A New Type of Osmium–Post-transition Metal Complex containing Four Metal Atoms

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COMPOUNDS containing metal–metal bonds between dissimilar metal atoms can be prepared by various oxidative procedures. These include the oxidation (by simple or co-ordinated metal halides) of monomeric complexes of metals in low oxidation states,[1]

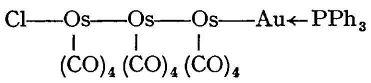
$$e.g.\ (Ph_3P)_2(CO)ClIr + HgCl_2 \longrightarrow (Ph_3P)_2(CO)Cl_2Ir\text{–}HgCl$$

and of dimeric compounds also,[2] *e.g.*

$$[(C_5H_5)(CO)_3Cr]_2 + Ph_3P{\rightarrow}AuCl \longrightarrow (C_5H_5)(CO)_3Cr\text{–}Au{\leftarrow}PPh_3 + (C_5H_5)(CO)_3Cr\text{–}Cl$$

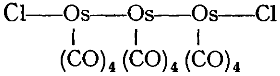
We have now prepared a series of complexes containing *four* metal atoms by oxidising the triangular cluster $Os_3(CO)_{12}$ with co-ordinated gold halides according to the reaction:—

$$Ph_3P{\rightarrow}AuCl + Os_3(CO)_{12} \longrightarrow$$

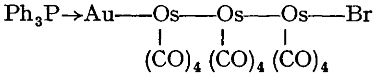


$$Cl\text{—}\underset{(CO)_4}{Os}\text{—}\underset{(CO)_4}{Os}\text{—}\underset{(CO)_4}{Os}\text{—}Au{\leftarrow}PPh_3$$

The red product (satisfactory analyses for $C_{30}H_{15}AuClO_{12}Os_3P$) is monomeric in chloroform and has an i.r. spectrum in the C–O stretching region (2098m, 2046s, 2016sh, 2011s, 1984m, 1979sh, 1967m cm.$^{-1}$ in cyclohexane) which is consistent with linear arrangement of the Au—Os—Os—Os moiety (C_{4v}). Although the tetrahedral arrangement of four metal atoms is well established, *e.g.*

in $Co_4(CO)_{12}$, and the pyramidal in $MeSn[Co(CO)_4]_3$ this seems to be the first probable case of a linear arrangement of four covalent bonded metal atoms. It is a nonconductor in nitromethane and melts sharply at 168°. The compound is similar to the even more symmetrical derivative (D_{4h} symmetry)  $Cl-\underset{(CO)_4}{Os}-\underset{(CO)_4}{Os}-\underset{(CO)_4}{Os}-Cl$ recently prepared by ewis Johnson, and Kilty.[3]

The corresponding red bromo-compound



$$Ph_3P\rightarrow Au-\underset{(CO)_4}{Os}-\underset{(CO)_4}{Os}-\underset{(CO)_4}{Os}-Br$$

has also been isolated and has properties similar to those of the chloride. Decomposition products were obtained when we tried to prepare the analogus iodo-, and triphenylarsine-gold derivatives. These include $Os(CO)_2(PPh_3)_2X_2$ (X = Hal) which have been prepared previously by the reaction of the carbonyl halides with the appropriate ligands.[4] Attempts to make Os–Cu and Os–Ag derivatives using the reaction of $(PPh_3)_3CuCl$ and $(PPh_3)_3AgBr$ with $Os_3(CO)_{12}$ were unsuccessful, triphenylphosphine substituted derivatives of the type $Os_3(CO)_{12-x}(PPh_3)_x$ [$x = 1, 2$, or 3] being formed. Previously, only the tri-substituted derivative was known, this having been prepared[5] by direct reaction between $Os_3(CO)_{12}$ and Ph_3P.

The reaction with the co-ordinated gold halides is in marked contrast to the reaction of $Os_3(CO)_{12}$ with mercuric halides; this reaction forms derivatives of the type $(CO)_4Os(HgCl)_2$ and $(CO)_4Os(Cl)HgCl$, all three Os–Os bonds being broken.[6] Further work on this problem with other metal halides aimed at elucidating the factors which decide whether all three, or only one, Os–Os bond will be ruptured is in progress.

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