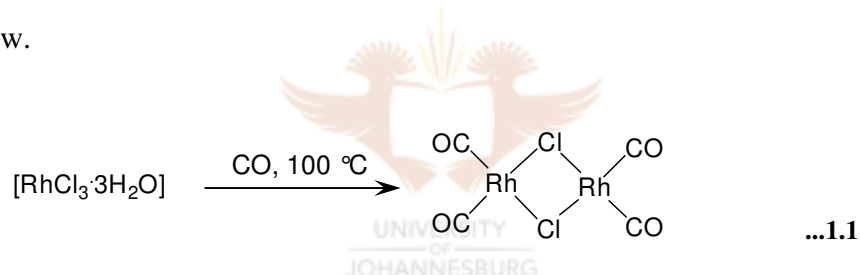


Chapter 1

Aim of Study

1.1 Introduction

Rhodium was discovered in 1804 by William Hyde Wollaston (1766–1828)^{1,2}. Rhodium is one of the least abundant elements in the earth crust ($\sim 10^{-7}$ % abundance), and the first compound containing a rhodium-carbon bond was synthesised by Manchot and König³ only in 1925. The above mentioned authors formulated the red, crystalline, volatile material obtained by treatment of $[\text{RhCl}_3]$ with CO as a carbon monoxide complex of rhodium oxychloride as, $[\text{Rh}_2\text{Cl}_2\text{O}\cdot 3\text{CO}]$. It was in 1943 that Hieber and Lagally⁴ correctly identified and formulated this compound as the halide bridged dimer, $[\text{Rh}_2(\mu\text{-Cl})_2(\text{CO})_4]$, see Eq. 1.1 below.



Rhodium forms organometallic compounds in oxidation states ranging from (+IV) to (-III), although by far the most common ones are Rh(I) and Rh(III). The rhodium(I) oxidation state has a d^8 -electron configuration and its organometallic complexes usually form either four-coordinate square planar⁵ or five-coordinate trigonal bipyramidal⁶ structures.

¹ W.P. Griffith, *Platinum Metals Rev.*, **47**, 2003, 175.

² W. H. Wollaston, *Phil. Trans. Roy. Soc.*, **94**, 1804, 419.

W. H. Wollaston, *J. Nat. Philos., Chem. Arts*, **10**, 1805, 3.

³ W. Manchot, J. König, *Chem. Ber.*, **58B**, 1925, 2173.

⁴ W. Hieber, H. Lagally, *Z. Anorg. Allg. Chem.*, **251**, 1943, 96.

⁵ S.S. Basson, J.G. Leipoldt, A. Roodt, J.A. Venter, *Inorg. Chim. Acta*, **118**, 1986, L45.

⁶ S.S. Basson, J.G. Leipoldt, J.A. Venter, *Acta Cryst.*, **C46**, 1990, 1324-1326.

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The rhodium(III) oxidation state has a d^6 -electron configuration and often an octahedral conformation^{5, 7}, and are commonly the product of the oxidative addition of rhodium(I) complexes. The reversibility of such reactions connecting the Rh(I) and Rh(III) oxidation states are responsible for many of the catalytic organic transformations⁷ which are encountered in organorhodium chemistry.

A large number of rhodium(I) complexes are known, most of these compounds involve π -bonding ligands such as CO, PR_3 , RNC, alkenes, cyclopentadienyl and arenes. One of the best known complexes is the rhodium analogue of *trans*-[Ir(Cl)(CO)(PPh₃)₂], which was first prepared by Angoletta⁸, and later correctly formulated by Vaska and DiLuzio⁹, and is known to exhibit catalytic activity. The rhodium complex¹⁰ was already known at that time and investigated to some extent¹¹. Today, complexes with the general formula *trans*-[M(X)(CO)(L)₂] (M = Rh(I), Ir(I); X = halide or pseudo-halide; L = neutral ligand) are considered analogues to Vaska's complex¹².

Catalysts are (chemical) compounds that accompany a catalytic process by having a major, even decisive, influence on its course without themselves undergoing any resultant change at the end of the process. Catalysts have thus well defined identity. The reason for the use of a catalyst is that it lowers the activation energy of a process (Figure 1.1), *i.e.*, the energy needed for a reaction to start taking place. Thus, the energy requirement of a catalytic process can be very efficient compared to an uncatalysed process. Accordingly, catalysts are not without a profile; on the contrary, a special *reaction profile* in combination with a *steric profile* is the essential condition in order that other substances can meet at the active center to join together or to undergo other transformations.

