Studies towards the Isomerisation of Olefins

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1. Introduction

The way how synthetic organic chemistry is exercised to construct molecules depends of course heavily on the target molecule, but reactions involving C=C π-bonds are almost always present in a multistep synthesis. This can be attributed to their versatile chemistry due to the lower bond energy of a π-bond in comparison with an σ-bond and its ability to coordinate (transition)-metals. Therefore it is not surprising, that a wide variety of synthetically invaluable reactions dealing with π-bonds have been developed. Among theme are many which start from alkenes or produce them. Therefore the formation and manipulation of olefins is of central interest in organic chemistry. Among them are well known reactions like WITTIG-olefinations, olefin metathesis and less common ones like the RAMBERG-BÄCKLUND-olefination and many more, but none of them is able to cover all types of olefins. In certain cases, when classical methods reach their limits, the geometric- and regio-isomerisation of olefins can serve to supplement these methods in order to access otherwise more difficult targets and to make use of a broader array of starting materials.

The isomerisation of olefins was considered for a long time as an undesired side reaction of many catalytic transformations, like the homogeneous and heterogeneous hydrogenation, hydroformylation or metathesis of olefins, which led to more or less useless by-products. It can be however also employed intentionally to affect preparative useful reactions. To accomplish olefin isomerisations in a desirable fashion, it is of course necessary to gain a proper understanding of the operating mechanisms and to use carefully chosen conditions and catalysts. The preparation of several isomerisation catalysts and the exploration of their application is the topic of the present work.

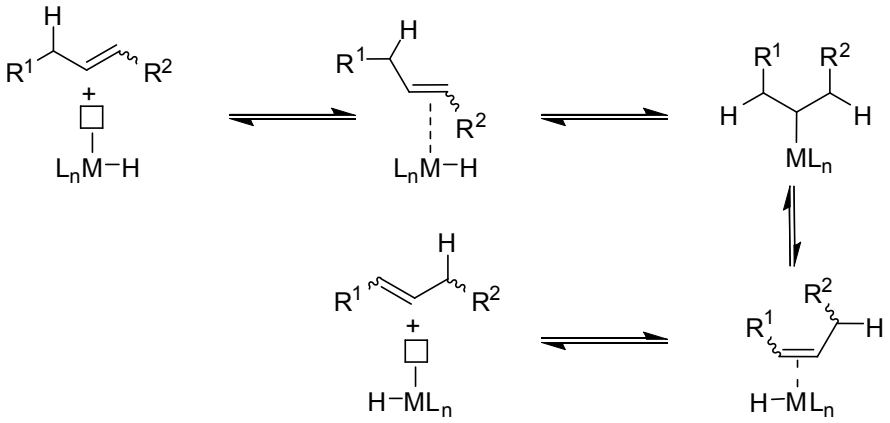
2. General Part

2.1. Isomerisation of Olefins in General

Since a C=C double bond can be defined by its position and geometry relative to the rest of the molecule, these two parameters can be influenced by isomerisation. Therefore both geometric (*E/Z*) isomers as well as regioisomers can be interconverted under properly chosen conditions. To achieve such isomerisations, as one might guess, the π-system of the olefin has to be activated. Different means of doing so have been described in literature, for example with strong acids,[1] bases,[2] radicals,[3] halogens,[4] or UV-irradiation,[5] but this thesis will focus mainly on transition metal catalysed isomerisations. Like for any catalytic process, the catalyst only lowers the activation barrier, but does not influence the equilibrium. Therefore a thermodynamic driving force is required to yield one isomer in excess over the other possible isomers. The following sections will be organized according to the type of isomerisation and the responsible driving force.

2.2. Mechanistic Aspects of Olefin Isomerisation

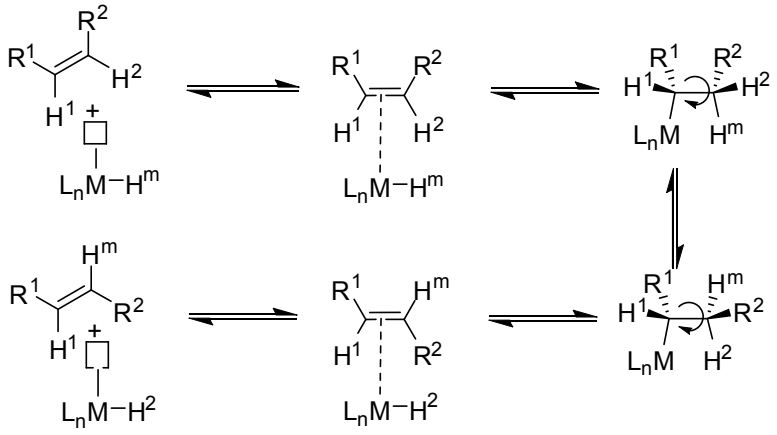
The overwhelming majority of transition metal catalysed olefin isomerisation, as well geometric- as regio-isomerisation, is believed to follow two more or less general mechanisms. These are on the one hand reversible insertion of the olefin into a transition metal-hydrogen bond followed by β-hydrogen elimination and on the other hand reversible oxidative addition of a transition metal into an allylic carbon-hydrogen bond. Of course both pathways have different requirements in terms of the catalyst.



Scheme 1: Isomerisation via insertion and β-hydrogen elimination

In the case of the insertion into a metal-hydrogen bond, an active catalyst needs, in addition to the obvious hydride ligand a vacant coordination site or a weakly bound ligand to generate

one to coordinate the substrate olefin (Scheme 1). After the olefin has coordinated to the metal hydride complex, it has to insert into the M-H bond to yield a σ-alkyl complex, which can freely rotate around the metal carbon bond, to allow β-hydrogen elimination of another hydrogen atom than the initial one. This β-hydrogen elimination produces a metal olefin complex, which can dissociate into the isomerised olefin and the restored catalyst. In the case of geometric isomerisation, the β-hydrogen elimination occurs from the same carbon atom, to which initial hydride has been added, but another hydrogen atom must be available to allow for the *E/Z* isomerisation (Scheme 2).

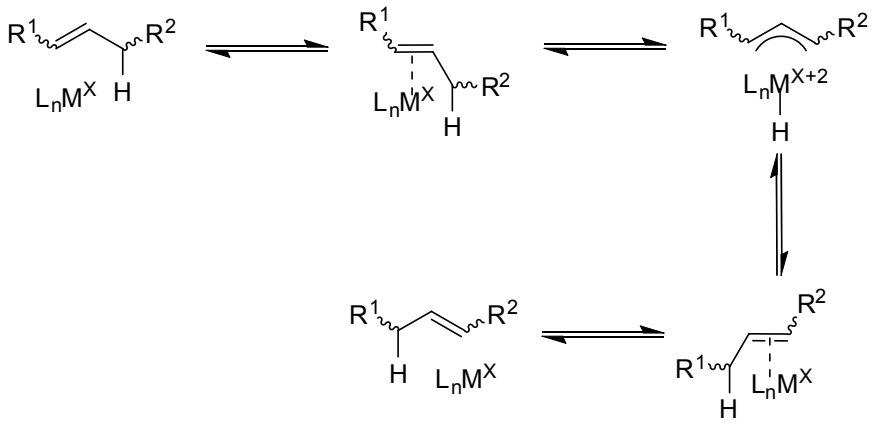


Scheme 2: Geometric isomerisation via transition metal hydride

Therefore it can be concluded, that only alkenes which possess at least one olefinic hydrogen atom can be geometrically isomerised via this mechanism.

Effective catalysts which are suspected to operate via this mechanism contain usually a late transition metal, most often part of the so called platinum group as central atom. Among them Ru, Rh and Pd, the representatives of the second row transition metals are predominant. These metals can form stable, well characterised hydride- and olefin complexes and have proven to catalyse olefin isomerisations, not only by intention but also often as undesired side reaction during homogeneous hydrogenation, hydroformylation or HECK-reaction.

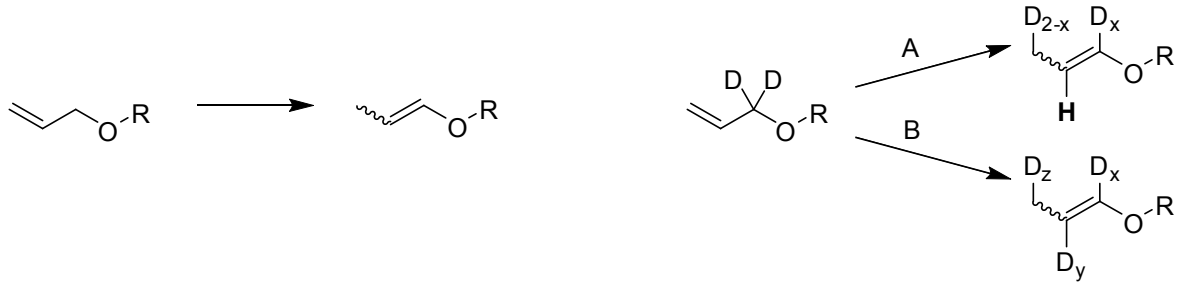
In the case of the second mechanism the substrate olefin coordinates to the central metal, which has to be in a low oxidation stage at first. Then the metal performs an oxidative addition into the allylic C-H bond to produce a η^3-allyl hydrido complex. This complex can later collapse again in a reductive elimination step to restore the catalyst and the isomerised (or unchanged) olefin (Scheme 3).



Scheme 3: Isomerisation via oxidative addition and reductive elimination

For this mechanism to operate, an active catalyst has to meet requirements different than for the first one. It must be able to provide three coordination sites in total to accommodate the intermediary allyl- and hydride ligand and most important, the central metal must be able to conduct a reversible oxidative addition into a C-H bond. This narrows the choice of proper metals down to only very few candidates. This can be rationalised by the higher energy of the σ* antibonding orbital of a C-H bond compared to other C-LG bonds which are more commonly activated in allylic substitution like the TSUJI-TROST reaction. To overcome this difficulty, the metal centre must either show a very low redox potential for the formal two electron oxidation or be able to form very stable and low in energy allyl- and hydride complexes. Two typical examples for these types of catalysts are tricarbonyliron $(CO)_3Fe^0$-fragments representing the strongly reducing metal centre and iridium(I)complexes, which can form quite stable iridium(III)allyl and -hydride complexes.

To distinguish these mechanisms or at least get a hint about the operating mechanism, different labelling experiments have been conducted. The most practical and common possibility to do so is to monitor the fate of the hydrogen atoms involved in the isomerisation step. This is usually done by deuterium labelling and monitored via ^{1}H-NMR or less common ^{2}H-NMR spectroscopy. A typical experiment is e.g. the isomerisation of an 1,1-dideuterioallylether to the corresponding propenylether (Scheme 4).



Scheme 4: Isomerisation of a deuterium-labelled allylether

Two possible findings could either be a clean formal 1,3-shift of the deuterium (path A) or scrambling of the label over all three carbon atoms (path B). The scrambling of path B could be rationalized by an insertion – β-hydrogen elimination mechanism, because the initial hydride can remain on the substrate and the metal has to abstract a deuterium to bring about the isomerisation. The thus newly formed metal-deuteride can again transfer the deuterium to any carbon atom that is part of a double bond via insertion, therefore deuterium will be present in all three positions. The clean 1,3-shift on the other hand can be explained very well by the oxidative addition – reductive elimination mechanism, since in this case C-H bond of C-2 is never affected, but the hydride (or deuteride) of the η^3-allyl intermediate can be transferred only from C-1 to C-3 and *vice versa*.[6,7]

Beside these two mechanisms other mechanisms have been proposed in some cases and will be discussed elsewhere.

It is, however, always important to keep in mind, that these "mechanisms" are only proposals that can be in accordance with experimental results or maybe quantum chemical calculations, but should never be regarded as the absolute truth.

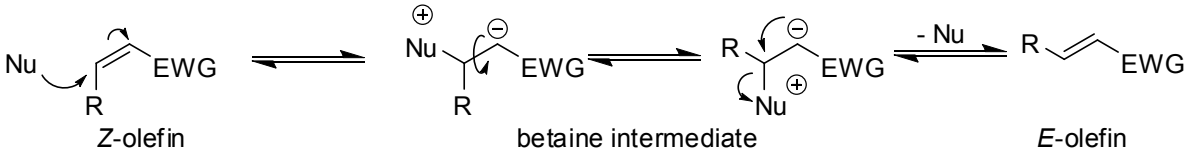
2.3. Geometric Isomerisations

Nowadays there is a plethora of methods available to synthesize alkenes with a defined geometry, often with good to excellent selectivity for the desired geometry.[8] But there are still cases, especially in more complex molecules,[9] where the selectivity of these methods drop below satisfying levels or even the wrong geometric isomer is produced. Furthermore in some cases the course of a multistep synthesis can create the need to invert a double bond geometry.

Different driving forces can operate in *E/Z* isomerisations, the most common one is the thermodynamic preference for the *E* over the *Z* configuration in acyclic olefins due to stereoelectronic reasons. On the other hand in cyclic olefins with a ring size between 8 and 10 ring atoms the *Z* isomer is lower in energy because of the ring strain [10].

Independent of the driving force of the olefin isomerisations, one has to keep in mind, that especially transition metal catalyzed *E/Z* isomerisation is often accompanied by regio isomerisation if the structure of the substrate molecule offers the possibility. To prevent such unproductive side reactions, the desired regioisomers have to be thermodynamically favourable over the others. This feature is often secured by conjugation to a π-system or a heteroatom.

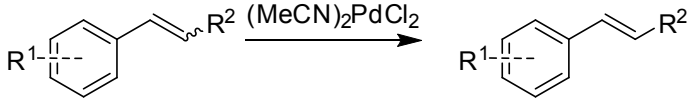
A particularly simple method of achieving this isomerisation to produce the more stable *E*-isomer in case of Michael acceptors is the reversible addition of nucleophiles, to produce betaine intermediates, which can freely rotate and then eliminate the former nucleophile as a leaving group to restore the olefin (Scheme 5).



