A New Hydridocarbonyl Complex of Osmium(II)

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Summary The reaction of K_2OsCl_6 with tricyclohexylphosphine in alcohols leads to the hydridocarbonyl complex $OsHCl(CO)(PCy_3)_2$.

THE hydridocarbonylphosphine complexes with the formula $MHX(CO)(PPh_3)_3$ where M = Ru or Os and X = Cl or Br may be obtained directly from the metal halides, triphenylphosphine, and alcohols.[1] Stephenson and Wilkinson[2] describe the preparation of the complex $RuCl_2(PPh_3)_3$ by refluxing a methanolic solution of PPh_3 and $RuCl_3$ under nitrogen.

I now report the isolation of the complex $OsHCl(CO)(PCy_3)_2$ (PCy_3 = tricyclohexylphosphine). On boiling a solution of PCy_3 and K_2OsCl_6 in 2-methoxyethanol in an atmosphere of nitrogen for 48 h, a red complex, $OsHCl(CO)(PCy_3)_2$, was obtained. The complex had satisfactory analytical data.

The complex decomposes at 210° and is slightly soluble in organic solvents. It is diamagnetic (measured between room temperature and $-150°$) indicating a low spin d^6-configuration.

The i.r. spectrum (KBr) in the range 2100—1850 cm^{-1} shows two bands attributable to ν(CO) stretching modes at 1932s and 1887m cm^{-1} and one band at 2012 cm^{-1} assigned to ν(M–H). On performing the reaction in deuteriated ethanol, the expected frequency shift for a covalent osmium–hydrogen band was found [ν(M–D) at 1508w cm^{-1}], the other two bands being unchanged. The split nature of the carbonyl bands, which is maintained in benzene solution, suggests that the complex is a mixture of geometrical isomers. So far, attempts to separate isomers have not succeeded. On shaking $OsHCl(CO)(PCy_3)_2$ in an excess of pyridine a yellow complex, $OsHCl(CO)(PCy_3)_2Py$, was obtained. The pyridine complex shows two i.r. absorption bands (KBr) at 2119m and 1870s cm^{-1} attributable to ν(CO) and one weak band at 2040 cm^{-1} assigned to ν(M–H).

In the mass spectrum there is a cluster, with the lowest fragment ion having *m/e* 808 which is in agreement with the formula $^{184}OsH^{35}Cl(CO)(PCy_3)_2$. The relative abundances of the peaks in this cluster agree with the calculated ratios. Fragment ions with higher masses than $OsHCl(CO)(PCy_3)_2$ could not be detected. Comparison of the mass spectra of $OsHCl(CO)(PCy_3)_2$ and its deuteriated derivative, prepared as described above, showed appreciable deuteriation of PCy_3 indicated by the presence of peaks at *m/e* 280—290. As a result we found that the ratios of the cluster of peaks due to $OsDCl(CO)(PCy_3)_2$ differed from the calculated $OsDCl(CO)(PCy_3)_2$ ratios in which the PCy_3 is non-deuteriated. These data suggest an exchange reaction between the complex and deuterium during the preparation of the complex.

All attempts to prepare $OsHCl(CO)(PCy_3)_3$ by addition of an excess of PCy_3 were unsuccessful. The fact that this complex could not be isolated may be due to the steric hindrance of the cyclohexyl groups.[3]

The structure of this complex is probably related to that of the complexes $RuHX(PPh_3)_3$,[4] the diamagnetic complex $RuX_2(SbPh_3)_3$,[2] and $RuCl_2(PPh_3)_3$. An *X*-ray study by La Placa and Ibers[5] has shown a quasi-octahedral structure for $RuCl_2(PPh_3)_3$.

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