NEW STATIONARY PHASES WITH DIAMINEBIS(PHOSPHINE)RUTHENIUM(II) COMPLEXES FOR THE CATALYTIC HYDROGENATION OF CARBONYL COMPOUNDS

NEUE STATIONÄRE PHASEN MIT DIAMINOBIS(PHOSPHIN)RUTHENIUM(II)-KOMPLEXEN FÜR DIE KATALYTISCHE HYDRIERUNG VON CARBONYLVERBINDUNGEN

DISSERTATION

der Fakultät für Chemie und Pharmazie
der Eberhard-Karls-Universität Tübingen
zur Erlangung des Grades eines Doktors
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Tag der mündlichen Prüfung:	15. Juli 2005
Dekan:	Prof. Dr. Stefan Laufer
1. Berichterstatter:	Prof. Dr. Hermann A. Mayer
2. Berichterstatter:	Prof. Dr. Ekkehard Lindner

Die vorliegende Arbeit wurde am
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„Phantasie ist wichtiger als Wissen, denn Wissen ist begrenzt."

Albert Einstein (14.03.1879 - 18.04.1955)

Meinen Eltern

1 CONTENT

2 ABBREVIATIONS AND UNITS

2.1 List of Abbreviations

Anal.	-	analysis
atm	-	atmosphere
B^-	-	base
B_0	-	magnetic field
BET	-	Brunauer-Emmett-Teller
BINAP	-	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
Calcd.	-	calculated
C=C	-	olefinic double bond
CME	-	chemically modified electrode
C=N	-	imine double bond
C=O	-	carbonyl double bond
d	-	doublet (NMR)
dB	-	decibel
DAIPEN	-	1,1-di(anisyl)-2-isopropyl-1,2-ethylenediamine
DEPT 135	-	distortionless enhancement by polirisation transfer (decoupler pulse 135°)
DiPEA	-	N-ethyldiisopropylamine
DMF	-	dimethylformamide
DPEN	-	diphenylethylenediamine
dppb	-	diphenylphosphinobutane
dppp	-	diphenylphosphinopropane
dppp*	-	T-silyl-functionalised diphenylphosphinopropane
ee	-	enantiomeric excess
E_λ	-	extinction
F	-	area

FAB	-	fast atom bombardement
FID	-	flame ionisation detector
FT-ATR-IR	-	fourier transform attenuated total reflection IR
FT-IR	-	fourier transform infrared spectroscopy
H^+	-	hydrogenium ion
H^-	-	hydride ion
HOBt	-	1-hydroxy-1H-benzotriazole
HPLC	-	high performance liquid chromatography
Hz	-	Hertz
GC	-	gas chromatography
IR	-	infrared spectroscopy
K^+	-	potassium cation
KO^iPr	-	potassium-*iso*-propanolate
KO^tBu	-	potassium-*tert*-butoxide
LB	-	line broadening (NMR)
m	-	multiplet (NMR)
m	-	mass
M	-	molar mass
M^+	-	molecular ion peak (mass spectrometry)
MAS	-	magic-angle spinning
max.	-	maximal
ML_n	-	reactive centre
m/z	-	mass/charge ratio
NH	-	amine group
$^nJ_{ij}$	-	coupling constant of nuclei i, j via n bonds
NMR	-	nuclear magnetic resonance
$^-O^tBu$	-	*tert*-butoxide anion
$-OCH_3$	-	methoxy group
OH	-	hydroxyl group
^-OH	-	hydroxide anion
$^-O^iPr$	-	*iso*-propanolate anion
p.a.	-	pro analysi
PASP	-	polymer assisted solution phase

PEG	-	polyethylene glycol
Ph	-	phenyl group
PPh_3	-	triphenylphosphine
ppm	-	parts per million
pta	-	1,3,5-triaza-7-phosphaadamantane
puriss.	-	purissimum
REM	-	raster electron microscopy
R_f	-	device-, substance-, and column-specific constant in GC
R^n	-	organic rest
r.t.	-	room temperature
[Ru]	-	ruthenium complex
solv	-	solvent
SP	-	Stöber particle
t	-	time
T	-	Tesla
TBTU	-	o-(benzotriazole-1-yl)-N,N,N',N'-tetramethyluroniumtetra-fluoroborate
THF	-	tetrahydrofurane
TMS	-	tetramethylsilane
TOF	-	turn-over frequency
TolBINAP	-	2,2'-bis(di-4-tolylphosphino)-1,1'-binaphthyl
UR	-	Ultraresin
UV	-	ultraviolett
VACP	-	variable-amplitude cross-polarisation
V	-	Volts
VIS	-	visible
vs.	-	versus
W	-	Watt
X	-	hydrolysable group
XylBINAP	-	2,2'-bis(di-3,5-xylylphosphino)-1,1'-binaphthyl

δ	-	chemical shift
ΔT	-	elevated temperature
ε_λ	-	extinction coefficient
η^n	-	hapticity
λ	-	wavelength
ν	-	valence oscillation
$\nu_{1/2}$	-	linewidth (NMR)

2.2 Prefixes

M	-	mega (10^6)
k	-	kilo (10^3)
c	-	centi (10^2)
m	-	milli (10^{-3})
µ	-	micro (10^{-6})
n	-	nano (10^{-9})

2.3 Schemes

2.4 Figures

2.5 Tables

3 INTRODUCTION

Due to an increasing interest of society in environmental issues chemical and pharmaceutical industry are challenged to optimise their procedures towards ecologically acceptable conditions. A possible way to reach the aim of a so called "green chemistry" is the use of well-designed homogeneous transition metal complexes[1-6] as catalysts. Owing to their high reactivity and selectivity reactions proceed more efficiently, i.e. they help to avoid toxic compounds and the formation of environmentally endangering by-products. Besides, energy is saved.

Among the diaminedichlorobis(phosphine)ruthenium(II) complexes developed by Noyori and co-workers[7,8] there are examples, which have already been introduced to industrial fine chemical synthesis. But although there are lots of advantages in the application of homogeneous transition metal catalysts one disadvantage remains. After the catalytic reaction the catalyst has to be separated from the reaction products. This procedure very often is a time, energy, chemicals, and therefore money consuming process. Moreover, the catalyst could decompose during the recycling process. All this antagonises the usage of homogeneous transition metal catalysts. A possibility to overcome this problem is the employment of heterogeneous catalysts, which in contrast to homogeneous catalysts are not soluble. Generally heterogeneous catalysts consist of a solid body with a large surface, on which the catalytic reaction takes place. Heterogeneous catalysts have the big advantage that they can easily be removed from a reaction mixture, by filtration for example. But indeed transportation processes like diffusion play a very important role and hence can influence the rate of conversion, which commonly is low as is selectivity. Another aspect in this context is the anchoring of homogeneous structurally well-defined transition metal complexes on surfaces of organic or inorganic polymers. More than twenty years ago first trials were made to transfer the principles of solid phase synthesis to transition metal complexes[9]. In this way it was supposed to combine the advantages of homogeneous and heterogeneous catalysis. In first trials carbonyl complexes were directly bound to organic polymers,

poly-2-vinylpyridine for example[10,11]. A disadvantage of the direct anchoring was the fact, that just a small amount of transition metal complexes could be attached. As a consequence a method was developed to immobilise metal complexes via a donor ligand molecule that was covalently bound to the polymer. With this method a larger range of metal complexes could be heterogenised[12-19]. The anchoring of the transition metal complex to the polymeric matrix was achieved by the exchange of a ligand molecule bound to the metal centre by an immobilised donor ligand. In a second approach a functionalised ligand molecule was coordinated to the metal centre. The metal complex functionalised in this manner was then added to the reaction mixture during the polymerisation of the organic support. In this way it was estimated to obtain polymers containing a selected amount of bound complexes with a well-defined structure. However, the latter method was not useful because the sensitive metal complexes decomposed during the polymerisation process[16,17]. At the beginning polystyrene and styrene/divinylbenzene copolymers (Merrifield-resins) were the commonly applied carrier materials[20]. In the following years polyvinyls[10-13], polyacrylates[18,21,22], and cellulose[23,24] were employed, too. In spite of the large variety of different organic polymer supports they commonly show low mechanical, thermal, and chemical stability. Moreover, they are sensitive towards aging[9].

Therefore efforts were made to immobilise transition metal complexes on the surface of inorganic supports. The donor ligands were provided with functional groups that could easily be hydrolysed, for example $-SiX_3$ (X = hydrolysable group like $-OCH_3$). By that a linkage with surface hydroxyl groups on an inorganic matrix could be achieved. As inorganic carrier materials first silica gel[25,26], later γ-Al_2O_3, zeolithes and glass[27] were applied. Until now the most often applied inorganic supporting material is silica gel[25,28-33], because it is neutral, its properties are well investigated[34-36], and possible modifications of its surface are well known[37-39]. However, common problems of these supports are leaching, reduced accessibility and reactivity of the immobilised reactive centres.

About ten years ago the concept of “Chemistry in Interphases”[40,41] was introduced to catalysis. With this method active centres can be incorporated into a mostly porous and swellable organic or inorganic polymer network, e.g. by employing a sol-gel process. By this means it was expected to overcome the problems of leaching and reduced accessibility. Due to porosity and swellability of the supporting material it was estimated

to imitate homogeneous conditions in the environment of the immobilised reactive centre and hence to combine the advantages of homogeneous and heterogeneous catalysis.

For fine chemical and pharmaceutical industry catalytic hydrogenation of polar double bonds such as C=O or C=N and especially the asymmetric version of this reaction plays an important role. With this key method it is possible to produce chiral alcohols or amines as precursors in the production of pharmaceutically interesting products[7,8,42]. For almost 40 years ruthenium homogeneous hydrogenation catalysts have been known[43,44]. Until now they have been proving their utility for this application due to their favourable reactivity and selectivity. To date for the hydrogenation of polar double bonds with ruthenium complexes two main catalytic cycles are known and accepted[45]. With these it is possible to explain the fact why some special ruthenium complexes with amine ligands are more active than other ruthenium complexes for the direct hydrogenation of ketones[7,8]. Often this high activity involves high enantioselectivity for the hydrogenation of prochiral ketones and a high chemoselectivity of carbonyl double bonds over olefinic double bonds[7,8,46]. Therefore the immobilisation of these ruthenium(II) complexes is of great interest.

As new supports for hydrogenation in interphases highly swellable ULTRARESINS, which already had been successfully introduced to solid phase synthesis[47], were modified with regard to the anchoring of ruthenium(II) complexes. In comparison to this organic matrix as inorganic support for a T-silyl functionalised ruthenium(II) complex spherical non-porous silica particles, so called Stöber particles[48] were applied. Hence the catalytic activity of analogous homogeneous ruthenium(II) complexes has already been reported[46,49], the new organic and inorganic supported stationary phases were employed in the catalytic hydrogenation of acetophenone. As hydrogenation methods both direct hydrogenation with H_2 gas as hydrogen source and transfer hydrogenation, in which the solvent provides the hydrogen, were applied. The organic and inorganic interphase catalysts were compared according to catalytic performance, recycle ability and leaching.

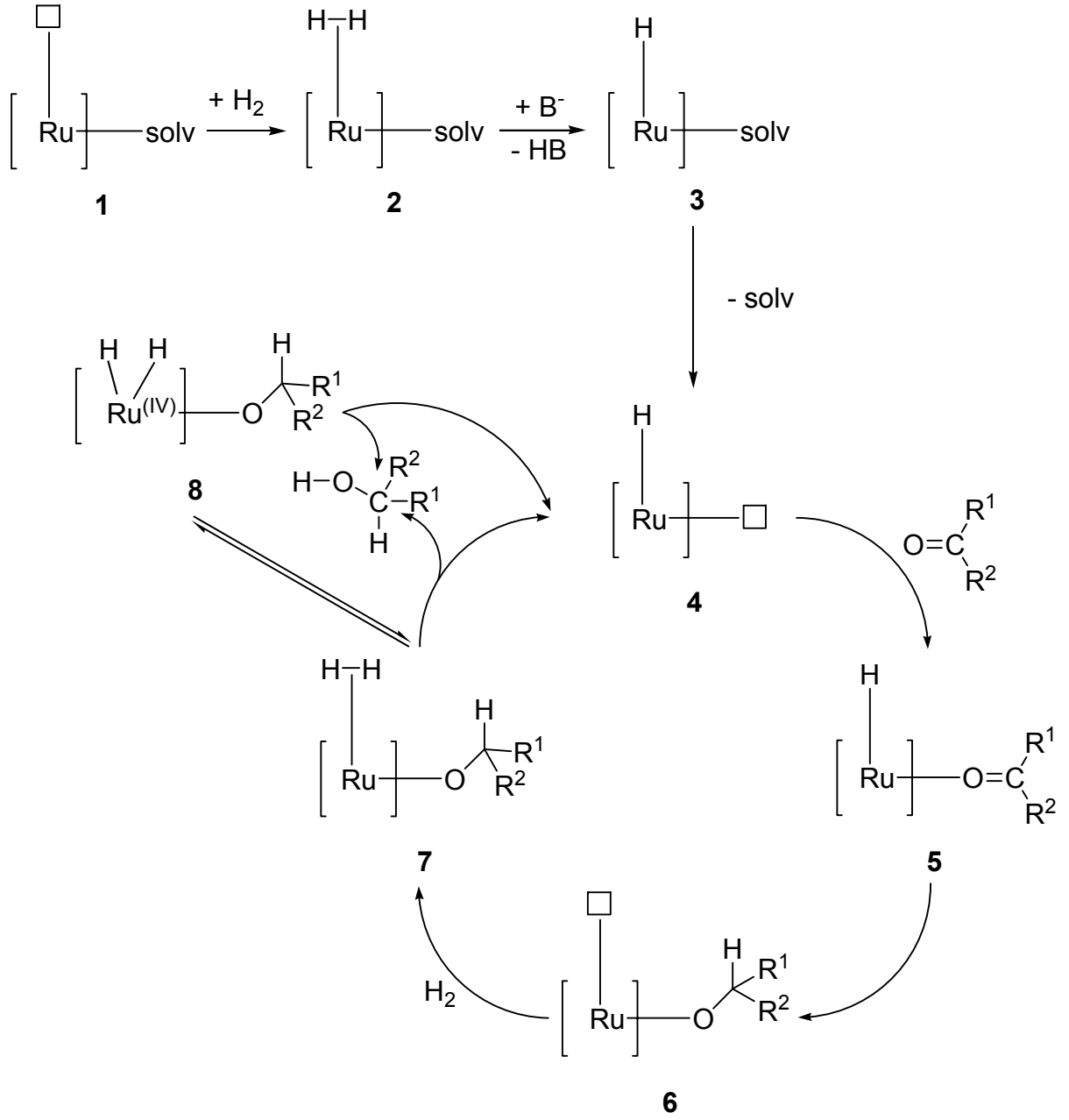
4 GENERAL SECTION

4.1 Catalytic Hydrogenation of Polar Double Bonds with Ruthenium Complexes

Ruthenium homogeneous hydrogenation catalysts have been proven to be some of the most useful catalysts for the catalytic hydrogenation of polar double bonds such as C=O or C=N due to their favourable reactivity and selectivity. In general, hydrogenation reactions with ruthenium catalysts can be classified by their reaction mechanisms[45] in direct hydrogenation with hydrogen gas as hydrogen source and transfer hydrogenation in which an organic source serves as hydrogen donor. The classical mechanisms of transition metal homogeneous catalysis involve the reactants forming products while bound to the central metal. So it is assumed that for the hydrogenation of polar bonds it is necessary that the ketone or imine binds to a free coordination site on the ruthenium(II). Because of the low hydride affinity of C=O or C=N it is crucial that the ruthenium complexes are sufficiently hydridic showing the following properties: Auxiliary ligands on the metal centre stabilise the positive charge that is left on the ruthenium after the hydride transfer step. These ligands contain for example strongly basic hydride, phosphine, and cyclopentadienide with electropositive donor elements (H, P, C). When these ligands are *trans* positioned to the leaving hydride they assist the weakening of the Ru-H bond because of their high *trans* influence. A negative charge on the ligands will promote the reaction[50-55].

4.2 Mechanisms of Hydrogenation Reactions in the Inner Coordination Sphere

4.2.1 Direct Hydrogenation



Scheme 1. Catalytic cycle for the direct hydrogenation of polar double bonds in the inner coordination sphere

For inner sphere hydrogenation reaction the generalised catalytic cycle in Scheme 1 is proposed[45]. In general precursor complexes are applied, because very often they are stable and storable in comparison to the active species which easily can be generated *in situ* during the hydrogenation process[56-60]. During the *in situ* preparation of an active species from precatalyst **1** in direct hydrogenation usually hydrogen gas first coordinates to a vacant site at the metal centre as a η^2-dihydrogen ligand (**2**)[61-64]. Normally this ligand undergoes heterolytic cleavage to give a ruthenium hydride (**3**) and a protonated base. By removal of a ligand, a solvent molecule for example, a free coordination site is created (**4**). In the next step the substrate binds to the free coordination site of the unsaturated hydride species (**5**). The coordination in the inner sphere leads to an electrophilic activation of the carbon of the carbonyl group so that a *cis*-hydride on the metal centre can migrate to the linked β carbon. Noyori and Ohkuma found evidence[7] for a high activation barrier for this inner sphere attack coming from a drastic change of ground state structures for the interaction between the Ru-H bond and the π face of the carbonyl. In some cases an ancillary ligand, usually containing an acidic hydrogen bond donor group, provides additional activation of the unsaturated substrate towards the hydride attack. By hydride migration from the catalyst to the substrate a new unsaturated ruthenium species **6** is generated, to which dihydrogen coordinates. The dihydrogen species **7** now can react in two ways: i) Protonation of the substrate leads to the product. The regenerated catalyst **4** is released. ii) By oxidative addition coordinated dihydrogen adds to the metal centre. This affords a Ru(IV) species (**8**). By elimination of the product the active catalyst **4** is regenerated. Normally it is not possible to experimentally differentiate between the two reaction paths. Catalytic reactions following the inner sphere hydrogenation cycle have several features in common[45]:

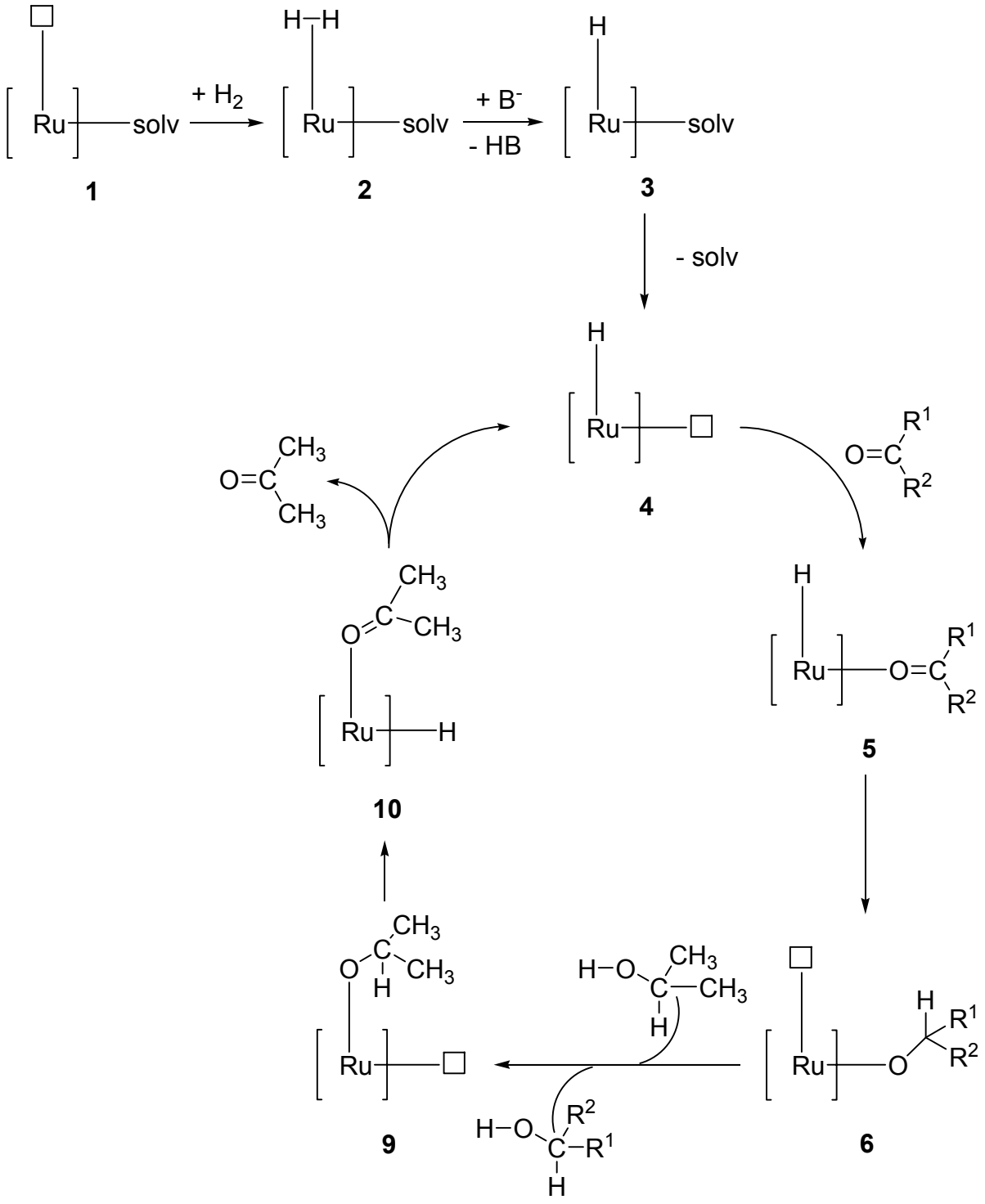
- They require high temperatures.
- They need high hydrogen pressures.
- The catalyst to substrate ratio is very small.
- No additives are required.
- They lose selectivity for C=O over C=C bonds[65,66].

One example for a catalytic system following the inner sphere coordination mechanism is [RuH{(R)-BINAP}{N≡C-CH_3}{(1-3-η):(5,6-η)-C_8H_{11}}](BF_4) (BINAP=2,2'-bis(diphenyl-phosphino)-1,1'-binaphthyl) developed by Bergens and co-workers[56,57]. During the hydrogenation in methanol, THF, or acetone (solv) with less than 1 atm H_2 pressure the hydride species [RuH{(R)-BINAP}{N≡C-CH_3}$_m$(solv)$_{3-m}$]BF_4, the actual catalyst is generated. The system serves for the hydrogenation of various unsaturated compounds, α- and β-ketoesters for instance. As a second example an interesting catalytic system has been developed by Laurenczy et al.[67]. The catalytic activity of the precursor complex $RuCl_2(pta)_4$ (pta=1,3,5-triaza-7-phosphaadamantane) during the hydrogenation reaction of CO_2 is depending on the pH of the water solution.

4.2.2 Transfer Hydrogenation

The proposed mechanism for the transfer hydrogenation process (Scheme 2)[45,68,69] of C=O bonds is similar to the direct hydrogenation explained above (Scheme 1). In contrast to the direct hydrogenation the hydride bound to the metal centre is derived from hydrogen transfer reagents such as 2-propanolate in 2-propanol/base mixtures or formate in formic acid/triethylamine mixtures via β-elimination reactions[70] (Scheme 2). Then starting from a hydride species of the ruthenium(II) complex with a free coordination site (**4**) the substrate coordinates to this complex. A hydride is transferred from the catalyst to the β–position of the substrate whereupon the unsaturated species of complex **6** is generated. The coordinated alkoxide species of the product is protonated by the hydrogen transfer agent and the product is released from the complex whereas the deprotonated hydrogen transfer agent coordinates to ruthenium complex **9**. By β-hydride elimination a hydride from the hydrogen donor is delivered to the metal centre (**10**). The elimination of the oxidised hydrogen transfer agent completes the cycle. Mizushima et al. for example demonstrated in their work[71,72] that the complex *cis*-$Ru(H)_2(PPh_3)_4$ is a very active precatalyst for the hydrogenation of ketones with 2-propanol as hydrogen donor following the proposed catalytic cycle (Scheme 2). Pamies and Bäckwall[73,74] suggested a slightly different mechanism for $Ru(H)_2(PPh_3)_3$ as catalyst which is generated from $RuCl_2(PPh_3)_3$ in the presence of a base in 2-propanol. They discussed the creation of a Ru(0) species by reductive elimination of the product

from complex species **5**. After oxidative addition of the O-H bond of the hydrogen transfer agent the reaction proceeds as explained above (Scheme 2).