Scheme 5: Isomerisation via Michael addition and consecutive elimination

The nucleophile is most often an amine like DMAP or DABCO, in fewer cases a phosphine. However this approach is far from general, but works only well for good Michael acceptors with e.g. EWG is –CHO or $–NO_2$, which are not too sterically congested at the β-carbon.

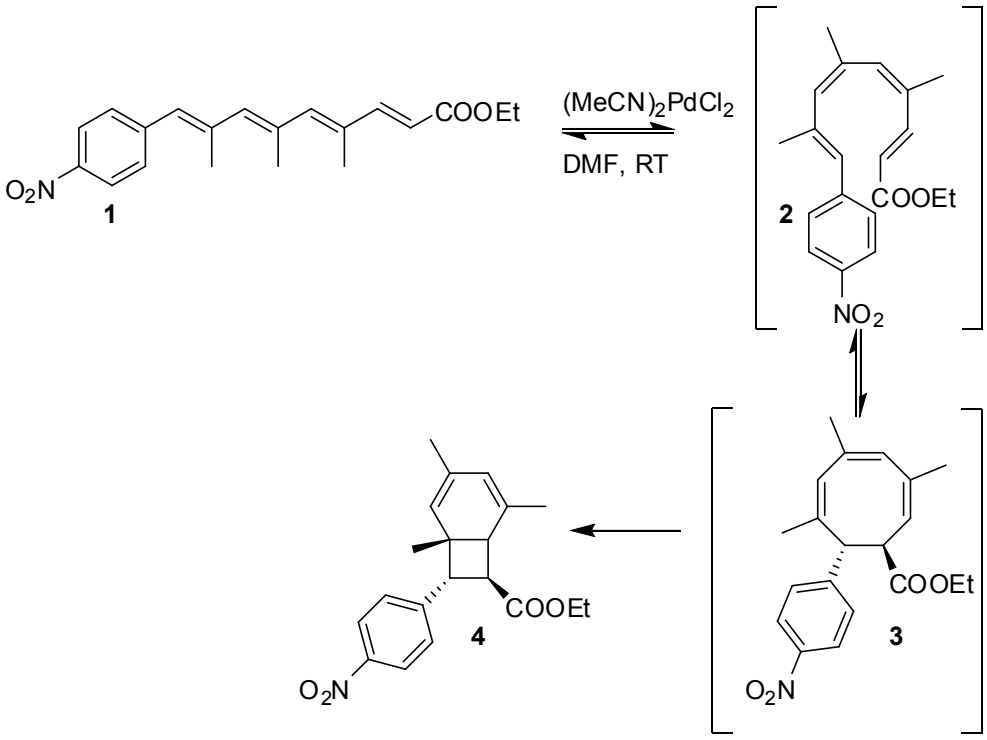
Other methods of broader scope rely on transition metal catalysts, which also accept other conjugated olefins than Michael acceptors. Among them $PdCl_2$ nitrile complexes are worth mentioning because of there availability and convenient use. These catalysts have been used to accomplish the thermodynamically driven *Z* to *E* isomerisation of different aryl conjugated olefins, produced e.g. by WITTIG-olefination.[11] This can be useful since the WITTIG-olefination produces predominantly the *Z* alkene and the SCHLOSSER-modification predominantly the *E* alkene, but both of them often not in perfect isomeric purity (Scheme 6).



Scheme 6: $(MeCN)_2PdCl_2$ catalyzed *Z/E* isomerisation of aryl olefins

By the virtue of this and other olefin isomerisations the isomeric mixture, which might evolve from these olefinations can be converted into the clean *E* isomer with excellent selectivity in many cases.

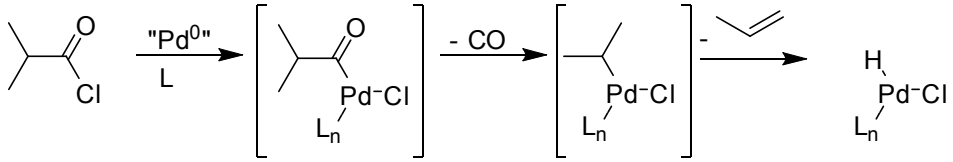
A particularly elegant application of this method has been reported by Baldwin[12,13] in the biomimetic synthesis of SNF4435C 1 and SNF4435D 2, two immunosuppresants isolated from *Steptomyces spectabilis*. $(MeCN)_2PdCl_2$ was used to isomerise the *E,E,E,E*-octatetraene derivative **1** into its *E,Z,Z,E* isomer **2**, which is capable to undergo two consecutive electrocyclic ringclosures to give finally the racemic bicyclic product **4**, via the monocyclic intermediate **3**, in 35 % yield. Since the *E,Z,Z,E* isomer is the only geometrical isomer which can undergo the desired cyclisations, it is selectively removed from the equilibrium to drive the thermodynamically unfavourable *E* to *Z* isomerisation forward (Scheme 7).



Scheme 7: $(MeCN)_2PdCl_2$ catalyzed E/Z isomerisation followed by electrocyclic cyclisations

The actual mechanism of this type of isomerisation has not been elucidated yet, but it seems likely that the $(R\text{-}CN)_2PdCl_2$ precatalyst is reduced to give a Pd-H species *in situ*. This can be supported by the fact, that a catalytically competent species is formed upon treatment of palladium(II)acetate with tributyltinhydride in the presence on triethylamine.[14] On the other hand Pd-stabilized carbocations have been proposed as intermediates.[11]

One more Pd-based catalytic system deserves to be mentioned. It was developed by Skrydstrup et al. to affect ene-yne-coupling in a HECK-like fashion. The precursors are $^tBu_3P$, $Pd(dba)_2$ and ^{i}PrCOCl and they are believed to produce a ligand stabilized palladium-chloride-hydride complex *in situ* via oxidative addition into the C-Cl bond of ^{i}PrCOCl, followed by extrusion of carbon monoxide and β-hydrogen elimination (scheme 8):



Scheme 8: Proposed generation of Skrydstrup's active catalyst

The isomerisation activity of this system was discovered and also systematically explored. It turned out, that facile *Z/E* isomerisation of conjugated olefins could be achieved also that non conjugated olefins migrate into conjugation under the same conditions, *vide infra.*[15]

2.4. Isomerisation into a higher substituted Isomer

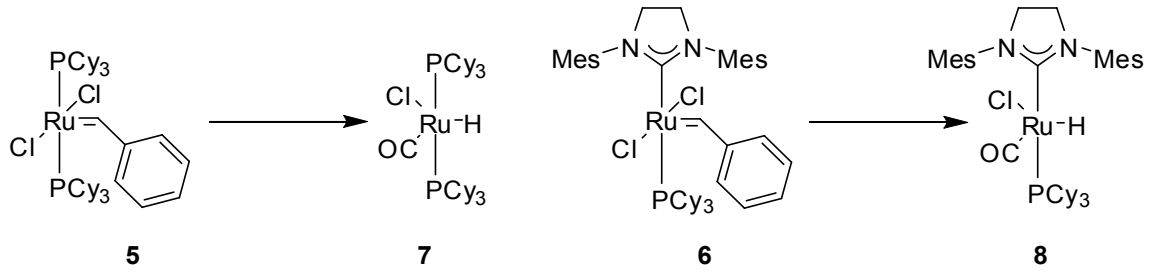
The isomerisation of a terminal olefin to give an internal isomer or in fewer cases the isomerisation of internal olefins to produce their higher substituted counterparts have been known for a long time, but seldom exploited for synthetic purposes. The thermodynamic preference for higher substituted olefins over lower substituted ones can be rationalised by hyperconjugation between the double bond π- and π*-orbitals and the σ and σ*-orbitals of substituents on the allylic carbon atoms. The energy gain due to this hyperconjugation is lower than for "true" conjugation to another sp^2 hybridized carbon atom or heteroatom, but still sufficient to shift the equilibrium in favour of internal higher substituted olefins.

A general trend is that the higher the starting olefin is substituted the slower the conversion will occur. This seems to hold true regardless of the catalyst used or the mechanism that operates, because in any case the olefin needs to coordinate to the metal centre in the first step, but the effect can be more or less pronounced depending on the specific catalyst. This is not necessarily a disadvantage, but can be used to perform only a single isomerisation e.g. of a 1-olefin to a 2-olefin with a catalyst which will not proceed any further due to steric congestion.

Different catalysts have been shown to affect this type of isomerisation. Among them ruthenium- and rhodium-based catalysts are the most prominent ones, but also palladium and iridium-complexes have to be mentioned.

The ruthenium derived catalysts are mostly hydrido-complexes or precatalysts, which can react to catalytically active metal hydrides under the reaction conditions. Some examples of this type of (pre)catalysts are $(Ph_3P)_3RuCl_2$,[16] $(Ph_3P)_3Ru(CO)HCl$,[17] or $(Ph_3P)_3Ru(NO)H$.[18]

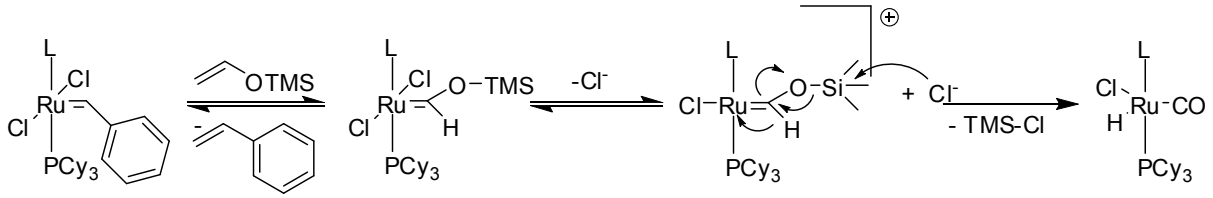
Two more Ru-derived catalysts differ from these simple examples. From the practical point of view catalysts derived from GRUBBS II ruthenium carbene by "thermal degradation" are interesting because of the commercial availability of GRUBBS catalysts and the ease of their preparation and use also for non inorganic or organometallic chemists. The catalytically competent species produced from the originally well defined metathesis catalyst are not fully elucidated and may depend on the reaction conditions (solvent, additives) but it has been shown, that Grubbs I and II catalysts **5** and **6** react/decompose into **7** and **8** respectively in the presence of methanol, ethylvinylether or trimethylsilylvinylether (Scheme 9).[19,20]



5 **7** **6** **8**

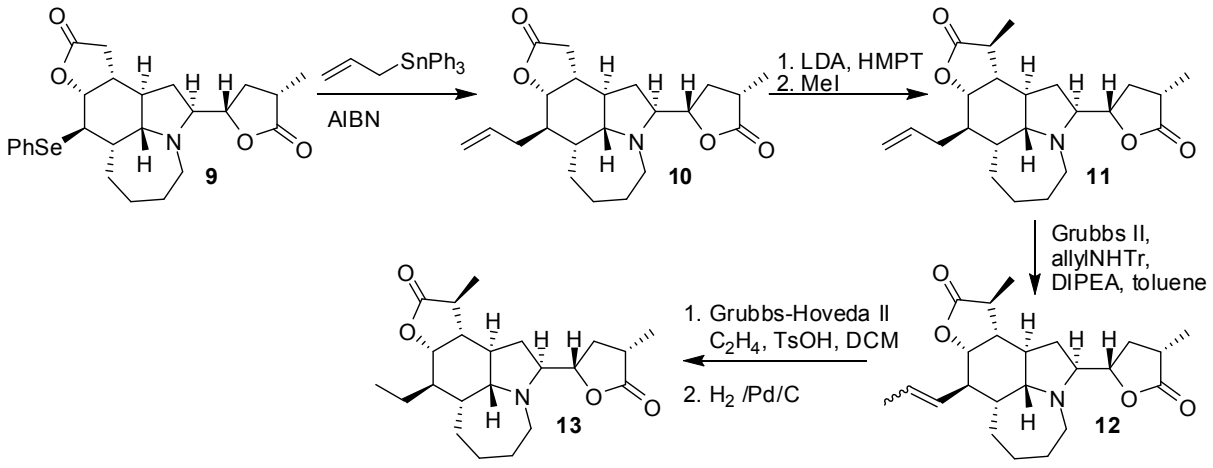
Scheme 9: Conversion of Grubbs I and II catalyst to ruthenium hydride complexes

This decomposition could be rationalised by an α-hydrogen elimination pathway: After initial olefin metathesis to generate a trimethylsilyloxy carbene complex, it might be possible, that a chloride ligand dissociates off to yield a vacant coordination site *cis* to the carbene ligand. This arrangement would allow α-hydrogen elimination, maybe assisted by nucleophilic attack of the chloride at the silicon atom (Scheme 10).



Scheme 10: Possible decomposition mechanism of Grubbs-type catalysts to metal hydride species

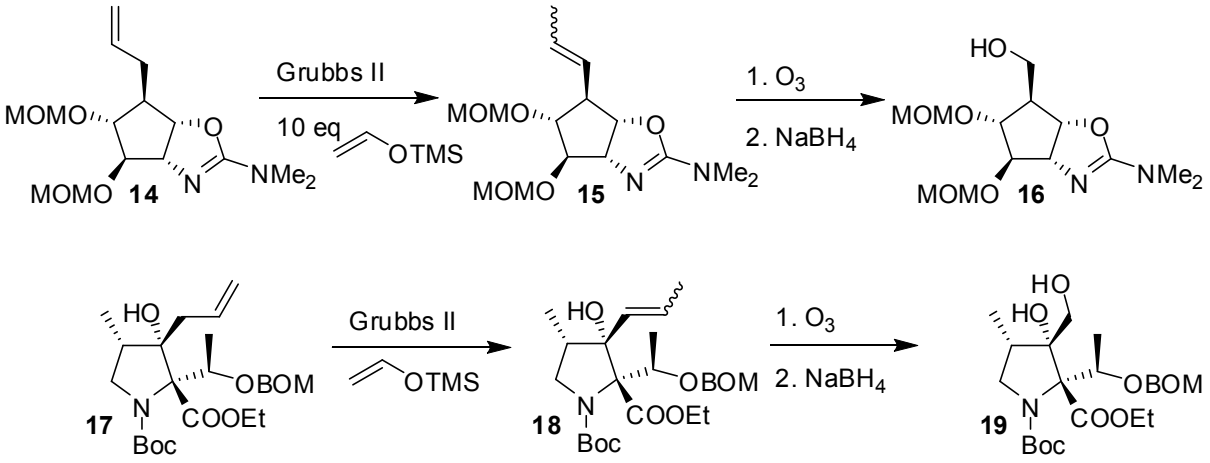
One interesting application of this type of isomerisation is the late stage functionalisation in the synthesis of natural products and complex molecules. An example is the introduction of an ethyl-group in the end of the synthesis of Tuberostemonine by Wipf. This reaction sequence starting from **9** consists of KECK-radical-allylation to produce **10**, isomerisation to the internal olefin **11** and cross metathesis with ethylene to introduce a vinyl in **12** group, which can be further hydrogenated if desired to yield an ethyl-group in the product **13** (Scheme 11) [21].



