Preparation and Crystal Structure of Dichloro(chloromercury)(nitrosyl)bis(triphenylphosphine)osmium(II)

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Summary The osmium-mercury compound, OsCl$_2$ (HgCl)-(NO)(PPh$_3$)$_2$ is formed by oxidative addition of HgCl$_2$ to OsCl(CO)(NO)(PPh$_3$)$_2$; its crystal structure reveals octahedral co-ordination about osmium with an Os–Hg distance of 2·577 Å and a linear Os–N–O linkage.

THE addition of mercuric chloride to d^8 complexes of the platinum metals frequently results in the formation of compounds containing covalent metal–mercury bonds, *e.g.*, (PPh$_3$)$_2$(CO)Cl$_2$Ir–HgCl[1] and [(PPh$_3$)$_2$(CO)$_3$ClOs–HgCl]-HgCl$_3$.[2] Definitive structural information on these compounds is lacking. (π-C$_5$H$_5$)Co(CO)$_2$ also forms a 1 : 1 adduct with mercuric chloride but here structural analysis shows the compound must be formulated as a Lewis acid–base adduct.[3]

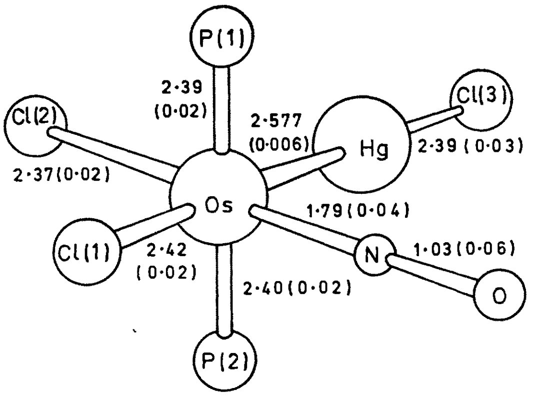

FIGURE. $\angle$OsHgCl(3) 177(1)°; $\angle$ OsNO 178(2)°.

The zerovalent osmium nitrosyl complex, OsCl(CO)(NO)-(PPh$_3$)$_2$,[4] reacts readily with mercuric chloride, with loss of CO, to yield yellow crystals, m.p. 267—269°, analysing for OsCl$_2$(HgCl)(NO)(PPh$_3$)$_2$, (ν_{NO} = 1820 cm^{-1}). The far-i.r. spectrum shows strong bands at 317 and 297 cm^{-1} (ν_{Os-Cl}) and 268 cm^{-1} (ν_{Hg-Cl}) and a band of medium intensity at 173 cm^{-1} which is probably to be associated with Os–Hg stretching. The compound is light-sensitive and, in strong light, mercury is deposited and OsCl$_3$(NO)(PPh$_3$)$_2$ (ν_{NO} 1850 cm^{-1}) formed. The same reaction occurs under *X*-rays and this decomposition has made collection of accurate data difficult.

The yellow crystals have trigonal diffraction symmetry with a = 44·26 ± 0·02, c = 11·983 ± 0·006 Å, space group $R\bar{3}$, z = 18. The structure was solved by Patterson and Fourier methods from *X*-ray data recorded by a Hilger–Watts four-circle automatic diffractometer with Mo-K_α radiation. At the current stage of least-squares refinement R = 0·114 for 1388 independent reflexions.

Octahedral co-ordination is found about the osmium atom (see Figure), metal–phosphorus and metal–chlorine distances having the expected values. The osmium–mercury distance seems short by comparison with the bond lengths found between mercury and first-row transition metals in the complexes Fe(CO)$_4$(HgCl,py)$_2$ (2·552 Å)[5] and Hg[Co-(CO)$_4$]$_2$ (2·50 Å),[6] and also the osmium–osmium bond distance of 2·88 Å found in Os$_3$(CO)$_{12}$.[7] Also of interest is the linearity of the co-ordinated nitrosyl group. The osmium–nitrogen and nitrogen–oxygen bond lengths of 1·79 and 1·03 Å, respectively, although inaccurate, are nevertheless in line with previously reported values.[8]

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