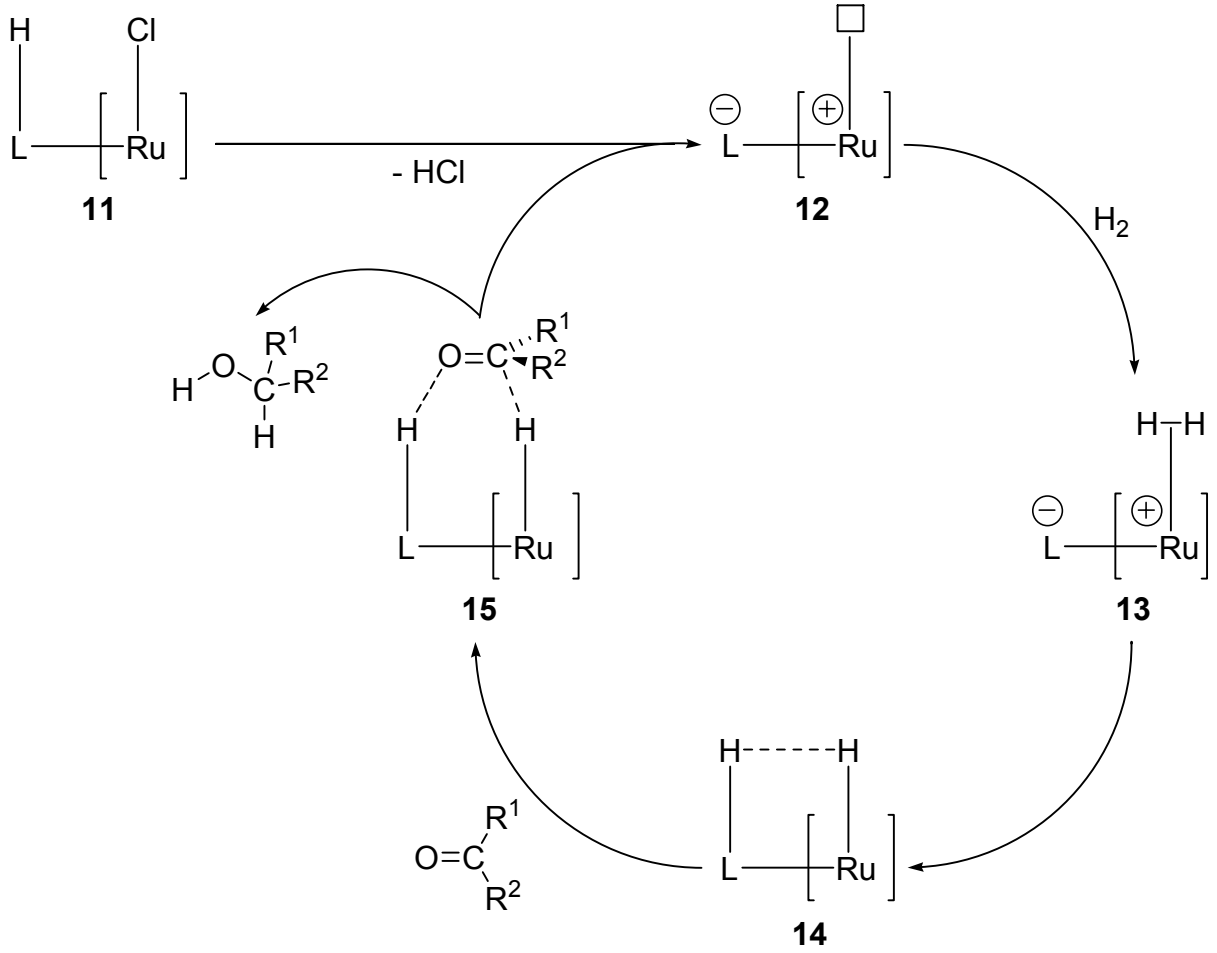
Scheme 2. Catalytic cycle for the transfer hydrogenation of polar double bonds in the inner coordination sphere of a ruthenium complex

4.3 Mechanisms of Hydrogenation Reactions in the Outer Coordination Sphere

4.3.1 "Metal-Ligand Bifunctional Catalysis" - Direct Hydrogenation of Carbonyl Functions in the Outer Coordination Sphere of Ruthenium(II) Complexes with Ancillary Ligand

Scientific interest moved away from direct hydrogenation reactions in the outer coordination sphere of ruthenium complexes[75,76] that do not require an auxiliary ligand, due to the discovery of the so-called "N-H" effect by Noyori and co-workers[7,8,42,77]. "N-H" effect means that the addition of diamines, for example ethylenediamine to $RuCl_2(PPh_3)_3$ and a base in 2-propanol increases the activity of the catalyst in the direct hydrogenation of ketones in an extraordinary way[7,78] whereas tertiary diamines are ineffective. Following the arguments of Noyori the hydride transfer to the substrate proceeds in the outer coordination sphere of the catalyst. The low hydride affinity of the carbon in C=O bonds usually requires an electrophilic activation. This can be achieved by an external electrophile or by an electrophile attached to an auxiliary ligand *cis* to the hydride of the ruthenium complex. To refer to catalytic systems that operate with ancillary ligands Noyori has coined the term "Metal-Ligand Bifunctional Catalysis"[68,79]. In these cases it is typical that the auxiliary ligand provides a proton as electrophile on the ligand. This means that the ligand must have an NH- or OH-group or an associated electrophile, for example a potassium cation[80]. In a cyclic six-membered transition state (**15**) the proton and the hydride are transferred in a concerted manner (Scheme 3). This catalytic behaviour leads to a charge alternation which seems to be an important factor that favours H_2-transfer to the polar C=O bonds over the non-polar C=C bonds.

The proposed mechanism[45] for this type of reaction (Scheme 3) starts with the generation of the active species **12**. It is derived from precatalyst **11** by dehydrochlorination. For this step a strong base, for example ^-OH, $^-O^iPr$ or $^-O^tBu$ is crucial. The 16-electron species **12** normally is stabilised by π-donation from the deprotonated ligand into the empty d-orbital of the metal. At the free coordination site on the metal centre a hydrogen molecule can coordinate to form the dihydrogen intermediate or transition state **13**. By heterolytically splitting the coordinated hydrogen the active hydrido species **14** is formed. Here a facial proton of the auxiliary ligand and



Scheme 3. Catalytic cycle for the direct hydrogenation of polar double bonds in the outer coordination sphere of a ruthenium(II) complex with an ancillary ligand

the hydride on the metal centre form a hydridic-protonic interaction (**14**). The substrate coordinates to complex **14** in a six-membered cyclic transition state (**15**). In doing so the polar double bonds of the substrate interact in the outer sphere with the proton of the ancillary ligand and the hydride at the metal centre. The simultaneous transfer of the hydride and the proton to the coordinated substrate yields the product and the 16-electron species **12**.

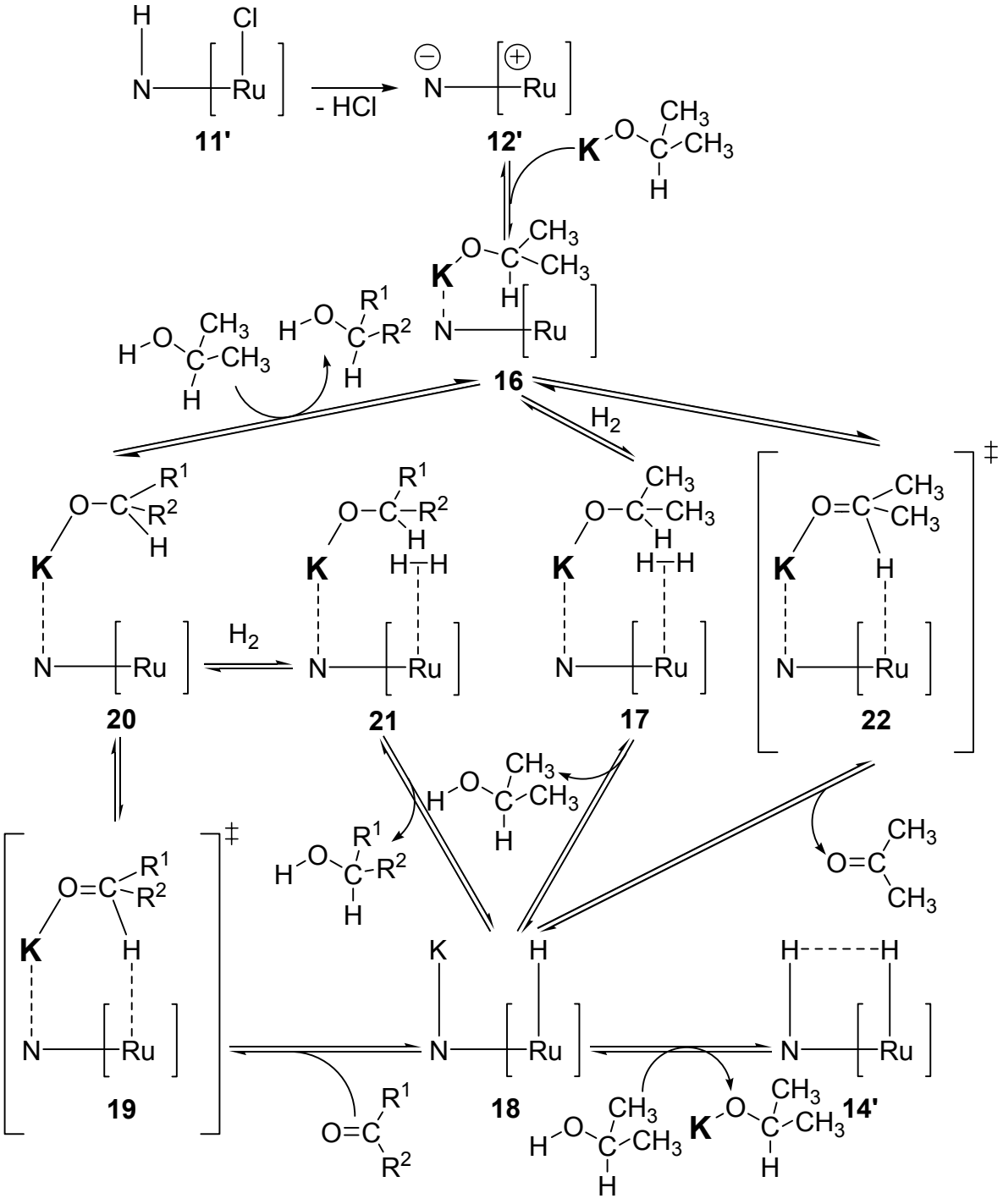
A main focus was not only the chemoselective hydrogenation of ketones and aldehydes but also the development of catalytic systems hydrogenating C=O bonds enantioselectively. Because of the many structural differences of the substrates it is not possible to find just one catalyst that meets all demands. By choosing suitable chiral

ligands it is possible to obtain enantiopure alcohols from prochiral ketones or aldehydes by asymmetric induction. Extraordinary examples for this type of ruthenium(II) catalysts with ancillary ligands offering an NH-group were developed by Noyori and co-workers[7,8,42,59,81,82]. A lot of stable catalyst precursors bearing a *trans*-[$RuCl_2$(diphosphine)(1,2-diamine)] basic structure were developed by Noyori's group and were investigated according to their catalytic activity in the hydrogenation of carbonyl compounds. A well-established and approved system of this type contains as bisphosphine ligand optically pure BINAP, TolBINAP (2,2'-bis(di-4-tolylphosphino)-1,1'-binaphthyl), or XylBINAP (2,2'-bis(di-3,5-xylylphosphino)-1,1'-binaphthyl) and as diamine ligand optically pure DPEN (diphenylethylenediamine), or DIAPEN (1,1-di(anisyl)-2-isopropyl-1,2-ethylenediamine) and hydrogenates C=O bonds with a TOF (turn-over frequency) up to 259 000 h^{-1} and enantioselectivity up to 99 % *ee*[7,82]. Inspired by these results other groups designed similar catalyst precursor systems and tested their catalytic behaviour in the hydrogenation of ketones[46,49,83-85]. The research of Morris et al. has led from *trans*-[RuClH(diphosphine)(1,2-diamine)] complexes as catalyst precursors operating only with a base in 2-propanol[60] to *trans*-[RuH_2(diphosphine)(1,2-diamine)] complexes. They could show that the dihydrido complexes[86,87] do not require a base to be catalytically active because they were proven to be the actual catalysts. In solution they lose H_2 to give the 16-electron species of the ruthenium(II) complex, which could be isolated and characterised. Similar results were gained once again by Noyori's group by developing a *trans*-[RuH(η^1-BH_4)-(diphosphine)(1,2-diamine)] system that hydrogenates carbonyl compounds in the outer coordination sphere[77,88]. Further investigations of Noyori's *trans*-[$RuCl_2${(*S*)-BINAP}-{(*S*,*S*)-DPEN}] system by Chen[80] resulted in the following conclusions:

- For the dehydrochlorination a base is necessary but it is not sufficient to get high activities.
- By elevating the concentration of alkali metal cation at constant base concentration the reactivity of the system is increased.
- The alkali metal cation not only is required to start the catalytic process but to continue the reaction.
- The speed of the reaction is influenced by alkali metal cations in the following order: K>Na~Rb>Li.

- ❖ A Lewis acid preferably an alkali metal cation is crucial for the hydrogenation of carbonyl compounds in the outer sphere of the *trans*-[$RuCl_2${(*S*)-BINAP}{(*S*,*S*)-DPEN}] system.

As an explanation the mechanism in Scheme 4 is proposed[80]. In the first step of the hydrogenation reaction the 16-electron species **12'** has to be generated from the catalyst precursor (**11'**) by dehydrochlorination. In contrast to the catalytic cycle shown in Scheme 3 KO^{i}Pr coordinates to the metal centre via the deprotonated amine ligand (**16**). Several competing reactions now can succeed: i) At the free coordination site of ruthenium H_2 coordinates (**17**). The hydrogen is heterolytically cleaved to yield 2-propanol and complex **18**. In a six-membered transition state (**19**) the substrate coordinates via the potassium cation to the ruthenium complex in the outer coordination sphere and a hydride is transferred to yield complex **20**. The product alcohol can be released in two ways. One possibility is the coordination of H_2 to the complex and its heterolytic splitting to yield the product and the hydride species **18**. The second possibility is the protonation of the coordinated alkoxide by 2-propanol leading to complex **16**. ii) Via a six-membered transition state (**22**) a hydride is transferred from the coordinated KO^{i}Pr to ruthenium to yield complex **18**. Now the catalytic cycle can proceed as explained. By exchanging the coordinated potassium ion with a proton from 2-propanol the ruthenium(II) hydride complex **14'** is generated. The catalytic cycle can advance as in Scheme 3. It was proposed that H_2 cleavage is favoured over dehydrogenation of 2-propanol, which is reflected in higher TOFs for direct hydrogenation than for transfer hydrogenation[80] but only takes place in the presence of a Lewis acid such as a potassium cation. Because of this the intermediate stages **17** and **21** are preferred. The 16-electron species **12'** is not basic enough to split hydrogen efficiently because no hydrogenation takes place without Lewis acid, which could be experimentally proven. In this case the competing dehydrogenation of 2-propanol takes place. By coordination of an alkali metal cation to the Ru-amido nitrogen the electron density of the metal centre is diminished. In this way the coordinated H_2 gets more acidic and can be easily deprotonated by a coordinated alkoxide. By the use of potassium cation as Lewis acid an increase of the reactivity is achieved in particular because of sterical reasons[80].



Scheme 4. Catalytic cycle for the hydrogenation of C=O groups by *trans*-[$RuCl_2${(S)-BINAP}{(S,S)-DPEN}] proposed by Chen[80] (Here KO^{i}Pr was used as base and K^+ as Lewis acid)

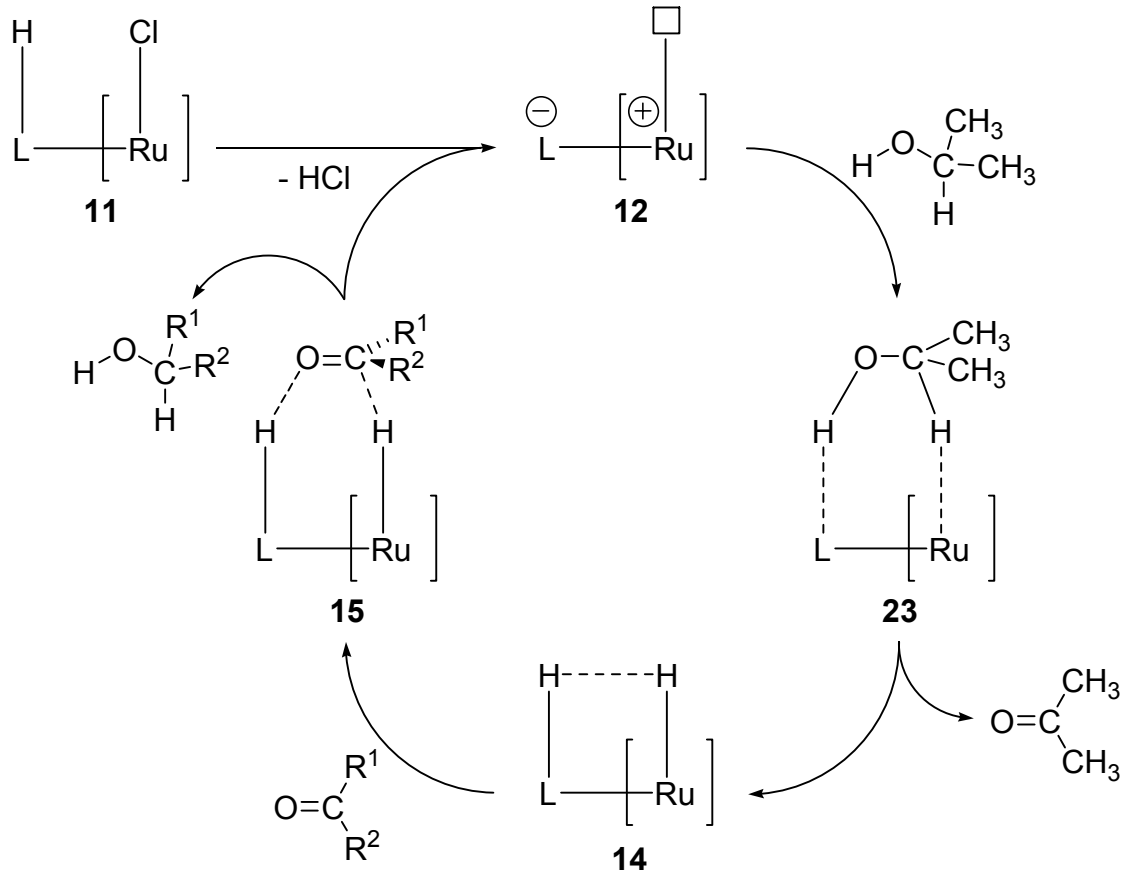
4.3.2 "Metal-Ligand Bifunctional Catalysis" - Transfer Hydrogenation of Carbonyl Functions in the Outer Coordination Sphere of Ruthenium(II) Complexes with Ancillary Ligand

As well as for the direct hydrogenation there are examples known for transfer hydrogenation that operate in the outer coordination sphere without ancillary ligand[89]. But as for direct hydrogenation the discovery of the "NH"-effect by Noyori and co-workers[68,90-94] led to a breakthrough for ruthenium transfer hydrogenation catalysts. As for the direct hydrogenation the catalytic cycle[45] (Scheme 5) starts with the generation of a 16-electron species by dehydrochlorination (**12**). Hydrogen transfer from 2-propanol to complex **12** in a six-membered transition state (**23**) produces the catalytically active hydride species **14**. Then the catalytic cycle proceeds as explained for direct hydrogenation (Scheme 3). As a progression of Noyori's results in direct hydrogenation of α,β-unsaturated ketones with diaminedichlorobis[(methoxyethyldiphenyl)phosphine]-ruthenium(II) complexes[49,85] Lindner et al. prepared a library of novel diaminedichloro-bis[(methoxyethyldimethyl)phosphine]ruthenium(II) complexes and showed that they are excellent catalyst precursor complexes for transfer hydrogenation[95]. They assumed that these operate following the cycle shown in Scheme 5.

4.3.3 "Metal-Ligand Bifunctional Catalysis"- Conclusion

In "Metal-Ligand Bifunctional Catalysis" the ligand plays an extraordinary role[45]. Its task is:

- the activation of the carbon of the carbonyl compound so that a nucleophilic hydride attack is possible by hydrogen bonding to the oxygen of the substrate,
- to provide a six-membered cyclic transition state for H^+/H^- transfer,
- to serve as a proton donor, which is transferred concerted with the hydride,
- to allocate a point of interaction for enantioselective recognition.



Scheme 5. Catalytic cycle for the transfer hydrogenation of carbonyl compounds in the outer coordination sphere of ruthenium(II) complexes with ancillary ligand

4.4 Chemistry in Interphases

A lot of problems make immobilised transition metals both on organic supports and on inorganic surfaces unattractive for their commercial use[41]:

i. The lifetime of these catalysts is very short due to leaching of the reactive centres caused by poor anchoring.

ii. The accessibility of the transition metal complexes is reduced due to sterical effects of the heterogeneous matrix.

iii. The influence of the supporting material on reactivity and selectivity of the reactive centre as well as the activity of the matrix itself in a catalytic process is not known.

iv. The reactive centres lose homogeneity because of minor changes in their structure. As a consequence reduced activity and selectivity of the catalyst is observed[38,96].

v. It is difficult to control the density of immobilised metal complex within the material or on its surface[96,97].

To overcome these problems in a recent approach (1995) the concept of "Chemistry in Interphases"[40,41] first introduced to reversed-phase chromatography[98-100] was transferred to catalysis[101]. An interphase is defined as a region within a material, in which a stationary phase and a mobile phase penetrate each other on a molecular level (Figure 1). The stationary phase is a combination of an organic, inorganic, or organic/inorganic hybrid inert support, a flexible spacer, and an active centre, for example a transition metal complex. The mobile phase consists of a solvent, a gaseous, a liquid, or a dissolved reactant. In an ideal interphase the reactive centre is uniform and well-defined; if the interphase contains a swellable polymeric support it is able to imitate homogeneous conditions: the active centres become highly mobile simulating the properties of a solution and hence they are accessible for substrates. On the other hand an interphase has the advantages of a heterogeneous catalyst because of its insolubility. For the preparation of interphase catalysts the sol-gel process is a powerful tool[40,41,102-105]. Under smooth and low-temperature conditions suitable polysiloxane networks can be obtained. By variation of the reaction conditions a large range from flexible to rigid materials is accessible[40,41]. Moreover porosity and swellability of the

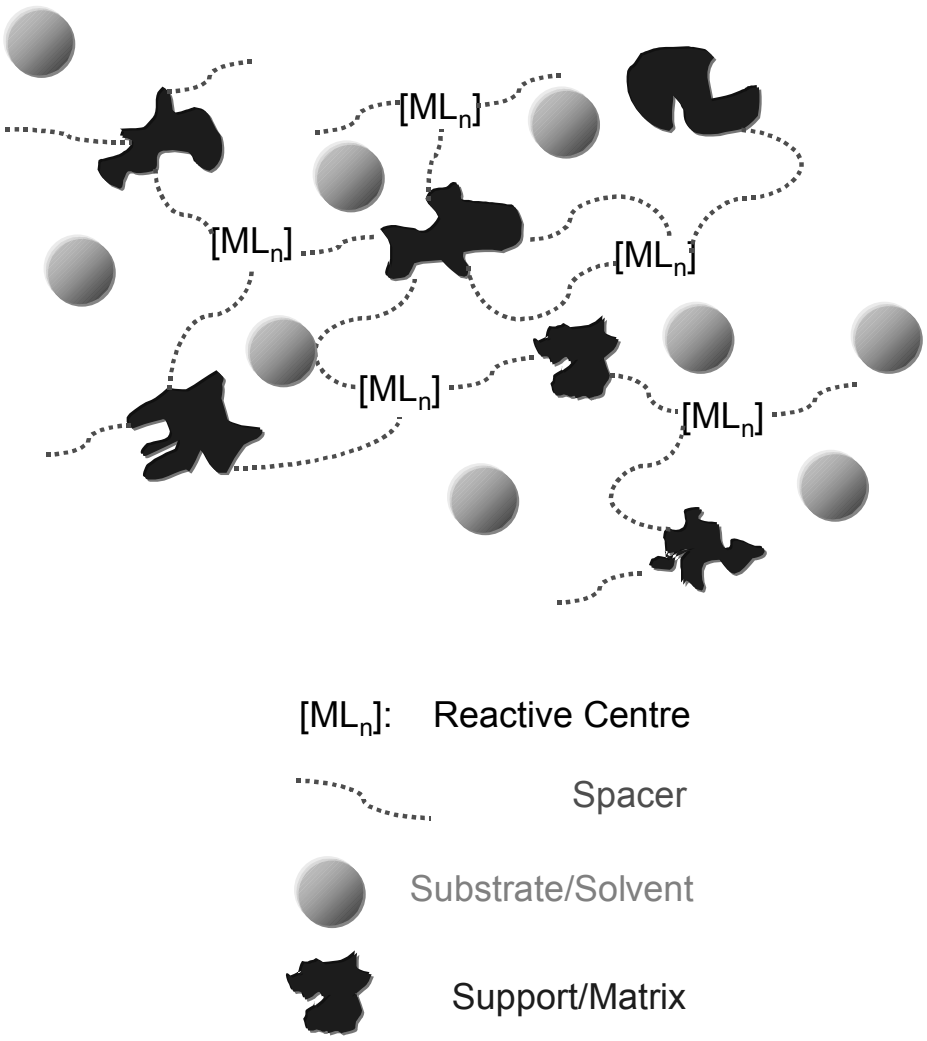


Figure 1. Schematic representation of an interphase

materials are adjustable. The derivatisation of a ligand molecule with a spacer, which coordinates to a transition metal, results in a functionalised complex. By simultaneous co-condensation of silyl functionalised metal complexes with alkoxysilanes a large variety of well-defined materials is accessible. If one considers these materials to be an ideal interphase, the reactive centres are nearly homogeneously distributed across a chemically and thermally inert polymer matrix. A second possibility for the immobilisation of transition metal complexes into an interphase is the covalent linkage of a functionalised ligand molecule to the matrix followed by the coordination of a homogeneous precursor complex. The problem of this method is the fact, that it is not

possible to detect the actual amount of reactive centres bound to the incorporated ligand molecules.

Recently attempts have been made to immobilise Noyori-type diaminedichloro-bis(phosphine)ruthenium(II) complexes and diaminedichlorobis(etherphosphine)-ruthenium(II) complexes with two hemilabile ether-phosphine ligands into a polysiloxane network via a sol-gel process with and without templates[106-109]. The analogous homogeneous complexes are excellent chemoselective catalysts for the direct hydrogenation of an α,β-unsaturated ketone[46,49,84]. These newly synthesised stationary phases showed a promising catalytic behaviour in the chemoselective hydrogenation of α,β-unsaturated ketones and some of them could be recycled several times without remarkable loss of activity[107-109].

