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SUPPORTED  
METAL COMPLEXES

*A New Generation of Catalysts*

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*A New Generation of Catalysts*

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## PREFACE

It is now 15 years since the first patents in polymer supported metal complex catalysts were taken out. In the early days ion-exchange resins were used to support ionic metal complexes. Soon covalent links were developed, and after an initially slow start there was a period of explosive growth in the mid to late 1970s during which virtually every homogeneous metal complex catalyst ever reported was also studied bound to a support. Both polymers and inorganic oxides were studied as supports, although the great preponderance of workers studied polymeric supports, and of these polystyrene was by far the commonest used. This period served to show that by very careful design polymer-supported metal complex catalysts could have specific advantages over homogeneous metal complex catalysts. However the subject was a complicated one. Merely immobilising a successful metal complex catalyst to a functionalised support rarely yielded other than an inferior version of the catalyst.

Amongst the many discouraging results of the 1970s, there were more than enough results that were sufficiently encouraging to demonstrate that, by careful design, supported metal complex catalysts could be prepared in which both the metal complex and the support combined together to produce an active catalyst which, due to the combination of support and complex, had advantages of activity, selectivity and specificity not found in homogeneous catalysts. Thus a new generation of catalysts was being developed. If heterogeneous and homogeneous catalysts are regarded as the first and second generations of man-made catalysts then supported metal complex catalysts are the third generation. Hence the title of this book *Supported Metal Complexes: A New Generation of Catalysts*.

This book is in many ways an update of the review I wrote between 1975 and 1976 (published in 1977). It describes both how supported metal complex catalysts have been prepared and used and suggests ideas for future developments. To date no supported metal complex catalysts have been used in large scale commercial processes; however I believe that this situation will change gradually, particularly as research into mechanically robust supports increases at the expense of investigation into mechanically weak supports such as polystyrene. The considerable opportunities that supported metal complex catalysts

offer for combining both the support and the metal centre in such a way as to obtain high activity, selectivity and specificity combined with easy separation of the catalyst from the reaction products will, I am sure, lead to commercial successes within the next decade. By attempting to summarise the current state of the art I hope that this book will hasten that event.

A book such as the present one is never merely the product of one man's pen alone. I owe a great deal, firstly to that international company of chemists who have provided the raw material for this work, and secondly to my own research students both at Southampton and Shrivenham. I should particularly like to thank Mr P. N. Vezey, Dr D. J. A. McCaffrey, Dr P. N. Nicholson, Professor J. A. Davies and Mr A. T. Sayer, all of whom have worked with me in this field. Not only has Dr S. G. Murray worked closely with me in this field, but this book would probably never have appeared without his encouragement of me to get on and write it. Mrs P. Trembath and Mrs K. J. Hunt helped with some of the typing. I am most grateful to Professors Brian James and Renato Ugo for inviting me to contribute this book to the *Catalysis by Metal Complexes* series and to Mr Ian Priestnall of Reidel's for so sympathetically living with the inevitable delays in writing a book during the period of major turbulence that has beset tertiary education in the United Kingdom in the 1980s. Finally I acknowledge with a deep sense of gratitude the understanding of my wife and daughters during the long hours of preparation. It is to them that this book is dedicated.

FRANK HARTLEY

Shrivenham  
1984

## ABBREVIATIONS

Ac	acetyl	EXAFS	extended X-ray absorption fine structure
acac	acetylacetonate		
albn	azobisisobutyronitrile	$\gamma$ -	gamma-
Ar	aryl	hfacac	hexafluoroacetylacetone
bipy	bipyridyl	$\mu$ -	bridging ligand
Bu	butyl	MAS	magic angle spinning
Bz	benzyl	Me	methyl
cod	1,5-cyclooctadiene	nbd	norbornadiene
cot	1,3,5-cyclooctatriene	NMR	nuclear magnetic resonance
Cp	cyclopentadienyl		
CP	cross-polarisation		
Cys	cystine	$\odot$	polymer (usually polystyrene)
dba	dibenzylideneacetone	Ph	phenyl
diop	2,3-o-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane	Pr	propyl
dma	dimethylacetamide	pvc	polyvinylchloride
dm-bq	2,6-dimethyl-1,4-benzoquinone	py	pyridyl
dme	dimethoxyethane	R	alkyl group
dmf	dimethylformamide	rad	unit of radiation
dmso	dimethylsulphoxide	{Si}	silica
dppe	bis(1,2-diphenylphosphino)ethane	thf	tetrahydrofuran
dpq	3,3',5,5'-tetramethyldiphenylquinone	tmeda	tetramethylethylenediamine
		Tos	tosyl
		TPP	tetraphenylporphyrin
$\eta$ -	hapto-	UV	ultra-violet
ESCA	electron spectroscopy for chemical analysis	XPS	X-ray photoelectron spectroscopy
ESR	electron spin resonance		
Et	ethyl		
eV	electron volt		