⁷ B. Cornils, W.A. Herrmann, "Applied Homogeneous Catalysis with Organometallic Compounds", VHC Publishers, Weinheim, 1996.

⁸ M. Angoletta, *Gazz. Chim. Ital.*, **89**, 1959, 2359.

⁹ L. Vaska, J.W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 1961, 2784.

¹⁰ L. Vallarino, *J. Chem. Soc.*, 1957, 2287.

¹¹ J. Chatt, B. Shaw, *Chem. Ind.*, 1961, 290.

¹² M. Selke, W.L. Karney, S.I. Hahn, C.S. Foote, *Inorg. Chem.*, **34**, 1995, 5715, for example.

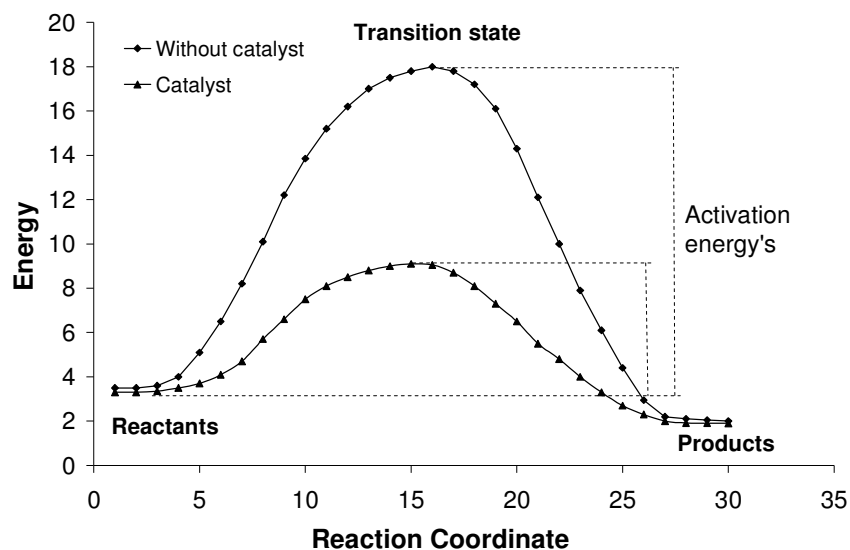


Figure 1.1 Reaction profile exemplifying the goal of a catalyst, the lower activation energy with a catalyst present in a reaction is clearly depicted in the figure.

An example worthy of mentioning is the new synthesis (Figure 1.2) of vitamin K_3 ¹³, which is used ubiquitously in veterinary medicine in the USA and is important as an anticoagulation vitamin for newborn babies in human medicine. Classically, vitamin K_3 is produced by the oxidation of 2-methylnaphthalene using chromic acid. This furnishes 16 kg of toxic, chromium-containing waste per kg of product. The new catalytic route uses hydrogen peroxide in combination with the very efficient homogeneous catalyst methyl(trioxo)rhenium, CH_3ReO_3 ¹³, with no notable production of waste products or toxic substances.

The same catalyst also enables the oxidative preparation of vanillin from biowastes¹⁴ and the oxidation of starches¹⁵, in both cases in combination with the cheap, environmentally harmless oxidizing agent hydrogen peroxide.

¹³ W. Adam, W.A. Herrmann, J. Lin, C.R. Saha-Möller, R.W. Fischer, J.D.G. Correia, *Angew. Chem. Int. Ed. Engl.*, **33**, 1994, 2475.

¹⁴ W. A. Herrmann, T. Weskamp, J.P. Zoller, R.W. Fischer, *J. Mol. Cat. A: Chemical*, **153**, 2000, 49.

¹⁵ W. A. Herrmann, J. P. Zoller, R. W. Fischer, *J. Organomet. Chem.*, **579**, 1999, 404.

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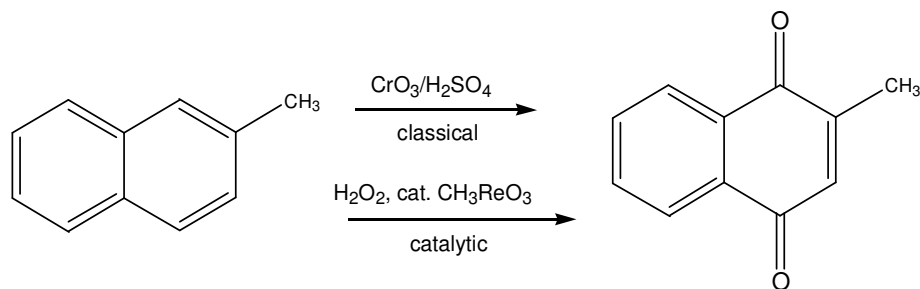


Figure 1.2 Schematic presentation indicating the classical synthetic and the catalytic route in the synthesis of vitamin K₃.