Scheme 11: Final steps in Wipf's Tuberosteminine synthesis

To achieve the crucial isomerisation step a particular convenient catalytic system, namely Grubbs II catalyst in presence of allyltritylamine was used in toluene. It is very likely, that the Grubbs II catalyst is actually the precursor to the active isomerisation catalyst.

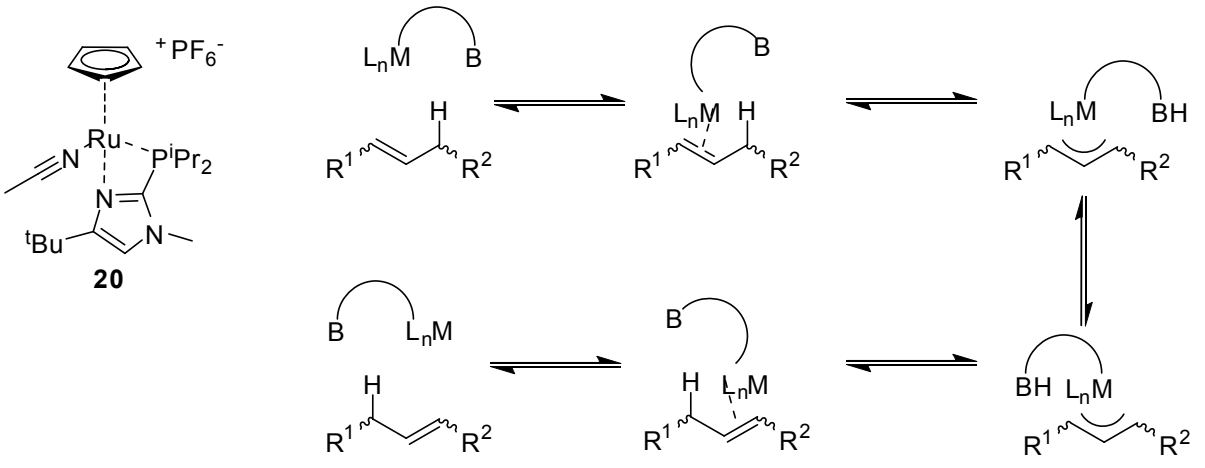
In two somehow similar cases an isomerisation-ozonolysis sequence was applied to convert an allyl- into a hydroxymethyl-group (Scheme 12).[22,23]



Scheme 12: Isomerisation – ozonolysis sequences in two total syntheses

The allyl-substituted starting materials **14** and **17** were isomerised to the corresponding propenyl derivatives **15** and **18**, which were finally converted to the alcohols **16** and **19** via ozonolysis and reductive workup.

The second extraordinary ruthenium-based catalyst **20** was developed by Grotjahn *et al*. It is interesting on the one hand because it is believed to operate via a mechanism strikingly different from all the catalysts mentioned yet and on the other hand it performs very efficiently for multiple consecutive isomerisations of one substrate molecule.[24,25]



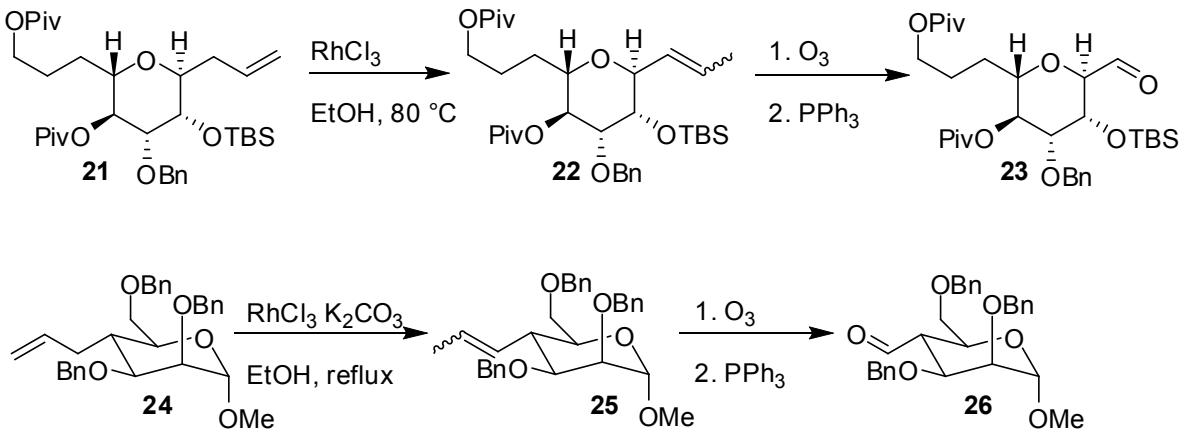
Scheme 13: Grotjahn's catalyst and a generalised metal-assisted deprotonation-reprotonation isomerisation mechanism

The suggested mechanism (Scheme 13) of action starts as usual with the coordination of the olefin to the metal centre, but then a base, which is tethered to the metal deprotonates an allylic hydrogen atom to produce an allyl-metal-complex as intermediate. This deprotonation of an olefin would require very strong bases like e.g. n-BuLi*KO^{t}Bu (SCHLOSSER's base) for the free olefin, but in case of the coordinated olefin the transition metal, in this case a cationic Ru(II) centre, very efficiently withdraws electron density from the π-bond without much back donation, to stabilize the resulting allyl fragment. Therefore a weak amine base like an imidazole derivative is sufficiently basic to affect the deprotonation. Then the allyl-complex can be reprotonated at the other side to restore the catalyst and the isomerised olefin.

In Grotjahn's catalyst a few remarkable features are present, which definitely enhance its activity. At first the precatalyst possesses a very labile acetonitrile ligand, which can be readily replaced by a substrate molecule. Second the whole complex is positively charged, to render it even more electron withdrawing. And last but not least, the weak base is part of a P,N-chelate ligand with a quite small bite angle. This small bite angle facilitates the dissociation of the imidazole part of the ligand, to offer a free coordination site and a base both in proper position to generate the metal-allyl intermediate.

In terms of rhodium-based catalysts for olefin isomerisation mainly two simple but effective catalysts have to be named. The prototype and more or less parent compound of nearly all rhodium derived isomerisation catalysts, hydrated rhodium(III)chloride, is itself precursor to a very active but not well defined catalytic species. The active catalyst is suspected to be a rhodium-hydride that is formed upon e.g. heating of rhodium(III)chloride in an alcoholic solvent and sometimes a base. This catalytic system was first reported by Grieco[26] and offers a couple of advantages. Rhodium(III)chloride hydrate, albeit not cheap, is still one of the more affordable sources of Rh and can be stored without exclusion of air. Furthermore the catalyst operates ligand free and is therefore not too sensitive to steric congestion at the substrate. This allows even isomerisations involving highly substituted and cyclic alkenes which are usually difficult to accomplish with many other catalysts.

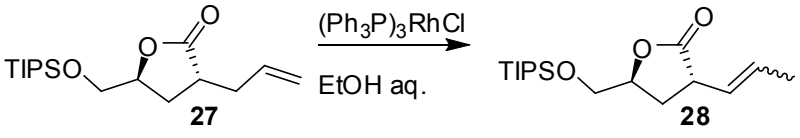
In its preparative applications, however it is often used in similar ways as the previously described Ru based catalysts. Again the two allyl-groups of **21** and **24** are isomerised to propenyl-groups in **22** and **25**, which are then cleaved by ozonolysis to yield the formyl-groups in **23** and **26** (Scheme 14).



Scheme 14: Two isomerisation-ozonolysis sequences

The $RhCl_3$ catalyst system shows, albeit it requires somewhat elevated temperatures, a very broad functional group tolerance, as shown by these examples[27,28]. Two noteworthy features about these isomerisations in alcoholic medium are, that transfer hydrogenation was not reported as a disturbing side reaction and that the isomerisation stops after one carbon atom and does not proceed further to reach the highest possible substituted double bond isomer. For the sake of completeness it has to be mentioned, that comparable isomerisations have been conducted over Rh/C and Rh/Al_2O_3 activated with HCl, albeit slower.[29]

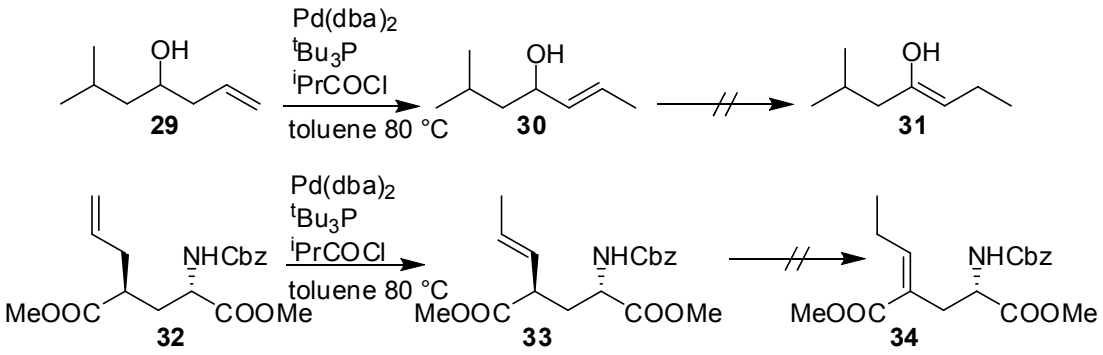
The second important rhodium derived "isomerisation catalyst" to be discussed here is $(Ph_3P)_3RhCl$, better known as WILKINSON'S catalyst. This complex was among the first if not the first practically useful homogeneous hydrogenation catalysts. Isomerisation of terminal to internal olefins was soon recognized as a side reaction during the hydrogenations, but it took longer until this feature of the catalyst was realized to be useful. When it is used in alcoholic solvents, it performs similar to $RhCl_3$ aq., but it can be also employed in aprotic solvent like e.g. THF if it is previously activated with e.g. n-BuLi or silanes.[30-35] This allows circumventing transfer hydrogenation, which has been reported as competing reaction in ethanol. In the given example, the easily accessible α-allyl-lactone **27** was isomerised to the otherwise more difficult to prepare α-propenyl-lactone **28** (Scheme 15).



Scheme 15: $(Ph_3P)_3RhCl$ catalysed isomerisation

Two other important classes of isomerisation (pre)catalysts are Pd(II)- and Ir(I)-complexes. The palladium derived catalysts have been treated shortly in the section about geometric isomerisation. It is not surprising, that the suspected active palladium-hydride species can also

catalyse regio-isomerisation. Again, compared to the already mentioned $PdCl_2$-nitrile complexes, Skrydstrup's catalyst system ($Pd(dba)_2$ + $^tBu_3P$ + ^iPrCOCl, *vide supra*) is particularly interesting. It was shown to selectively isomerise the linear 1-olefins **29** and **32** to the 2-olefins **30** and **33** but does not lead to further internal products **31** and **34**, even in presence of heteroatoms or carbonyl groups, which should offer a substantial energy gain in case of conjugation (scheme 16).[36]

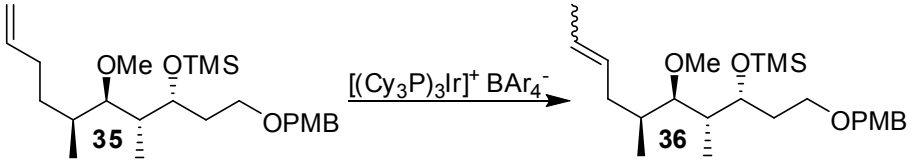


Scheme 16: Selective single double bond isomerisation by Skrydstrup's catalyst system

This selectivity might be a consequence of the bulky $^tBu_3P$ ligand that is employed, but is anyway a valuable complementation to the "exhaustive" isomerisation that can be achieved by different catalysts.

The iridium-based catalysts which are presented here are not among the most active catalysts in comparison, but they deserve to be mentioned because of their selectivity. From the mechanistic point of view, most Ir(I) catalysts are suspected to react via an oxidative addition – reductive elimination pathway, which can be rationalised by the pronounced tendency of coordinativly unsaturated Ir(I) complexes to undergo oxidative addition, which can be further enhanced by the use of rather electron donating ligands, and the relative high stability of iridium-hydrides.[37]

Their synthetic application does not differ very much from the previously discussed catalysts, but they offer some interesting possibilities.

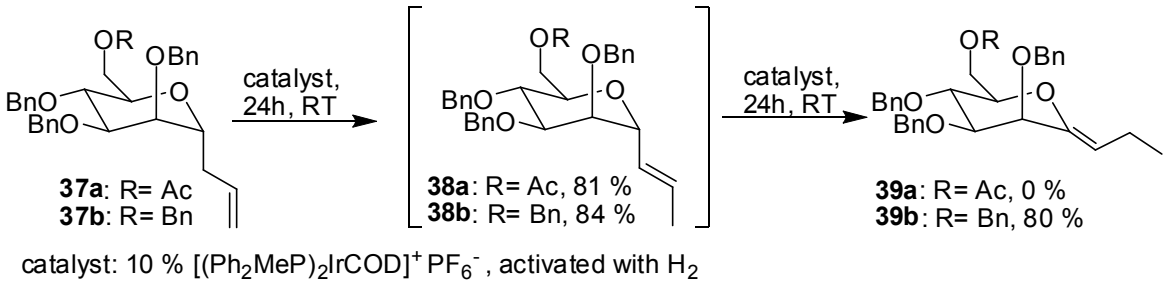


Scheme 17: Isomerisation by a cationic iridium complex

The cationic iridium catalyst is able to affect a selective double bond migration of **35** over only one position to **36** and stops afterwards (Scheme 17).[38] This fact can be explained by

the bulkiness of the ligands similarly as for Skrydstrup's catalyst, but this Ir-complex is in contrast well defined and probably even air stable, two advantages which definitely facilitate reproducible preparative work.