## CONTENTS

PREFACE	xiii
ABBREVIATIONS	xv
CHAPTER 1. <i>Introduction</i>	1
1.1. Catalysis	1
1.2. Reasons for Supporting Metal Complexes	3
1.3. Catalyst Requirements	9
1.4. Types of Support	9
1.4.1. Organic Polymers	11
1.4.2. Inorganic Supports	14
1.5. Chemically Modified Electrodes	16
1.6. Immobilised Enzymes and Reagents for Organic Syntheses	16
1.7. Triphase Catalysis	16
1.8. Heterogenisation of Metal Complex Catalysts	18
1.8.1. Phase Transfer	19
1.8.2. Supported Liquid and Gas Phase Catalysts	19
1.8.3. Use of Melts	23
1.8.4. Lattice Metal Complexes	23
1.8.5. Water Soluble Complexes	24
1.9. Polymer Supported Metal Catalysts	25
References	26
CHAPTER 2. <i>Preparation of the Supports</i>	34
2.1. General Considerations for Organic Polymers	34
2.2. Styrene Based Systems	38
2.2.1. Functionalisation of Preformed Polystyrene	38
2.2.2. Copolymerisation of Functionalised Styrenes	48
2.3. Non-Styrene Polymers	51
2.4. Radiation Grafting	
2.4.1. Techniques of Radiation Grafting	
2.4.2. Reactions Occurring under the Influence of Radiation	60
2.4.3. Factors Affecting Radiation Grafting	62

2.5. Silica-Based Systems	67
2.6. Other Inorganic Supports	71
References	72
CHAPTER 3. <i>Introduction of Metals onto Supports</i>	80
3.1. Ion-Exchange-Based Catalysts	80
3.2. Functionalised Supports	81
3.3. Metal Complexes Bound to Polymeric Supports Through Metal-Carbon Bonds	87
3.4. Polymerisation of Functionalised Monomers	89
3.5. Direct Reaction Between Organometallic Compounds and Inorganic Oxide Surfaces	92
3.6. Surface Bonding of Metal Carbonyls on Inorganic Oxides	95
3.7. Supported Ziegler-Natta Catalysts	103
3.8. Surface Supported Metal Salts	105
3.9. Surface Complexes of Transition Metal Oxides on Oxide Supports	106
References	107
CHAPTER 4. <i>Characterisation of Supported Catalysts</i>	118
4.1. Microanalysis	118
4.2. Chromatographic Methods	119
4.2.1. Gel Chromatography	119
4.2.2. Temperature Programmed Decomposition Chromatography	120
4.3. Spectroscopic Methods	121
4.3.1. Infrared	121
4.3.2. Raman	124
4.3.3. Inelastic Electron Tunnelling	125
4.3.4. Ultraviolet and Visible	125
4.3.5. Nuclear Magnetic Resonance	125
4.3.6. Electron Spin Resonance	128
4.3.7. Mössbauer	131
4.3.8. Mass Spectrometry	132
4.3.9. ESCA	133
4.3.10. Extended X-ray Absorption Fine Structure	134
4.4. Electron Microscopy	135
References	136
CHAPTER 5. <i>The Use of Supported Metal Complex Catalysts</i>	141
5.1. Introduction	141
5.2. Optimisation of Conditions	142