The market for catalysts amounts to *ca.* 12 billion US dollar per year with an estimated product market of 1.2 – 6 quadrillion US dollar (factor of 100 – 500). Thus, > 80 % of the net product of the chemical industry alone is based on catalytic processes¹⁶.

Energy research would also not make much progress without catalysis¹⁷. The storage of energy, perhaps the major topic in energy research, is based on catalytic processes, irrespective of whether the chemical processes occurring in batteries or hydrogen technology are considered. A fuel cell is usually preceded by the chemical conversion of “stored energy”, *i.e.*, a catalytic reforming process (*e.g.*, methanol/water) with its sensitive dependence on pressure, temperature, and technical system. The demands for robustness and efficacy for such reforming catalysts are extremely high in the light of the expectation that within 20 years the proportion of fuel-cell driven vehicles will amount to about 20 %, *i.e.*, 10 million private motor vehicles in Germany. The safety problems associated with a vehicle fuel tank containing hydrogen under pressure will only be eliminated when an alternative fuel such as methanol can be efficiently converted by a catalytic process into a gas with high hydrogen content immediately prior to combustion.

It can be expected that catalysis for vehicle propulsion will achieve a similar success as that for cleaning vehicle exhaust gases. The three-way catalytic converter for the three pollutant groups: nitrogen oxides, carbon monoxide and hydrocarbons operates on a noble metal basis platinum, palladium and rhodium. In spite of its good performance, this is still an

¹⁶ Zukünftige Förderung der Katalysatorforschung, BMBF, Projektträger Neue Materialien und Technologien beim Forschungszentrum Jülich GmbH, Symposium am 13.01.2000 in Bonn.

¹⁷ <http://aci.anorg.chemie.tu-muenchen.de/wah/vortraege/catalysis.pdf>

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“end of the pipe” solution. Even so, the engines of motor vehicles remain the most abundant “chemical reactor” in the world (about 1 billion in number). They depend on gasoline, the sulfur and aromatic contents of which must again be drastically reduced to comply with EU regulations. Considering the round 180 million tons of gasoline consumed in Europe per annum, this represents an enormous challenge for catalyst technology, the only possibility to solve the problem.

