A New Hydridocarbonyl Complex of Osmium(II)
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Summary The reaction of \( \text{K}_2\text{OsCl}_6 \) with tricyclohexylphosphine in alcohols leads to the hydridocarbonyl complex \( \text{OsHCl}(\text{CO})(\text{PCy}_3)_2 \).

The hydridocarbonylphosphine complexes with the formula \( \text{MHX}(\text{CO})(\text{PPh}_3)_3 \) where \( M = \text{Ru or Os} \) and \( X = \text{Cl or Br} \) may be obtained directly from the metal halides, triphenylphosphine, and alcohols. Stephenson and Wilkinson describe the preparation of the complex \( \text{RuCl}_2(\text{PPh}_3)_3 \) by refluxing a methanolic solution of \( \text{PPh}_3 \) and \( \text{RuCl}_3 \) under nitrogen.

I now report the isolation of the complex \( \text{OsHCl}(\text{CO})(\text{PCy}_3)_2 \) \( (\text{PCy}_3 = \text{tricyclohexylphosphine}) \). On boiling a solution of \( \text{PCy}_3 \) and \( \text{K}_2\text{OsCl}_6 \) in 2-methoxyethanol in the atmosphere of nitrogen for 48 h, a red complex, \( \text{OsHCl}(\text{CO})(\text{PCy}_3)_2 \), 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 \( \nu(\text{CO}) \) stretching modes at 1932 s and 1887 m cm\(^{-1} \) and one band at 2012 cm\(^{-1} \) assigned to \( \nu(\text{M-H}) \). On performing the reaction in deuteriated ethanol, the expected frequency shift for a covalent osmium-hydrogen band was found at 1508 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 \( \text{OsHCl}(\text{CO})(\text{PCy}_3)_2 \) in an excess of pyridine a yellow complex, \( \text{OsHCl}(\text{CO})(\text{PCy}_3)_2\text{Py} \), was obtained. The pyridine complex shows two i.r. absorption bands (KBr) at 2119 m and 1870 s cm\(^{-1} \) attributable to \( \nu(\text{CO}) \) and one weak band at 2040 cm\(^{-1} \) assigned to \( \nu(\text{M-H}) \).

In the mass spectrum there is a cluster, with the lowest fragment ion having \( m/e \) 808 which is in agreement with the formula \( ^{185}\text{OsH}^{35}\text{Cl}(\text{CO})(\text{PCy}_3)_2 \). The relative abundances of the peaks in this cluster agree with the calculated ratios. Fragment ions with higher masses than \( \text{OsHCl}(\text{CO})(\text{PCy}_3)_2 \) could not be detected. Comparison of the mass spectra of \( \text{OsHCl}(\text{CO})(\text{PCy}_3)_2 \) and its deuteriated derivative, prepared as described above, showed appreciable deuteriation of \( \text{PCy}_3 \) 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 \( \text{OsDCl}(\text{CO})(\text{PCy}_3)_2 \), differed from the calculated \( \text{OsCl}(\text{CO})(\text{PCy}_3)_2 \) ratios in which the \( \text{PCy}_3 \) is non-deuteriated. These data suggest an exchange reaction between the complex and deuterium during the preparation of the complex.

All attempts to prepare \( \text{OsHCl}(\text{CO})(\text{PCy}_3)_3 \) by addition of an excess of \( \text{PCy}_3 \) were unsuccessful. The fact that this complex could not be isolated may be due to the steric hindrance of the cyclohexyl groups.

The structure of this complex is probably related to that of the complexes \( \text{RuH}(\text{PPh}_3)_3 \), the diamagnetic complex \( \text{RuCl}(\text{SbPh}_3)_3 \), and \( \text{RuCl}(\text{PPh}_3)_3 \). An X-ray study by La Placa and Ibers has shown a quasi-octahedral structure for \( \text{RuCl}(\text{PPh}_3)_3 \).

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