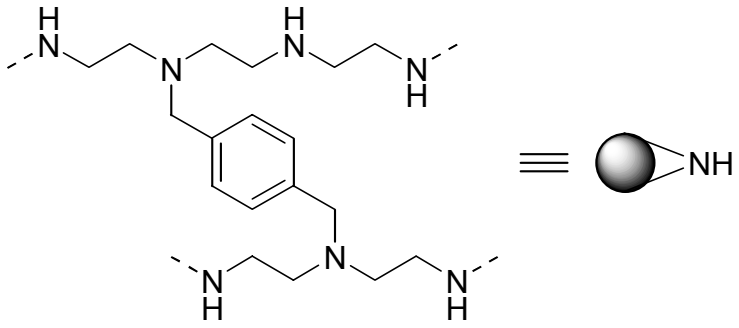
In this work two other types of heterogenised catalysts are introduced. In the first part of this thesis new interphases were synthesised and characterised using highly crosslinked polyethylene imine resins, so called ULTRARESINS[47,110,111] as organic matrices. Dichlorobis[1,3-bis(diphenylphosphine)propane]ruthenium(II) and dichlorobis-[(methoxyethyldiphenyl)phosphine]ruthenium(II) were immobilised on ULTRARESINS by coordination to a covalently bound diamine spacer. In the second part of the thesis a stationary phase with inorganic support was synthesised and characterised. Therefore dichlorobis[(methoxyethyldiphenyl)phosphine]ruthenium(II) was anchored on the surface of spherical silica particles with a diameter of 800 nm via a T-silyl functionalised 1,2-diamine spacer with a mixed primary-secondary diamine. The stationary phases were applied as interphase catalysts in hydrogenation reactions. As model system the reduction of acetophenone to 1-phenylethanol served. As hydrogenation methods both direct hydrogenation with H_2 as hydrogen source and transfer hydrogenation with 2-propanol as hydrogen donor were employed. The results of the different stationary phases were compared regarding catalytic performance, stability of the interphase catalyst, and leaching of the active centres.

4.5 ULTRARESINS

About forty years ago Merrifield introduced polymer-supported methods for peptide synthesis[112]. Insoluble polymeric supports for chemical transformations now belong to the most important and far-reaching innovations of the last decades[113-115]. Until now they have been more and more improved, e. g. polypeptides[116], polynucleotides[117], or oligosaccharides[118] are synthesised automatically with solid state synthesis. In the last years polymeric supports not only were applied for the synthesis of polymeric compounds but also for the preparation of non-polymeric molecules in solid state supported synthesis in solution[119-125]. So far for solid state supported synthesis functionalised swellable crosslinked polystyrenes were applied as polymeric materials[126]. If resins of higher polarity were necessary polystyrenes plugged with polyethylene glycols (PEG) were preferred[127]. Polymer assisted solution phase synthesis (PASP-synthesis) differs from solid phase synthesis in the point that the polymer does not operate as an anchor for any reagent in solution, i.e. the polymer actively participates in the reaction in solution but in PASP-synthesis the substrate is never covalently bound to the resin. Depending on the function of the polymeric material during the reaction it can be modified in various ways. For example polymeric supports are used as scavenger reagents for by-products or educts[128], as carriers in heterogeneous catalysis[129], or for purification of reaction mixtures after the “catch-and-release” mechanism[130].

But a fundamental disadvantage of polymer-supported methods is the fact that it is not competitive to synthesis in solution because of its low atom economy. Moreover the use of polystyrene resins is limited due to the fact of its low chemical acceptance of solvents and its low thermal and chemical stability[131].

Therefore a new class of polymeric supports was developed[47,110,111]. Starting from soluble polyethylene imines, polyethylene imine resins crosslinked with terephthal aldehyde, so called ULTRARESINS were prepared (Scheme 6)[47,110,111]. Because of the large amount of secondary amines in the polymer backbone these resins have a high loading capacity so that this class of new polymeric supporting materials promises to be more efficient than the common polystyrene supports. The secondary amines can be functionalised in various ways very efficiently and consequently can improve solid phase synthesis because of their enlarged atom economy.



UR1

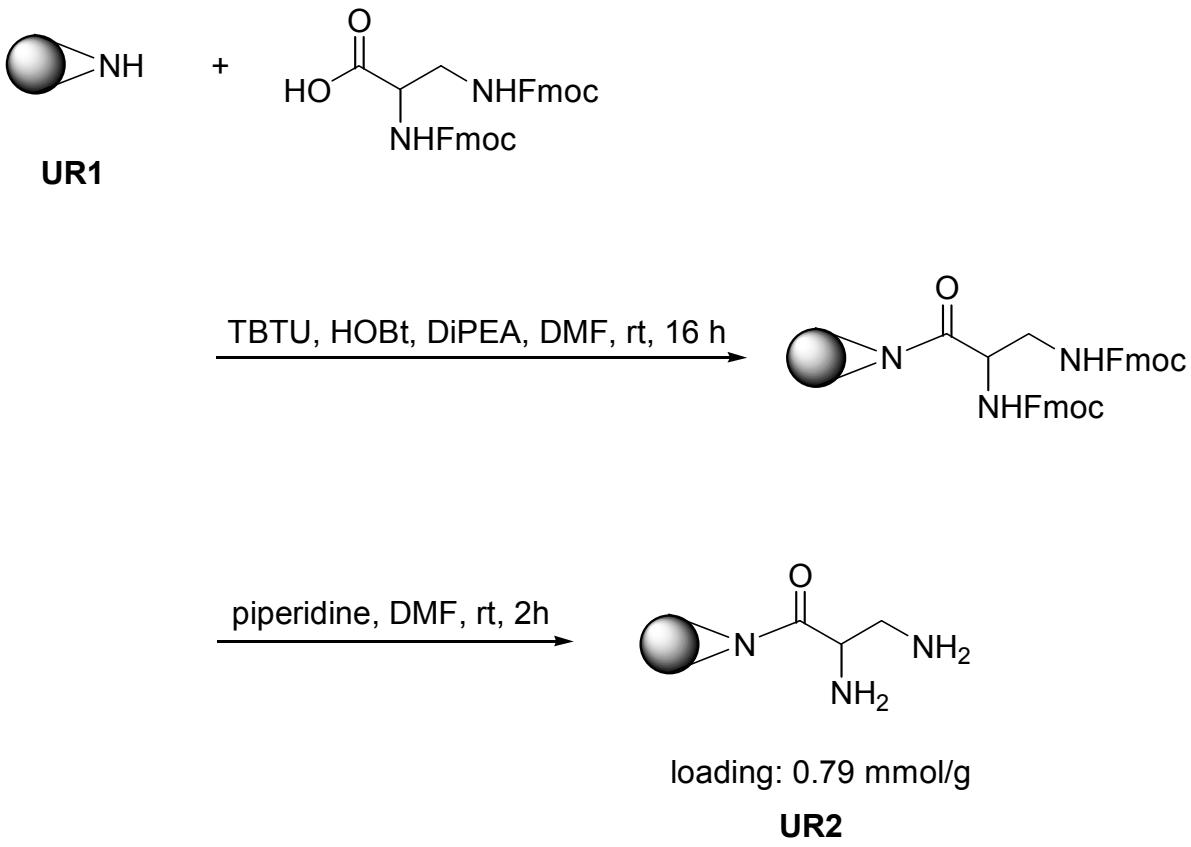
Scheme 6. With terephthal aldehyde crosslinked polyethylene imine (ULTRARESIN)

4.6 ULTRARESINS as Polymeric Support for Diaminedichlorobis-(phosphine)ruthenium(II) Interphase Catalysts

Until now different organic polymeric supports for the heterogenisation of transition metal complexes are known[10-13,20-23,129]. A completely new approach to create an interphase catalyst was made by the application of highly swellable ULTRARESINS as organic polymer matrix. A spacer, which provides a 1,2-diamine structure was bound to the support via an amide bond (Table 1). By the coordination of two types of dichlorobis(phosphine)ruthenium(II) precursor complexes to the immobilised spacers four different interphase materials were obtained (Table 2 and 3).

4.6.1 Preparation of the Modified ULTRARESIN UR2 with 1,2-Diaminopropionic Acid as Spacer

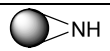
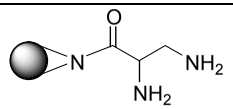
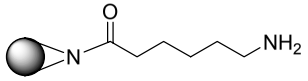
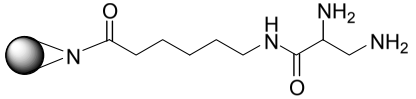
For the coupling of 1,2-diaminopropionic acid to ULTRARESIN **UR1** the TBTU/HOBt[132] (TBTU = o-(benzotriazole-1-yl)-N,N,N',N'-tetramethyluroniumtetrafluoroborate; HOBt = 1-hydroxy-1H-benzotriazole) method was used (Scheme 7). Therefore to a certain amount of the secondary amines in **UR1** Fmoc-1,2-diaminopropionic acid (Fmoc = fluorenylmethoxycarbonyl protecting group) was coupled in DMF with DiPEA (N-ethyldiisopropylamine) as a base. By addition of DiPEA the diaminopropionic acid and HOBt are neutralised as well as their nucleophilic character increased. Under these



Scheme 7. Preparation of the modified ULTRARESIN **UR2**

reaction conditions the active ester of HOBt and the Fmoc-diaminopropionic acid forms as an intermediate. This compound undergoes a nucleophilic attack (-OBt is a very good leaving group) by a secondary amine of the resin. In this way the 1,2-diamine derivative is bound to the resin via an amide bond. Typically the loading of the resulting resin with Fmoc-1,2-diaminopropionic acid would have been determined by Fmoc cleavage with piperidine in DMF and Fmoc determination by UV/VIS spectroscopic methods (see Experimental Part). Due to the low amount of Fmoc-1,2-diaminopropionic acid the Fmoc protecting group is cleaved by the remaining secondary amines in the ULTRARESIN during the coupling reaction. Because of that the primary amines of the 1,2-diamine derivative are partly deprotected so that a capping step with acetic anhydride and DiPEA as a base to inactivate residual secondary amines in the ULTRARESIN could not be carried out. In the next step remaining Fmoc-protecting groups of the coupled Fmoc-1,2-diaminepropionic acid are removed in a two-step reaction with the secondary base piperidine (20 % piperidine in DMF). Piperidine abstracts the β-

Table 1. Different modified ULTRARESINS

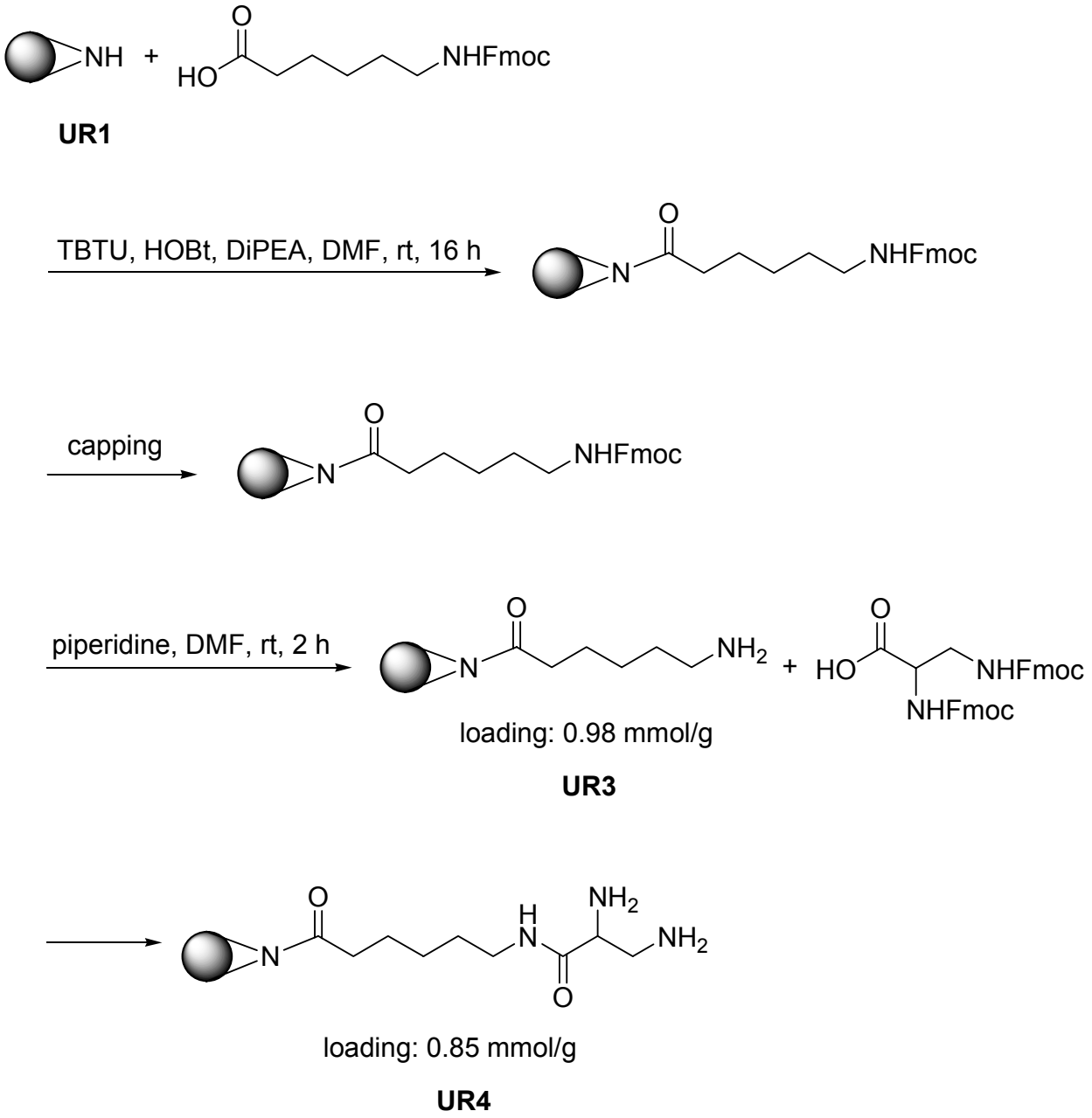
No.	Structure of the ULTRARESIN	Kaiser-test	IR-Data ν [cm^{-1}]	Suspension $^{31}P\{^{1}H\}$ NMR	Solid State ^{31}P NMR	Loading [mmol/g]
UR1	 Polyethylene imine crosslinked with terephthal aldehyde	positive	3260 (N-H) 3015 (C-H) 2888, 2809 (aliphatic C-H) 1510 (N-H) 1451 (aliphatic C-H)			
UR2	 1,2-diaminopropionic acid coupled to **UR1** without spacer	positive	3421 (N-H) 2921 (aliphatic C-H) 1627 (NC=O)			0.79
UR3	 aminohexanoic acid coupled to **UR1**	positive				0.98
UR4	 1,2-diaminopropionic acid coupled to **UR3**	positive	3298 (N-H) 2933 (aliphatic C-H) 1632 (NC=O)			0.85

proton of the Fmoc-group. In this way a carbanion intermediate is formed. In a process following an $E1_{cB}$ mechanism dibenzofulvene and carbon dioxide are eliminated. The use of polar solvents such as DMF accelerates the deprotection. In this manner the modified ULTRARESIN **UR2** is prepared. The loading of colourless ULTRARESIN **UR2** with 1,2-diaminopropionic acid was determined from the starting amount of Fmoc-1,2-diaminopropionic acid to give 0.79 mmol/g. Because of the undesirable Fmoc cleavage from the 1,2-diaminopropionic acid during the amide coupling to the resin a capping step to inactivate remaining secondary amines in the resin backbone could not be carried out. This leads to undesirable properties of the polymeric support for the immobilisation of diaminedichlorobis(phosphine)ruthenium(II) complexes. As was already shown [46,83,133-138] not only primary diamines are able to coordinate to ruthenium(II) precursor complexes, but also secondary amines[46,83,136-138], imines[133], and heterocycles[46,83,134,135]. This means that during the immobilisation step the coordination of the ruthenium(II) complexes could not be controlled because of the huge amount of diamine structures in the polymeric matrix. A second disadvantage of **UR2** is that the spacer of the diamine derivative is very short (one C-atom). Therefore it was supposed that mobility as well as activity of the immobilised catalyst precursor would be diminished[9].

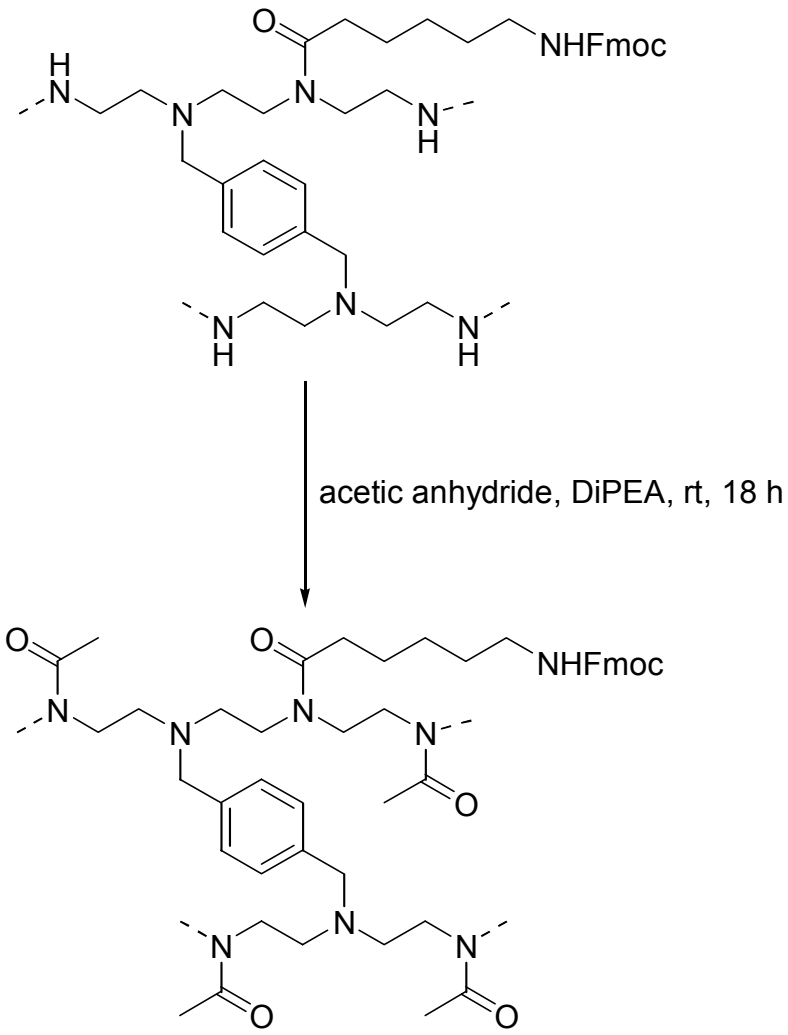
4.6.2 Preparation of an ULTRARESIN with 1,2-Diaminohexanoic Acid as Spacer

To avoid these disadvantages a second approach was made (Scheme 8). Fmoc-aminohexanoic acid as spacer molecule was coupled to ULTRARESIN **UR1** according to the TBTU/HOBt method[132] in the way explained above. By this an elongation of the spacer molecule of seven atoms is achieved. Now the remaining secondary amines in the resin backbone were inactivated in a capping step (Scheme 9). The capping proceeded with a 1 : 1 mixture of acetic anhydride and DiPEA in DMF at room temperature for 18 h. To couple a 1,2-diamine derivative to the spacer first the Fmoc-protecting group had to be cleaved from the spacer. The cleavage proceeded as explained with piperidine in DMF. By UV/VIS spectroscopy (see Experimental Part) a loading of the resin **UR3** with aminohexanoic acid of 0.98 mmol/g was determined. Like in ULTRARESIN **UR2** Fmoc-1,2-diaminopropionic acid was chosen as diamine derivative. The coupling of the diamine to the anchored spacer once again proceeds as explained

after the TBTU/HOBt method[132] with DiPEA as base in DMF for 16 h at room temperature. A Kaisertest (see Experimental Part) indicated that no free amines were left in the colourless resin. After Fmoc cleavage the loading with diamine structure on the organic support **UR4** is determined to 0.85 mmol/g.



Scheme 8. Preparation of the second modified ULTRARESIN **UR4** with long spacer



Scheme 9. Capping of the secondary amines with acetic anhydride and DiPEA

The progress of the synthesis of **UR2** and **UR4** could be followed via IR spectroscopy (for **UR4** see Figure 2). By coupling the Fmoc-spacer to the resin the appearance of an amide band at 1627 cm^{-1} was observed. The Fmoc-protecting group could be detected as well in a band for the carbamate part of the Fmoc-protecting group at 1705 cm^{-1} and in fluorene deformation bands at 760 cm^{-1} and 738 cm^{-1}. The latter are characteristic for Fmoc. When the resin is capped with acetic anhydride the amide band at 1627 cm^{-1} increases due to the appearance of additional amide bonds. After the Fmoc protecting group had been removed the typical bands disappear. For resin **UR4** the reaction procedure was repeated when Fmoc-1,2-diaminopropionic acid was coupled to the spacer and the appearance and disappearance of the typical IR bonds could be observed. **UR4** remained colourless.

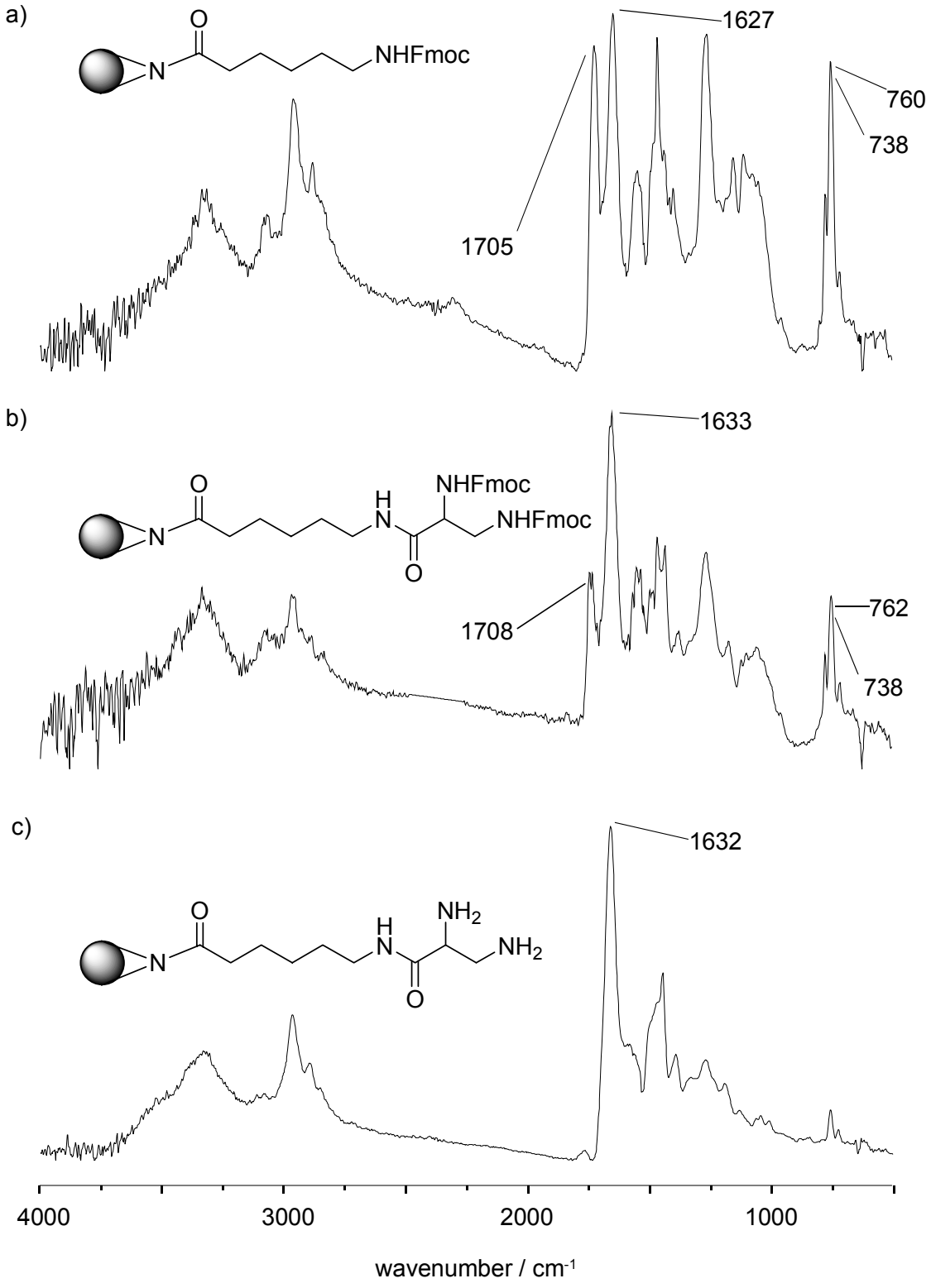
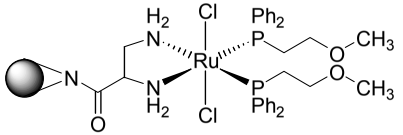
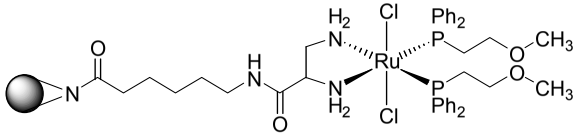