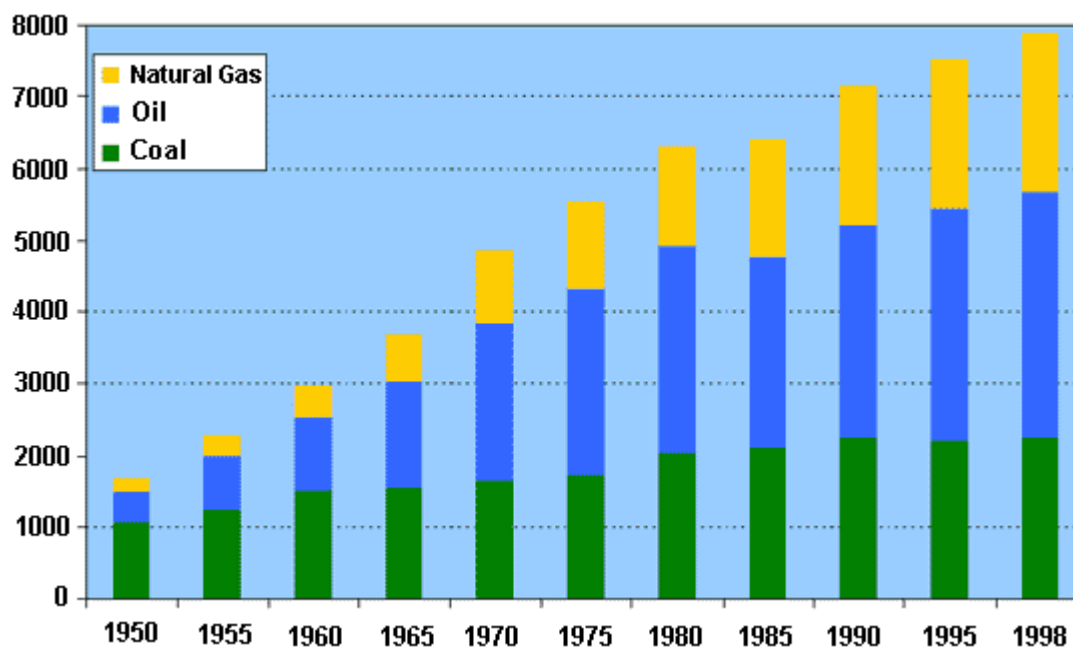


Figure 1.3 Diagram displaying World Fossil Fuel Consumption per Source, 1950-1998 (in million of tons of equivalent oil). Over the last 50 years, while consumption of fossil fuels grew substantially, the world undertook a transition in its usage of fossil fuels, from solids (coal), to liquids (oil) to gases (natural gas). While coal accounted for 62% of all fossil fuel consumption in 1950, this share dropped to 28% in 1998 equivalent to the share of natural gas. The share of oil substantially increased between 1950 and 1980, where it peaked at 45% of fossil fuel use, then declined to 43%¹⁸.

Catalysis is also the method of choice for avoiding pollutants irrespective of whether they are of natural or man-made origin. The large-scale example of motor vehicle exhaust gas catalysts is an adequate illustration and the use of fuel cell technology for the primary objective of reducing vehicle emissions has been mentioned above. All major automobile concerns are active in this field. Selective, efficient, and long-lasting catalysts are the key to

¹⁸ <http://people.hofstra.edu/geotrans/eng/ch8en/conc8en/worldfossil.html>

success. It has just recently been reported in *Nature* that the use of natural gas as a fuel is possible with the help of copper and samarium oxide-containing catalysts¹⁹.

1.2 Aim of Study

It is clear from the introduction that catalysts have a large role to play in the chemical industry and in human lives in general. In homogeneous catalysis with rhodium(I) complexes whether it is in hydroformylation, hydrogenation or carbonylation^{7, 20}, substitution of ligands plays an integral role in the catalytic cycle. A study of the effects that influence the mechanistic pathway and rate constants of substitution, is of prime importance in designing improved future catalysts.

In this study, a model complex of general formula $[\text{Rh}(\text{X})(\text{CO})\{\text{P}(\text{Obtbp})_3\}_2]$ ($\text{X} = \text{Cl}^-$, OAc^-), with possible catalytic properties to be explained in future, was selected. The incorporation of the bulky phosphite ligand is expected to make the metal centre more electron poor and thus inhibit oxidative addition and also to introduce a sterically crowded environment. Furthermore, the substitution behaviour of a polyatomic anionic acetate moiety (OAc^-) as good leaving group in the complex could be studied on the electron poor, sterically crowded rhodium(I) metal centre. This included the electronic and steric parameters of the tertiary aryl phosphites involved in coordination to the rhodium(I) centre.

With the above in mind, the following stepwise aims were set for this study.

1. Preparation of model complexes such as *trans*- $[\text{Rh}(\text{X})(\text{CO})\{\text{P}(\text{Obtbp})_3\}_2]$ ($\text{X} = \text{Cl}^-$, OAc^-) that contain a bulky phosphite ligand of which the $\text{P}(\text{Obtbp})_3$ was chosen, and to study the solid state and solution properties thereof, also with respect to the effects of electronic and steric interactions.

¹⁹ S. Park, J.M. Vohs, R.J. Gorte, *Nature*, **404**, 2000, 265.

²⁰ P.W.N.M. van Leeuwen, "Homogeneous Catalysis (Understanding the Art)", Kluwer Academic Publ., Dordrecht, 2004.

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2. The crystallographic characterisation of a free phosphite ligand ($\text{P}(\text{Obtbp})_3$) and the square planar pseudo Vaska-type complex synthesised from that ligand (*trans*- $[\text{Rh}(\text{OAc})(\text{CO})\{\text{P}(\text{Obtbp})_3\}_2]$) to study the coordination mode, bond lengths and distortion (if any) of the phosphite ligand.
3. Investigation of the equilibrium that exist between the four-coordinate complexes *trans*- $[\text{Rh}(\text{OAc})(\text{CO})\{\text{P}(\text{Obtbp})_3\}_2]$ and *trans*- $[\text{Rh}(\text{Cl})(\text{CO})\{\text{P}(\text{Obtbp})_3\}_2]$.
4. Kinetic study of the substitution of the acetate ligand by chloride in the four-coordinate *trans*- $[\text{Rh}(\text{OAc})(\text{CO})\{\text{P}(\text{Obtbp})_3\}_2]$ complex.

