

Stoichiometric Hydrogenation of Olefins using $\text{HRuCl}(\text{PPh}_3)_3$ and Formation of an *ortho*-Metallated Ruthenium(II) Complex

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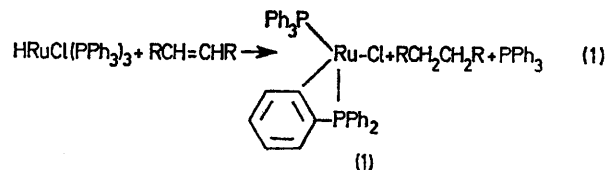
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Summary Stoichiometric hydrogenation of olefins using $\text{HRuCl}(\text{PPh}_3)_3$ in the absence of hydrogen results in formation of the dimer $[(\text{Ph}_3\text{P})\text{ClRu}(o\text{-C}_6\text{H}_4\text{PPh}_2)]_2$; this complex reacts with H_2 , and HCl , to yield in solution the catalytically important bisphosphine complexes $\text{RuXCl}(\text{PPh}_3)_2$ ($\text{X} = \text{H}, \text{Cl}$).

WE report the isolation of the *ortho*-metallated product (1) via a novel synthesis employing the stoichiometric hydrogenation of an olefin with $\text{HRuCl}(\text{PPh}_3)_3$ *in vacuo* [equation (1)]. *ortho*-Metallated complexes, which are of current interest,^{1,2} have not been reported previously for ruthenium(II) phosphine systems, although a related phosphite complex³ $[(\text{PhO})_3\text{P}]_3\text{RuCl}[o\text{-OC}_6\text{H}_4\text{P}(\text{OPh})_2]$ has been made by thermal loss of H_2 from $\text{HRuCl}[\text{P}(\text{OPh})_3]_4$.

A variety of olefins have been used for reaction (1) but activated ones that co-ordinate more strongly give more efficient syntheses. For example, compound (1) is readily

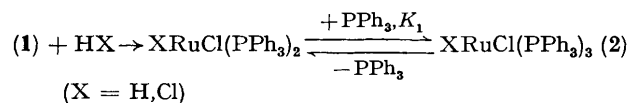
formed and isolated from solutions containing the hydride and maleic acid in a 1:1 ratio maintained at 60° for 4 h, and the complete stoichiometry of reaction (1) has been



demonstrated. Compound (1) analyses correctly; no hydride ligands are present. Mol. wt. data indicate a monomer in dioxan, and a dimer-monomer equilibrium in benzene; a C-H out-of-plane deformation at 720 cm^{-1} and $\nu(\text{C}-\text{C})$ at 1510 cm^{-1} are characteristic of *ortho*-metallation.¹

Yellow solutions of (1) in benzene react with H_2 (1:1) probably via a $\text{Ru}^{\text{IV}}\text{H}_2$ to give a red bisphosphine hydrido-

complex $\text{HRuCl}(\text{PPh}_3)_2$ (not isolated); addition of one mole of phosphine regenerates the readily isolable violet trisphosphine hydrido-complex. Corresponding reactions with HCl give $\text{RuCl}(\text{PPh}_3)_2$ and $\text{RuCl}_2(\text{PPh}_3)_3$, equation (2).



The bisphosphine complexes are important because these are believed to be involved in catalytic systems using the trisphosphine complexes.⁴ Preliminary spectrophotometric data on the K_1 equilibrium (X = H) give $K_1 > 10^6 \text{ M}^{-1}$ at 25° in benzene, indicating that the $\text{HRuCl}(\text{PPh}_3)_3$ is little dissociated at 'catalytic' concentrations of 10^{-3} M .

Solutions of (1) readily absorb 1 mole of CO. Acyl formation by insertion into the C-Ru bond does not occur;⁵ the i.r. spectrum of the product and chemical analysis is consistent with the formulation $(\text{PPh}_3)_2\text{Ru}(\text{CO})\text{Cl}(o\text{-C}_6\text{H}_4\text{PPh}_2)$.

Utilisation of phenyl hydrogens for olefin hydrogenation has been suggested from results of exchange studies for a number of homogeneous catalytic systems,⁵ although to our knowledge the overall stoichiometry of a reaction such as (1) with isolation of the transition-metal product has not been reported previously. The stoichiometric process is unimportant in hydrogenations catalysed by $\text{HRuCl}(\text{PPh}_3)_3$ under H_2 which are very much more rapid⁶. Spectrophotometric data indicate that both the stoichiometric and catalytic hydrogenations likely proceed *via* the same alkyl intermediate but the subsequent hydrogenolysis step is faster than the intramolecular hydrogen transfer step. Regeneration of the hydride by reaction (2) is also slower than the catalytic hydrogenations.

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