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PRELIMINARY COMMUNICATION

NEW HYDRIDO COMPLEXES OF OSMIUM CARBONYL AND SOME RELATED DERIVATIVES

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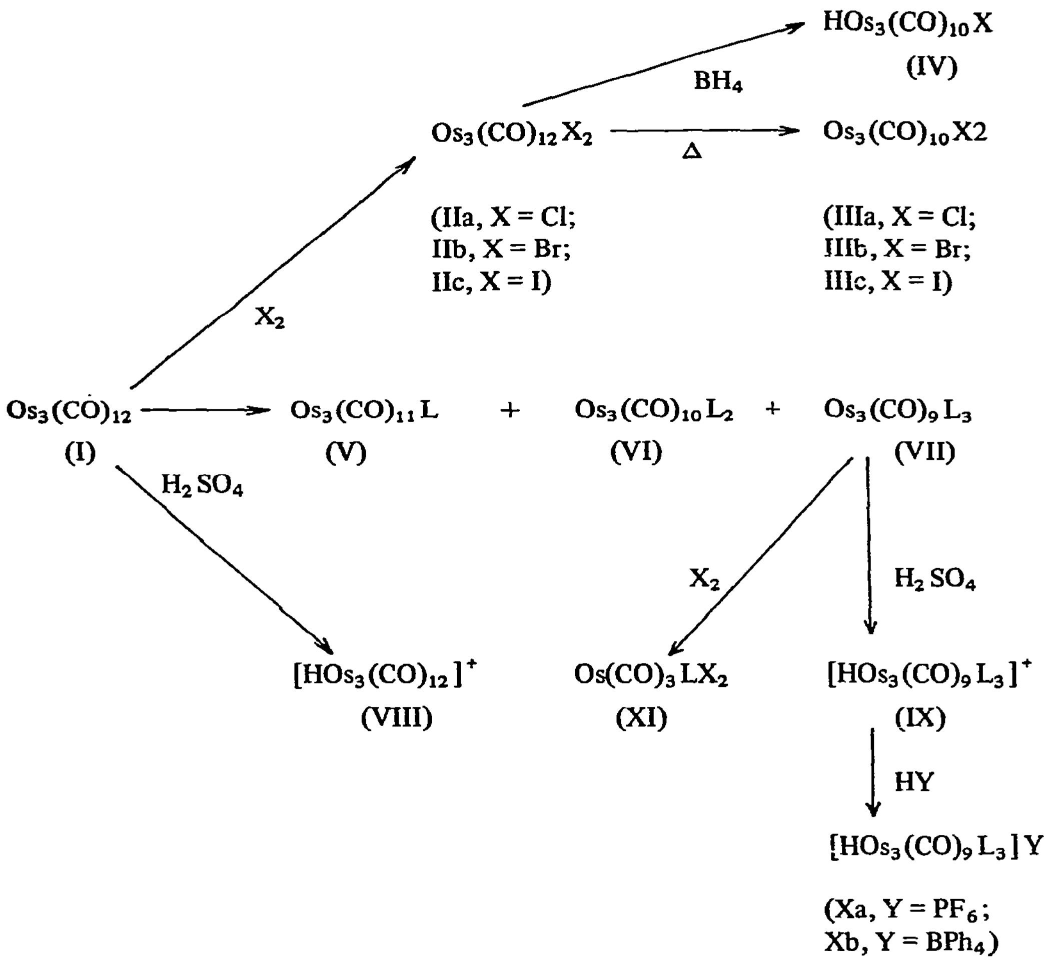
Reaction of dodecacarbonyltriosmium (I) with halogens (X_2) in benzene under reflux has been shown to yield the *linear* complexes $Os_3(CO)_{12}X_2$ (II) as the initial products[1] We now report that on prolonged heating in benzene these complexes (II) are smoothly converted into the *cyclic* $Os_3(CO)_{10}X_2$ derivarives (III) with loss of two molecules of carbon monoxide. Satisfactory analyses were obtained in all cases (IIIa–IIIc) and the molecular weights and precise molecular formulae were derived from mass spectroscopic studies. The structure of the complex $Os_3(CO)_{10}(OMe)_2$ of similar stoichiometry has been established[2] to be cyclic with two OMe groups bridging two osmium atoms. The structure of (III) is expected to be similar. In agreement the IR spectrum of (III) is closely related to that of the dimethoxy derivative and under electron impact ejection of halogen radical from the molecular ion was not observed and this is characteristic of systems containing halogens in bridged positions[3].

Treatment of (IIa) with sodium borohydride in tetrahydrofuran yields $HOs_3(CO)_{10}Cl$ (IV) in low yields. The presence of the hydrido ligand has been confirmed by mass spectroscopic measurements, *m/e* 892; $H^{192}Os_3(CO)_{10}{}^{35}Cl$, and the absence of $(M-Cl)^+$ species is as expected for a system containing a bridging halogen. Other similar complexes, *e.g.*, $HOs_3(CO)_{10}(ER)$ (E = O or S; R = Alkyl or aryl) have been reported earlier[1,4]. For the ethyl mercapto complex, $HOs_3(CO)_{10}SEt$, a cyclic structure involving a bridging thiol group has been established from single crystal X-ray studies[2]. This structure is related to that of $Os_3(CO)_{10}(OMe)_2$ and the hydrido ligand is considered to occupy a bridging position.

Reaction of (I) with ligands such as triethyl- or diethylphenyl-phosphine gave mono- (V), di- (VI), and tri-substituted (VII) complexes which were conveniently separated on an alumina column. In all cases the stoichiometry was established by analytical and mass spectroscopic data. Substitution derivatives of dodecacarbonyl-triiron[5] -triruthenium[6], and -triosmium[7] have been obtained previously but only for iron monosubstituted complexes[5] have been reported. Only one of the several possible isomers of these complexes has been obtained in each case and the stereochemistries which are at present unknown are under investigation. Halogenation of (VII) gives the monomeric complex $OsX_2(CO)_3L$ suggesting that in (VII) one phosphine ligand is coordinated to each osmium atom.



Several hydrido-carbonyl compounds of osmium are known: mononuclear $H_2Os(CO)_4$[8], trinuclear $H_2Os_3(CO)_{10}$[1] and $HOs_3(CO)_{10}(ER)$[1,4], and tetranuclear complexes $H_2Os_4(CO)_{13}$ and $H_4Os_4(CO)_{12}$[1]. We now report that (I) readily dissolves in *concentrated* sulphuric acid giving the cation $[HOs_3(CO)_{12}]^+$ (IX); dodecacarbonyltriruthenium shows similar behaviour. [The NMR spectra are irreversibly temperature- and time-dependent, and signals at 29.9τ (20°), 30.3τ (100°, 1 h), and 18.5τ (100°, 6 h) are observed. The species giving rise to the signal at 18.5τ is the most stable.] The phosphine substituted derivatives of (I) are also soluble in this acid and with $Os_3(CO)_9(PEt_3)_3$ (VII) the salts $[HOs_3(CO)_9(PEt_3)_3]PF_6$ (or BPh_4) (X) have been isolated (broad resonance at 29.2τ in H_2SO_4).

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