Even more fascinating, an example has been published how remote protecting groups can influence the extent of the double bond migration:



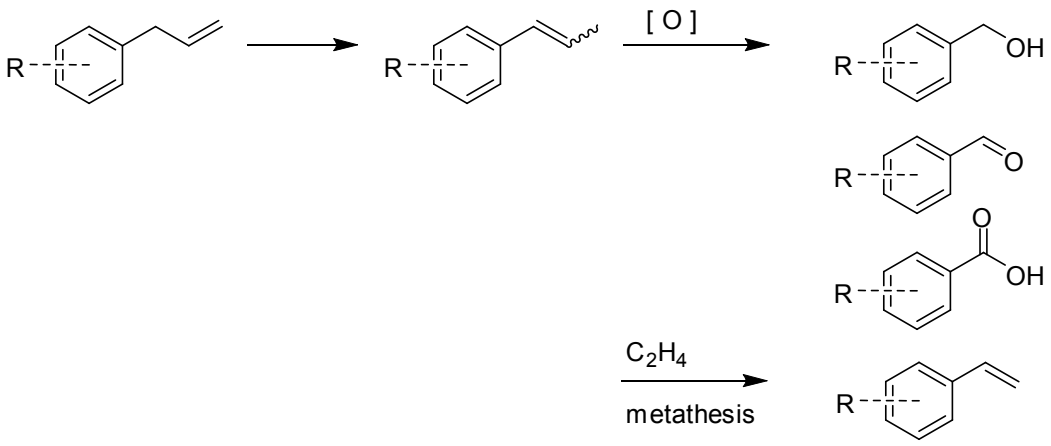
Scheme 18: Ir catalysed isomerisation in dependence of the protecting group

The terminal double bond of the 1-α-allyl mannose derivatives **37a** and **37b** can be shifted to give the 2-olefin **38a** and **38b** regardless of the 6-*O*-protecting group in 24 h, but if the reaction time is prolonged, it depends on this protecting group, whether the isomerisation proceeds further to the corresponding *exo*-glycal or not. Only the 6-*O*-benzyl derivative **38b** is further converted to **39b**, whereas **39a** is not formed (Scheme 18).[39]

The activation of the precatalyst with hydrogen in this example might lead to the impression that an iridium-hydride species could be the actually active catalyst, but it is most likely that the only purpose of this pre-treatment is to remove the COD ligand to generate the required coordination sites.

2.5. Isomerisation into π-Conjugation with Arenes

The migration of isolated olefins into conjugation with arenes or heteroarenes is one idealized application for isomerisation catalysts. The energy gain of conjugation is usually big enough to shift the equilibrium completely to the side of the products. Furthermore many aromatic substrates and the corresponding products are chemically sufficiently stable, that side reactions due to the catalyst are rare. An important practical application of this type of isomerisation is the processing of essential oils. Their main constituents are often substituted derivatives of allylbenzene, which present proper starting materials for isomerisation. The product propenylbenzene derivatives on the other hand are often useful intermediates for further syntheses. Before the advent of transition metal catalysis, the same transformations e.g. from 2-hydroxyallylbenzene to 2-hydroxypropenylbenzene have been conducted with strong base at high temperatures.[40]

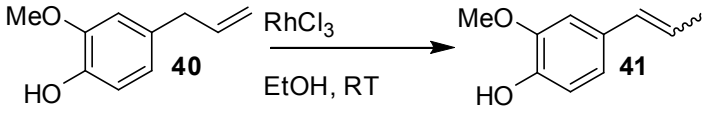


Scheme 19: Isomerisation of allylbenzenes and further reactions of the products

The propenylbenzene derivatives can be further converted to e.g. benzylic alcohols, aromatic aldehydes, carboxylic acids or styrenes with substitution patterns which might be difficult to obtain otherwise (Scheme 19).[41]

In terms of catalysts, there is not much difference to those mentioned in the previous section, but in some instances more forcing reaction conditions can be employed due to more robust starting materials and products. So again the "usual suspects", ruthenium-, rhodium-, palladium- and iridium-complexes are the most important catalysts for these transformations.

An especially economic example for an isomerisation of this type has been reported as early as 1977. The complete conversion of eugenol (**40**) to isoeugenol (**41**) was accomplished on multigram scale with only 0.016 % of $RhCl_3$ in ethanol at ambient temperature in 24 h (Scheme 20) [42]:

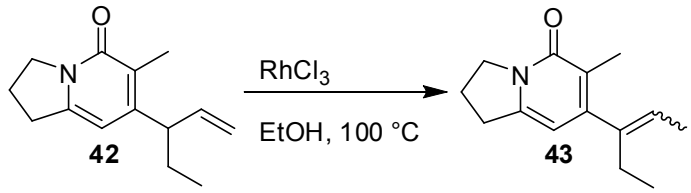


Scheme 20: Isomerisation of eugenol to isoeugenol under rhodium catalysis

Comparable efficient palladium- and ruthenium-catalysed procedures that uses $[^tBu_3PPdBr]_2$ and $(Ph_3P)_3RuCl_2$ as catalyst and a catalyst loading of 0.05 % and 0.077 % respectively were developed later. These reactions reach completion in toluene at 50 °C after 2 h and in refluxing ethanol after 3 h.[43, 44]

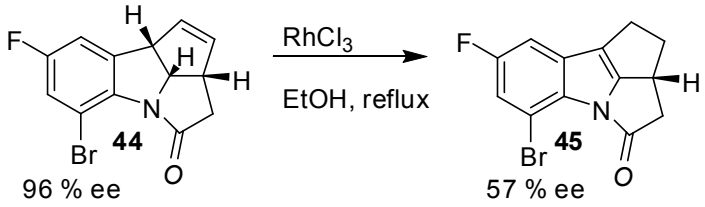
Also Grubbs II catalyst that has been "thermally degraded" (*vide supra*) performs well in similar reactions[45] and a polymer-supported Ir(I) catalyst has been reported to affect these type of transformations cleanly in quantitative yield.[46]

The isomerisation towards heteroarenes works in many cases equally well, as shown in the synthesis of mappicine ketone.[47] The terminal olefin **42** was isomerised cleanly to the conjugated internal olefin **43** (Scheme 21).



Scheme 21: $RhCl_3$ catalysed isomerisation into conjugation with a pyridone

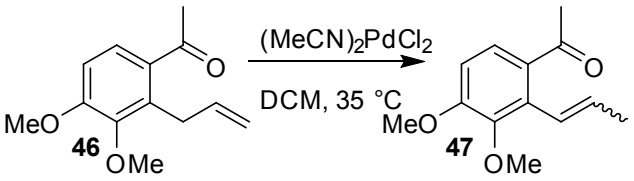
Another, sterically more challenging example for the high efficiency of $RhCl_3$ to promote isomerisations is the following transformation:



Scheme 22: $RhCl_3$ catalysed isomerisation- aromatisation

This remarkable isomerisation shows the ability of $RhCl_3$ to move the double bond of **44** over two positions in this highly rigid tetracyclic framework to yield the indole-derivative **45**. Unfortunately this reaction was accompanied by an unacceptable degree of racemisation and was therefore rejected in favour of a two step hydrogenation – oxidation/aromatisation sequence with virtually no racemisation.[48]

Finally also the $(MeCN)_2PdCl_2$ catalyst has been used to convert allylbenzene-derivative **46** into the corresponding propenylbenzene derivatives **47** (Scheme 23).[49]



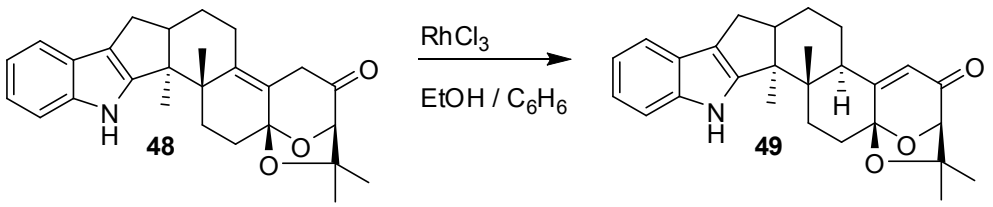
Scheme 23: $(MeCN)_2PdCl_2$ catalysed isomerisation of an allylbenzene derivative

2.6. Isomerisation into π-Conjugation with an EWG

The isomerisation of double bonds towards electron withdrawing groups offers a high degree of energetic stabilisation due to conjugation of the populated π-orbital with a low lying empty orbital of the EWG. However, this empty MO also renders most EWGs more or less electrophilic and susceptible for reductions. Therefore these isomerisations are somewhat more difficult to accomplish cleanly without side reactions compared to isomerisation into conjugation with an arene. For example ruthenium-hydrides show in some cases, depending

on the ligand sphere, pronounced complex-hydride-like and therefore reducing behaviour (see NOYORI reduction/hydrogenation). Because of these reasons, mainly isomerisations in contact with esters and ketones, which represent less reactive electrophiles compared with e.g. aldehydes and nitro compounds, have been described. Again $RhCl_3$ is the most popular catalyst for these transformations.

One elegant application of this reaction is the final step in A. B. Smith's total synthesis of Paspalicine:



Scheme 24: isomerisation of the β-γ-unsaturated isomer to Paspalicine

In the penultimate step, a PFITZNER-MOFFATT oxidation, a mixture of Paspalicine **49** and its β,γ-unsaturated isomer **48** were produced in an unfavourable ratio of only 1:5. Fortunately the double bond isomer could also be converted into the desired product **49** upon treatment with rhodium(III)chloride in an ethanol/benzene mixture (Scheme 24).[50] Similar double bond migrations over one position are also often affected by bases, e.g. during OPPENAUER-oxidation,[51] but such conditions might also cause epimerisations or other deleterious side reactions.

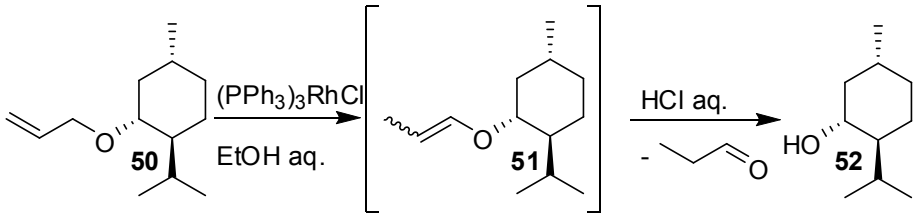
2.7. Isomerisation into π-Conjugation with a Heteroatom

The conjugation of a C=C double bond to a heteroatom, like it is present for instance in an enol ether of an enamine, offers a substantial energy gain in comparison to the isolated olefin. This effect originates, in contrast to the previously discussed conjugation to an EWG, from the binding interaction between the heteroatoms nonbonding lonepairs with the empty π*-antibonding orbital of the olefin. Of course this explanation works only for heteroatoms that are located on the right side of carbon in the periodic table and possess lonepairs. However the main focus of this section will be the isomerisation of allylether, allylamines and allylsulfides, therefore this criterion is fulfilled.

The use of allylethers as protecting group for alcohols, especially in glycol-chemistry, is very feasible and wide spread. Allylethers are easy to introduce via WILLIAMSON-etherification and are stable to alkaline and mildly acidic conditions. To cleave off allylethers, different procedures have been described.[52] The earliest way to do so was to convert the allylether into a propenylether under sometimes harsh alkaline conditions, followed by acidic hydrolysis thereof. Such a sequence is of course only suitable for sufficiently robust substrates and

products. A complementation to the acidic hydrolysis is the ozonolysis of the intermediate propenylether to form a formate ester, which is susceptible for alkaline hydrolysis.[53] A different approach to the cleavage of allylethers is to oxidise it with selenium dioxide to an acrolein hemiacetal, which is very labile towards hydrolysis.[54]

A milder alternative to these protocols based on rhodium catalysed isomerisation of the allyl- to a propenylether was described by E. J. Corey. Allyl menthyl ether (**50**) was isomerised to menthyl propenyl ether (**51**), which is susceptible for acidic hydrolysis to yield menthol (**52**) (Scheme 25).[55]



Scheme 25: Cleavage of allylmenthylether via isomerisation and hydrolysis

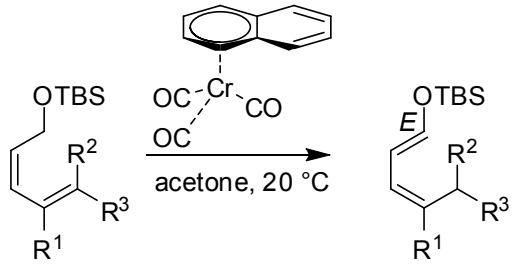
Similar procedures have been further developed via pre-activation of the catalyst with n-BuLi to conduct the first step of the reaction in an aprotic medium and suppress transfer hydrogenation from the alcoholic solvent.[32-35,56-58]

Also Ir-based catalysts, especially $[(Ph_2MeP)_2IrCOD]^+ PF_6^-$, have been employed to achieve similar isomerisations of allyl- to propenylethers. The resulting enolethers can also be cleaved with other electrophiles than H^+ if acidic or protic conditions have to be avoided. For example NIS and Hg^{2+} salts work well for this purpose.[59-61]

It has to be mentioned at this point, that if stereochemistry of the enolethers produced via isomerisation is an issue, suitable catalysts are available to generate the *E* as well as the *Z* isomer. The already described Ir catalyst $[(Ph_2MeP)_2IrCOD]^+ PF_6^-$affords usually good to excellent *E* selectivity, whereas DPPB-$NiCl_2$ activated with $LiEt_3BH$ leads to almost perfect *Z* selectivity in many cases.[62-65] Such enolethers with well defined stereochemistry can participate in e.g. CLAISEN rearrangements with a very predictable stereochemical outcome.

