os_3$ triangle, whereas in complexes III–V this ligand bridges the longest Os–Os bond. It is known that the $\mu_2$-hydride ligand causes metal–metal bonds to lengthen, but this effect is not usually found in cases where the metal–metal bond is also bridged by a $\mu$-carbon atom [7]. Evidently, the above-mentioned difference in the structures of $\mu$-carbyne complexes II and III–V is due to the presence of a donor–acceptor interaction between the $Os(CO)_4$ unit and the carbyne carbon atom in the latter complexes, where the carbyne bridge, in contrast to II, has in fact not $\mu_2$- but $\mu_3$-character.

Complex II easily eliminates phosphine or carbonyl ligand at the rhenium atom, yielding $\mu$-acyl complex I or its phosphine-substituted derivative [1]. Therefore, it may be suggested that the formation of I in the reaction of $HOs_3(CO)_{10}$ ($\mu$-$\eta^2$-C≡CPh) (V) with alkyne $(OC)_5ReC{\equiv}CPh$ proceeds through a $\mu$-carbyne intermediate, $HOs_3(CO)_{10}\{\mu\text{-CC(Ph)=C=C(Ph)Re(CO)}_5\}$.

Reactions of V with other alkynes and the chemistry of II are currently under investigation.

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