5.3. Laboratory Application	145
5.4. Industrial Application	145
References	147
<b>CHAPTER 6. <i>Hydrogenation</i></b>	149
6.1. Introduction	149
6.2. Nature of the Support	150
6.3. Effect of Cross-Linking	151
6.4. Nature of the Solvent	151
6.5. Nature of the Metal Complex	152
6.6. Activity of Supported as Compared to Homogeneous Catalysts	152
6.7. Selectivity	153
6.8. Stability	154
6.9. Survey of Supported Hydrogenation Catalysts	152
6.9.1. Titanium, Zirconium and Hafnium	154
6.9.2. Chromium, Molybdenum and Tungsten	156
6.9.3. Iron, Ruthenium and Osmium	157
6.9.4. Cobalt	162
6.9.5. Rhodium	163
6.9.5.1. Analogues of $[Rh(PPh_3)_3Cl]$	163
6.9.5.2. Other Rhodium(I)-Phosphine Complexes	170
6.9.5.3. Rhodium(I)-Phosphinite Complexes	173
6.9.5.4. Rhodium Carbonyl Complexes	173
6.9.5.5. Organometallic Rhodium Complexes	174
6.9.5.6. Rhodium Carboxylate Complexes	176
6.9.5.7. Rhodium Amide and Imidazole Complexes	177
6.9.5.8. Rhodium Thioether Complexes	177
6.9.5.9. Organorhodium(III) Complexes	177
6.9.6. Asymmetric Hydrogenation	178
6.9.7. Iridium	185
6.9.8. Nickel	187
6.9.9. Palladium and Platinum	189
6.9.10. Actinides	194
6.10. Reduction of Inorganic Molecules	194
6.11. Michael Addition	195
References	196
<b>CHAPTER 7. <i>Hydrosilylation</i></b>	204
<b>CHAPTER 8. <i>Reactions Involving Carbon Monoxide</i></b>	216
8.1. Introduction	216

8.2. Hydroformylation	218
8.2.1. Cobalt Hydroformylation Catalysts	220
8.2.2. Rhodium(I) Hydroformylation Catalysts	223
8.2.3. Asymmetric Hydroformylation	228
8.2.4. Other Transition Metal Hydroformylation Catalysts	228
8.3. Carbonylation of Methanol	229
8.4. Fischer-Tropsch Reaction	235
8.4.1. Fischer-Tropsch Formation of Paraffins	236
8.4.2. Fischer-Tropsch Formation of Olefins	237
8.4.3. Fischer-Tropsch Formation of Alcohols	240
8.5. Water Gas Shift Reaction	240
8.6. Alkoxycarbonylation of Olefins	243
8.7. Isocyanates Formed by Carbonylation of Nitro Compounds and Azides	243
8.8. Syntheses of Aldehydes and Ketones	244
8.9. Substitution of Carbonyl Ligands in Metal Carbonyls	245
References	246
 CHAPTER 9. <i>Dimerisation, Oligomerisation, Polymerisation, Disproportionation and Isomerisation</i>	 252
9.1. Olefin Dimerisation	252
9.2. Olefin Trimerisation	255
9.3. Oligomerisation and Cyclooligomerisation of Dienes	255
9.4. Oligomerisation of Acetylenes	257
9.5. Polymerisation of Olefins	258
9.5.1. Inorganic Oxide Supported Olefin Polymerisation Catalysts	259
9.5.2. Polymer Supported Olefin Polymerisation Catalysts	261
9.6. Diene Polymerisation	262
9.7. Acetylene Polymerisation	264
9.8. Copolymerisation of Propylene Oxide with Carbon Dioxide	264
9.9. Olefin Metathesis	265
9.10. Olefin Isomerisation	268
9.10.1. Zirconium Complexes	269
9.10.2. Iron, Ruthenium and Osmium Carbonyl Complexes	269
9.10.3. Ruthenium(II) and Rhodium(I) Carbonyl and Carboxylate Complexes	270
9.10.4. Silica Supported Rhodium Catalysts	273
9.10.5. Nickel Catalysts	273
9.10.6. Palladium Catalysts	274

9.11. Quadricyclane-Norbornadiene Isomerisation	274
9.11.1. Quadricyclane to Norbornadiene Isomerisation	274
9.11.2. Norbornadiene to Quadricyclane Isomerisation	276
9.12. Grignard Cross-Coupling Reactions	276
References	277
 CHAPTER 10. <i>Oxidation and Hydrolysis</i>	 285
10.1. Hydrocarbon Oxidation	285
10.2. Decomposition of Peroxides	288
10.3. Oxidation of Organic Compounds	289
10.4. Oxidation of Inorganic Compounds	291
10.5. Chlorination	292
10.6. Ammoxidation	293
10.7. Hydroxylation of Aromatic Compounds	293
10.8. Hydroxylation of Olefins	293
10.9. Carboxylation of Olefins and Aromatic Compounds	294
10.10. Vinyl Ester and Ether Exchange	295
10.11. Nitrile Hydrolysis	295
10.12. Nucleophilic Substitution of Acetate Groups	295
10.13. Stereoselective Hydrolysis of Esters	296
References	296
 CHAPTER 11. <i>Conclusions And Future Possibilities</i>	 299
11.1. Sequential Multistep Reactions	299
11.2. Selectivity Enhancement	304
11.3. Activity	306
11.4. Organic versus Inorganic Supports	308
11.5. Future Developments	309
References	310
 INDEX	 313