Similarly silylenolethers can be prepared from their allylic isomers. These silylenolethers with a defined geometry are sometimes difficult to produce by conventional routes, or require at least rigorously anhydrous condition, strong bases and toxic additives like HMPT during their synthesis. On the other hand, they are highly valuable intermediates in organic synthesis, they can be used e.g. as precursors to enolates, in REETZ-alkylation or MUKAIYAMA-aldol reaction to name a few applications.

A special example for the isomerisation of allylethers is the transformation of 1-(silyloxy)methylbutadiene derivatives into their isomeric silyldienolethers:



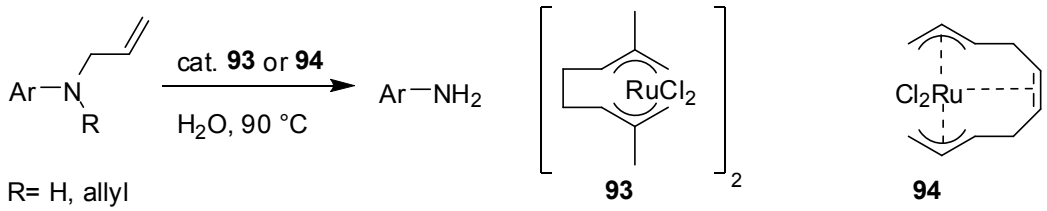
Scheme 26: Stereoselective isomerisation of 1-(siloxymethyl)butadiene derivatives

This interesting reaction occurs in presence of 20 % $NpHCr(CO)_3$ in acetone with complete stereoselectivity in favour of the *E* isomer (Scheme 26). This selectivity is attributed to a metal assisted sigmatropic 1,5-H shift, that should proceed through a highly ordered transition state.[62,66,67] The produced silyldienolethers are useful dienes for various DIELS-ALDER reactions.

The chemistry stays quite similar, when the heteroatom changes from oxygen to nitrogen. Allylamines can be isomerised to yield enamines analogously to allylethers. Somewhat different catalysts can be used, for instance cationic Rh(I)-complexes[68,69] have found broad application in this area and to a lesser extent also Co(I)[70] and Ti(IV)[71] catalysts are used, but also the common catalysts like WILKINSON'S catalyst or thermally treated Grubbs II catalyst were used with success.[72,73] This reaction can be used to deprotect allylamines, but also to generate enamines which are excellent nucleophiles and useful intermediates for further reactions.

The allyl-group is probably not the most common nitrogen protecting group compared to Boc, Cbz etc., but it can be cleverly employed to achieve orthogonal protection/deprotection conditions. For the sake of completeness, it is necessary to mention, that isomerisation is not the only feasible method to cleave *N*-allylgroups, but Pd-catalysed TSUJI-reduction with e.g. Bu_3SnH or TSUJI-TROST allylation of some other nucleophile also offers a reliable alternative. Their disadvantages are the toxicity and stench of the required organotin reagents as well as the necessary removal the unavoidable by-products.

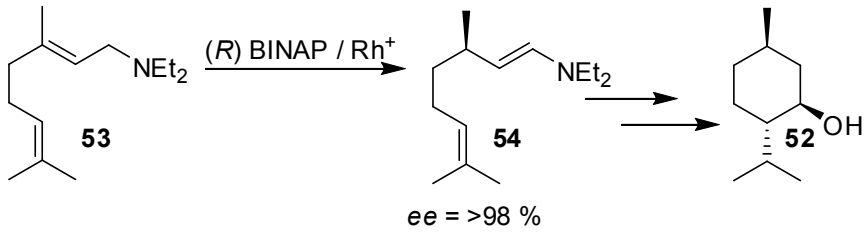
In terms of isomerisation, besides the "usual suspects", some interesting catalysts have been developed (Scheme 27).



Scheme 27: One-pot isomerisation-hydrolysis sequence of mono- and diallylamines

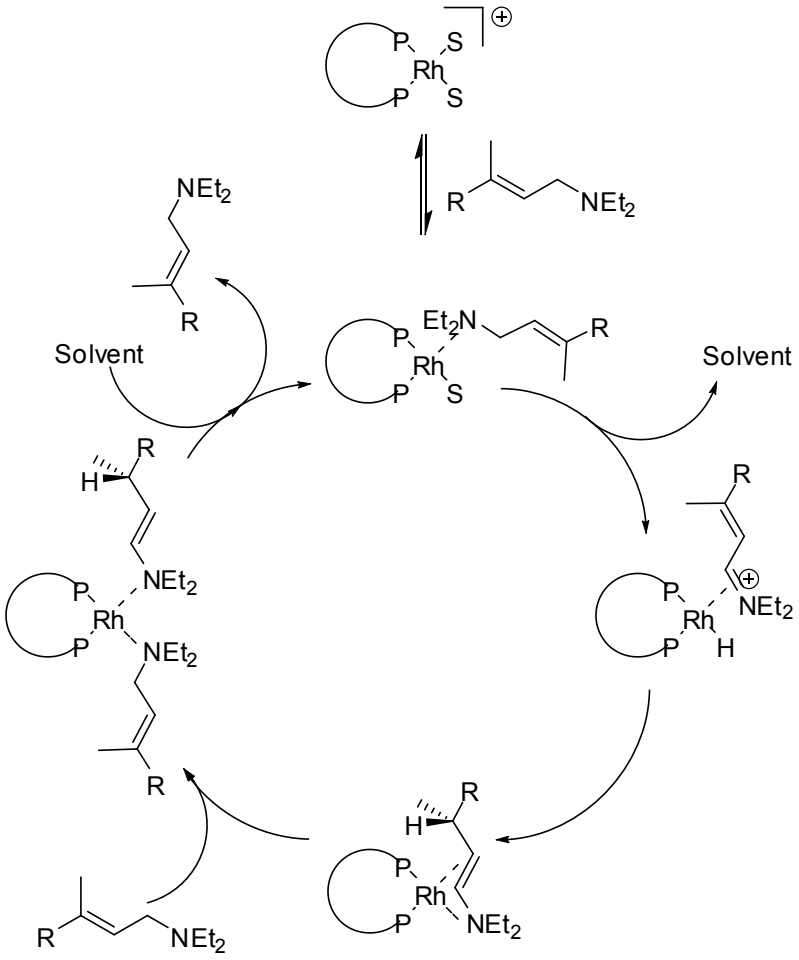
Mono- and diallylamines can be isomerised and the resulting enamines can be hydrolysed in a one-pot sequence catalysed by these Ru(IV) complexes in water. This procedure offers close to quantitative yields of the deprotected products and very environmentally benign reaction conditions.[74]

Another entirely different but very important application of the isomerisation of allyamines belongs to the realm of asymmetric synthesis. The BINAP-Rh(I) catalysed asymmetric isomerisation of prochiral allylamines to enantioenriched enamines is a very well established method to create a stereogenic centre. The most famous application of this atom economic and highly efficient reaction is probably the synthesis of almost optically pure (>98 % *ee*) citronellal diethyl enamine (**54**) from diethylgeranylamine (**53**). This transformation is the key step in the industrial production of several monoterpenes, of which menthol (**52**) is the most important (Scheme 28).



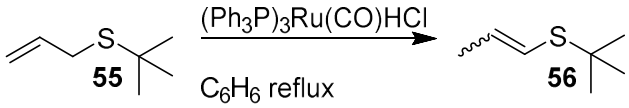
Scheme 28: Asymmetric isomerisation of diethylgeranylamine to citronellal enamine

The mechanism of this highly enantioselective isomerisation is believed to start, after coordination of the nitrogen to the Rh(I) centre, with a β-hydrogen elimination to yield a rhodium-hydride intermediate to which the newly formed iminium is still coordinated. Now the stereogenic centre is set by a suprafacial transfer of the hydride to the electrophilically activated prochiral β-carbon atom. After this crucial step, another fresh allylamine molecule coordinated to the rhodium centre and the product enamine gets displaced by a solvent molecule (Scheme 29).[71,75]



Scheme 29: Proposed mechanism of the crucial asymmetric isomerisation step

Also allylsulfides have been isomerised via transition metal catalysis to their corresponding vinylsulfides, but to considerable lesser extent than allylethers or allylamines. This fact can be attributed to the good coordinating properties of organic sulfides, which might cause inactivation of transition metal catalysts. Such deleterious catalyst poisoning can be overcome by employing allylsulfides with a very bulky residue like ^{t}butyl or trityl located on the sulphur atom to suppress coordination. In fact the isomerisation of allyl^{t}butylsulfide (**55**) to propenyl sulfide **56** can be conducted without difficulties with 2 % of $(Ph_3P)_3Ru(CO)HCl$ (Scheme 30).[76]



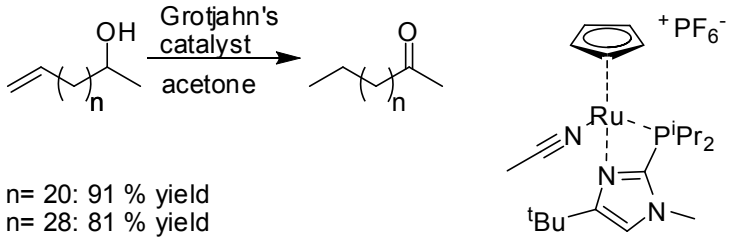
Scheme 30: Ruthenium catalysed isomerisation of allyl^{t}butylsulfide

The resulting vinylsulfides can be further used e.g. as electrophiles in iron-catalysed cross-coupling reactions.[77]

2.8. Isomerisation driven by a consecutive reaction

Until now, only thermodynamically favoured isomerisation reactions have been reviewed, but also energetically neutral or even counter thermodynamic isomerisations can be performed, if they are coupled to consecutive reactions, that have a sufficiently high negative ΔG to provide the required driving force. Among them keto-enol tautomerism, hydroformylation, hydroboration and hydrosilylation will be discussed.

It is well known, that the keto-form of carbonyl compounds is substantially lower in energy than the corresponding enol-form and is therefore orders of magnitude more abundant in equilibrium. Thus it is not surprising, that a once formed enol will predominantly tautomerise into its keto-form and will not be available for any further isomerisation. This simple concept was impressively demonstrated by Grotjahn *et al*. (scheme 31):

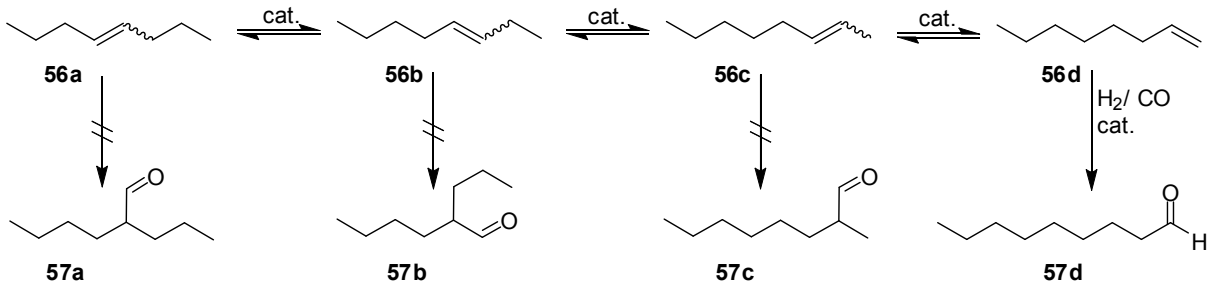


Scheme 31: Multiple isomerisations along an aliphatic chain towards an alcohol function

The terminal double bond could be shifted all the way towards the hydroxyl group to produce an enol intermediate and the corresponding ketone in the end. Though this type of transformation would be probably easier more productive to achieve in a two step procedure consisting of hydrogenation and separate oxidation, this example definitely highlights the power of this well designed catalyst.[24,25]

Another, more practically important, application of the same principle is a very sophisticated hydroformylation procedure. It was discovered quite early, that hydroformylation of terminal olefins was always accompanied by isomerisation to their internal counterparts, which gave rise to *i*-aldehydes instead of the desired *n*-aldehydes. This side reaction was considered deleterious for a long time and much effort was put into ligand- and catalyst design to suppress it. However recently the situation changed, and by the virtue of new catalyst systems it became possible to convert the drawback of undesired isomerisation into a valuable advantage. With catalysts that promote both the isomerisation as well as the hydroformylation reaction, but are selective enough to convert only terminal olefins into aldehydes, these can be removed from the mixture to shift the equilibrium in their favour. In the given example the

isomeric octenes **57a-c** are interconverted, but only 1-octene (**56d**) is further converted to n-nonanal (**57d**), none of the iso-aldehydes **57a-c** is formed in substantial amounts (Scheme 32).



Scheme 32: Selective hydroformylation of 1-octene out of the equilibrium

This does not only avoid undesired by-products, but allows also to feed the reaction with a technical mixture of regio-isomeric olefins instead of a more expensive pure starting material.[78-80]

The improvements in cross-coupling reactions, to accept sp^3-hybridized nucleophiles created the demand to synthesize a variety of alkylboranes or -boronates and alkylsilanes for SUZUKI- and HIYAMA-DENMARK coupling respectively. Two quite feasible and atom economic ways to do so are hydroboration and hydrosilylation. In contrast to hydroboration, which also works uncatalysed, hydrosilylation of olefins does not proceed without catalysis. Both reactions have been involved with many different catalysts transition metal hydride species, which are often also active in olefin isomerisation reactions. Again, similar to the situation in the case of hydroformylation, this side reaction was turned from a disadvantage into a benefit. It allows analogously to convert internal olefins or mixtures of regio isomers of olefins into the valuable terminal products [81, 82].