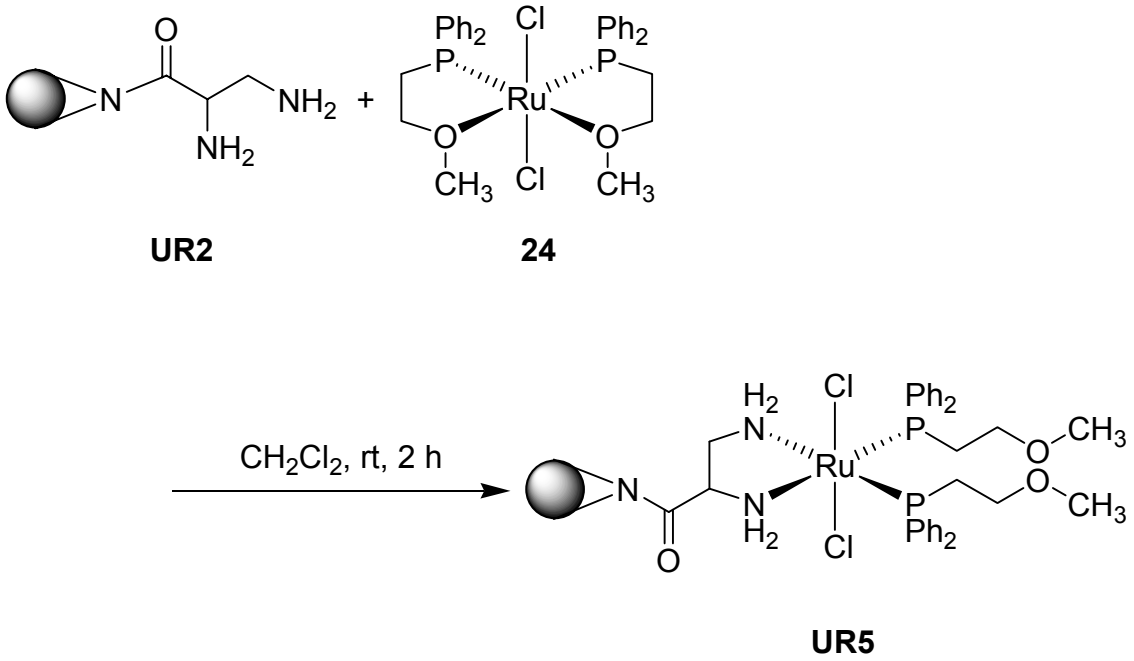
Figure 2. IR spectra of intermediate products during the preparation of **UR4** a) after coupling of Fmoc-aminohexanoic acid to **UR1** b) after coupling of Fmoc-1,2-diaminopropionic acid to **UR3** c) IR spectrum of **UR4**

4.6.3 Synthesis of the Immobilised Diaminedichlorobis[(methoxyethyldiphenyl)-phosphine]ruthenium(II) and Diaminedichloro[1,3-bis(diphenylphosphine)-propane]ruthenium(II) Complexes UR5-UR8

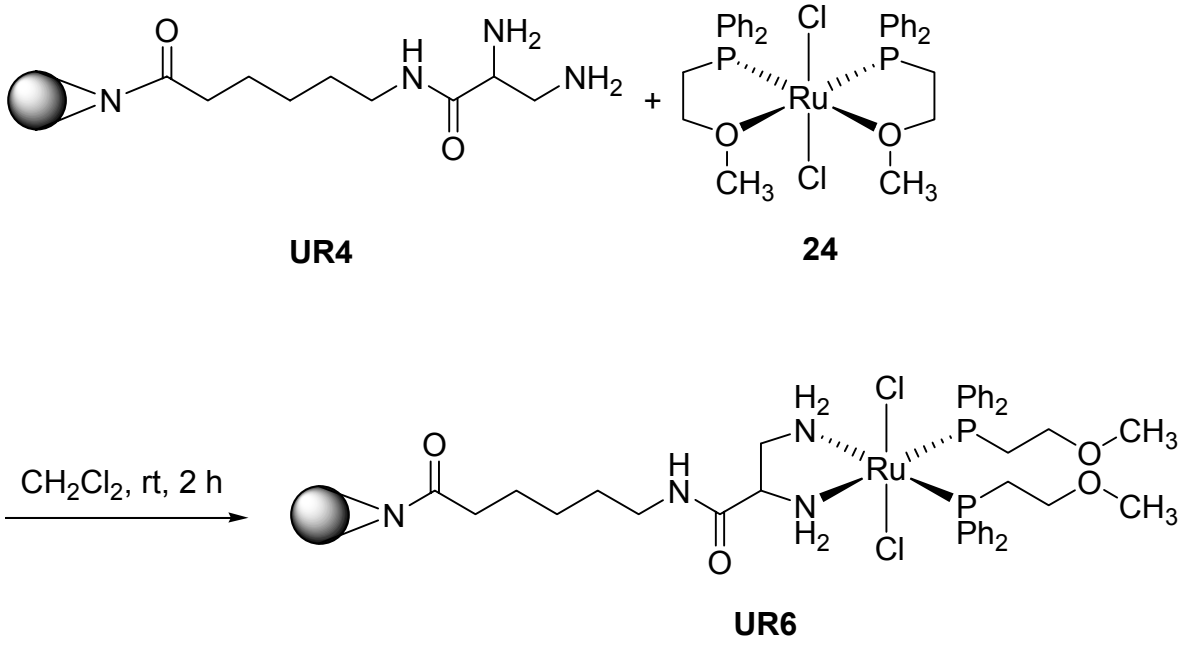
For the anchoring of the precursor complexes dichlorobis[(methoxyethyldiphenyl)-phosphine]ruthenium(II) (**24**) and dichlorobis[1,3-bis(diphenylphosphine)propane]-ruthenium(II) (**25**) to the immobilised 1,2-diamine derivative on **UR2** and **UR4** methods for the analogous homogeneous complexes already introduced in literature[46,83] were employed (Scheme 10-13). As the red complex **24** and the bright brown complex **25** were stable in air, all procedures could be carried out without inert gas atmosphere. This allows to apply the same working technique, which is used for the preparation of ULTRARESINS. When the dissolved complexes **24** and **25** were added to the swollen colourless resins **UR2** and **UR4** gradual colour changes indicated the coordination of the precursor complexes. With ruthenium(II) complex **24** the colourless resins **UR2** and **UR4**, respectively changed to green stationary phases **UR5** and **UR6** (Scheme 10 and 11) whereas the solution changed in colour from red to green. With the second complex **25** the yellow materials **UR7** and **UR8** (Scheme 12 and 13) were obtained. For the coordination of dichlorobis[(methoxyethyldiphenyl)phosphine]ruthenium(II) (**24**) advantage was taken from the hemilabile character of the methoxyethyl(diphenyl)-phosphine ligands[83,139-141]. By the attack of the bis[(methoxyethyldiphenyl)-phosphine]ruthenium(II) complex **24** at the immobilised diamine ligand the hemilabile bond to oxygen is cleaved. Thus the 1,2-diamine can coordinate. For complex **25** the bonding to the immobilised 1,2-diamine proceeds easily in a ligand exchange reaction as was already reported for the analogous homogeneous complexes[46]. The complete coordination of the complex to the modified resin could be shown with a Kaisertest.

Table 2. Stationary phases with ruthenium etherphosphine complex

No.	Structure of the ULTRARESINS	Kaiser-test	IR-Data ν [cm^{-1}]	Suspension $^{31}P\{^{1}H\}$ NMR	Solid State ^{31}P NMR	Loading [mmol/g]
UR5	 dichlorobis[(methoxyethyldiphenyl)-phosphine]ruthenium(II) **24** coordinated to **UR2**	positive	3636–3198 (N-H) 2921 (aliphatic CH_2) 1641 (NC=O)	δ 35.6 ppm $\nu_{1/2}$=506.8 Hz	δ 34.9 ppm $\nu_{1/2}$=1010.7 Hz	0.79
UR6	 dichlorobis[(methoxyethyldiphenyl)-phosphine]ruthenium(II) **24** coordinated to **UR4**	negative	3417, 3307, 3267 (N-H) 2933 (aliphatic CH_2) 1629 (NC=O)		δ 37.6 ppm $\nu_{1/2}$=1177.8 Hz	0.85



Scheme 10. Preparation of the new stationary phase **UR5** from **UR2** and ruthenium(II) complex **24**



Scheme 11. Preparation of the new stationary phase **UR6** from **UR4** and ruthenium(II) complex **24**

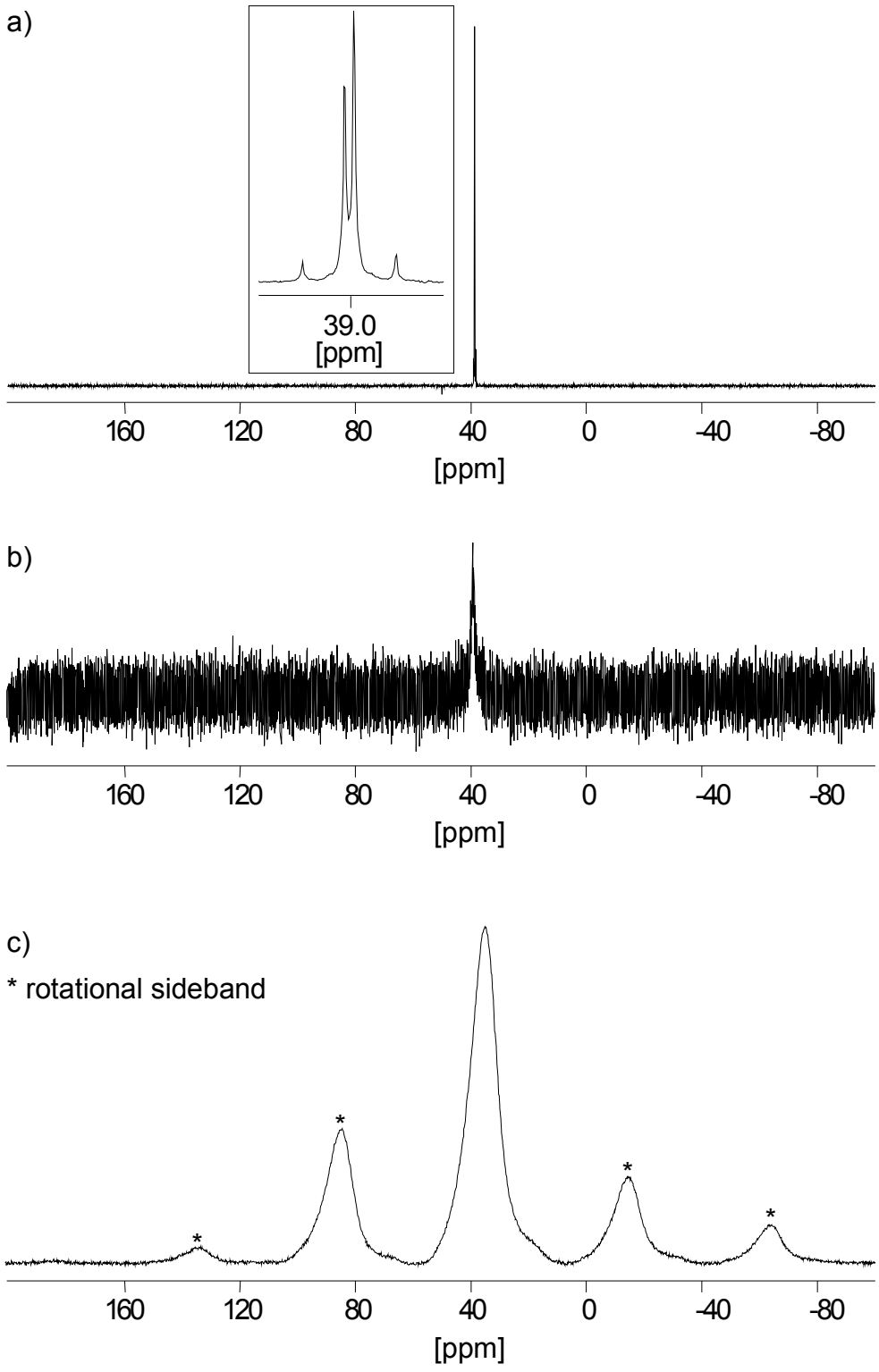
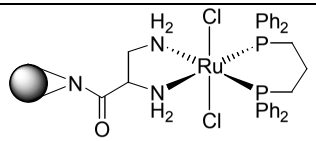
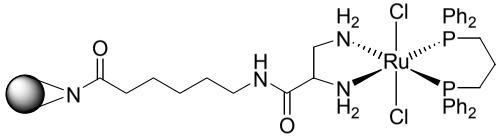
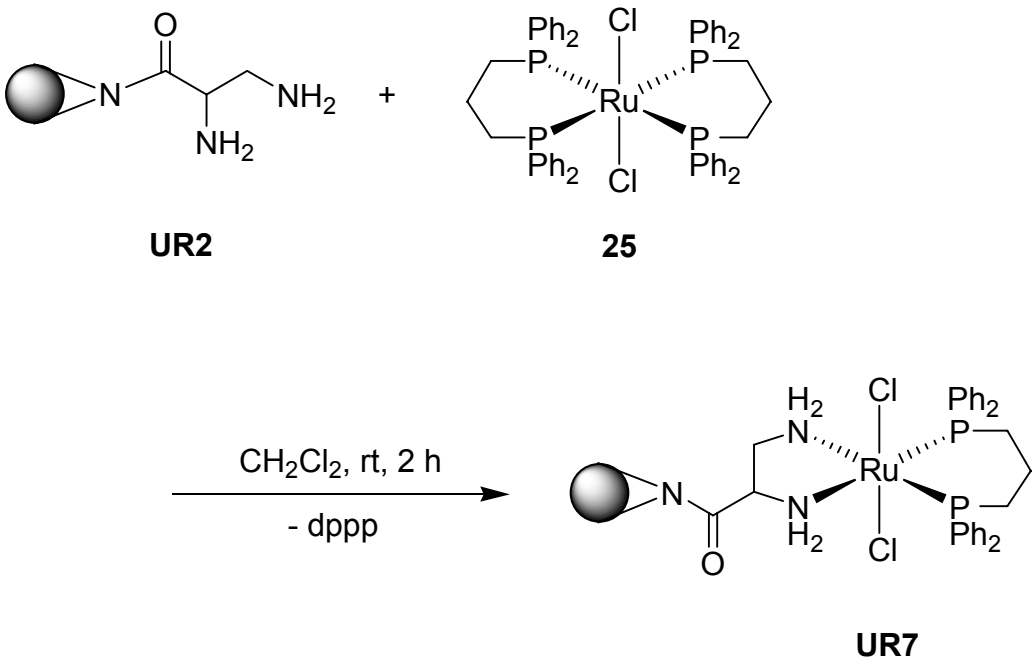


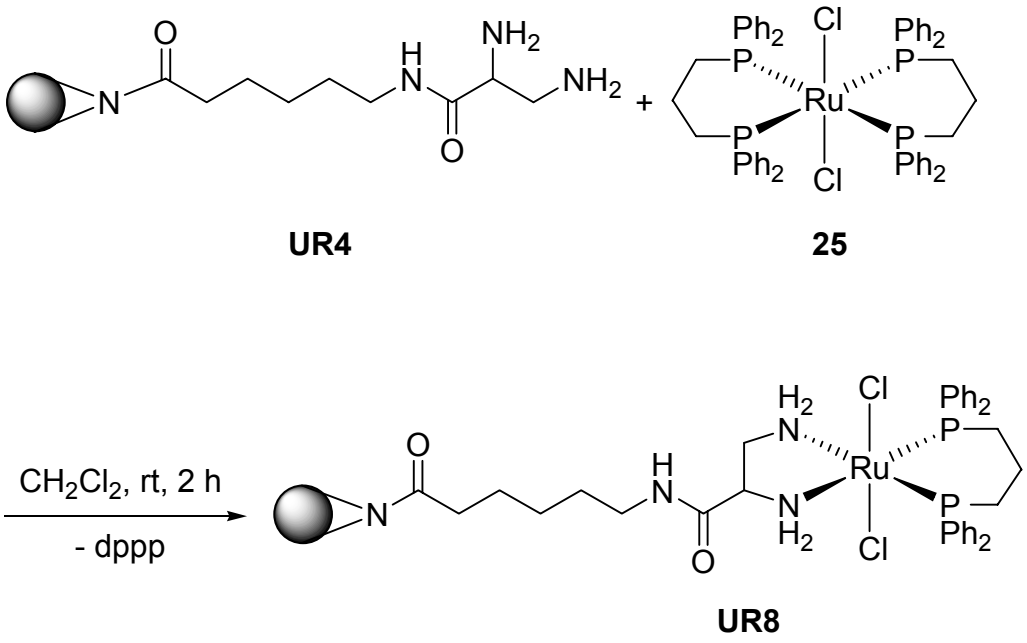
Figure 3. a) High resolution $^{31}P\{^{1}H\}$ NMR spectrum of the homogeneous complex **26**
b) $^{31}P\{^{1}H\}$ Suspension NMR spectrum of the new stationary phase **UR5**
c) ^{31}P VACP/MAS NMR spectrum of the stationary phase **UR5**

Table 3. Stationary phases with ruthenium dppp complex

No.	Structure of the ULTRARESINS	Kaiser-test	IR-Data ν [cm^{-1}]	Suspension $^{31}P\{^1H\}$ NMR	Solid State ^{31}P NMR	Loading [mmol/g]
UR7	 *trans*-bis[1,3-bis(diphenylphosphino)-propane]dichlororuthenium(II) **25** coordinated to **UR2**	positive	3658-3190 (N-H) 2922 (aliphatic C-H) 1630 (NC=O)	δ 43.1 ppm $\nu_{1/2}$=136.8 Hz δ 41.0 ppm $\nu_{1/2}$=244.7 Hz	δ 46.2 ppm $\nu_{1/2}$=629.8 Hz δ 35.8 ppm $\nu_{1/2}$=646.8 Hz	0.79
UR8	 *trans*-bis[1,3-bis(diphenylphosphino)-propane]dichlororuthenium(II) **25** coordinated to **UR4**	negative	3701-3177 (N-H) 2933 (aliphatic C-H) 1630 (NC=O)		δ 47.1 ppm $\nu_{1/2}$=580.1 Hz δ 36.2 ppm $\nu_{1/2}$ = 667.1 Hz	0.85



Scheme 12. Preparation of the new stationary phase **UR7** from **UR2** and ruthenium(II) complex **25**



Scheme 13. Preparation of the new stationary phase **UR8** from **UR4** and ruthenium(II) complex **25**

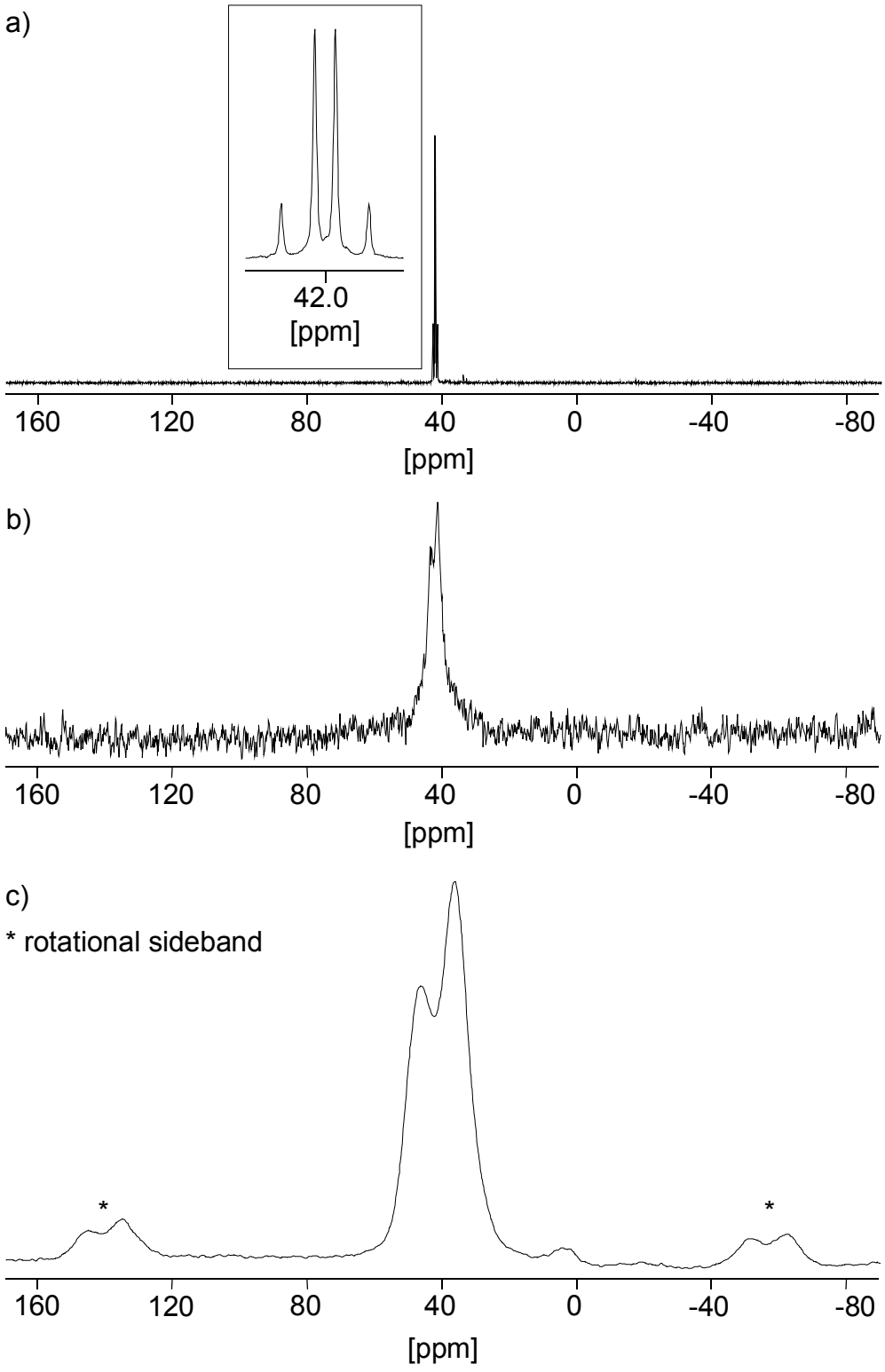
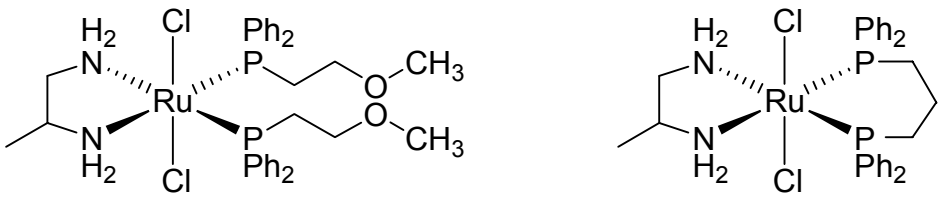


Figure 4. a) High resolution $^{31}P\{^{1}H\}$ NMR spectrum of the homogeneous complex **27**
b) $^{31}P\{^{1}H\}$ Suspension NMR spectrum of the new stationary phase **UR7**
c) ^{31}P VACP/MAS NMR spectrum of the stationary phase **UR7**

In the ^{31}P VACP/MAS NMR spectra of **UR5**-**UR8** broad signals in the range of 7 to 66 ppm indicate that the metal complex fragments have been immobilised successfully to **UR2** and **UR4**. This broad chemical shift range has to be compared to the rather small chemical shift difference of the two inequivalent phosphine groups of the analogous homogeneous complexes **26** and **27** (Scheme 14) in solution (**26**: δ 39.1, 38.9, AB pattern, $^2J_{PP}$ = 36.7 Hz[83]; **27**: δ 41.5, 42.3, AB pattern, $^2J_{PP}$ = 52.2 Hz[46]). In general going from solution into materials like **UR5**-**UR8** leads to increased line widths of the signals and the loss of the fine structure due to enhanced dispersion of the chemical shifts but not to large differences in chemical shifts as observed for **UR5**-**UR8**. Previous results for comparable diaminebis(phosphine)ruthenium complexes have demonstrated that they may isomerise when going from solution to the solid state[46,49,83,95,142]. According to that the complexes in **UR5**-**UR8** may either form an all-*cis*-$RuP_2N_2Cl_2$ or a *cis*-*cis*-*trans*-$RuP_2N_2Cl_2$ structure. The broad range of chemical shifts in the ^{31}P VACP/MAS NMR spectra of **UR5**-**UR8** are fully compatible with the diaminebis(phosphine)ruthenium complexes **26** and **27**, however, different structures have to be considered. This is in agreement with the NMR data of the stationary phases **UR5** and **UR7** in suspension.



26 **27**

Scheme 14. Analogous homogeneous complexes **26** and **27**

By IR spectroscopy no characteristic bands for the immobilised ruthenium complexes are detected for the stationary phases **UR5**-**UR8**. Typical bands of the ULTRARESIN matrix partly overlay the bands. Furthermore the strong amide band, due to the large amount of amide bonds in the resin, obscures the bands of the immobilised complexes. Swelling factors specify the total volume of resin and absorbed solvent with respect to the mass of the resin. For a macroscopic detection of the swelling factor a certain

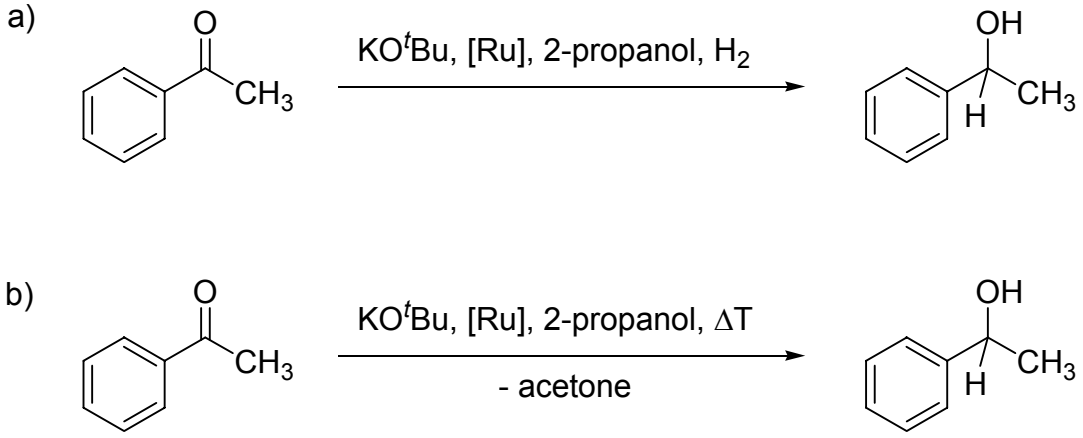
amount of dry resin is weighed, solvent is added and the mixture shaken for a certain time. After one hour of rest for equilibration the excessive solvent is removed. Then the volume of the swollen resin is determined. By the ratio of volume to mass of the dry resin the swelling factor is calculated[143]. For the stationary phases **UR7** and **UR8** swelling factors were measured in 2-propanol and methanol (Table 4). The stationary phases do not swell in 2-propanol and the swelling ability in methanol is diminished in contrast to pure ULTRARESINS **UR1**[47]. The sort of linker molecule, here spacer with immobilised ruthenium(II) complex, seems to play an important role in the swelling of the resin. This is in agreement with previous results[47]. Because of high loading with spacer and complexes the influence of the ULTRARESIN backbone on the swellability is reduced. The sort of linker appoints the swelling of the modified ULTRARESINS **UR7** and **UR8**.