## CHAPTER 1

### INTRODUCTION

#### 1.1. Catalysis

Although the subject of catalysis has been around ever since the first enzyme 'catalysed' an organic reaction it first began to develop into a science in 1836 when Berzelius used the word 'catalysis' to describe a number of previous experimental observations including Thenard's (1813) that ammonia was decomposed by metals and Dobereiner's (1825) that manganese dioxide modifies the rate of decomposition of potassium chlorate. Berzelius developed the word *κατάλυσις* from two Greek words *κατα-* a prefix meaning down and *λυσειν* a verb meaning to split or break. Presumably Berzelius saw a catalyst as something that broke down the inhibitions of molecules towards reaction. Indeed this is consistent with the alternative Greek meaning of *κατάλυσις* which is variously described as meaning either an inn or tavern [1] or the consequences of a failure of social or ethical restraints, such as a riot [2]. The popular press now uses the word catalysis in its alcoholic sense of 'bringing together' rather than its more literal sense of 'breaking down'. A catalyst may be defined as 'a substance which increases the rate at which a chemical reaction approaches equilibrium without being consumed in the process'. As befits a committee a longer, although more precise, description has been suggested by the UK Science Research Council [3]: "A system is said to be 'catalysed' when the rate of change from state I, to state II, is increased by contact with a specific material agent which is not a component of the system in either state, and when the magnitude of the effect is such as to correspond to one or more of the following descriptions:

- (a) Essentially, measurable change from state I to state II occurs only in the presence of the agent.
- (b) A similarly enhanced rate of change is found with the same sample of agent in repeated experiments using fresh reactants.
- (c) The quantity of matter changed is many times greater than that of the agent."

Man's earliest attempts to emulate the enzymes generally led to catalysts

that existed in a separate phase to the reactants with a distinct interface between them; such catalysts are described as 'heterogeneous'. However more recently a number of catalysts have been developed which operate in the same phase as the reactants and are consequently known as 'homogeneous'. Of these, for our present purposes, by far the most important are the metal complex catalysts that dissolve in a solution containing the reactants. Although such homogeneous catalysts were first used for acetylene reactions as early as 1910 (e.g. reaction (1)),



their use only really began to be developed in the 1940s when wartime restrictions on raw materials forced the Germans to investigate both carbon monoxide and acetylene based processes for the production of fuels and plastics. The inherently greater difficulty of separating a homogeneous catalyst from the products at the conclusion of a reaction led industry to adopt a rather conservative attitude to the introduction of homogeneously catalysed processes in place of heterogeneous processes in which the catalyst could often be separated by some form of coarse filtration such as a cyclone filter. However the greater selectivity of homogeneous catalysts, arising out of their molecular nature, which ensures that only one type of active site is present, conveys an ability to produce pure products in high yield that the heterogeneous catalysts, whose activity is often based on 'defect sites' on their surface, of which there may be several different types, are hard pressed to match. Accordingly a significant number of homogeneously catalysed industrial processes have been brought on stream in recent years [4-5a].

The high selectivity of homogeneous catalysts [5b], arising from their molecular nature has led industrial and academic chemists into a search for catalysts that combine such 'molecular sites' with the ease of separation of heterogeneous catalysts. The first approach used was to support the molecular catalyst on an insoluble support. This followed from the work of Merrifield in supporting enzymes for polymer synthesis and degradation on polystyrene resin [6, 7]. The first published work on supported metal complex catalysts, involving the support of cationic metal complexes such as  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  on sulphonated polystyrene, was published in 1969 [8-11]. After a slow initial start, work has expanded to the extent that several hundreds of papers are published annually on supported metal complex catalysts. A number of good reviews have been written [12-33], of which 18, 23, 28, 30 and 33 are particularly recommended. To date only one book has appeared in the West [34]. Reviews in Japanese [35-37] and Russian [38, 39] reflect the world-wide importance of the subject. Except for the specialised field of Ziegler-Natta catalysis (Section 9.5) no commercial processes involving supported metal

complex catalysts have yet been developed although it is the present author's view that this is only a few years away because of the enhanced selectivity that can be achieved when both support and metal complex combine together. Indeed it is reported [40] that Mobil did take a polymer-supported rhodium hydroformylation process up to pilot plant scale in the mid-1970s. Further development of a commercial-scale plant was only halted because the existing and projected markets were not large enough to justify the construction of a new plant. Had they been so, then the supported catalyst would have been the catalyst of choice.