3. Scientific Task

The task of the present work was to develop effective catalysts for the (regio)-isomerisation of olefins and also to establish preparative useful applications for them. The interest in this type of catalysis came mainly from its beneficial features like excellent atom economy and the possibility to conduct it without additional required reagents. Such features seemed highly desirable in the context of "green chemistry" and the development of environmentally benign reactions. These virtues have been demonstrated in a couple of sophisticated syntheses like e.g. the previously mentioned Takasago-menthol-process. As beautifully illustrated by this example, all carbon atoms of two equivalents of isoprene are conserved and transformed in a concise sequence into highly enantioenriched citronellal, which can be further converted to menthol. As proven by such great showcases, it is possible, in certain cases, to circumvent the use of reagents in stoichiometric quantities by the prudent employment of catalysed (olefin)-isomerisation.

Furthermore, the chance of coupling it with other catalytic transformations seemed attractive. By such means, it might become possible to broaden the applications of unsaturated renewable resources like e.g. oleic acid derivatives. These could be eventually transformed into useful bifunctional building blocks via double bond migration and selective ω-functionalisation.

Under these aspects it appeared promising to investigate this type of reaction.

4. Results and Discussion

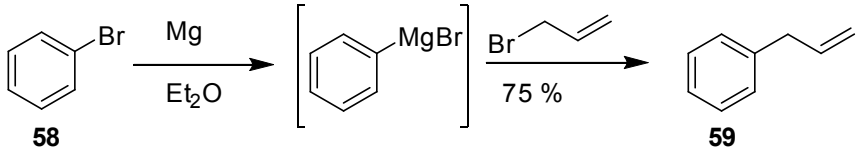
4.1. Concept

The isomerisation of olefins via the transition metal hydride insertion-β-hydrogen elimination mechanism seemed more promising in terms of potentially active catalysts systems than the η^3-allyl-hydride mechanism. This preference was based on the knowledge, that almost all transition metals form hydride complexes, which might be more or less suitable as isomerisation catalysts, but on the other hand only few examples for oxidative addition of transition metals into, albeit allylic, C-H bonds are known. Furthermore, the catalysts, which are believed to operate via such a mechanism, are mainly iridium based, which is a rare and precious metal. Therefore the following work was mainly focussed on hydrido-complexes of ruthenium, which is not cheap, but affordable in comparison to iridium, and has been shown to give rise to active catalyst for olefin isomerisation.

4.2. Preparative Work

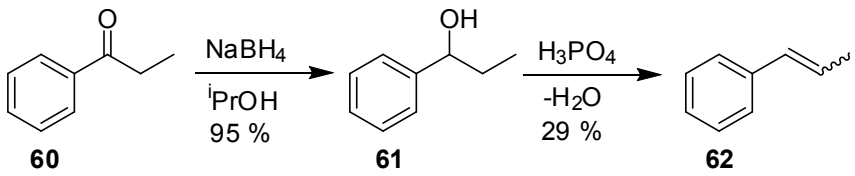
4.2.1. Test system

To test the different catalysts, allylbenzene (**59**) was chosen as substrate. It is easily prepared from bromobenzene (**58**) via uncatalysed GRIGNARD-coupling with allylbromide (Scheme 33), and the reaction to its conjugated isomerisation products *E*- and *Z*-propenylbenzene can be conveniently monitored via GC-MS.



Scheme 33: Synthesis of allylbenzene

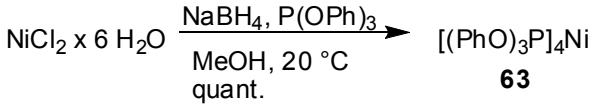
The product of the isomerisation reaction propenylbenzene was prepared as reference material from propiophenone (**60**) via reduction with sodium borohydride to the corresponding benzylic alcohol **61**, followed by acidic dehydration to yield predominantly *E*-propenylbenzene (**62**) (Scheme 34).



Scheme 34: Synthesis of propenylbenzene from propiophenone

4.2.2. Nickel-Hydrides

Several catalysts for the isomerisation of olefins which are based on nickel are known, a few of them have been previously reviewed. Those were derived from Ni(II)precursors via reduction with a complex hydride like e.g. super-hydride $LiB(Et)_3H$, *vide supra*. There is a second type of catalytically active nickel hydrides, which is accessible via protonation of Ni(0)complexes at the metal centre with a strong acid to give formally cationic Ni(II)hydrides. The Ni(0)precursors require ligands with pronounced π-acceptor properties like phosphites to stabilize the low-valent nickel centre. The catalytic properties of such complexes like $[(MeO)_3P]_4Ni\text{-}H^+$ and $[(EtO)_3P]_4Ni\text{-}H^+$ are known for a long time and well documented.[83] However these complexes are usually prepared via reduction of an Ni(II)salt by a slight excess of trimethyl- or triethylphosphite as reducing agent in the presence of a base in an alcoholic solvent. This route is sensitive to the exact stoichiometry and rate of the addition of the reagents and the resulting products are somewhat airsensitve. On the other hand the triphenylphosphite-analogue **63** can be prepared much easier by the reduction of a Ni(II)salt in the presence of $P(OPh)_3$ by $NaBH_4$ (Scheme 35).[84]



Scheme 35: Synthesis of tetrakis(triphenylphosphite)nickel

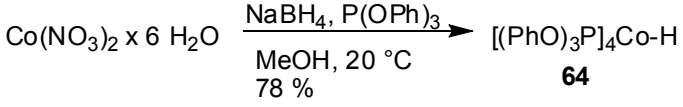
This complex also showed activity for the isomerisation of allylbenzene to propenylbenzene in the presence of an equimolar amount of sulphuric acid in $CHCl_3$ at 20 °C (Table 1).

Table 1: Isomerisation of allylbenzene at 20 °C in the presence of 2 % $[(PhO)_3P]_4Ni/H_2SO_4$ in $CHCl_3$.

TIME [MIN]	ALLYLBENZENE [%]	*Z*-PROPENYLBENZENE [%]	*E*-PROPENYLBENZENE [%]
60	**75.9**	**6.5**	**17.6**
120	**32.9**	**14.5**	**52.6**
180	**16.3**	**17.3**	**66.4**

4.2.3. Cobalt-Hydrides

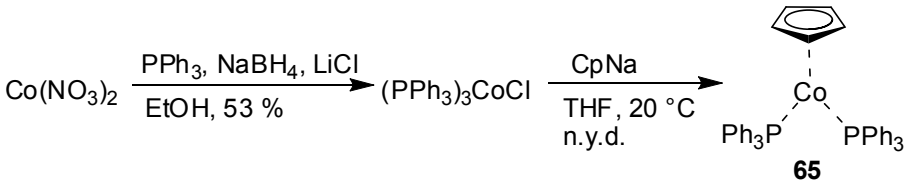
Encouraged by the catalytic activity of $[(PhO)_3P]_4Ni\text{-}H^+$, the isoelectronic complex $[(PhO)_3P]_4Co\text{-}H$ (**64**) was prepared (Scheme 36).[85]



Scheme 36: Synthesis of tetrakis(triphenylphosphite)cobalt(I)hydride

Unfortunately this complex showed no catalytic activity, in contrast to the also isoelectronic $(CO)_4Co\text{-}H$, which is, albeit volatile and toxic, a surprisingly simple example for a catalyst, that is able to promote olefin isomerisation as well as selective hydrosilylation of terminal olefins.[86]

Then also $CpCo(PPh_3)_2$ (**65**) was prepared in the hope, that it could be protonated analogous to $[(PhO)_3P]_4Ni$ at the metal centre, a reaction which is known in the case of its trimethylphosphine analogue $CpCo(PMe_3)_2$.[87] It was prepared in a two step sequence from $Co(NO_3)_2$ via $(PPh_3)_3CoCl$ (Scheme 37).[88]

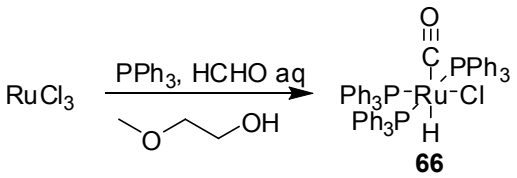


Scheme 37: Synthesis of $CpCo(PPh_3)_2$

However the complex showed no catalytic activity towards allylbenzene in the presence of either H_2SO_4 or TFA.

4.2.4. Ruthenium-Hydrides

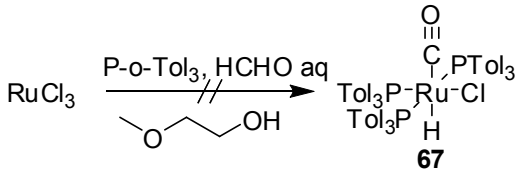
The first Ru-based complex that was prepared was tris(triphenylphosphine)carbonyl ruthenium(II)chloride hydride (**66**). This complex is a very well known, relatively stable and easily accessible compound. It can be prepared from ruthenium(III)chloride and triphenylphosphine via carbonylative reduction with aqueous formaldehyde in an alcoholic solvent, from which the product precipitates (Scheme 38):



Scheme 38: Synthesis of $(Ph_3P)_3Ru(CO)HCl$

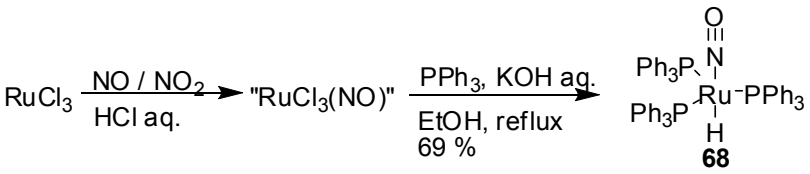
This short preparation as well as its well documented catalytic properties rendered it a quite suitable starting point.

It was attempted to prepare also its tris(tri-o-tolylphosphine)-analogue **67**, to get an idea of steric influences of the ligand while mostly retaining the electronic properties, but this venture failed (Scheme 39). This might be due to the increased steric bulk of the ligand, which could have led to a coordinativly unsaturated and therefore unstable complex.



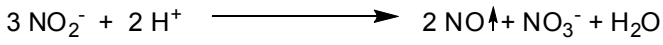
Scheme 39: Attempt to prepare $(Tol_3P)_3Ru(CO)HCl$

The next step was to switch from the above mentioned carbonyl-hydrido-complex **66** to its nitrosyl-hydrido-analogue **68**. This complex, $(Ph_3P)_3Ru(NO)H$, is also literature known, but less common than $(Ph_3P)_3Ru(CO)HCl$, probably because of its a bit tougher two step synthesis employing gaseous nitrous oxides in the first step (Scheme 40).



Scheme 40: Synthesis of $(PPh_3)_3Ru(NO)H$

The required mixture of NO and NO_2 can be easily generated via oxidation of NO with air, the NO itself can be liberated from sodium nitrite by treatment with a strong acid (Scheme 41).[89]



Scheme 41: Generation of NO via protonation of nitrite

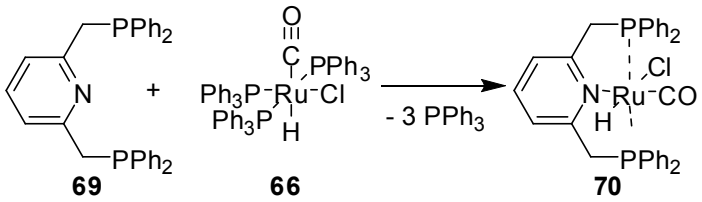
In this specific case, concentrated HCl was used as acid, to avoid the contamination of the reaction mixture with traces of another acid or the corresponding anion. The exact ratio of NO and NO_2 is not too important for the success of the reaction, but the presence of NO_2 is. The formation of the nitrosyl-ruthenium-chloride-complex could be very conveniently monitored by a change in colour of the reaction mixture. The initially dark brown solution turned to deep purple, as soon as the $RuCl_3$ was completely consumed. The purple solution was concentrated and used directly in the next step, from which the product was obtained in good yield.

In contrast to the inconvenience of handling obnoxious nitrous oxides, the nitrosyl-ligand promised a big advantage, based on its ability to coordinate metals either in a linear or bent fashion. The difference between the two isomeric forms is that the nitrosyl-ligand donates (formally) three electrons in its linear conformation, but only one electron in the bent conformation (if the NO-ligand is considered neutral), thereby creating the demand for two more electrons at the metal centre. This demand can be expressed as coordinative unsaturation or more common a vacant coordination site. Since the initial step of the proposed catalytic cycle (*vide supra*) is the coordination of the substrate olefin to the metal centre, it is crucial to provide a coordination site. This is most often achieved by ligand dissociation, but a simple flip of the nitrosyl-ligand was expected to be much faster. In fact this complex performed quite well in toluene at 50 °C (Table 2).

Table 2: Isomerisation of allylbenzene in the presence of 0.8 % $(PPh_3)_3Ru(NO)H$ at 50 °C in toluene

TIME [MIN]	ALLYLBENZENE [%]	*Z*-PROPENYLBENZENE [%]	*E*-PROPENYLBENZENE [%]
5	**62.7**	**6.6**	**30.7**
10	**22.9**	**8.8**	**68.3**
20	**14.8**	**9.6**	**75.6**

The importance of a free coordination site for successful catalysis was demonstrated by the synthesis of a coordinatively saturated and quite robust complex **70** from complex **66** and ligand **69** (Scheme 42), which showed no tendency to loose any ligand in order to generate a coordination site.



Scheme 42: Synthesis of the inert complex **67**

Therefore it was not surprising, that it did not show any catalytic activity.