Table 4. Swelling factors of **UR7** and **UR8**

Resin	**Dry [mL/g]**	**2-Propanol [mL/g]**	**Methanol [mL/g]**
UR7	2.35	2.35	5.87
UR8	2.32	2.32	7.89
UR1			16.50[47]

4.7 Catalytic Hydrogenation of Acetophenone with Stationary Phases UR5-UR8

The new stationary phases **UR5**-**UR8** were assumed to show similar catalytic properties[46,49] than analogous homogeneous ruthenium(II) complexes. The reduction of acetophenone to 1-phenylethanol was chosen as model reaction for the hydrogenation process (Scheme 15) owing to the fact that in the reaction only one defined product is possible apart from enantioselectivity. The conditions, under which these homogeneous ruthenium(II) complexes are catalytically active, are already known[7,8,46,49,80]. Therefore comparable conditions (2-propanol, KO^{t}Bu as alkaline base) were chosen as a basis for the catalytic tests of the newly prepared stationary phases.



Scheme 15. Reduction of acetophenone as model reaction for the a) direct hydrogenation, b) transfer hydrogenation

4.7.1 Direct Hydrogenation

The direct hydrogenation was carried out in a hydrogenation station, for which on-line acquisition of consumed hydrogen and graphical illustration of these data is computerised[144]. A typical hydrogenation reaction can be classified into three parts (Figure 5):

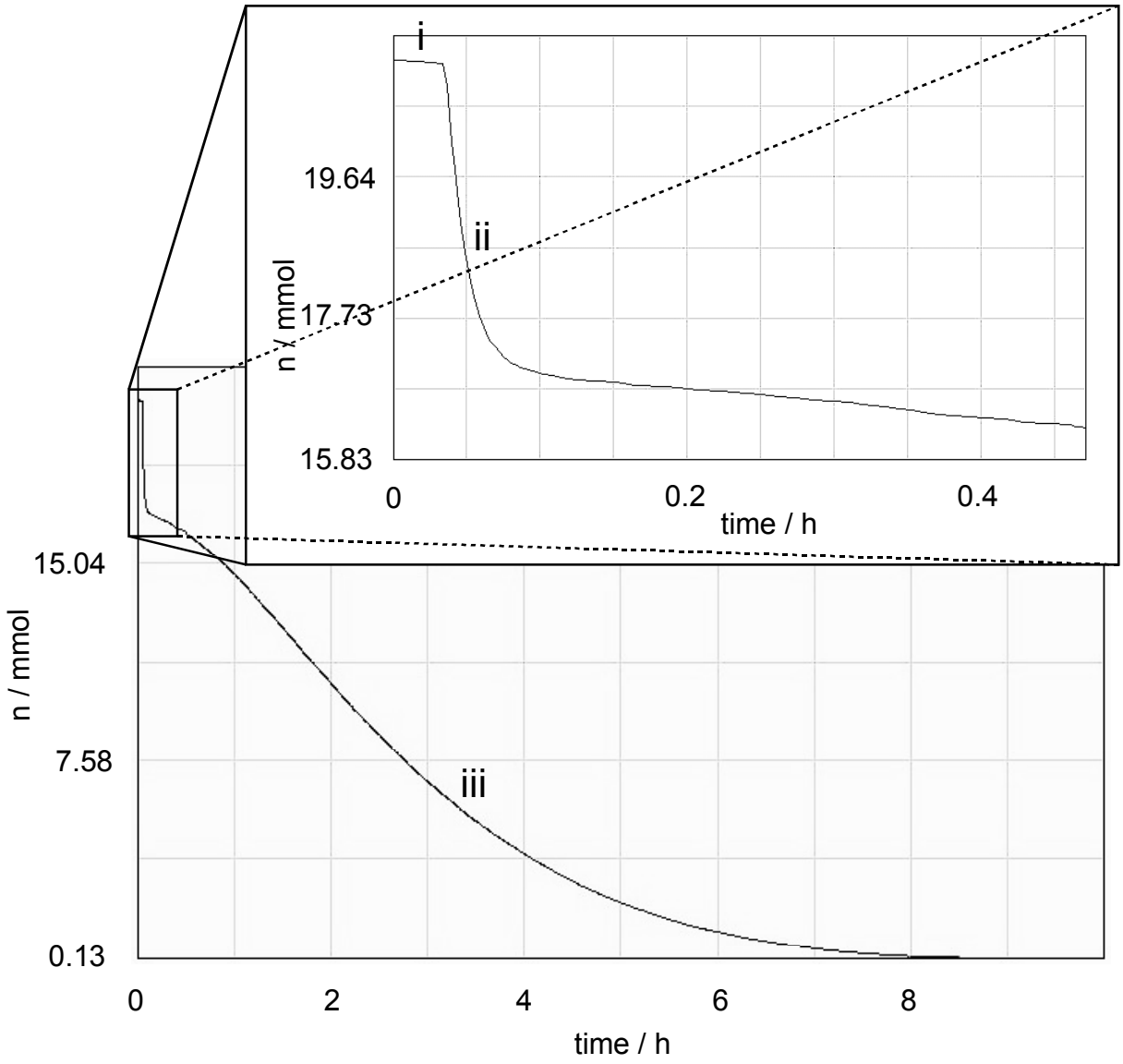


Figure 5. Graphical illustration of the hydrogenation reaction of acetophenone with complex **27** (Table 5, entry 17) with the three typical phases i, ii and iii

i. *Phase of waiting:* The graph of pressure vs. time in the supplementary vessel shows an almost horizontal progression. Hydrogen just diffuses into the solution, so that only surface reactions can take place. Therefore with the catalyst to substrate ratio applied only minimal conversion is expected.

ii. *Phase of insertion by stirring:* With start of stirring the hydrogen dissolves depending on its pressure and solubility. The graph shows an almost vertical decrease in pressure. After the phase of insertion a further phase of waiting or phase of activation can appear.

iii. *Phase of hydrogenation:* During the hydrogenation the pressure in the supplementary vessel decreases. The experimentally observed progression follows an exponential function.

Before the new stationary phases were tested for their catalytic activity in the hydrogenation of acetophenone the system itself was investigated concerning catalytic activity of the employed autoclave and the applied co-catalyst (Table 5, entries 13 and 14). For basic alkali cation salts as KO^{t}Bu it is established that they can act as catalysts in the hydrogenation of carbonyl functions themselves by means of a Meerwein-Ponndorf-Verley reduction[145] in 2-propanol as solvent. With a conversion of 7 % and 3 % and a TOF of about 0.1 h^{-1} the performance of the co-catalyst would be negligible for an immobilised catalyst working with a manifold higher TOF. In a first hydrogenation run under low hydrogen pressure the new stationary phase **UR5** was applied (Table 5, entry 1). No conversion of the employed substrate acetophenone was observed. As it was not possible to cap residual secondary amines in the polymer backbone of **UR5** the ruthenium(II) complex **24** is able to coordinate to these amines and for that is supported within the ULTRARESIN. It is assumed, that the mobility of the immobilised ruthenium(II) complex by coordination to the polymer backbone and the short spacer molecule respectively, is confined as was already reported for other polymeric supports[20]. Due to the rigid structure of the stationary phase (Table 4) the accessibility of the complexes for the bulky co-catalyst KO^{t}Bu is diminished. An attack of the sterically hindered alkoxide anion is crucial for the *in situ* generation of the active species of the immobilised ruthenium(II) complex (Scheme 4). Besides, the rigid structure of **UR5** leads to a reduced accessibility of substrate to the active metal centres. Because of that no conversion during the hydrogenation could be observed. In contrast to that ULTRARESIN **UR8** is equipped with a spacer molecule (Table 3, Scheme 13), which was expected to ensure the mobility and accessibility of the reactive ruthenium(II) centres. In analogy to **UR5** for **UR8** in a first reaction low hydrogen pressure and room temperature were chosen (Table 5, entry 2) as reaction conditions. Only negligible conversion was obtained. By increasing pressure and reaction time (Table 5, entries 3 and 4) a maximal conversion of 3 % is achieved. As a consequence the reaction temperature was elevated to obtain higher reactivity (Table 5, entry 5). However, the activity of the immobilised ruthenium(II) complex could not be enhanced. The conversion of 8 % and TOF of 0.58 h^{-1} is in the range of the blank tests with co-catalyst as catalyst. As was

reported[145] the elevated temperature promotes the activity of the potassium cation under basic conditions. Moreover, at high temperatures the immobilised ruthenium(II) complex is destroyed as could be shown by solid state ^{31}P NMR spectroscopy. In comparison to that the analogous homogeneous complex **27** presented 100 % conversion of acetophenone within 10 hours (Table 5, entry 16) at 35 °C.

In order to improve the catalytic activity of stationary phase **UR8** the composition of the hydrogenation mixture was changed. Two hydrogenation reactions with the heterogenised catalyst **UR8** were performed in water (Table 5, entries 7 and 8). The hydrogenation of the acetophenone proceeds very slowly. A maximum TOF of 1.11 h^{-1} was reached. In water the immobilised ruthenium(II) complex is transformed. It is assumed that metalic ruthenium is generated, which is responsible for the conversion of acetophenone. Since the formation of the actual catalyst species of ruthenium is a very slow process, the hydrogenation reaction proceeds very slowly.

As new co-catalyst so-called “superhydride” ($LiHB(C_2H_5)_3$) was chosen. It was considered that with this co-catalyst a chloride of the immobilised dichlororuthenium(II) species could be exchanged by a hydride. In this way the catalytically active complex species would be generated *in situ*. Although in a blank test with superhydride as catalyst (Table 5, entry 15) a conversion of 100 % with a TOF of 3.57 h^{-1} was achieved it was used as co-catalyst in further hydrogenation runs (Table 5,entries 9-12). An interesting progression was observed. By adding the stationary phase **UR8** to this hydrogenation mixture the catalytic activity of the superhydride is reduced (Table 5, entries 9 and 10). For the conversion of the immobilised transition metal complex the $LiHB(C_2H_5)_3$ is consumed and therefore is not available for the hydrogenation reaction anymore. Entries 11 and 12 in Table 5 show that the presence of 2-propanol is crucial for the catalytic activity of the superhydride; in toluene as solvent no conversion is observed. Recycling of the stationary phases is difficult after a hydrogenation run in an autoclave. The stationary phases are grinded due to friction between the reaction vessel an the magnetic stirring bar.

Table 5. Results from the direct hydrogenation reaction of acetophenone in a batch slurry reaction.

No.	Resin	Substrate Concentration [mol/l]	Molar Ratio Catalyst:Cocatalyst: Substrate	H_2 Pressure [bar]	Temperature [°C]	Reaction Time [h]	Conversion with GC[%] (with HPLC)	TOF [h^{-1}] (from HPLC)
1	**UR5**	0.67	1 : 4 : 94	1.5	rt	16	(0)	
2	**UR8**	0.21	1 : 8 : 100	1.5	rt	20	(3)	(0.15)
3	**UR8**	0.36	1 : 5 : 838	9-30	25	27	(3)	(0.93)
4	**UR8**	0.13	1 : 5 : 838	30	25	48	(0)	
5	**UR8**	0.35	1 : 4 : 876	30	50-80	116	8	0.58
6	**UR8**	0.13	1 : 4 : 1006	75	25	72	0	
7[a]	**UR8**	0.20	1 : 5 : 196	30	35	158	89	1.11
8[a]	**UR8**	0.20	1 : 5 : 196	15	35	238	42	0.35
9[b]	**UR8**	0.50	1 : 10 : 1006	30-70	25	110	40	3.69
10[b]	**UR8**	0.25	1 : 12 : 1007	30	35	136	21	1.55
11[c]	**UR8**	0.46	1 : 5 : 867	10-45	32	120	0	
12[c]	**UR8**	0.55	1 : 5 : 1012	30	35	62	1	0.12
13	-	0.44	0 : 1 : 192	40	35	134	7	0.10
14	-	0.08	0 : 1 : 199	30	35	41	3	0.15
15[b]	-	0.12	0 : 1 : 86	30	35	24	100	3.57
16[d]	**27**	0.44	1 : 4 : 1019	30	35	10	100	101.93
17[d]	**27**	2.18	1 : 6 : 7168	20-40	25-35	309	97	22.60

[a] Water as solvent

[b] $LiHB[C_2H_5]_3$ as co-catalyst

[c] The reaction was carried out in dry toluene with $LiHB[C_2H_5]_3$ as co-catalyst

[d] Analogous homogeneous catalyst

4.8 Transfer Hydrogenation

The transfer hydrogenation processes were performed in glass flasks under reflux conditions. When the acetophenone or another carbonyl compound was added to the colourless KO^{t}Bu/2-propanol solution, it darkened to yellow, and even became orange during the heating. As was already reported[145] this was accredited to the strong basic conditions, which might lead to aldol additions. A bathochromic shift in the resulting products causes a colouration of the reaction mixture. The addition of the stationary phases **UR5**-**UR8** did not lead to a visible change of the solution. As for direct hydrogenation first two blank tests (Table 6, entries 14 and 15) should ensure the performance of the stationary phases. As expected[145] the co-catalyst KO^{t}Bu showed catalytic activity. The reduction of acetophenone proceeded slowly with TOFs in the range as for direct hydrogenation. The performance of the stationary phase **UR5** (Table 6, entry 1) was better under transfer conditions than for direct hydrogenation. A TOF of 2.18 h^{-1} was determined. It is possible that the swelling ability of the resin is increased when heated, thus the accessibility of the reactive centres is enhanced. Due to the longer spacer molecule it was estimated that in **UR6** the activity of the active centres would be better than for **UR5**. After 20 h a conversion of 31 % was detected (Table 6, entry 2). With a TOF of 15.5 h^{-1} **UR6** was more active than **UR5**, but the performance of these systems was still not satisfactory. In comparison to **UR5** and **UR6** stationary phase **UR8** showed a better performance under the same conditions (Table 6, entry 3). Hence trials to vary the reaction conditions of the transfer hydrogenation were performed with this stationary phase. Entries 3-6 of Table 6 show the dependency of the catalytic activity of the modified ULTRARESIN from the concentration of co-catalyst. By increasing the amount of KO^{t}Bu the activity of the immobilised complex could not be improved. However, the conversion of 29 % and TOF of 12.76 h^{-1} was even worse. By raising the base concentration in the reaction solution the conditions for a competing aldol addition are promoted[145] and lead to a lowered acetophenone concentration. This means that the acetophenone has to be removed from a pre-equilibrium, which causes a reduced performance of the catalyst **UR8**. When the concentration of base in the hydrogenation mixture was lowered (Table 6, entries 5 and 6) to minimise or even avoid the competing aldol addition the catalytic performance of the immobilised catalyst decreased. This is in good agreement with similar homogeneous ruthenium(II)

Table 6. Results from the hydrogen transfer hydrogenation reaction of acetophenone in a batch slurry reaction

No.	Resin	Substrate Concentration [mol/l]	Molar Ratio Catalyst:Cocatalyst: Substrate	Temperature [°C]	Reaction Time [h]	Conversion with GC[%] (with HPLC)	TOF [h^{-1}] (from HPLC)
1	**UR5**	0.23	1 : 4 : 98	105	17	(38)	(2.18)
2	**UR6**	2.00	1 : 5 : 1000	90	20	(31)	(15.50)
3	**UR8**	2.00	1 : 5 : 1000	90	20	(44)	(22.00)
4	**UR8**	2.00	1 : 11 : 1000	90	23	29	12.76
5	**UR8**	2.00	1 : 1 : 1000	90	16	(2)	(1.25)
6	**UR8**	2.00	1 : 0 : 1000	90	16	(0)	
7	**UR8**	2.00	1 : 5 : 1000	rt	16	(0)	
8	**UR8**	0.10	1 : 5 : 106	120	48	33	0.73
9	**UR8**	0.04	1 : 6 : 104	92	43	31	0.75
10	**UR8**	0.05	1 : 5 : 89	92	64	63	0.87
11[a]	**UR8**	2.02	1 : 5 : 995	90	20	(44)	(21.88)
12[b]	**UR8**	0.20	1 : 5 : 101	115	48	0	
13[c]	**UR8**	0.04	1 : 5 : 104	92	43	89	2.15
14	-	2.03	0 : 1 : 189	90	23	8	0.66
15	-	0.06	0 : 1 : 20	92	66	11	0.03
16[c]	-	0.04	0 : 1 : 22	92	28	70	0.55

[a] Application of recycled ULTRARESIN **UR8**

[b] Water as solvent

[c] Usage of $LiHB(C_2H_5)_3$ as co-catalyst

complexes: For the generation of the catalytically active species a strong base in a certain amount is crucial[80]. Therefore a compromise for the base concentration is necessary.

Reflux conditions are very harsh and could lead to the decomposition both of the immobilised ruthenium complexes and the ULTRARESIN. Thus it was tried to hydrogenate acetophenone in 2-propnol at ambient temperature (Table 6, entry 7), which led to no conversion. By reducing the amount of substrate in the reaction mixture the reactivity of the catalyst is decreased (Table 6, entries 8-10). It is assumed that the reaction rate is dependent on the acetophenone concentration. The chance of a substrate molecule to reach an immobilised ruthenium complex is the better the more molecules are present in the reaction mixture. Another approach was made by applying the recycled resin **UR8** that had already been used for direct hydrogenation (Table 5, entry 2) for transfer hydrogenation. The investigation of this stationary phase had shown that the immobilised complex had not been destroyed during direct hydrogenation. Recycled **UR8** showed the same performance with a similar TOF as fresh **UR8** (Table 6, entries 3 and 11).

Under the same consideration as for direct hydrogenation the combination of the reaction mixture was changed with respect to solvent and co-catalyst (Table 6, entries 12, 13, and 16). It turned out that water as solvent is not suitable for the transfer hydrogenation. For $LiHB(C_2H_5)_3$ the same problems appeared as for direct hydrogenation. The superhydride showed a high catalytic activity in the hydrogenation under reflux conditions and therefore was not suitable as co-catalyst.

The catalytic activity of the stationary phases **UR5**, **UR6**, and **UR8** is (in contrast to their homogeneous analogues) better in transfer hydrogenation than in direct hydrogenation. However, ^{31}P solid state NMR showed that due to the harsh conditions during transfer hydrogenation the reactive centres on the ULTRARESINS had decomposed and therefore could not be recycled.

4.9 Spherical Silica Particles

To overcome the disadvantages of the ULTRARESINS as organic support (thermal and mechanical instability of the stationary phases **UR5**-**UR8**) inorganic supports have been chosen. One favourable material as a matrix is silica gel. By functionalisation of highly active and selective, well-defined homogeneous transition metal catalysts these reactive centres can be incorporated into an inert silica support in micro- and mesopores via co-condensation with alkoxysilanes. In materials of that kind the amount of immobilised complex is known as well as its structure, because the reactive centre can be characterised while still being homogeneous by the common methods like high resolution NMR, IR etc.[40]. For most applications of those materials diffusion of molecules to the reactive centres and away from them plays a crucial role and is the rate-limiting step for the reaction in question. However, the accessibility of the transition metal complexes within a material for gases and liquid or dilute reactants during a reaction still is not obvious. Furthermore a disadvantage of this materials is a lack of information about the chemical environment of the reactive centres. Various approaches have been made to overcome these problems[146,147]. One possibility is the modification of spherical, non-porous, monodisperse silica particles, so-called Stöber particles[48,148,149]. In this case the modification only is possible on the surface of this material by functionalisation of surface silanol groups. It is therefore estimated to ensure the accessibility of immobilised reactive centres. Moreover, it is assumed that all centres are in a homogeneous environment.

One application of surface modified spherical silica particles is in chromatography[150], for example in the separation of big analyte molecules that do not need to diffuse into pores but can interact with reactive centres on a surface.

In electrochemistry spherical silica particles are used to extend a lateral system of a chemically modified electrode (CME) to a three-dimensional concept. In a recent report ruthenium(II) complexes were immobilised to a platinum electrode via a silyl functionalised diamine spacer[137,138]. The same ruthenium complexes were covalently bound to spherical 800 nm silica particles[136,137], which spontaneously adsorb on the surface of an electrode. It was suggested to employ spherical monodisperse non-porous particles as support in order to obtain a defined and simple surface geometry of the electrode for the investigation of diffusion processes. Another concept was the

comparison of the redox activity of the ruthenium complex modified particles with that of similar homogeneous ruthenium complexes. These diaminedichlorobis(phosphine)-ruthenium(II) complexes are catalytically active in the hydrogenation of α,β-unsaturated ketones[49]. In a recent approach a correlation between electrochemical behaviour and catalytic activity of these complexes is assumed[151]. As an implication of all those results it is considered that modified 800 nm silica particles are catalytically active in the hydrogenation of ketones. To confirm this claim in the second part of this work spherical 800 nm silica particles modified with ruthenium(II) complexes were prepared and characterised. They were applied in the direct and transfer hydrogenation of acetophenone as model substrate. However, the employment of surface modified Stöber particles as interphase catalysts is a compromise:

i. Due to a lower surface area of the spherical support than of porous materials a smaller loading with reactive centres has to be accepted.

ii. A possible decrease of stability with regard to leaching as was reported for other surface modified materials[96,97] has to be taken into account.

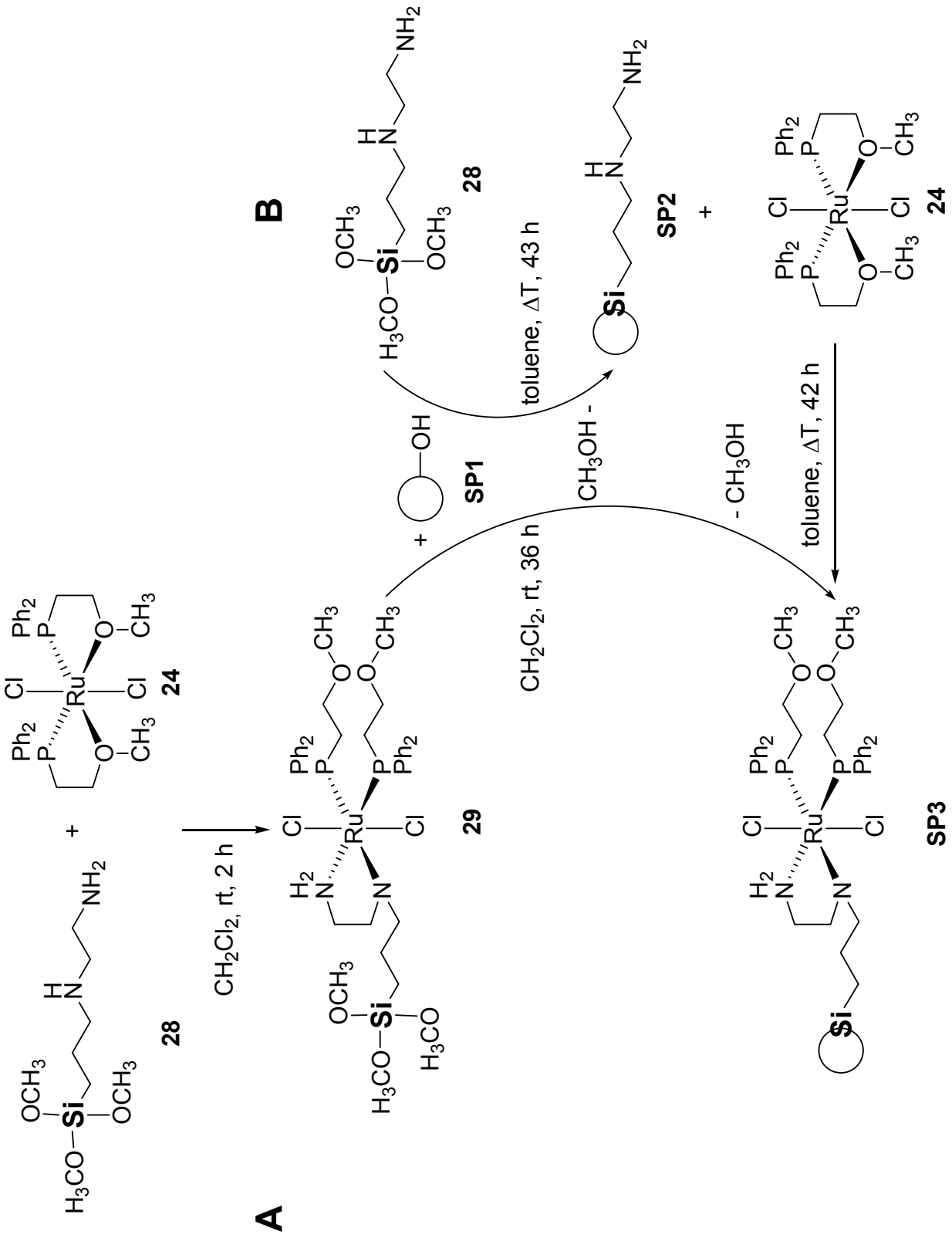
iii. It is considered, that the binding sites on spherical particles are much more homogeneous than for porous silica. This means, that all reactive centres are in a homogeneous environment.