Supported metal complex catalysts form the subject of this book. In the present chapter we shall examine the pros and cons of homogeneous and heterogeneous catalysts as a way of identifying the advantages and disadvantages we may expect for supported metal complex catalysts. We shall then examine other areas of chemistry where supported reagents are used, in order to promote an awareness of fields in which those wishing to develop supported metal complex catalysts should look for relevant developments. This chapter concludes with a brief account of alternative approaches to the present one for combining the advantages of homogeneous catalysts, accruing from their molecular nature, with the ease of separation of heterogeneous catalysts. In the remainder of the book we consider first the preparation of the supports (Chapter 2), then the introduction of metal complexes on to them (Chapter 3) and then the characterisation of the products (Chapter 4). After a brief look at the chemical engineering implications of supported metal complex catalysts in Chapter 5, the use of these catalysts in a number of reactions is considered (Chapters 6-10). The book concludes with some suggestions for the future in Chapter 11.

## 1.2. Reasons for Supporting Metal Complexes

In order to appreciate the reasons for the present interest in supported complex catalysts, which may be called the 'third generation' catalysts, it is useful to look at the advantages and disadvantages of the heterogeneous and homogeneous catalysts under a number of headings:

(a) *Separation of the catalyst.* The major disadvantage of homogeneous catalysts is the problem of separating the very expensive catalyst from the products at the end of the reaction. With heterogeneous catalysts this can be achieved by some kind of coarse filtration whereas with homogeneous catalysts a very efficient distillation or ion-exchange process is required. Distillation is inevitably an endothermic process and is therefore expensive and unless it is efficient it will result in small catalyst losses which may (a) render the process uneconomic

and/or (b) contaminate the product which, in the case of a foodstuff, for example, would be unacceptable. It should be pointed out that two of the commercially successful homogeneously catalysed processes, namely the Wacker process for oxidation of ethylene to acetaldehyde [41] and the Monsanto process for the carbonylation of methanol to yield acetic acid [42], depend in part for their success on the relatively low boiling-points of the products (acetaldehyde 20.8 °C; acetic acid 117.9 °C). Of course, in some cases such as the hydrogenation of soft oils to yield components suitable for incorporation into margarine, the products decompose before their boiling-points (even under reduced pressure) so that distillation is not a practical method for separation of the catalyst in such cases. Distillation is also impossible in the case of reactions where there are high-boiling side-products which would steadily build up in concentration if they were not removed.

(b) *Efficiency*. In a heterogeneous system, the catalytic reaction must necessarily take place on the surface of the catalyst so that all atoms or molecules of the catalyst not present at the surface remain unused. By contrast all the molecules in a homogeneous catalyst are theoretically available as catalytic centres so that these catalysts are potentially more efficient in terms of the amount of catalyst needed to catalyse a given amount of reaction.

(c) *Reproducibility*. Homogeneous catalysts have the advantage over heterogeneous catalysts of being totally reproducible because they have a definite stoichiometry and structure; by contrast the structure of the surface of a heterogeneous catalyst is heavily dependent on both its method of preparation and its history subsequent to preparation.

(d) *Specificity*. A given homogeneous catalyst will generally have only one type of active site and therefore will often be more specific than a heterogeneous catalyst where several types of active site may be present in the form of different surface defects. These defects are extremely difficult to control. The specificity of a homogeneous catalyst can often be selectively modified by altering the other ligands present in such a way as to alter either the electronic nature or the steric requirements of the site.

(e) *Controllability*. Closely related to specificity is the fact that because a homogeneous catalyst has a definite structure it is much easier to modify it in order to control a reaction. Thus when the homogeneous catalyst  $[\text{Rh}(\text{acac})(\text{CO})_2]$  is altered to  $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$  the ratio of normal to branched aldehydes obtained when 1-hexene is hydroformylated is altered from

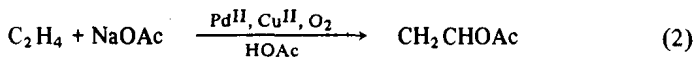
1.2 : 1 to 2.9 : 1 [43]. Substitution of  $\text{PPh}_3$  by  $\text{PPh}_2(p\text{-styryl})$  further enhances this ratio to 3.9 : 1 [44]. By contrast the ill-defined active sites of a heterogeneous catalyst make systematic design and improvement very difficult.