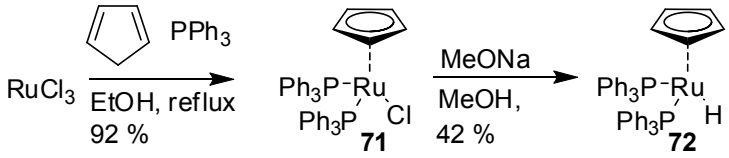
The next candidate to be synthesized was $CpRu(PPh_3)_2H$ (**72**). It was prepared to investigate the influence of the cyclopentadienyl-ligand on the catalytic properties of a ruthenium-hydride-complex. The Cp-moiety is a pretty common ancillary ligand in transition-metal organic chemistry, especially famous for sandwich-complexes like ferrocene. It is capable of donating up to 6 electrons (in η^5-coordination mode, counted as Cp^-) to the metal, two of them

as an σ-bond and the remaining four as π-bonds. It also possesses two degenerate empty MOs which can serve to accept δ-back bonding from populated d-orbitals of the metal, but these orbitals are relatively high in energy and therefore most often little electron withdrawal is recognized.[90] So in conclusion, the Cp-ligand can be viewed as "tridentate" ligand occupying three facial coordination sites,[91] that is relatively small and strongly electron donating. The thus resulting electron-rich metal-centre, when engaged in an olefin-complex, can be expected to accept only weak σ-donation, but to give rise to stronger π-back donation. Therefore electron rich olefins will bind more loosely, but electron poor olefins, that carry electron withdrawing substituents and have due to them a low lying π*-antibonding orbital, should bind stronger, in accordance to the Chatt-Dewar-Duncanson model.

The low steric demand of the Cp-ligand does not accelerate a dissociation of the triphenylphosphine-ligands, therefore the availability of vacant coordination sites is less likely and this will impair the coordination and isomerisation of substrates.

Its catalytic performance reflects these predictions, the complex is capable to isomerise allylbenzene, but relativly slowly.

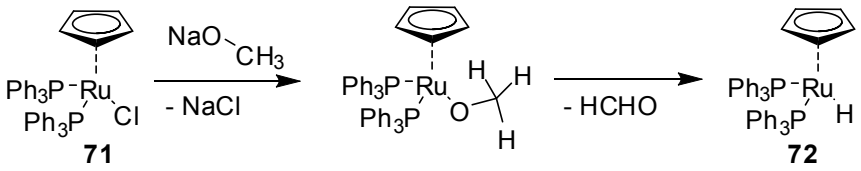
The complex **69** was prepared in a two step sequence from $RuCl_3$, via $CpRu(PPh_3)_2Cl$ (**71**) as intermediate (Scheme 43).



Scheme 43: Synthesis of $CpRu(PPh_3)_2H$

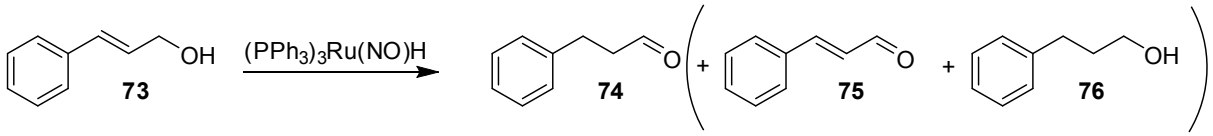
Since $CpRu(PPh_3)_2Cl$ is a common CpRu-halfsandwich precursor and frequently used Lewis acidic/σ-accepting catalyst, its synthesis is not only literature known, but well optimized. The use of freshly cracked cyclopentadiene, albeit employed in vast excess of 20 eq, is mandatory to achieve high yields.

The second step to substitute the chloride- with a hydride-ligand could be conducted by different means. Frequently complex-hydrides, most often tetrahydroborates, but also DIBAL-H have been used, but in the case some noble transition-metals a more elegant way is possible. The desired substitution can be affected by treatment with different alkoxides, or even alcohols in the presence of bases, as long as the employed alcohols possess α-hydrogens. The mechanism of this reaction is believed to involve the substitution of the chloride by an alkoxide as first step, followed by β-hydrogen-elimination (Scheme 44).



Scheme 44: Possible mechanism of the alkoxide-mediated reduction of **71** to **72**

These catalysts were tested not only with allylbenzene, but also with cinnamyl alcohol (**70**) as substrate, to test the idea of keto-enol-tautomerism as driving force to move a double bond out of conjugation with the aromatic core and to get an idea about functional group tolerance. It turned out, that e.g. $(PPh_3)_3Ru(NO)H$ served well to isomerise cinnamyl alcohol (**70**) to dihydrocinnamic aldehyde (**71**), but a significant degree of cinnamic aldehyde (**72**) and dihydrocinnamyl alcohol (**73**) were formed as byproducts, presumably due to transfer hydrogenation (Scheme 45).

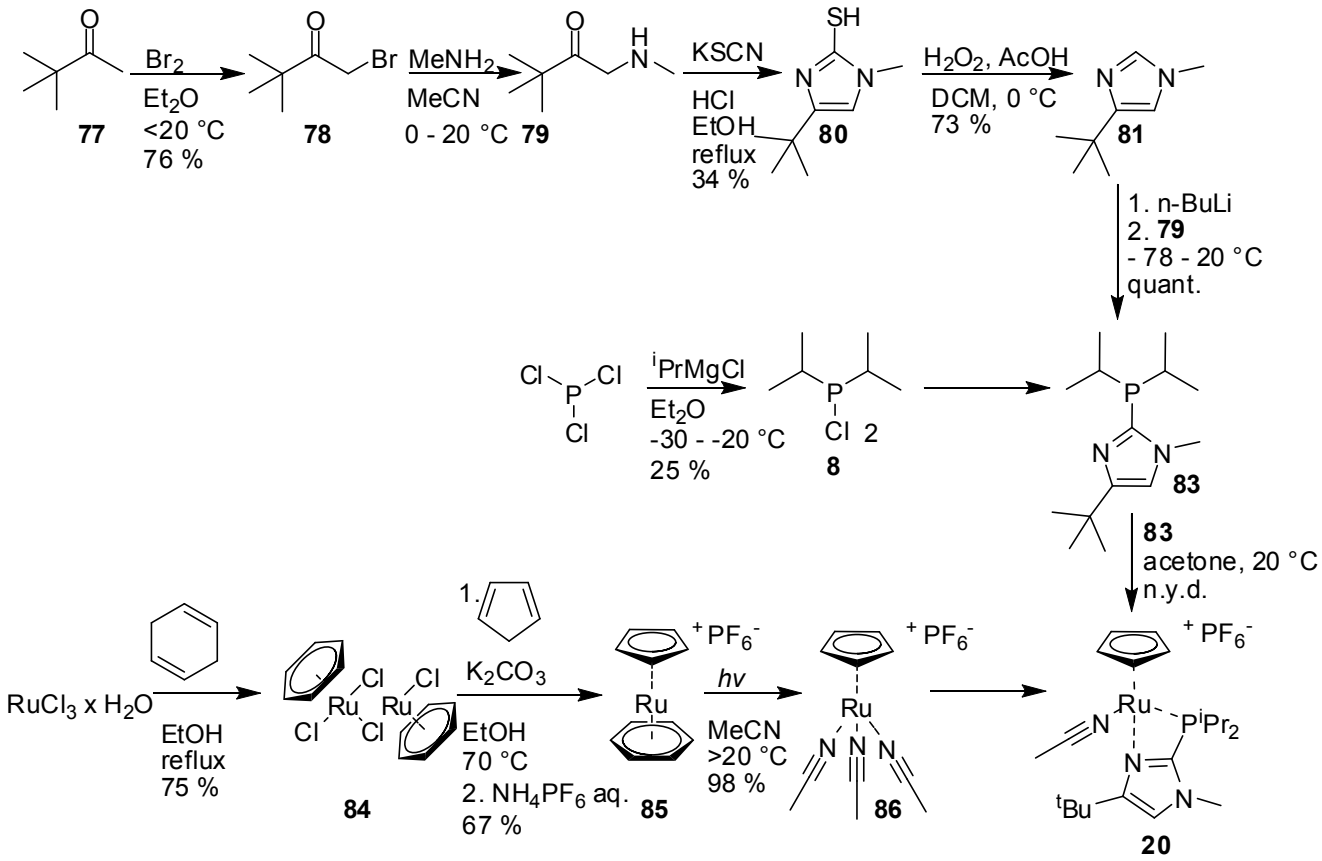


Scheme 45: Isomerisation of cinnamyl alcohol accompanied by transfer hydrogenation

This property of ruthenium-hydride-complexes is well known and has also been exploited synthetically.[92]

4.2.5. Grotjahn's Catalyst

For comparison to the above mentioned ruthenium-hydride catalysts, also the ruthenium-based Grotjahn-catalyst was prepared. Albeit it is commercially available, it was tempting to synthesize it from scratch. This synthesis was derived from Grotjahn's own synthesis, but with some minor changes mainly caused by availability of starting materials and lacking special equipment. The general course of the synthesis is outlined (Scheme 46).

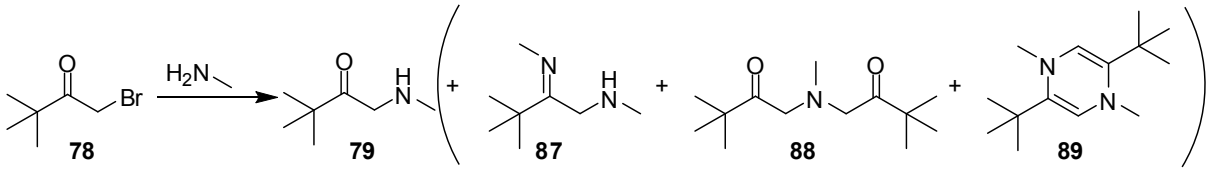


Scheme 46: Synthetic route to Grotjahn's catalyst

Surpisingly the synthesis of the ligand **83** imposed more difficulties, than the organometallic part to access the $CpRu(MeCN)_3^+$-precursor **86**.

To prepare the 1-methyl-4-^{t}butyl-imidazol core of the ligand **83**, Grotjahn *et al*. have published a concise synthesis starting form the α-methylaminoketone **79**, via MARCKWALD-cyclisation and oxidative desulfurization.[93,94] To enter this well established path, it was necessary to prepare the α-aminoketone **79**. It was planned to convert pinacolone (**77**) into α-bromopinacolone (**78**), which should be aminated with methylamine to yield **79**. The bromination worked excellent, but the conversion to the α-aminoketone **79** could never be achieved cleanly. The desired product was formed in modest yield, but always accompanied

by other amine-byproducts. This was not too surprising, since on the one hand the α-bromoketone **78** possesses two electrophilic sites which can react with the good nucleophile methylamine to give also imine **87**, and on the other hand the desired α-methylaminoketone **76**, was still nucleophilic to be alkylated again on the nitrogen to form **88**. Furthermore it might be possible that two molecules of **79** could cyclise to form 1,4-dihydropyrazine **89** (Scheme 47).



Scheme 47: Amination of α-bromopinacolone and possible side products

This variety of side-products which all had similar polarities prevented the isolation of **79**, which in turn was not expected to be very stable itself. Fortunately this problem was overcome by subjecting the crude product mixture directly to the conditions of the MARCKWALD-cyclisation. This consisted of prolonged heating under reflux in ethanolic HCl in presence of excess KSCN, so that at least the imine- and enamine-byproducts might have been hydrolysed to give **79** again, which could react to the expected 2-mercaptoimidazole-derivative **80**. In this way **80** was obtained as a semi-solid paste, still contaminated with the dialkylated side-product **88**, which was identified via GC-MS, but the crude product could be fortunately purified via recrystallisation from toluene. The next step, the oxidative desulfurisation with *in situ* generated peracetic acid worked fine according to the published protocol, to yield imidazole **81** as volatile yellow oil of skatol-like odour.

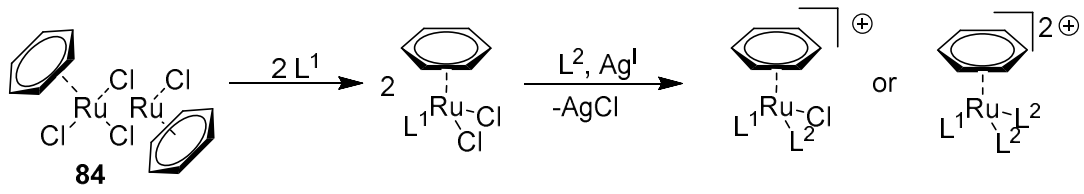
To introduce the diisopropylphosphino-group, chlorodiisopropylphosphine (**82**) was required. Albeit also commercially available, this compound was prepared by twofold alkylation of PCl_3 with isopropylmagnesiumchloride in diethyl ether, according to an Organic Syntheses procedure.[95]

Now with these two "halves" of the ligand in hand, it was only necessary to connect them to finish the synthesis of the ligand **83**. To do so, the imidazole **81** was lithiated selectively at the most acidic 2-position and the resulting lithio-imidazole could be coupled with a slight excess of chlorodiisopropylphosphine to yield **83**.

On the organometallic side of the catalyst, $CpRu(MeCN)_3^+$ PF_6^- (**86**) served as direct precursor to the active catalyst. This complex presents an even more useful precursor to CpRu-halfsandwich complexes and catalysts derived thereof than $CpRu(PPh_3)_2Cl$, because the three acetonitrile-ligands are only very weakly bound to the metal-centre and can be

substituted easily by almost any donor. Because of these benefits, different syntheses of this valuable compound are known. They rely most often on the displacement of a η^6-arene-ligand by the three acetonitrile-ligands. The conditions under which this substitution is conducted depend mainly on the nature of the involved arene. Whereas naphthalene is replaced simply during stirring in excess acetonitrile at 20 °C, benzene for instance needs to be cleaved via photolysis in acetonitrile.[96] The procedure relying on the replacement of benzene, albeit more difficult to conduct with standard laboratory equipment, was finally chosen because of the easier purification of the product. Unlike in the case of naphthalene as side-product, benzene can be evaporated together with the acetonitrile, to leave the virtually pure product behind. A facile synthesis of **86** starting from benzene-ruthenium(II)chloride-dimer (**84**), which in turn is easily prepared from $RuCl_3$, has been published by Trost *et al.*[97] To prepare $[(C_6H_6)RuCl_2]_2$, ruthenium(III)chloride was refluxed in ethanol with an excess of 1,4-cyclohexadiene, to yield the product as brown precipitate.[98] Comparable η^6-arene-complexes can also be produced from other substituted 1,3- or 1,4-cyclohexadiene-derivatives, for instance phellandrene, in an analogous fashion, but the benzene-parent compound offers a higher tendency to crystallise due to its higher symmetry.