4.9.1 Preparation of the Modified 800 nm Silica Particles

The 800 nm silica particles were prepared by the Stöber process. For catalytic application the particles can be modified in two different ways (Scheme 16):

A. A diaminebis(etherphosphine)ruthenium complex (**29**) is homogeneously prepared from a T-silyl functionalised diamine (**28**) and a bis(etherphosphine)-ruthenium(II) complex (**24**)[83]. The functionalised complex is immobilised on the surface of the silica particles (**SP1**) to yield the modified particles **SP3**.

B. A T-silyl functionalised diamine derivative spacer molecule (**28**) is covalently bound to the silica particles (**SP1**) by reaction with surface silanol groups. The anchoring of a bis(etherphosphine)ruthenium complex (**24**) to the diamine modified particles **SP2** proceeds as was reported in literature[83] for homogeneous complexes.



Scheme 16. Two possible reaction pathways for the modification of 800 nm silica particles with diaminedichlorobis(etherphosphine)ruthenium(II) complex **24**

For the covalently bonding of the T-silyl functionalised species high temperatures are required. It is considered that the T-silyl functionalised homogeneous ruthenium complex **29** could be partly destroyed during the anchoring process because of the harsh reaction conditions. Hence first the thermally and chemically stable spacer 3-(2-aminoethyl)aminopropyltrimethoxysilane (**28**) was bound to **SP1** (Scheme 16). For the coordination of the precursor complex **24** to the immobilised mixed primary-secondary diamine spacer (**SP2**) relatively smooth conditions can be realised[136]. When the colourless modified silica particles **SP2** were reacted with a red solution of complex **24** the solution became green as well as the wet particles after some time. The colour change of the "solution" is a consequence of "nano" scaled silica particles that are not in suspended but in a quasi-diluted state. If so the green colour is attributed ruthenium(II) complexes anchored to these particles whose homogeneous analogue is yellow to green. During the washing process these particles were removed.

In the ^{31}P VACP/MAS NMR spectrum of **SP3** a broad signal at a range of 5 to 72 ppm indicates that the metal complex fragments have been immobilised successfully to **SP2**. Despite of the large chemical shift range this result is in agreement with the chemical shift in solution $^{31}P\{^{1}H\}$ NMR spectroscopy for the analogous homogeneous complex **29** (AB pattern, δ 38.8, 35.6, $^{2}J_{PP}$ = 36.29 Hz) (Figure 6). With the same arguments as for the ULTRARESINS (page 41) the immobilisation of the complex could be established. To probe the chemical stability of the surface immobilised ruthenium complexes and of the silica particles, **SP3** was extracted in a Soxhlet extractor with different solution mixtures of dichloromethane and 2-propanol (**SP4** and **SP5**). Light scattering and SEM investigations showed that **SP3** and the extracted silica particles **SP5** had approximately the same size like the pure particles **SP1**[136]. In addition to that the SEM micrographs manifested the spherical shape and monodispersity of **SP5** (Figure 7). From elemental analysis of **SP3** a loading of 26 % of the surface OH-groups[150,152] (see Experimental Part) with ruthenium complexes is estimated. After solvent treatment the loading remained unchanged.

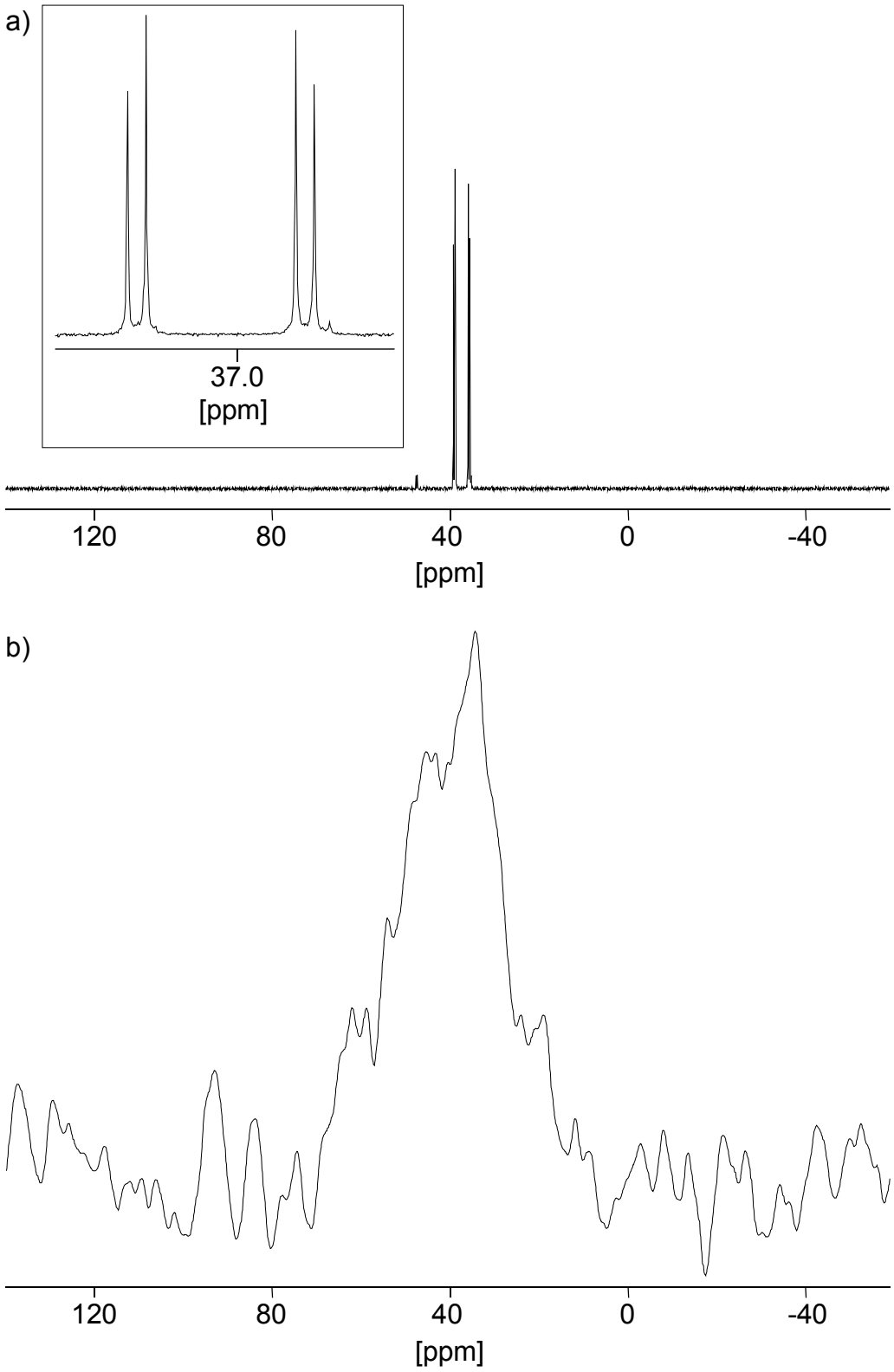


Figure 6. a) $^{31}P\{^{1}H\}$ high resolution NMR spectrum of the homogeneous complex **29**
b) ^{31}P VACP/MAS NMR spectrum of the stationary phase **SP3**

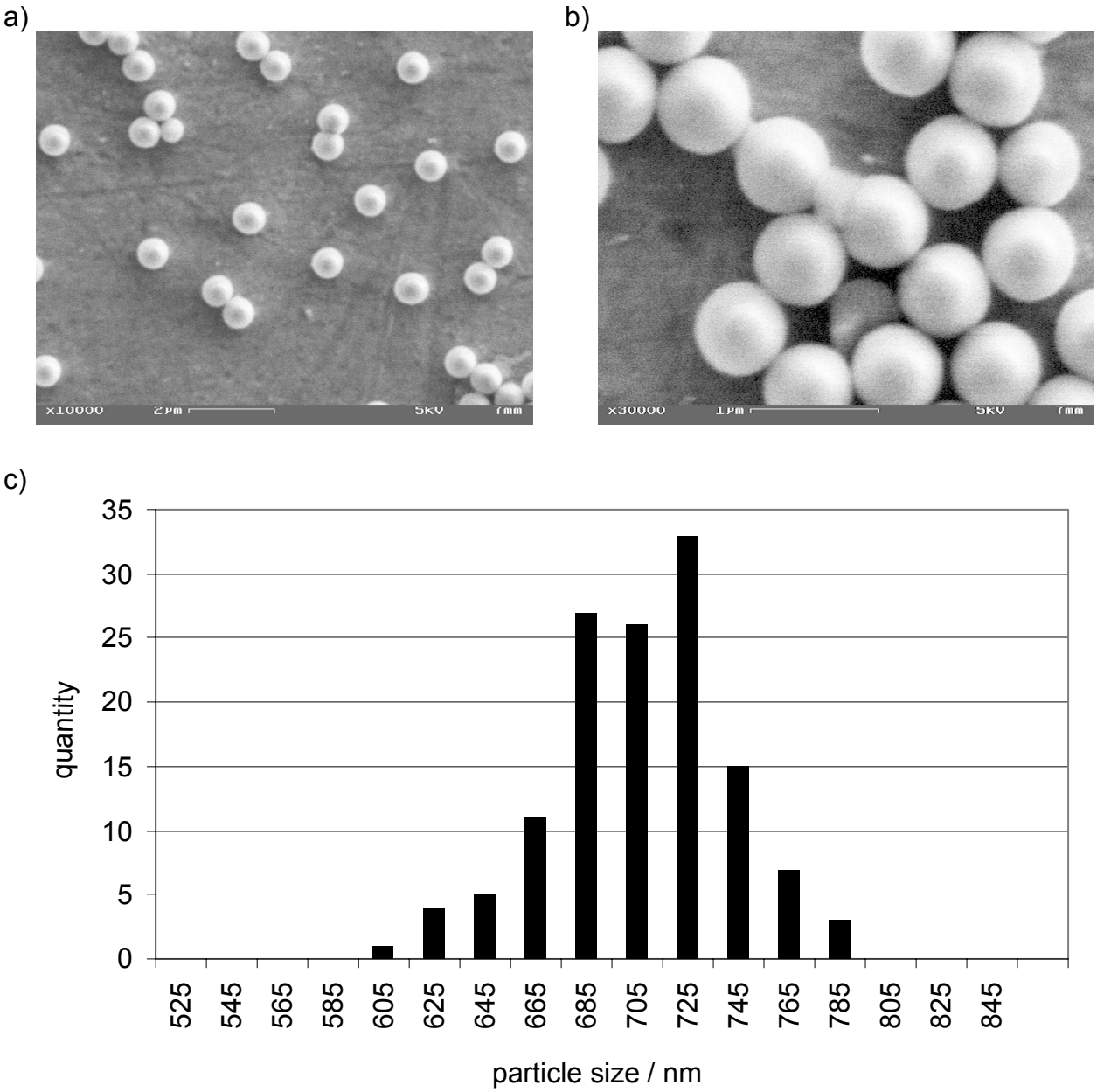


Figure 7. a) SEM micrographs of **SP5** (scalebar corresponds to 2 µm); b) SEM micrographs of **SP5** (scalebar corresponds to 1 µm); c) size distribution of **SP5** derived from SEM micrographs

4.10 Catalytic Hydrogenation with Modified Spherical Silica Particles

As for the stationary phases **UR5**-**UR8** the surface modified silica particles **SP3**-**SP6** were tested for their catalytic activity in the hydrogenation of acetophenone to 1-phenylethanol (Scheme 15).

4.10.1 Direct Hydrogenation

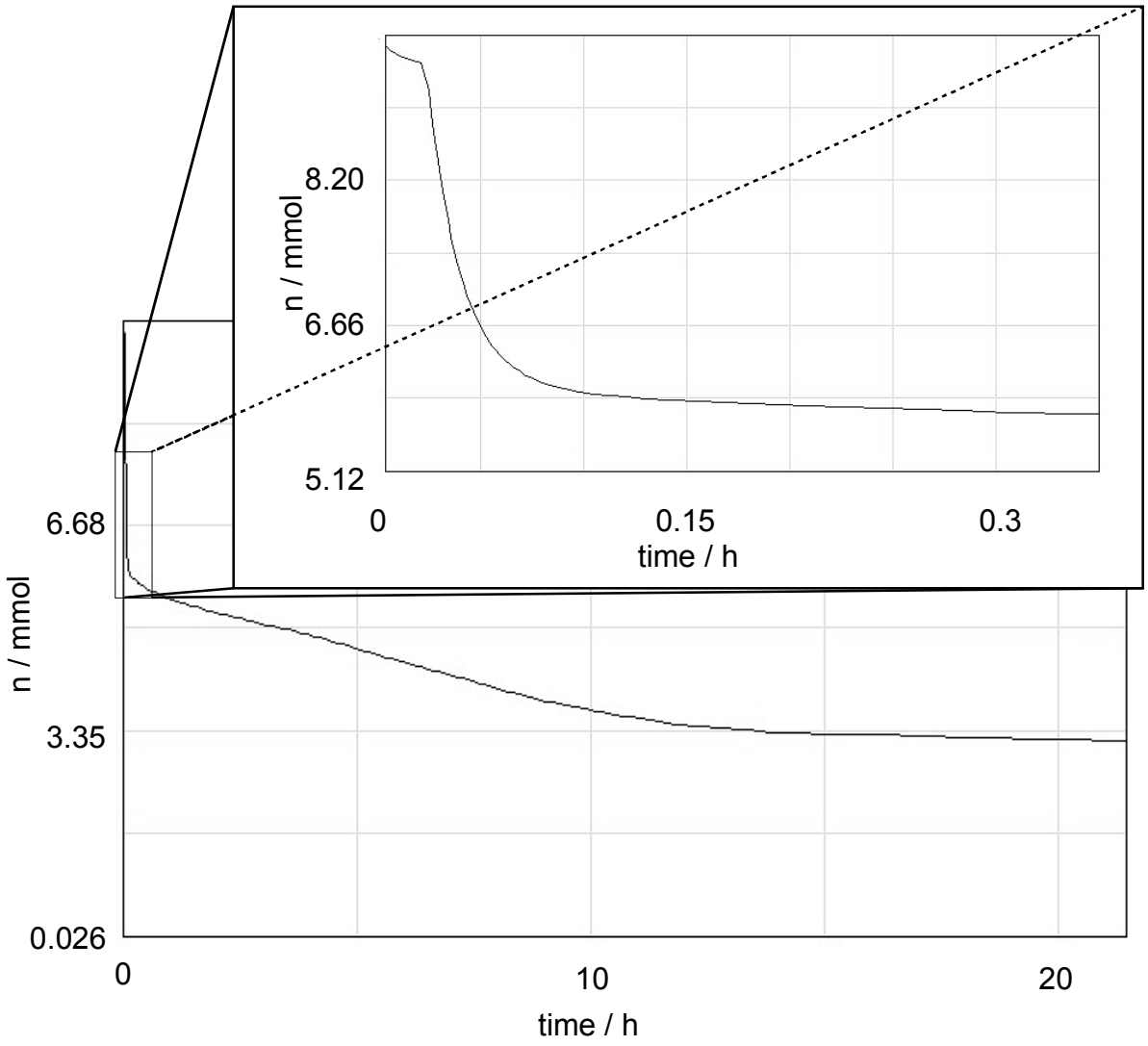


Figure 8. Graphical illustration of the hydrogenation reaction of acetophenone with stationary phase **SP3** (Table 7, entry 4) with the three typical phases i, ii and iii

Blank tests of the hydrogenation system were performed to confirm the results from reaction runs with the stationary phases **SP3**-**SP6**. In a mixture with pure silica particles **SP1** in 2-propanol with KO^{t}Bu as co-catalyst (Table 7, entry 16) no conversion of the substrate was observed. With light scattering experiments it is detected that some of the pure silica particles agglomerate during the hydrogenation process, some are destroyed, i.e. they are not chemically stable. A reaction just with co-catalyst in 2-propanol (Table 7, entry 17) led to negligible production of 1-phenylethanol. To ensure a possible catalytic activity of immobilised ruthenium complex the performance of the homogeneous ruthenium(II) complex **29** was determined (Table 7, entries 19 and 20). As expected the transition metal complex converted acetophenone completely to 1-phenylethanol with a TOF of up to 100 h^{-1}. For completion of data the homogeneous educt **24** was used to hydrogenate acetophenone (Table 7, entry 22). After 40 hours the substrate was converted completely. However, by analysing the graph of the hydrogenation it is observed that just little hydrogen gas is consumed. In agreement with literature the bis(etherphosphine)ruthenium(II) complex transfers hydrogen from the base/2-propanol mixture to the carbonyl function. With the spherical silica particles **SP3** 100 % conversion was achieved within 14 hours with a TOF of ca. 6.5 h^{-1} (Table 7, entries 1 and 4). The graph of the hydrogenation reaction had the typical shape (Figure 8), in which all phases of a hydrogenation process are present. To ensure that the catalyst of this reaction was the immobilised ruthenium complex and not leached and/or dissolved fractions of the complex, the solid parts of the reaction suspension were separated from the liquids. No 1-phenylethanol was found after the solutions were reused in hydrogenation without further purification just by adding acetophenone (Table 7, entries 2 and 5) or acetophenone and co-catalyst (Table 7, entry 7), respectively. Therefore it was concluded that no leaching had taken place during the hydrogenation reaction. Residual stationary phase **SP3** of the hydrogenation runs was recycled and than reused as catalyst (Table 7, entries 3 and 6). The particles still showed catalytic activity. However, the performance was strongly reduced in comparison to freshly prepared **SP3**. By evaluating the detected data it was found that the recycled particles **SP3** needed four hours time for activation. Then an increased consumption of hydrogen gas started, which after a total reaction time of about 20 hours was reduced to a minimum. This could be due to partly decomposition of the surface immobilised complexes or to destruction of the particles. With light scattering

Table 7. Catalytic hydrogenation of acetophenone with modified silica particles **SP3**-**SP6**; all direct hydrogenation processes were performed under 30 bar H_2 pressure at 35 °C

No.	Material	Substrate Concentration	Molar Ratio Catalyst: Cocatalyst: Substrate	Time [h]	Conversion [%]	TOF [h^{-1}]
1	**SP3**	0.053	1 : 5 : 102	19	100	5.37
2	Solution of 1	0.063		98	0	
3[a]	**SP3**	0.022	1 : 6 : 101	70	8	0.11
4	**SP3**	0.049	1 : 5 : 90	14	100	6.45
5	Solution of 4	0.024		21	0	
6[a]	**SP3**	0.043	1 : 5 : 100	91	56	0.62
7	Solution of 6	0.123	0 : 1 : 30	48	0	
8	**SP4**	0.047	1 : 5 : 92	92	86	0.86
9	**SP4**	0.024	1 : unknown : 106	41	63	1.62
10[a]	**SP4**	0.025	1 : 6 : 101	43	34	0.80
11	**SP5**	0.033	1 : 5 : 100	41	65	1.59
12	Solution of 11	0.033	0 : 1 : 23	41	37	
13	**SP6**	0.005	1 : 4 : 85	41	1	0.02
14[b]	**SP3**	0.021	1 : 6 : 100	68	100	1.47
15	Solution of 14	0.021	0 : 1 : 18	45	11	
16	SiO_2	0.049	1 : 6 : 92	20	0	
17	KO^tBu	0.083	0 : 1 : 199	41	3	0.13
18[b]	KO^tBu	0.056	0 : 1 : 20	66	11	0.03
19[c]	**29**	0.081	1 : 5 : 100	1	100	100.00
20[c]	**29**	0.700	1 : 5 : 1031	20	100	51.56
21[b]	**29**	0.658	1 : 5 : 992	16	76	48.52
22[d]	**24**	0.073	1 : 5 : 100	40	100	2.50

[a] Recycled silica particles

[b] Transfer hydrogenation under reflux

[c] Homogeneous catalysis with corresponding complex **29**

[d] Homogeneous catalysis with precursor complex **24**

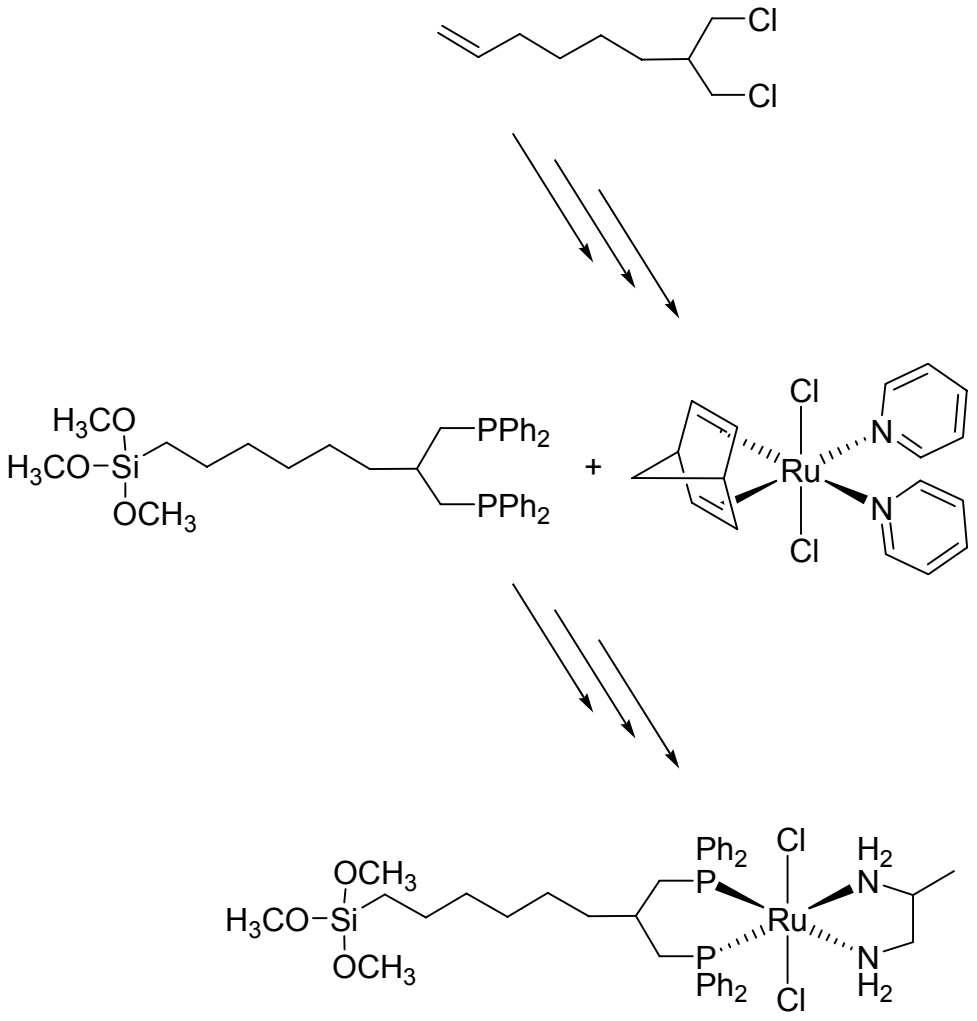
investigations particle sizes over the whole colloidal range were obtained after two consecutive hydrogenation runs. When the catalytic activity of the extracted silica particles **SP4** was investigated (Table 7, entries 8 and 9), a reduced performance in the hydrogenation of acetophenone in comparison to **SP3** was observed. As for recycled **SP3** the data showed after about four hours with low activity a period of good activity, which then was followed by a drop of hydrogen consumption after 20 hours in total. But after the recycling procedure in a Soxhlet extractor **SP4** still displayed activity in a consecutive hydrogenation run with similar TOF (Table 7, entry 10).
When the specially treated silica particles **SP5** were applied for catalysis (Table 7, entry 11) their catalytical performance was in the range of that of **SP4**. The consumption of hydrogen started rapidly but after 16 hours a drop of activity was observed. Only to make sure the liquid parts of the reaction mixture were reused in a hydrogenation run with additional acetophenone and KO^{t}Bu (Table 7, entry 12). After 41 hours 37 % of the total amount of acetophenone was converted. That means that leaching had proceeded during the hydrogenation with **SP5**.
200 nm silica particles (**SP6**) were applied for catalysis (Table 7, entry 13) to compare them with modified 800 nm silica particles. But their conversion was negligible.

4.10.2 Transfer Hydrogenation

As for the ULTRARESINS the spherical silica supported complexes were employed for transfer hydrogenation. The performance of the co-catalyst in a blank test (Table 7, entry 18) was in an acceptable range. When the homogeneous ruthenium(II) complex **29** was used as catalyst (Table 7, entry 21) the TOF was comparable to that in direct hydrogenation under the same conditions (Table 7, entry 20). Due to the hydrolysable T-silyl group at the diamine spacer of the complex condensation was expected owing to 2-propanol, but after the reaction this was not apparent. The modified silica particles **SP3** (Table 7, entry 14) converted acetophenone to 100 % to 1-phenylethanol within 68 hours. After that time a GC sample was taken. With dynamic light scattering experiments it was shown that after transfer hydrogenation the silica particles agglomerated due to the drastic reaction conditions (reflux, base as co-catalyst). Moreover in another hydrogenation run with the liquid parts of this reaction (Table 7, entry 15) leaching was observed.