(f) *Thermal Stability.* The thermal stability of heterogeneous catalysts, such as pure metals and metal oxides, is often much higher than that of homogeneous catalysts. Since the rate of most reactions increases with temperature, a high operating temperature may be an advantage. It should be noted that high temperatures are not always ideal because some reactions involve a pre-equilibrium step which may be disfavoured by increasing the temperature. This is particularly true of reactions involving olefins where the entropy change on metal-olefin complex formation is almost invariably negative so that the stability of metal-olefin complexes decreases with increasing temperature [45]. The lower thermal stability of homogeneous catalysts is often compensated for by their significantly higher activities at lower temperatures and pressures.

(g) *Oxygen and moisture sensitivity.* Homogeneous catalysts are often organo-metallic compounds with metals in low oxidation states. Accordingly many of them are sensitive to oxygen and moisture. However heterogeneous catalysts are frequently subject to poisoning by 'soft' ligands to a much greater degree than homogeneous catalysts.

(h) *Solvent.* Whereas the range of suitable solvents for a homogeneous catalyst is often limited by the solubility characteristics of the catalyst, this clearly presents no problem for a heterogeneous catalyst.

(i) *Corrosion and plating out.* The use of some homogeneous catalysts on a commercial scale has led to a number of practical problems such as corrosion and plating out on the reactor walls that are not immediately obvious when the reaction is carried out in all-glass apparatus on the laboratory scale. The oxidative acetylation of ethylene to vinyl acetate catalysed by palladium(II) (reaction (2)) is an example of a process that suffers severe corrosion problems.



Although the original driving force for supporting homogeneous catalysts was to combine most of the advantages of homogeneous catalysts that accrue from their molecular character, particularly their selectivity and controllability, with the paramount virtue of ease of separation of the heterogeneous catalyst,



experience has shown that the presence of both support and catalyst can have synergically beneficial effects. Thus the process of attachment to a support may have the following effects:

(i) The support may not be merely an inert back bone. It may take a positive role leading to preferred orientations of the substrate at the catalytic site so promoting selectivity [45a]. This, of course, is what the supporting back bones in many enzymes have been doing in nature for many millenia. It is this effect that is believed to be largely responsible for the  $3\frac{1}{2}$ -fold enhancement of the normal : branched aldehyde selectivity when 1-hexene is hydroformylated over polypropylene supported  $[\text{Rh}(\text{acac})(\text{Ph}_2\text{PC}_6\text{H}_4\text{CH}=\text{CH}_2-p)\text{CO}]$  as compared to catalysis by the same complex unsupported [44].

(ii) Organic functional groups covalently bound to the surface of crystalline solids or polymers are subject to special constraints which may alter their chemical reactivity relative to the analogous small molecules [45b]. Thus the chemical properties of supported metal complexes can be different to their homogeneous analogues.

(iii) Supporting a metal complex on what is effectively a multidentate ligand may alter the stereochemistry around the metal ion in a beneficial way. This is well illustrated by the selectivity of platinum on nylon catalysts in the hydrogenation of benzene [46]. Thus platinum anchored on Nylon 66, 6 and 610 catalyses the formation of cyclohexene whereas platinum on Nylon 3, although an active hydrogenation catalyst, yields cyclohexane exclusively.

(iv) Supporting a metal complex may alter the position of equilibrium between metal ions and their surrounding ligands. This undoubtedly occurs when rhodium(I) complexes are bound on phosphinated supports and accounts for the fact that much lower phosphorus : rhodium ratios give greater enhancements of selectivities in olefin hydroformylation in the case of supported catalysts than with homogeneous catalysts [44, 47].

(v) By supporting a complex it is sometimes possible to stabilise catalytically active but normally unstable structures. Often this arises through site separation that prevents dimerisation to form stable inactive species, a process that is an important deactivation mechanism for many rhodium(I) systems [48]. Activation through site isolation is very important in hydrogenations catalysed by titanocene hydrides [49] and olefin polymerisations catalysed by chromium oxides [50] which are considered in more detail in Chapters 6 and 9. Although there has been a lot of interest in developing supported catalysts in which the metal centres are isolated, these catalysts are often used in swelling solvents. An important paper examined the effect of swelling solvents on site isolation by studying reaction (3) using infrared spectroscopy [50a].