Univalent Osmium: Osmium Complexes with Triphenylphosphine and Triphenylarsine

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Other than one carbonyl Os(CO)$_3$ and two carbonyl halides of the type [OsX(CO)$_3$]$_2$ (X = Br, I), described by Hieber and Stallmann, there has been no reported evidence of compounds containing osmium in oxidation states lower than II. For the carbonyl monohalides, [OsX(CO)$_3$]$_2$, the authors propose the conventional halogen-bridged configuration, but no physical measurements are given to support this assumption and thus the univalency of osmium.

This communication reports a new series of osmium complexes, with triphenylphosphine and triphenylarsine, in which the central atom displays the oxidation state I, and an apparent quadricovalency which marks a pronounced departure from all previously known complexes of osmium. The compounds [OsCl(Ph$_3$P)$_3$], [OsBr(Ph$_3$P)$_3$], [OsCl(Ph$_3$As)$_3$] and [OsBr(Ph$_3$As)$_3$] are prepared directly from the corresponding hexahalogenoosmate(IV) and the appropriate ligand which is the sole reducing agent for osmium in the system.

$$\text{(NH}_4\text{)}_2\text{Os}^{IV}\text{Cl}_4 + 4.5 \text{Ph}_3\text{P} \rightarrow [\text{Os}^3\text{Cl}(\text{Ph}_3\text{P})_3] + 1.5 \text{Ph}_3\text{PCl}_2 + 2 \text{NH}_4\text{Cl}.$$ Extensive reduction of Os(IV) is achieved by employing relatively high temperatures ($120^\circ - 150^\circ$) and reaction media which prevent compounds of intermediate valencies from precipitating. Ethylene glycol monomethyl ether (b. p. 124$^\circ$) and various mixtures of ethanol and ethylene glycol (b. p. 196$^\circ$) have proved useful solvents in these preparations.

The crystals of these complexes are colorless or nearly so and stable in air (decomp. temperatures range from 156$^\circ$ to 198$^\circ$). They can be considered as essentially diamagnetic (at 25$^\circ$, $\mu = 0.3$ to 0.5 B. M.) which suggests exchange interaction between two neighboring osmium (I) atoms of $d^7$ configuration. As a consequence, the spatial arrangements of ligands ought to provide for a relatively short Os-Os distance. A dimeric structure, derived from two parallel square planes (each comprising a quadricovalent formula unit), appears to fulfill this requirement and is not inconsistent with the chemical evidence.

From precession and Weissenberg photographs a crystal of OsBr(Ph$_3$P)$_3$ was found to be orthorhombic with $a = 19.5$ Å, $b = 18.7$ Å, and $c = 25.6$ Å. It belongs to space group Pbca (No. 61) and has eight formula units per unit cell. The crystal is centrosymmetric and has a calculated density of 1.50. The X-ray powder diffraction patterns of OsBr(Ph$_3$P)$_3$, OsCl(Ph$_3$P)$_3$, OsBr(Ph$_3$As)$_3$ and OsCl(Ph$_3$As)$_3$ are all very similar, which suggests that these complexes are isomorphs. The stereochemistry of OsBr(Ph$_3$P)$_3$ is being studied by X-rays by Dr. P. Orioli of Istituto di Chimica Fisica della Università di Firenze.

The osmium(I) complexes are non-electrolytes in nitrobenzene. The observed values for their molecular weights in chloroform fall in the range expected for monomeric species. These results, however, are inconclusive, for they may equally well reflect dissociation of phosphine or arsine ligands from a polymeric complex. In fact, substances which are recovered after prolonged treatment with chloroform, contain only two ligand molecules per osmium, indicating a non-equivalence of one Ph$_3$P (or Ph$_3$As) with the two others in the original complex. Reactions with bromine, iodine, triethylphosphite or hydrazine reveal the same property: one neutral ligand molecule is replaced by the reagent. Reduction of OsBr(Ph$_3$P)$_3$ or OsCl(Ph$_3$P)$_3$ with hydrazine has yielded an apparently zerovalent osmium complex which is being studied.

Relatively low solubility of the Os(I) complexes and the instability of the dissolved species toward atmospheric oxidation have hindered determination of magnetic susceptility in solution. To avoid these difficulties, it is intended to study the nature of the dissolved complex by electron spin resonance.

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4. Details of this work, as well as that on bivalent, tervalent, and quadrivalent osmium complexes with triphenylphosphine and triphenylarsine, will be published elsewhere.