4.11 Catalytic Hydrogenation with Sol-Gel Processed Diaminebis-(phosphine)ruthenium(II) Complexes

In a recent approach[108] the synthesis of a T-silyl functionalised 1,3-(diphenylphosphino)propane derivative (dppp*)[153] with a spacer molecule containing six CH_2-groups was improved. With this dppp* ligand a diaminedichlorobis(phosphine)-ruthenium(II) complex was prepared[134] (Scheme 17). This new functionalised complex was incorporated into four different sol-gel materials with different amounts of the co-condensation agent methyltrimethoxysilane.



30

Scheme 17. Schematical synthesis of the T-silyl functionalised ruthenium(II) complex **30**

With solid state NMR, EXAFS and EDX it could be shown that the sol-gel processed complex did not undergo structural changes. The new homogeneous ruthenium(II) complex **30** as well as the new stationary phases were applied for the catalytic direct hydrogenation of *trans*-4-phenyl-3-butene-2-one as model substrate. Due to the aromatic, olefinic, and carbonyl double bond in the structure of this compound the chemoselectivity of the different interphase catalysts could be determined. The known system containing 2-propanol as solvent and KOH as base was employed. Hydrogenation reactions were carried out in a glass reactor under mild conditions, this means a H_2 pressure of 3 bar at 35 °C. It was shown that the sol-gel processed stationary phases were catalytically active in the interphase with a maximum TOF of 155 h^{-1} within the first hour. The sol-gel processed ruthenium(II) complexes converted the substrate to 100 % within 24 hours, whereas they showed appreciable chemoselectivity according to the alcohol product. The heterogenised catalysts were recycled after each hydrogenation run and could be reused eight times with no remarkable loss of activity and selectivity[108].

4.12 Comparison of the Catalytic Performance of Different Supported Diaminedichlorobis(phosphine)ruthenium(II)complexes

The new stationary phases **UR5**-**UR8** based on so-called ULTRARESINS, an organic support did not show remarkable catalytic activity in the direct hydrogenation of acetophenone. Conversion as well as turn-over frequency were in the range of activity of KO*t*Bu as catalyst with regard to a Meerwein-Ponndorf-Verley reduction[145]. A possible explanation for the low activity of the immobilised precursor complexes could be the rigidity of the polymeric material. The swelling ability of the resin is reduced after anchoring of spacer and complex[47]. Therefore the accessibility for activating co-catalyst and substrate is reduced. Moreover the material is mechanically grinded, which means it gets destroyed during the reaction in the autoclave. The performance of the chemically modified ULTRARESINS **UR5**-**UR8** in transfer hydrogenation was more promising but still not satisfactory. The activity of the supported precursor complexes probably is increased due to a diminished rigidity of the polymeric material under the applied reflux conditions of transfer hydrogenation. The elevated temperature leads to an enlarged swelling of the material and hence to a better accessibility of the reactive

centres. However, the elevated temperatures cause the decomposition of the immobilised ruthenium complexes. As was reported for previously employed organic supporting materials[9] the ULTRARESINS suffer from their insufficient chemical and thermal stability. Moreover, the accessibility of the immobilised reactive centres is not ensured. Nevertheless ULTRARESINS offer interesting possibilities for their employment in catalysis. In organic synthesis the use of resins as scavengers is wide spread[128]. ULTRARESINS could be applied as scavengers after transition metal catalysed processes in order to remove the catalyst from the reaction mixture. By effective functionalisation with suitable ligands catch-and-release mechanisms and so recycling of the catalyst could be reached. In this way it would be possible to profit by the advantages of homogeneous catalysis and polymer assisted solution phase synthesis.

A second approach was made by the immobilisation of catalyst precursor complexes on the surface of spherical 800 nm silica particles (**SP3**-**SP5**). It was expected to ensure a good accessibility of the ruthenium(II) complexes located in a homogeneous environment. The immobilised complexes (**SP3**) were catalytically active in the hydrogenation of acetophenone as was expected from their redox behaviour[125,136,137]. With a maximum TOF of about 6 h^{-1} the substrate was totally converted to 1-phenylethanol. The modified particles could be recycled successfully, but their treatment with solvents in a Soxhlet extractor led to a loss of activity. Moreover it was observed, that both recycled and treated particles **SP4** and **SP5** needed a phase of activation. After a total time of twenty hours the activity declined to a minimum. This was accredited to the inactivation of the immobilised ruthenium(II) complexes. Besides, leaching could not be excluded completely. After two successive hydrogenation runs or after transfer hydrogenation the spherical particles were partly destroyed, some were agglomerated. As a consequence from these results in a further approach nano scaled spherical particles should be applied as inorganic support. In doing so it is expected to increase the stability of the material with regard to mechanical and chemical stability. By reducing the size of the carrier material to nano size it could be achieved that during hydrogenation, for example the particles would not be in suspension but in a quasi diluted state. Hydrogenation then could proceed like in solution, which should increase the activity of the immobilised complexes. The separation of the small particles would get more difficult but could still be carried out by centrifugation.

The incorporation of functionalised ruthenium(II) complexes by a sol-gel process into a silica matrix via co-condensation with alkoxysilanes yields the most auspicious results. To optimise stability of the polysiloxane network and accessibility of the reactive centres several materials with different amount of co-condensation agent were applied. In this way an interphase catalyst is attained that shows exquisite performance in several consecutive hydrogenation runs with *trans*-4-phenyl-3-butene-2-one as substrate with negligible loss of activity and selectivity[108]. The immobilisation of the ruthenium(II) complexes proceeds in the last case in contrast to the ULTRARESINS and Stöber particles via a T-silyl functionalised diphosphine ligand[108]. In doing so it is possible to easily vary the diamine ligand at the metal centre, which opens up a method for a catalyst screening.

For the immobilisation two different types of diaminedichlorobis(phosphine)ruthenium(II) complexes were chosen. In the first case the complex was equipped with hemilabile etherphosphine ligands in the second case with chelating 1,3-(diphenyl)phosphino-propane derivatives. Both types of complexes were expected to work in the outer coordination sphere of the metal centre after the mechanism proposed for Noyori-type ruthenium(II) diamine bis(phosphine) complexes. But in recent work evidence was found that the mechanism for the etherphosphine complexes differs from the proposed one. After the abstraction of a chloride ion from the ruthenium centre $^{-}O^{t}Bu$ coordinates at the free coordination site. It seems that from that precursor the actual species of the complex is generated. A major part in this sort of catalytic cycle is attributed to the hemilabile ligands but it is still not clear-cut. To solve this issue still efforts are made.

For a future application for the catalytic hydrogenation of ketones in the interphase with diaminedichlorobis(phosphine)ruthenium(II) complexes the most promising supports are estimated to be materials, into which a well-defined functionalised complex is incorporated via a sol-gel process. Matrices of this type show good chemical stability, which means they can be recycled several times without loss of activity. The functionalisation of the phosphine ligand opens up the possibility for a catalyst screeening. In conclusion the sol-gel materials fit the demand for interphase catalysts that shall combine the advantages of homogeneous and heterogeneous catalysis.

5 EXPERIMENTAL PART

5.1 General Remarks

All reactions were performed under argon employing the usual Schlenk techniques if not mentioned otherwise. The applied solvents were dried with the usual methods and stored under argon. Toluene was distilled from sodium benzophenone ketyl, *n*-pentane was dried over $LiAlH_4$ and distilled. CH_2Cl_2 was distilled from CaH_2 and 2-propanol was dried over magnesium and distilled. Deionised H_2O and $CDCl_3$ for high resolution NMR measurements were degassed in three freeze-pump-thaw cycles and set under argon prior to use. Solvents for ULTRARESIN synthesis were purchased from Fluka Chemical Company in HPLC grade.

5.2 Materials and Instrumentation

$RuCl_2$(methoxyethyldiphenylphosphine)$_2$[83,139] and $RuCl_2$(1,3-diphenylphosphino-propane)$_2$[154] were synthesised according to literature methods. The precursor complex $RuCl_3 \cdot x\ H_2O$ was purchased from Strem Chemicals, Inc. Polyethylene imines, Fmoc-aminohexanoic acid, Fmoc-1,2-diaminopropionic acid, acetic anhydride, TBTU, HOBt and DiPEA were obtained from Sigma Aldrich Chemical Company, Fluka Chemical Company, Lancaster Synthesis GmbH Company, and Merck Chemical Company, respectively, and used without further purification.

The spherical silica particles with a diametre of 800 nm were prepared using the Stöber-process[48,148,149] and were a donation of the group of Prof. Speiser as well as the 200 nm 3-(2-aminoethyl)aminopropyldichlorobis[(methoxyethyldiphenyl)phosphine]-ruthenium(II) silica particles (**SP6**). 2-propanol was purchased from Aldrich Chemical Company (99.5 %, HPLC grade) and Merck Chemical Company (≥ 99.5 %, puriss.). *n*-pentane (≥ 99.0 %, for synthesis), $LiAlH_4$ (for synthesis), and CaH_2 (for synthesis) were obtained from Merck Chemical Company. $LiAlH_4$ and CaH_2 were stored under

argon. 3-(2-aminoethyl)aminopropyltrimethoxysilane, potassium-*tert*-butoxide, 1-phenylethanol and benzaldehyde were purchased from Fluka Chemical Company and used without purification. Acetophenone was employed as derived from Fluka Chemical Company or Riedel de Haën Chemical Company. $LiHB(C_2H_5)_3$ (1 M solution in THF) was obtained from Aldrich Chemical Company. Argon (purity 4.8) was purchased from Messer Griesheim Company. Hydrogen for catalysis was synthesised in a Whatman hydrogen generator with a Pd-tube as cathode in a solution of sodium hydroxide (Merck Chemical Company, p.a., ACS, max. 0.0002% K) and millipore H_2O (Millipore, Milli Q-Plus 185, Q PAK® 2) as electrolyte or purchased (purity 5.0) from Messer Griesheim Company. All solvents and reagents not mentioned were obtained from the chemicals store of the University of Tübingen.

5.3 Methods

5.3.1 Solid State NMR Measurements

Magic-angle spinning (MAS) phosphorus-31 variable-amplitude cross-polarisation (VACP) NMR spectra of powder samples were acquired in 4 mm o.d. zirconia rotors at 10 kHz spinning frequency using Bruker double-bearing MAS probes. Samples were measured on a Bruker AVANCE DSX-200 spectrometer (B_0 = 4.7 T) with 4.2 µs proton pulse widths and contact times of 2 ms, using a ramped amplitude (2 dB) on the phosphorus channel. Chemical shifts were referenced with respect to external 85% aq H_3PO_4 by setting the peak of external $NH_4H_2PO_4$ to 0.81 ppm.

5.3.2 NMR Spectroscopy in Solution or Suspension

The ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$, and $^{29}Si\{^{1}H\}$ solution or suspension nuclear magnetic resonance spectra (NMR) were recorded on a Bruker DRX 250 or a Bruker DRX 400 spectrometer at 295 K. Frequencies and standards are as follows:

$^{31}P\{^{1}H\}$ NMR: 101.26 MHz, the signals were referenced to external 85 % H_3PO_4.

$^{13}C\{^{1}H\}$ NMR: 62.90 MHz. The chemical shifts were measured relative to solvent peaks, which are reported relative to TMS.

$^{29}Si\{^{1}H\}$: 250.13 MHz. The chemical shifts were referenced to TMS.
^{1}H NMR: 250.13 MHz and 400.13 MHz, respectively. The signals were referenced relative to the residual proton signals of the solvent relative to TMS.
To support the assignment NMR DEPT 135 spectra were obtained.

5.3.3 FT-ATR-IR Measurements

FT-ATR-IR measurements were carried out on Bruker Vector 22 with a SplitPea® ATR-unit from Harrick. By pressing the sample directly to a Si crystal the IR-spectra were detected with 16 scans. An automatic ATR-correction was executed.

5.3.4 Infrared spectra

Infrared spectra were acquired on a Bruker FT-IR spectrometer IFS 48 covering the range of 4000 cm^{-1} - 400 cm^{-1}. Samples were prepared as pellets on KBr.

5.3.5 UV/VIS Measurements

UV spectra were recorded on a Lambda-5 UV/VIS-spectrometer of Perkin-Elmer (Überlingen).

5.3.6 Mass Spectrometry

FAB mass spectra were recorded on a Finnigan MAT 711 A modified by AMD company (10kV, 323 K).

5.3.7 Elemental Analysis

Elemental analyses were obtained on a Vario EL made by Elemental Company.

5.3.8 Light Scattering Experiments

Light scattering was performed on a Coulter® N4 Plus Submicron Particle Sizer with a 10 mW He-Ne laser at a wavelength of 632.8 nm with monochromatic polarized light at

298 K and a wave angle of 90°. For the measurements quartz cuvettes were used. Suspensions were made in filtered (Millipore) ethanol.

5.3.9 Scanning Electron Microscopy

SEM was carried out on a Zeiss DSM 962 with an acceleration voltage of 5 kV. Samples were not sputtered.

5.3.10 Ultrasonicator

For ultrasonic treatment a TRANSSONIC 460 of Elma® was applied.

5.3.11 Centrifuge

For centrifugation 50 mL flasks of Sarstedt in an Eppendorf Centrifuge 5810 R were employed.

5.3.12 General Procedure for the Determination of the Loading of the Resin via UV-Spectroscopic Fmoc Identification

To cleave the Fmoc protecting group from the resin 5-10 mg dried and washed samples of the resin were weighed and put into a 10 mL calibrated flask. The flask was filled with a solution of 20 % piperidine in DMF to the calibration line and shaken for 2 hours. At first a background measurement with pure piperidine/DMF solution is carried out at the UV-spectrometer at a wavelength area of 150-320 nm. Then the solution with the cleaved Fmoc is measured against this reference. The extinction values at the three absorption maxima of the UV-spectrum at λ_1= 267 nm, λ_2= 289 nm, and λ_3= 301 nm are evaluated with the following equation:

$$x\left[\frac{mmol}{g}\right] = \frac{10^5 \cdot E_\lambda}{\varepsilon_\lambda \cdot (sample\ weight)}$$

x : loading of the resin

E_λ : extinction

ε_λ : extinction coefficient

sample weight : mass of the resin in mg.

The following extinction coefficients were used:

ε_{267} = 17500 cm^{-1}

ε_{289} = 5800 cm^{-1}

ε_{301} = 7800 cm^{-1}.

The loading of the resin is the average of the calculated values at the three different wavelengths.

5.3.13 Kaisertest

Small resin particles are treated with the solutions I, II, and III in an Eppendorf cup, then heated to 110 °C for 5 minutes. If there is a colour change to blue, there are residual amines left. Solution I: 50 µL of 0.01 M aqueous KCN solution filled up to 25 mL with pyridine; solution II: 5 g ninhydrine in 100 mL *n*-butanol; solution III: 80 g phenol in 20 mL *n*-butanol.

5.3.14 Hydrogenation station

The employed hydrogenation station allows hydrogenation reactions under constant pressure between 1 and 100 bar. The temperature can be kept constant in a range between 10 °C and 150 °C with a tempered oil bath or water bath, respectively. During the reaction the pressure inside the autoclave is kept unchanged whereas pressure drop is measured in a supplementary vessel. On-line acquisition of detected data (consumed H_2 (mol) per time), their graphical illustration and analysis is carried out computerised with software developed at the University of Tübingen[144].

5.3.15 High Performance Liquid Chromatography

For HPLC separations a Beckman Gold System with controller system 406, pump system 126, autosampler 507 and diode array detector 168 was applied. As separation

column a Nucleosil 100 C-18 (5 µm, 2 x 250 mm, Grom Company, Herrenberg) was used. UV detection proceeded at λ = 214 nm.

For the determination of the conversion of the hydrogenation reactions the following equation was used:

$$conversion = \frac{area\ (phenylethanol)}{area\ (phenyethanol) + area\ (acetophenone)} \cdot 100\ \%.$$

5.3.16 Gas chromatography

GC measurements were carried out on a Carlo Erba Strumentazione HRGC 5300 Mega Series with a 20 m Carbowax Column (diameter 250 µm, film thickness 0.25 µm) under the following conditions: Temperature of the injector and FID-detector 250 °C, column temperature 140 °C, H_2 pressure 0.4 bar, fuel gas pressure for air and hydrogen 0.6 bar and split 20 mL/min. As integrator a Shimadzu C-R3A Chromatopac was used. Samples for GC measurements were taken after the hydrogenation without further purification for the ULTRARESINS. For the silica particles the solid material was separated from the reaction mixture before taking GC samples.

5.4 Modification of the ULTRARESINS

All reactions were carried out without inert gas in plastic syringes equipped with teflon filters.

5.4.1 Preparation of the Modified ULTRARESIN UR2

500 mg of resin **UR1** were swollen in DMF and reacted with 1 mmol each of Fmoc-1,2-diaminopropionic acid, TBTU, HOBt, and DiPEA in 10 mL of DMF for 16 h at room temperature. Removement of Fmoc proceeded with a 20 % solution of piperidine in DMF for 2 h at room temperature. The resulting colourless resin **UR2** was washed with DMF and CH_2Cl_2 and dried *in vacuo*. A loading with diamine of 0.79 mmol/g was determined from the applied amount of Fmoc-diaminopropionic acid. IR: ν = 3421 cm^{-1} (N-H), 2921 cm^{-1} (aliphatic C-H), 1627 cm^{-1} (NC=O).

5.4.2 Preparation of the Modified ULTRARESIN UR4

1 g of compound **UR1** was swollen in DMF and reacted with 3 mmol each of Fmoc-aminohexanoic acid, TBTU, HOBt and DiPEA in 20 mL of DMF at room temperature. After 16 h the product was washed with DMF and CH_2Cl_2 and dried. The resulting resin was capped with 7.5 mL each of acetic anhydride and DiPEA for 18 h in 30 mL of DMF. After washing with DMF and CH_2Cl_2 the removement of Fmoc proceeded with a 20 % solution of piperidine in DMF for 2 h at room temperature. UV/VIS measurement of the solution led to Fmoc-loading of the resin **UR3** of 0.98 mmol/g.
500 mg of resin **UR3** were swollen in DMF and reacted with 1 mmol each of Fmoc-1,2-diaminopropionic acid, TBTU, HOBt, and DiPEA in 10 mL of DMF for 16 h at room temperature. The resulting resin was washed with DMF and CH_2Cl_2 and dried *in vacuo*. Removement of Fmoc proceeded with a 20 % solution of piperidine in DMF for 2 h at room temperature and led to **UR4** as a colourless solid. UV/VIS measurement of the solution led to Fmoc-loading of resin **UR4** of 0.85 mmol/g. IR: ν = 3298 cm^{-1} (N-H), 2933 cm^{-1}(aliphatic C-H),1632 cm^{-1} (NC=O).

5.4.3 Preparation of the Stationary Phases UR5-UR8

One equivalent of ULTRARESIN **UR2** or **UR4**, respectively was swollen in 2 mL of CH_2Cl_2, then washed twice with 2 mL of the same solvent. One equivalent of dichlorobis-[(methoxyethyldiphenyl)phosphine]ruthenium(II) (**24**) or *trans*-bis[1,3-bis(diphenyl-phosphino)propane]dichlororuthenium(II) (**25**) respectively, dissolved in 5 mL of CH_2Cl_2 was added to the swollen resin. After shaking the suspension for 2 h at room temperature the coloured resin was washed several times with CH_2Cl_2. After drying *in vacuo* the stationary phase **UR5**-**UR8** were obtained.

UR5: green solid; suspension $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.6 ($P(C_6H_5)_2CH_2CH_2OCH_3$, $\nu_{1/2}$ = 506.8 Hz at LB = 10 Hz); ^{31}P VACP/MAS NMR: δ 34.9 ($P(C_6H_5)_2CH_2CH_2OCH_3$, $\nu_{1/2}$ = 1010.7 Hz at LB = 10 Hz); IR: ν = 3636-3198 $cm^{-}1$ (N-H), 2921 cm^{-1} (aliphatic CH_2), 1641 cm^{-1} (NC=O); Kaisertest positive.

UR6: green solid, ^{31}P VACP/MAS NMR: δ 37.6 ($P(C_6H_5)_2CH_2CH_2OCH_3$, $\nu_{1/2}$ = 1177.8 Hz at LB = 10 Hz); IR: ν = 3417 cm^{-1}, 3307cm^{-1}, 3267 cm^{-1} (N-H), 2933 cm^{-1} (aliphatic CH_2), 1629 cm^{-1} (NC=O); Kaisertest negative.

UR7: yellow solid, suspension ^{31}P{^{1}H} NMR ($CDCl_3$): δ 43.1 ($CH_2[CH_2P(C_6H_5)_2]_2$, $\nu_{1/2}$ = 136.8 Hz at LB = 100 Hz), 41.0 ($CH_2[CH_2P(C_6H_5)_2]_2$, $\nu_{1/2}$ = 244.7 Hz at LB = 100 Hz); ^{31}P VACP/MAS NMR: δ 46.2 ($CH_2[CH_2P(C_6H_5)_2]_2$, $\nu_{1/2}$ = 629.8 Hz at LB = 100 Hz), 35.8 ($CH_2[CH_2P(C_6H_5)_2]_2$, $\nu_{1/2}$ = 646.8 Hz at LB = 100 Hz); IR: ν = 3658-3190 cm^{-1} (N-H), 2922 cm^{-1} (aliphatic C-H), 1630 cm^{-1} (NC=O); Kaisertest positive.

UR8: yellow solid, ^{31}P VACP/MAS NMR: δ 47.1 ($CH_2[CH_2P(C_6H_5)_2]_2$, $\nu_{1/2}$ = 580.1 Hz at LB = 10 Hz), 36.2 ($CH_2[CH_2P(C_6H_5)_2]_2$, $\nu_{1/2}$ = 667.1 Hz at LB = 10 Hz); IR: ν = 3701-3177 cm^{-1} (N-H), 2933 cm^{-1} (aliphatic C-H), 1630 cm^{-1} (NC=O); Kaisertest negative.

5.5 Modification of the 800 nm Stöber Silica Particles

The spherical sub micron silica particles were prepared applying the Stöber-process. The surface area of 4.2 m^2g^{-1} for the 800 nm particles was determined by BET measurements[150]. The theoretical amount of silanol groups on the surface of Stöber particles[48] is 4.89 OH-groups per nm^2. With these values a theoretical amount of 34.10 $\mu mol \cdot g^{-1}$ OH-groups on the surface is estimated. For all considerations, in which the loading with ruthenium complex was taken into account a maximal loading was assumed.

5.5.1 Preparation of the 3-(2-Aminoethyl)aminopropyl Silica Particles (SP2)

For activation 800 nm silica particles (5.03 g, maximum n(SiOH) = 0.17 mmol) were heated up to 200 °C *in vacuo* overnight. Afterwards the particles were suspended in 30 mL toluene by ultrasonication. A four fold excess with reference to the maximum amount of surface OH-groups on **SP1** of 3-(2-aminoethyl)aminopropyltrimethoxysilane (0.15 g, 0.69 mmol) (**28**) was added under stirring and heated to reflux for 43 h. The resulting white particles were washed twice with 10 mL of toluene and once with 10 mL

of *n*-pentane. After drying *in vacuo* 4.91 g (97 %) of **SP2** were obtained as a white powder.

5.5.2 Preparation of the 3-(2-Aminoethyl)aminopropyldichlorobis[(methoxyethyldiphenyl)phosphine]ruthenium(II) Silica Particles (SP3)

A mixture of **SP2** (4,91 g, maximal loading with diamine spacer n = 0.17 mmol) and a two fold excess of dichlorobis[(methoxyethyldiphenyl)phosphine]ruthenium(II) (**24**) (0.22 g, 0.33 mmol) was suspended in 40 mL of toluene by ultrasonication and heated to 70 °C under stirring for 42 h. After cooling to room temperature the wet greenish particles were washed seven times with a total amount of 115 mL of toluene and three times with a total amount of 65 mL of CH_2Cl_2. After drying *in vacuo* 3.67 g (73 %) of **SP3** were obtained as a grey to green powder. ^{31}P VACP/MAS NMR: δ 34.2 ($P(C_6H_5)_2CH_2CH_2OCH_3$, $\nu_{1/2}$ = 1861.5 Hz at LB = 200 Hz); Elemental analysis: Anal. Calcd.: Cl: 0.25 %; Found: Cl: 0.13 %; Dynamic Light Scattering: ø = 727 nm.

5.5.3 Preparation of the 3-(2-Aminoethyl)aminopropyldichlorobis[(methoxyethyldiphenyl)phosphine]ruthenium(II) Silica Particles (SP4)

Silica particles **SP3** were extracted in a 15 mL Soxhlet extractor with 100 mL of dry CH_2Cl_2 for 48 h. The residual suspension in the Soxhlet hull was transferred to a Schlenk tube and the solvent evaporated *in vacuo*. **SP4** was obtained as a grey powder.

5.5.4 Preparation of the 3-(2-Aminoethyl)aminopropyldichlorobis[(methoxyethyldiphenyl)phosphine]ruthenium(II) Silica Particles (SP5)

Silica particles **SP3** were extracted in a 15 mL Soxhlet extractor with a mixture of 60 mL of dry CH_2Cl_2 and 80 mL of dry 2-propanol for 16 h. The residual suspension in the Soxhlet hull was transferred to a Schlenk tube and the solvent evaporated *in vacuo*. **SP5** was obtained as a grey powder. Elemental analysis: Anal. Calcd.: C: 1.59 %; H: 0.19 %; N: 0.10 %; Cl: 0.25 %; Found: C: 0.43 %; H: 0.56 %; N: 0.05 %;. the loading of ruthenium complex did not change in comparison to **SP3**; Light Scattering: ø = 745 nm.

5.5.5 Modified 200 nm Silica Particles SP6

For the modified 200 nm silica particles **SP6** a loading of 10 µg ruthenium(II) complexes per gram material was determined with elemental analysis.

