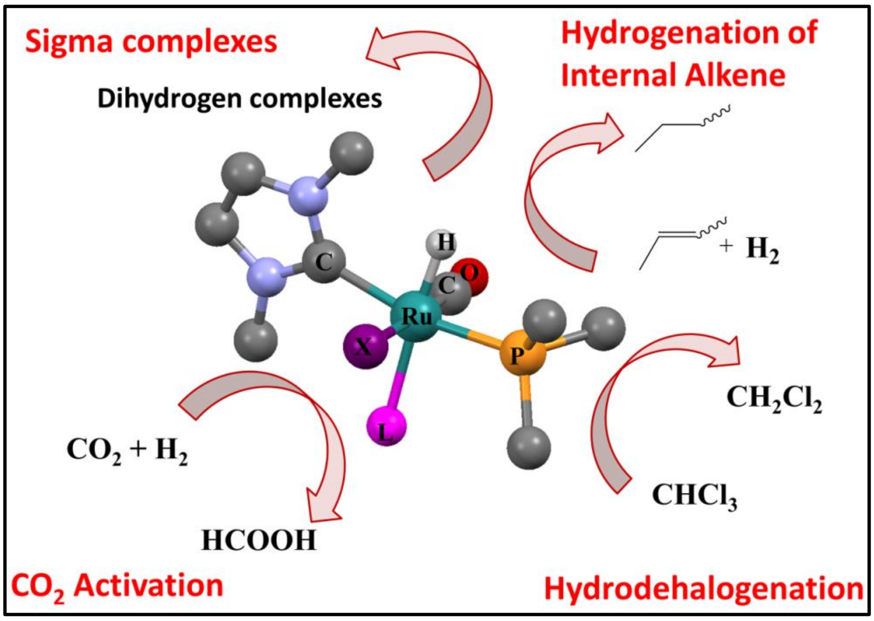
Synopsis

Chemistry of Ru(II) complexes bearing N-heterocyclic carbene, hydride, and dihydrogen ligands: Synthesis, mechanistic insights, and applications



Synopsis of the thesis entitled "Chemistry of Ru(II) complexes bearing N-heterocyclic carbene, hydride, and dihydrogen ligands: Synthesis, mechanistic insights, and applications", to be submitted by Deep Mala (S. R. No. 02-01-01-10-11-11-1-08733) under the supervision of Prof. Balaji R. Jagirdar, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, for the PhD degree of the institute under the faculty of science.

Introduction

N-heterocyclic carbenes (NHC) are strong σ donors and weak π acceptors. Also, NHC forms strong metal-carbon bonds in metal complexes and hence complexes bearing NHC ligands are in general, thermally stable. Chemistry of NHCs and their transition metal complexes has been explored extensively in catalysis. Metal hydride or dihydrogen complexes are reactive intermediates and also employed as catalysts in several catalytic reactions such as hydrogenation, transfer hydrogenation, and hydroformylation. The binding of H_2 to a metal center and its cleavage for the oxidative addition to a metal center are key steps in these catalytic reactions. There has been a substantial development in the field of dihydrogen chemistry. In particular, elongated dihydrogen complexes are of significant interest due to their relevance in hydrogenation reactions. A large number of elongated dihydrogen complexes have been reported. However, there has been no systematic study for the elongation of the H–H bond in dihydrogen complexes employing NHC's as a co-ligand.

Objectives

The objectives of this work are as follows:

i. Synthesis and characterization of ruthenium dihydrogen complexes bearing an NHC ligand.
ii. Systematic variation in the ligand environment around a metal center for the elongation of the H–H bond in the process of oxidative addition of H_2 to a metal center.
iii. To synthesize new ruthenium hydride and dihydride complexes and explore their activities in catalysis such as hydrogenation, hydrodehalogenation, and CO_2 activation.

Significant results

A series of dihydrogen complexes bearing NHC ligands of the type [RuCl(η^2–H_2)(CO)(IMes)(PPh_3)(L)](OTf) [L = pyridine (Py), 4-methylpyridine (4MePy), acetonitrile (MeCN), pivalonitrile (Me_3CCN)] have been prepared by the protonation of hydride complexes [RuHCl(CO)(IMes)(PPh_3)(L)] (L = Py, 4MePy, MeCN, Me_3CCN) with HOTf. The ligands (Py, 4MePy, MeCN, Me_3CCN) *trans* to the hydride were found to be labile in all the hydride complexes. The H–H bond distances in the η^2–H_2 ligands of dihydrogen complexes were found to be temperature dependent. The H–H bond distances got slightly elongated (0.98-0.93 Å) with an increase in the temperature (183-233 K). Phosphine analogues, [RuCl(η^2–H_2)(CO)(PPh_3)$_2$(L)](OTf) [L = Py, 4MePy) of NHC dihydrogen complexes were also synthesized. The H–H bond distances were temperature invariant (0.93 Å, 223-263 K) in these complexes.

A series of homobimetallic ruthenium hydride [{RuHCl(CO)(IMes)(PPh_3)}$_2$(NN)] (NN= 4,4′-bpy, 4,4′-dpyen, 4,4′-dpyan) [4,4′-bipyridine (4,4′-bpy); 1,2-bis(4-pyridyl)ethylene (4,4′-dpyen); 1,2-bis(4-pyridyl)ethane) (4,4′-dpyan)] complexes bearing an NHC ligand and their corresponding dihydrogen complexes of the type [{RuCl(η^2–H_2)(IMes)(PPh_3)(CO)}$_2$(NN)][OTf]$_2$ (NN= 4,4′-bpy, 4,4′-dpyen, 4,4′-dpyan) have been synthesized and characterized. They are the first examples of homobimetallic dihydrogen complexes bearing NHC ligands. In addition, hydrogenation of internal and terminal alkenes was carried out using these homobimetallic hydride complexes.

NHC/PMe_3 based cationic complexes of the type [RuH(CO)(IMes)(PMe_3)$_3$](X) (X = Cl, BPh_4) have been synthesized and characterized using NMR spectroscopy. Partial hydrodechlorination of $CHCl_3$ to CH_2Cl_2 was observed in the presence of both the complexes. In addition, these complexes were also found to be efficient for the activation of the C–Cl bond in CH_2Cl_2 to form [$CH_2Cl.PMe_3$]Cl salt in the presence of excess PMe_3. Notably, HD exchange in H_2 molecules via $CDCl_3$ was observed in the presence of both the complexes.

A new and efficient route has been developed for the synthesis of the ruthenium dihydride complexes $[\mathrm{Ru(H)_2(CO)(L)(PPh_3)_2}]$ (L = IMes, IPr, $\mathrm{PPh_3}$). The reaction pathway for the synthesis of these derivatives was established by isolation of few intermediates. Insertion of $\mathrm{CO_2}$ into one of the Ru–H bond of $[\mathrm{Ru(H)_2(CO)(L)(PPh_3)_2}]$ (L = IMes, IPr) complexes took place to afford bidentate formate complexes $[\mathrm{RuH}(\eta^2\text{-}\mathrm{O_2CH)(CO)(L)(PPh_3)_2}]$ (L = IMes, IPr). Structure formulation of these complexes was done using NMR spectroscopy.