5.5.6 Preparation of the 3-(2-Aminoethyl)aminopropyldichlorobis[(methoxyethyldiphenyl)phosphine]ruthenium(II) Complex (29)

Dichlorobis[(methoxyethyldiphenyl)phosphine]ruthenium(II) (**24**) (0.250 g, 0.378mmol) was dissolved in 20 mL of CH_2Cl_2. 3-(2-Aminoethyl)aminopropyltrimethoxysilane (0.085 g, 0.382 mmol) was added under stirring. The colour changed immediately from dark red to green. The solution was stirred for 3 h at ambient temperature and CH_2Cl_2 afterwards reduced in volume to 1 mL. After addition of 25 mL of *n*-pentane a yellow solid precipitated. Another 75 mL of *n*-pentane were added and the product was filtered and washed three times with 25 mL of *n*-pentane. After drying *in vacuo* 0.161 g (48 %) of complex **29** was obtained as a green solid. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 38.8 (d, AB, $^2J_{PP}$ = 36.29 Hz), 35.6 (d, AB, $^2J_{PP}$ = 36.29 Hz); ^{1}H-NMR ($CDCl_3$): δ 7.08-7.85 (20H, m, C_6H_5), 5.29 (1H, s, CH_2NH), 3.57 (9H, s, $SiOCH_3$), 2.32-3.36 (22H, m, $SiCH_2CH_2$, $SiCH_2CH_2CH_2$, $NHCH_2CH_2NH_2$, $NHCH_2CH_2NH_2$, PCH_2, PCH_2CH_2, $P(CH_2)_2OCH_3$), 2.21, 1.84 (1H, m, PCH_2), 1.40 (1H, m, $SiCH_2CH_2$), 0.37 (1H, m, $SiCH_2CH_2$), 0.01 (2H, m, $SiCH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ127.9-136.9 (m, C_6H_5), 69.2 (m, CH_2OCH_3), 57.9 (OCH_3), 57.8 (OCH_3) 54.4 ($SiCH_2CH_2CH_2$), 50.7 ($Si(OCH_3)_3$), 49.3 ($NHCH_2CH_2NH_2$), 42.8 ($NHCH_2CH_2NH_2$) 26.9 (d, PCH_2, $^2J_{CP}$ = 26.58 Hz), 24.8 (d, PCH_2, $^2J_{CP}$ = 26.58 Hz), 21.9 ($SiCH_2CH_2$), 6.7 ($SiCH_2$); ^{29}Si; δ -22.8 (s, $Si(OCH_3)_3$); IR: ν = 3264-3346 cm^{-1} (NH, NH_2), 3053 cm^{-1} (aromatic CH_2), 2935 cm^{-1} (aliphatic CH_2), 1576 cm^{-1} (R_1R_2NH), 1433 cm^{-1} (-O-CH_2), 1191 cm^{-1} (P-O-CH_3), 1087 cm^{-1}(-CH_2-NH_2); MS (FAB): *m/z* 882 [M], 847 [M-Cl], 659 [M-diamine ligand], 393 [M-2 etherphosphine ligands], 245 [etherphosphine ligand].

5.6 Direct Hydrogenation with UR5 and UR8 under Low Hydrogen Pressure with 2-Propanol as Solvent

The stationary phases **UR5** and **UR8** were mixed with the co-catalyst KO^{t}Bu in a 50 mL Schlenk tube. The solid mixture was set under argon. Afterwards dried 2-propanol and acetophenone were added under stirring. The reaction mixture was degassed in three freeze-pump-thaw cycles. The degassed suspension was set under a hydrogen pressure of 1.5 bar while stirring. The hydrogenation system was closed. After 30 minutes of stirring to allow hydrogen to diffuse into the solution the Schlenk tube was set under a hydrogen pressure of 1.5 bar again. The system was closed and stirred at room temperature for the reaction time. After the hydrogenation reaction the Schlenk tube was flushed several times with argon to remove hydrogen gas. An HPLC sample was taken from the reaction mixture without further purification (Table 5, page 47).

5.6.1 Direct Hydrogenation with Stationary Phase UR5 under Low Hydrogen Pressure with 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of **UR5** with four equivalents of KO^{t}Bu and 100 equivalents of acetophenone in 2-propanol.

5.6.2 Direct Hydrogenation with Stationary Phase UR8 under Low Hydrogen Pressure with 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of **UR8** with 8 equivalents KO^{t}Bu and 100 equivalents of acetophenone in 2-propanol.

5.6.3 Recycling of the Stationary Phases UR5 and UR8

After the hydrogenation reactions the reaction mixtures were washed into a plastic syringe with teflon filter to remove liquids. The residual solid resins **UR5** or **UR8**, respectively were washed several times with 2-propanol, methanol, and CH_2Cl_2. The resulting solids were dried *in vacuo*.

UR5: brown solid, ^{31}P VACP/MAS NMR: δ 35.6 ($CH_2[CH_2P(C_6H_5)_2]_2$, $\nu_{1/2}$ = 1242.1 Hz at LB = 10 Hz).

UR8: brown solid, ^{31}P VACP/MAS NMR: δ 50.6 ($CH_2[CH_2P(C_6H_5)_2]_2$, $\nu_{1/2}$ = 630.5 Hz at LB = 50 Hz), 39.2 (($CH_2[CH_2P(C_6H_5)_2]_2$, $\nu_{1/2}$ = 712.9 Hz at LB = 50 Hz); IR: ν = 3701-3177 cm^{-1} (N-H), 2933 cm^{-1} (C-H), 1630 cm^{-1} (NC=O).

5.7 General Procedure for the Direct Hydrogenation with Stationary Phase UR8 under High Hydrogen Pressure

Stationary phase **UR8** was filled into an autoclave of ca. 75 mL content. The co-catalyst was added. The solid mixture was set under argon. Then the solvent and acetophenone were added under stirring. The autoclave was sealed and the suspension degassed. The hydrogenation suspension was tempered at 35 °C for 30 minutes. Then it was set under hydrogen pressure without stirring. After one minute the suspension was stirred so that hydrogen gas could diffuse into the suspension and dissolve. With a supplementary hydrogen vessel the hydrogen pressure in the autoclave was kept constant during the reaction time. After the reaction time the autoclave was cooled to room temperature. From the reaction mixture a GC or HPLC sample was taken without further purification (Table 5, page 47).

5.7.1 Direct Hydrogenation with Stationary Phase UR8 under High Hydrogen Pressure with 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of **UR8** with 4 or 5 equivalents of KO^{t}Bu and 838, 876 or 1006 equivalents of acetophenone respectively, in 2-propanol.

5.7.2 Direct Hydrogenation with Stationary Phase UR8 under High Hydrogen Pressure with 2-Propanol as Solvent and LiHB(C_2H_5)$_3$ as Co-catalyst

One equivalent of **UR8** with 10 or 12 equivalents of a 1 M solution of LiHB(C_2H_5)$_3$ in THF and 1006 or 1007 equivalents of acetophenone in 2-propanol.

5.7.3 Direct Hydrogenation with Stationary Phase UR8 under High Hydrogen Pressure with Toluene as Solvent and $LiHB(C_2H_5)_3$ as Co-catalyst

One equivalent of **UR8** with 5 equivalents of a 1 M solution of $LiHB(C_2H_5)_3$ in THF and 867 or 1012 equivalents of acetophenone in toluene.

5.7.4 Direct Hydrogenation with Stationary Phase UR8 under High Hydrogen Pressure with Deionised Water as Solvent and KO^tBu as Co-catalyst

One equivalent of **UR8** with 5 equivalents of KO^tBu and 196 equivalents of acetophenone in deionised H_2O.

5.7.5 Direct Hydrogenation with the Homogeneous Catalyst 27 under High Hydrogen Pressure with 2-Propanol as Solvent and KO^tBu as Co-catalyst

One equivalent of complex **27** was put into a 5 mL Schlenk tube, set under argon, and dissolved in 5 mL of 2-propanol. 4 or 6 equivalents of KO^tBu were filled into a ca. 75 mL autoclave. The autoclave was closed and the solid was set under argon. Under stirring first 2-propanol was added to the co-catalyst to dissolve it, then the catalyst solution. Afterwards 1019 or 7168 equivalents of acetophenone were mixed with the solution in the autoclave. The autoclave was closed. The reaction solution was degassed, then tempered, and set under constant hydrogen pressure for the reaction time.

5.7.6 Direct Hydrogenation with Co-catalyst KO^tBu in 2-Propanol without Catalyst (Blank Test)

One equivalent of co-catalyst KO^tBu with 192 or 199 equivalents of acetophenone in 2-propanol.

5.7.7 Direct Hydrogenation with Co-catalyst $LiHB(C_2H_5)_3$ in 2-Propanol without Catalyst (Blank Test)

An autoclave of ca. 75 mL content was set under argon, then filled with 35 mL 2-propanol and one equivalent of a 1 M solution of $LiHB(C_2H_5)_3$ in THF. After adding 86

equivalents of acetophenone the autoclave was closed. The reaction mixture was degassed, then tempered, and set under constant hydrogen pressure for the reaction time.

5.8 General Procedure for the Transfer Hydrogenation with the Stationary Phases UR5, UR6, and UR8

In a 5 mL Schlenk tube or a 50 mL round flask equipped with reflux condenser and pressure valve the stationary phases **UR5**, **UR6**, and **UR8** were mixed with co-catalyst and set under argon. Under stirring the solvent and acetophenone were added. Without degassing the reaction mixture was heated to reflux in an oil bath equipped with contact thermometer and stirred at constant temperature for the reaction time. Then the mixture was cooled to room temperature and a sample for GC or HPLC was taken without further purification (Table 6, page 49).

5.8.1 Transfer Hydrogenation with Stationary Phase UR5 with 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of **UR5** with 4 equivalents of KO^{t}Bu and 98 equivalents of acetophenone in 2-propanol.

5.8.2 Recycling of the Stationary Phase UR5

After the hydrogenation reaction the reaction mixture was washed into a plastic syringe with teflon filter to remove liquids. The residual solid resin was washed several times first with 2-propanol, then methanol, and CH_2Cl_2. The resulting brown solid was dried *in vacuo*. ^{31}P VACP/MAS NMR: δ 41.9 ($\nu_{1/2}$ = 1799.2 Hz at LB = 20 Hz).

5.8.3 Transfer Hydrogenation with Stationary Phase UR6 with 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of **UR6** with 5 equivalents of KO^{t}Bu and 1000 equivalents of acetophenone in 2-propanol.

5.8.4 Transfer Hydrogenation with the Stationary Phase UR8 with 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of **UR8** with 1 to 11 equivalents of KO^{t}Bu and 89 to 1000 equivalents of acetophenone in 2-propanol.

5.8.5 Transfer Hydrogenation with the Stationary Phase UR8 with 2-Propanol as Solvent without Co-catalyst

One equivalent of **UR8** with 1000 equivalents of acetophenone in 2-propanol.

5.8.6 Transfer Hydrogenation with the Stationary Phase UR8 with 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst at Room Temperature

One equivalent of **UR8** with 5 equivalents of KO^{t}Bu and 1000 equivalents of acetophenone in 2-propanol.

5.8.7 Transfer Hydrogenation with the Recycled Stationary Phase UR8 in 2-Propanol and KO^{t}Bu as Co-catalyst

One equivalent of the recycled stationary phase **UR8** with 5 equivalents of KO^{t}Bu and 933 equivalents of acetophenone in 2-propanol.

5.8.8 Transfer Hydrogenation with the Stationary Phase UR8 in Deionised Water and KO^{t}Bu as Co-catalyst

One equivalent of **UR8** with 5 equivalents of KO^{t}Bu with 101 equivalents of acetophenone in deionised water.

5.8.9 Transfer Hydrogenation with the Stationary Phase UR8 in 2-Propanol and LiHB(C_2H_5)$_3$ as Co-catalyst

One equivalent of **UR8** with 5 equivalents of a 1 M solution of LiHB(C_2H_5)$_3$ in THF and 104 equivalents of acetophenone in 2-propanol.

5.8.10 Transfer Hydrogenation with KO^{t}Bu in 2-Propanol (Blank Test)

One equivalent of KO^{t}Bu with 20 or 189 equivalents of acetophenone, respectively in 2-propanol.

5.8.11 Transfer Hydrogenation with $LiHB(C_2H_5)_3$ in 2-Propanol (Blank Test)

One equivalent of 1 M solution of $LiHB(C_2H_5)_3$ in THF with 22 equivalents of acetophenone in 2-propanol.

5.9 General Procedure for the Direct Hydrogenation with the Silica Particles SP3-SP6 under High Hydrogen Pressure

The spherical silica particles **SP3**-**SP6** were filled into an autoclave of ca. 75 mL content. After the co-catalyst was added, the solid mixture was set under argon. Then the solvent and acetophenone were added under stirring. The autoclave was sealed and the suspension degassed. The hydrogenation suspension was tempered at 35 °C for 30 minutes. Then it was set under a hydrogen pressure of 30 bar without stirring. After one minute the suspension was stirred so that hydrogen gas could diffuse into the suspension and dissolve. With a supplementary hydrogen vessel the hydrogen pressure in the autoclave was kept constant at 30 bar. After the reaction time the autoclave was cooled to room temperature. Under air the reaction suspension was filled into a centrifugation vessel or under argon into a Schlenk tube. By centrifugation without protecting gas or by sedimentation under argon, respectively the liquid parts of the suspension were separated from the solid parts. From the liquids a GC sample was taken without further purification (Table 7, page 51).

5.9.1 Direct Hydrogenation with the 800 nm Silica Particles SP3 in 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of the silica particles **SP3** with 5 equivalents KO^{t}Bu and 90 or 102 equivalents of acetophenone in 2-propanol.

5.9.2 Direct Hydrogenation with the 800 nm Silica Particles SP4 in 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of the silica particles **SP4** with 5 equivalents of KO^{t}Bu and 92 or 106 equivalents of acetophenone in 2-propanol.

5.9.3 Direct Hydrogenation with the 800 nm Silica Particles SP5 in 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of the silica particles **SP5** with 5 equivalents of KO^{t}Bu and 100 equivalents of acetophenone in 2-propanol.

5.9.4 Direct Hydrogenation with the 200 nm Silica Particles SP6 in 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of the silica particles **SP6** with 4 equivalents of KO^{t}Bu and 85 equivalents of acetophenone in 2-propanol.

5.9.5 Recycling of the Liquid Parts of the Reaction Mixture without Inert Gas Atmosphere

After the hydrogenation reaction the suspension was collected in a 50 mL centrifugation vessel and centrifugated. The liquid parts of the hydrogenation reaction were decanted and reused in hydrogenation without further purification

5.9.6 Recycling of the Liquid Parts of the Reaction Mixture under Argon

After the hydrogenation reaction the suspension was collected under argon in a 50 mL Schlenk tube and kept there for several days until sedimentation of the solid parts of the suspension had occurred. The liquid parts of the reaction mixture were directly reused in a reaction run without further purification.

5.9.7 Recycling of the Solid Parts of the Reaction Mixture under Argon

The used silica particles **SP3** and **SP4** were recycled by treating them in a Soxhlet extractor for 48 h with a mixture of 100 mL CH_2Cl_2 and 50 mL 2-propanol. After drying the silica particles *in vacuo* they were set under argon.

5.9.8 Direct Hydrogenation with the Recycled Liquid Parts of the Hydrogenation Mixtures without Additional KO^{t}Bu as Co-catalyst

A ca. 75 mL autoclave was set under argon. The recycled liquids were put into the autoclave. Under stirring additional acetophenone was added. The autoclave was closed and the reaction mixture was degassed, then tempered, and set under constant hydrogen pressure for the reaction time.

5.9.9 Direct Hydrogenation with the Recycled Liquid Parts of the Hydrogenation Mixtures with Additional KO^{t}Bu as Co-catalyst

One equivalent of extra KO^{t}Bu as co-catalyst was put into an autoclave of ca. 75 mL content and set under argon. The recycled liquids and 18 to 30 equivalents of extra acetophenone were added under stirring. The autoclave was sealed and the reaction mixture was degassed, then tempered, and set under constant hydrogen pressure for the reaction time.

5.9.10 Direct Hydrogenation with the Recycled 800 nm Silica Particles SP3 or SP4 in 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of the recycled silica particles **SP3** or **SP4** respectively, with 5 or 6 equivalents of KO^{t}Bu and 100 or 101 equivalents of acetophenone in 2-propanol.

5.9.11 Direct Hydrogenation with the 800 nm Silica Particles SP1 in 2-Propanol as Solvent and KO^{t}Bu (Blank Test)

One equivalent of the silica particles **SP1** with 6 equivalents of KO^{t}Bu (with regard to surface OH-groups) and 92 equivalents of acetophenone in 2-propanol.

5.9.12 Direct Hydrogenation with Co-catalyst KO^{t}Bu in 2-Propanol without Catalyst (Blank Test)

One equivalent of co-catalyst KO^{t}Bu with 199 equivalents of acetophenone in 2-propanol.

5.9.13 Direct Hydrogenation with the Homogeneous Catalyst 29 under Hydrogen Pressure with 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of complex **29** was put under argon into a 5 mL Schlenk tube. It was dissolved in 5 mL of dry 2-propanol and ultrasonicated for one minute. 5 equivalents of KO^{t}Bu were filled into an autoclave. The autoclave was closed and the solid was set under argon. Under stirring 2-propanol was added to the co-catalyst to dissolve it, then the catalyst solution. Afterwards 100 or 1031 equivalents of acetophenone were mixed with the solution in the autoclave. The autoclave was closed. The reaction solution was degassed, then tempered at 35 °C, and set under a constant hydrogen pressure of 30 bar for the reaction time

5.9.14 Direct Hydrogenation with the Homogeneous Catalyst 24 under Hydrogen Pressure with 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of complex **24** was put into a 5 mL Schlenk tube and set under argon. It was suspended in 5 mL of dry *2*-propanol and ultrasonicated for one minute. 5 equivalents of the co-catalyst KO^{t}Bu were filled into an autoclave. The autoclave was closed and the solid was set under argon. Under stirring 2-propanol was added to the co-catalyst to dissolve it, then the catalyst suspension. Afterwards 100 equivalents of acetophenone were mixed with the suspension in the autoclave. The autoclave was closed. The reaction suspension was degassed, then tempered, and set under constant hydrogen pressure for the reaction time.

5.10 Transfer Hydrogenation with 800 nm Silica Particles SP3

5.10.1 Transfer Hydrogenation with the 800 nm Silica Particles SP3 with 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of silica particles **SP3** was mixed with 6 equivalents of KO^{t}Bu as co-catalyst in a 25 mL round bottom flask and set under argon. Under stirring 2-propanol and 100 equivalents of acetophenone were added. The reaction mixture was heated to reflux and stirred under constant temperature for 68 h. Then it was cooled to room temperature and a GC sample was taken after separating the solid parts of the reaction mixture from the liquids without further purification.

5.10.2 Transfer Hydrogenation with Complex 29 in 2-Propanol as Solvent and KO^{t}Bu as Co-catalyst

One equivalent of complex **29** was set under argon in a 100 mL round bottom flask, then dissolved in 40 mL of 2-propanol. 5 equivalents of KO^{t}Bu were filled into a 50 mL round bottom flask, set under argon, and dissolved in 25 mL of 2-propanol. Under stirring the dissolved co-catalyst and 992 equivalents of acetophenone were added to the catalyst. The reaction mixture was heated to reflux and stirred under constant temperature for 16 h. Then it was cooled to room temperature and a GC sample was taken without further purification.

5.10.3 Transfer Hydrogenation with KO^{t}Bu in 2-Propanol (Blank Test)

One equivalent of KO^{t}Bu was set under argon in a 25 mL round bottom flask and dissolved in 2-propanol. Under stirring 20 equivalents of acetophenone were added. The reaction mixture was heated to reflux and stirred under constant temperature for 66 h. Then it was cooled to room temperature and a GC sample was taken without further purification.

5.11 Determination of the Conversion of the Hydrogenation Reactions with GC

To quantify the amount of 1-phenylethanol and acetophenone in the solution after a hydrogenation process an internal standard was employed. An internal standard must fulfil the following conditions:

i. The standard substance must elute in a time similar to the analytes.

ii. A complete separation of all components is crucial.

iii. The internal standard should elute near the peaks of the substances whose peak areas will be analysed relatively to the peak area of the internal standard.

iv. The concentration of the internal standard should be similar to the concentration of the analytes.

v. The vapour pressure of the standard substance must be similar to the vapour pressure of the analytes under same conditions.

Benzaldehyde, which is structurally similar to acetophenone and 1-phenylethanol was applied. The amount of substance is proportional to the peak area of the substance. The constant of proportionality is difficult to determine. To handle this problem a correction factor R_f referred to the internal standard is introduced. The R_f value is a device-, substance- and column-specific constant. With a mixture of 100 µL acetophenone, 100 µL 1-phenylethanol, and 100 µL benzaldehyde in 10 mL of 2-propanol it is calculated from a chromatogram as follows:

$$R_f = \frac{m_x \cdot F_{ist}}{m_{ist} \cdot F_x},$$

with m_x : mass of the analyte

m_{ist} : mass of the internal standard

F_x : peak area of the analyte

F_{ist} : peak area of the internal standard

By repeating the experiment several times it was controlled that the R_f value was constant. With a second mixture of known concentration of acetophenone and

1-phenylethanol including 100 µL of benzaldehyde the R_f value could be verified by the following calculation:

$$m_x = \frac{R_f \cdot m_{ist} \cdot F_x}{F_{ist}}.$$

With the same equation the amount of acetophenone and 1-phenylethanol in a solution of unknown concentration could be calculated after adding 100 µL of benzaldehyde. The conversion of the hydrogenation reactions was determined with the following equations:

$$n(analyte) = \frac{m(analyte)}{M(analyte)}$$

and

$$conversion = \frac{area\ (phenylethanol)}{area\ (phenylethanol) + area\ (acetophenone)} \cdot 100\ \%,$$

with m : mass
M : molar mass.

5.11.1 Determination of the TOF

The turn-over frequency (TOF) of the hydrogenation reactions was calculated:

$$TOF = \frac{n\ (product)}{n\ (catalyst)} \cdot t^{-1},$$

with t : time in h.

6 REFERENCES

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7 SUMMARY

Catalytic hydrogenation of polar double bonds such as C=O or C=N is in demand of fine chemical and pharmaceutical chemistry, especially the asymmetric version of this reaction. Among the diaminedichlorobis(phosphine)ruthenium(II) complexes, there are examples of extraordinary catalytic performance. However, separation of these catalysts from other substrates after hydrogenation still is a time, energy, and chemicals consuming process. Moreover, the complexes might be destroyed during this procedure. Therefore the heterogenisation of these diaminedichlorobis(phosphine)-ruthenium(II) complexes is of great economical interest.

The aim of the present work was the preparation of two new types of interphase catalysts by immobilisation of diaminedichlorobis(phosphine)ruthenium(II) complexes and the investigation of their catalytic behaviour. As a model system the hydrogenation of acetophenone to 1-phenylethanol was employed. The reaction conditions were adapted from similar homogeneous ruthenium complexes (KO^tBu as co-catalyst, 2-propanol as solvent). Both direct and transfer hydrogenation were investigated.

In a first approach a highly crosslinked polyethylene imine resin, a so-called ULTRARESIN was applied as organic polymeric support. A diaminedichlorobis[(methoxyethyl-diphenyl)phosphine]ruthenium(II) and a diaminedichloro[1,3-bis(diphenylphosphino)-propane]ruthenium(II) complex were each successfully anchored to this matrix by coordination to two diamine spacers of different length. The diamine spacers were covalently linked to the resin via an amide bond. With this procedure four new stationary phases were prepared. FT-ATR-IR measurements served for the characterisation of the ULTRARESINS. To indicate the linkage of the complexes ^{31}P NMR spectroscopy was applied. The new interphase catalysts were employed for the catalytic hydrogenation of acetophenone. Their reactivity under H_2 pressure was negligible. The use of “superhydride” as cocatalyst led to a transformation of the stationary phase. Moreover, the superhydride itself converted the acetophenone with good activity. Water as solvent

caused a decomposition of the stationary phase. However, the resulting product that was assumed to be ruthenium metal converted the substrate very slowly.

The performance of the chemically modified ULTRARESINS in transfer hydrogenation was acceptable, but during the harsh conditions the active species on the resins were destroyed. It was not possible to recycle the interphase catalysts.

In a second approach spherical silica particles, so-called Stöber particles with a diametre of 800 nm served as inorganic support. The modification of these non-porous particles only can proceed by application of surface silanol groups. Therefore pure particles were equipped with 3-(2-aminoethyl)aminopropyl spacers in a condensation reaction. This spacer molecule provided a mixed primary-secondary diamine group to which a dichlorobis[methoxyethyl(diphenyl)phosphine]ruthenium(II) complex easily could coordinate. Here advantage was taken from the hemilabile character of the etherphosphine ligands. To determine size, shape, and monodispersity of these Stöber particles light scattering and SEM investigations were applied. Elemental analysis and ^{31}P NMR spectroscpy indicated the anchoring of the ruthenium(II) complex. The spherical particles equipped with a reactive centre were employed as well for direct as for transfer hydrogenation of acetophenone. When first used, the particles converted acetophenone to 100 % to 1-phenylethanol with a maximal TOF of 6 h^{-1}. After recycling or just treating the particles in a Soxhlet extractor they showed reduced catalytic activity. It is assumed that after 20 h the reactive centres on the surface were destroyed. Moreover, the particles themselves were not stable under the conditions applied for hydrogenation. After two consecutive runs under hydrogen pressure in an autoclave they were destroyed, whereas they agglomerated during transfer hydrogenation. Leaching was investigated and could not totally be excluded.

In comparison to the ULTRARESINS and Stöber particles as interphase catalysts sol-gel processed materials, into which a ruthenium complex is incorporated can be applied for catalysis in several consecutive runs without loss of activity and without leaching. In conclusion the sol-gel materials fit the demand for interphase catalysts, that shall combine the advantages of homogeneous and heterogeneous catalysis.

My academic teachers were:

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