This dimeric complex **84** is a suitable starting material for a variety of benzene-ruthenium-complexes as well as other ruthenium compounds. It is especially noteworthy, that due to the coordinative unsaturation of the corresponding monomer or in other words the bridging function of two of the chloride-ligands, the dimer can be easily cleaved via addition of a suitable donor. This reaction offers the opportunity to introduce selectively different ligands, at first by splitting the dimer and then by replacing one or two chloride-ligands, most often assisted by silver(I)salts to precipitate AgCl (Scheme 48).



Scheme 48: Possible application of $[(C_6H_6)RuCl_2]_2$

The first step of this approach has been used in the synthesis of a very simple but also effective photo-activated precatalyst for olefin metathesis.[99]

This behaviour can also serve to explain the ease of its reaction with cyclopentadiene and potassium carbonate in hot ethanol to produce the mixed sandwich complex **85**. Due to its

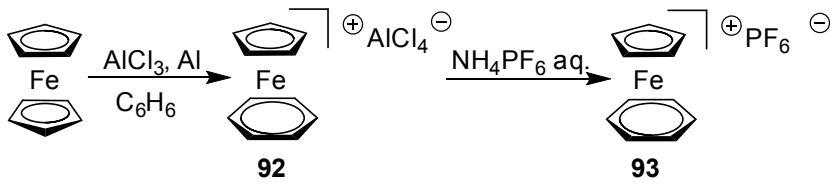
charge, this complex can be isolated conveniently via precipitation as its hexafluorophosphate-salt.

The crucial last step in the preparation of $CpRu(MeCN)_3^+ PF_6^-$ was the photolytic substitution of benzene by three equivalents of acetonitrile. It occurs most likely via excitation of electrons from a bonding MO into an antibonding orbital to reduce the bond order between the metal centre and the benzene-ligand, but details of the mechanism of this reaction are far beyond the scope of this text.

From the practical point of view, the reaction was carried out relatively straightforward via irradiation of a solution of complex **85** in degassed acetonitrile with a low-pressure mercury lamp. Due to the lack of a designated photo-reactor in our laboratory, an apparatus consisting mainly of an UV-C mercury lamp, which was extracted from an aquarium-water clearing/ sterilising device (type JBL AquaCristal UV-C 5W), immersed in a large NS 45/40 750 ml Schlenk tube was improvised. The electric power supply was fitted into the Schlenk tube through a rubber septum, which provided sufficient sealing against atmospheric oxygen to conduct the reaction sufficiently inert under a permanent positive pressure of nitrogen. The exclusion of oxygen during photochemical operations, except from intended oxidations and similar reactions, is crucial because the "common" kinetically stable triplet-oxygen $^3O_2$ can be excited under UV irradiation to highly reactive singlet-oxygen $^1O_2$, which would cause a variety of side-reactions. This excitation is facilitated by photosensitizers, like some transition metal complexes.

Fortunately the desired product could be obtained in almost quantitative yield with only traces of impurities detectable via ^{1}H-NMR, albeit darker in colour than described in literature. Now with both ligand **83** and metal precursor **86** in hand, the only thing left to produce the active catalyst was to mix them in equimolar ration in acetone and stir overnight. The catalyst was obtained in solution and used without further purification. It proved to be active in the isomerisation of cinnamyl alcohol (**73**) cleanly to 3-phenylpropanal (**74**) without any transfer hydrogenation, as with the other ruthenium-hydride catalysts.

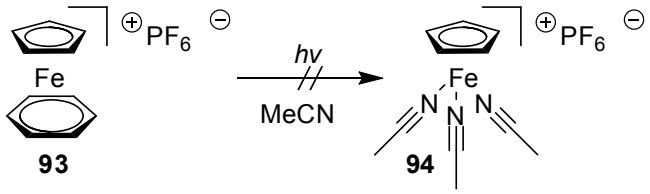
It was attempted to extend this chemistry to the lighter iron analogue, but only with limited success. The required precursor $CpFe(C_6H_6)^+ PF_6^-$ (**93**), as well as its p-xylene analogue, were prepared according to literature procedures from ferrocene under Lewis acidic, reducing conditions in the respective aromatic hydrocarbon as solvent via the corresponding tetrachloroaluminate **85** as intermediate (Scheme 49).[100]



Scheme 49: Conversion of ferrocene to $CpFe(C_6H_6)^+ PF_6^-$

It is noteworthy that the analogous reaction sequence also can be applied to ruthenocene, but since this is more than two orders of magnitude more expensive than ferrocene (Sigma-Aldrich 09.07.2014), the above outlined route to **86** seemed superior.

The following photolysis of the mixed sandwich complex **93** has been described to yield a "naked" $CpFe^+$ cation, which can be stabilised by suitable ligands.[101] However due to iron's tendency to oxidation and the only "semi-inert" conditions in the photolysis apparatus, no tris(acetonitrile)-complex **94** comparable to the more stable $CpRu(MeCN)_3^+ PF_6^-$ could be isolated (Scheme 50). On the other hand more or less stable CpFe-half-sandwich complexes with stronger π-acceptor ligands can be prepared by this method.

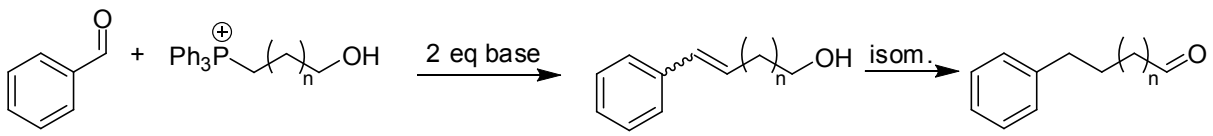


Scheme 50: Failed attempted to prepare $CpFe(MeCN)_3^+ PF_6^-$

4.3. Applications of Olefin Isomerisation

Now with several active catalysts at hand, it became necessary to explore potentially useful applications of them. Albeit it is very atomeconomic, the isomerisation of double bonds can only be employed with benefit in a well-tailored situation.

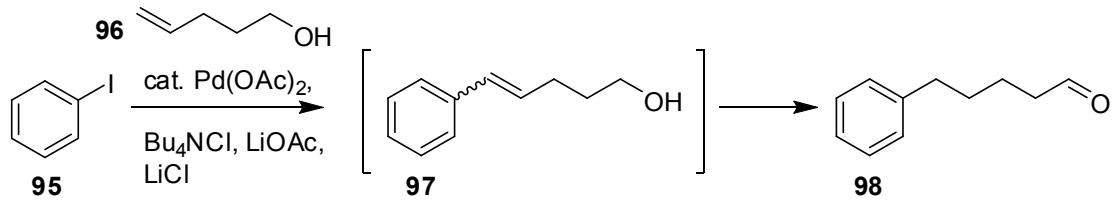
After the successful and clean isomerisation of cinnamyl alcohol to dihydro cinnamic aldehyde, it seemed interesting to test this reaction also for longer chain olefinic alcohols. Furthermore this reaction might offer the possibility to design a general method for the multi-carbon homologisation of aromatic aldehydes in a two step sequence (Scheme 51).



Scheme 51: WITTIG-olefination with ω-hydroxy phosphonium salts followed by isomerisation

It looked promising in the beginning, but after some literature search it turned out, that a much more efficient and elegant procedure for the synthesis of similar products via Heck-

reaction with consecutive double bond migration catalysed by in situ generated Pd-H species was already known. In the given example, iodobenzene (**95** undergoes HECK-reaction with 4-pentene-1-ol (**96**) to give at first the usual HECK-product **97**, which is further isomerised to the thermodynamically more stable aldehyde **98** (Scheme 52).[102-104]

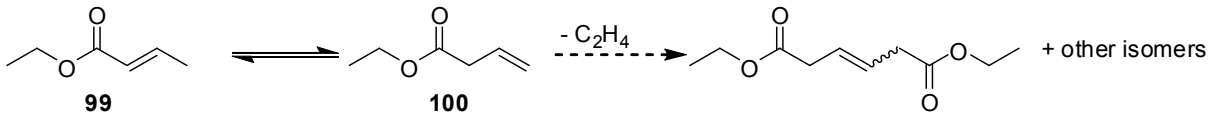


Scheme 52: Heck-reaction with consecutive isomerisation

The second idea which was considered, was to couple the olefin isomerisation with a second reaction to shift the equilibrium in a favourable way. Since this concept has been demonstrated to work fine with hydroformylation, hydroboration and hydrosilylation, other reactions of olefins were searched. Since catalytic reactions are always preferable over stoichiometric reactions, olefin-metathesis appeared as an interesting option. In this way, it was hoped, to conduct a counter-thermodynamic isomerisation to produce a lower substituted olefin in equilibrium with its higher substituted isomer(s) and sequester it selectivly via self- or cross-metathesis to produce eventually a useful product.

Grubbs I catalyst was considered to be suitable for this venture, because of its relatively low reactivity, compared to the more modern Grubbs II or Grubbs-Hoveda catalysts, which should enable it to ”wait” for the isomerised, lower substituted and therefore more reactive olefin instead of converting the starting internal olefin also. A very helpful survey on the reactivity of different types of olefins towards different catalyst has been published[105] that helps to judge whether certain reagent combination might react in the desired fashion or not. Therein the examined olefins were classified in four types depending on the behaviour towards specific catalysts.

At first, the isomerisation of a crotonic acid derivative like ethyl crotonate (**99**) to its nonconjugated isomer **100** followed by selective self-metathesis was considered, which might open a new route to (dehydro)adipic acid derivatives (Scheme 53).

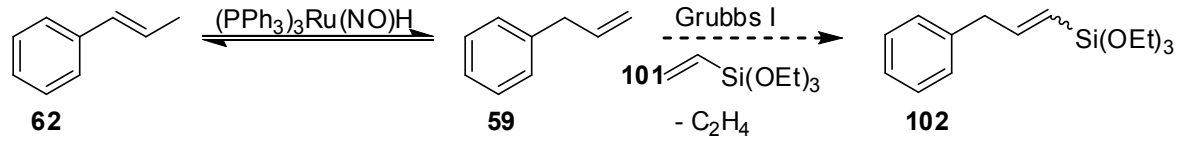


Scheme 53: Planned isomerisation and consecutive self-metathesis of ethyl crotonate

However after some fruitless experimentation this idea was abandoned in favour of cross-metathesis, which should offer the benefit, that at least one metathesis partner can be supplied in high concentration in contrast to the very low concentration of the counter thermodynamic isomer in equilibrium.

As metathesis partner, triethoxyvinylsilane, not to be confused with vinyl trimethylsilyl ether which has been use to decompose ruthenium-carbenes as mentioned earlier, was selected for two reasons. On the one hand, it is considered as a type 3 olefin in metathesis reactions catalysed by Grubbs I catalyst, which means, that it is susceptible to cross metathesis with a different olefin, but will not form a homo dimer under the same reaction conditions. This is important in order to perform an efficient (cross) metathesis, because the main driving force of the more or less enthalpically neutral olefin metathesis is the entropically beneficial loss of ethene or a similar volatile olefinic side-product. So the homocoupling of one of the reactants would "waste" the driving force futile without to produce the intended product. On the other hand, the expected product of the reaction, a substituted trialkoxyvinylsilane can be used in several reactions of preparative value, like for instance HIYAMA-DENMARK coupling or TAMAO-FLEMING oxidation.

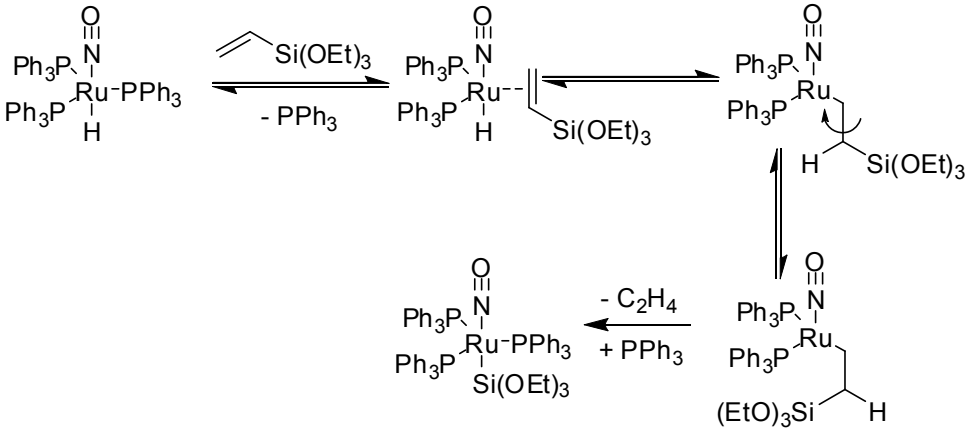
As test system again the allylbenzene – propenylbenzene pair was chosen, not only because of its availability, but also because the catalysts, especially $(Ph_3P)_3Ru(NO)H$, had been shown to catalyse the isomerisation into the thermodynamically favoured direction, but based on the principle of microscopic reversibility, they were expected to catalyse also the backward reaction. So the planned reaction consisted of the equilibration of propenylbenzene (**62**) to allylbenzene (**59**), which could be present only in very low concentration, followed by (selective) cross metathesis thereof with an excess of triethoxyvinylsilane (**101**) to yield triethoxy-3-phenylpropenylsilane (**102**) (Scheme 54).



Scheme 54: Planned isomerisation of propenylbenzene to allylbenzene with consecutive metathesis

The reaction was explored at different temperatures and concentrations in dichloromethane and chlorobenzene, however the desired product was never formed. Different reasons for this reaction not to occur can be considered.

It might be possible that the isomerisation catalyst gets poisoned by the triethoxyvinylsilane, which is present in excess with respect to the olefin, maybe via insertion into the Ru-H bond, followed by β-silicon elimination (Scheme 55).

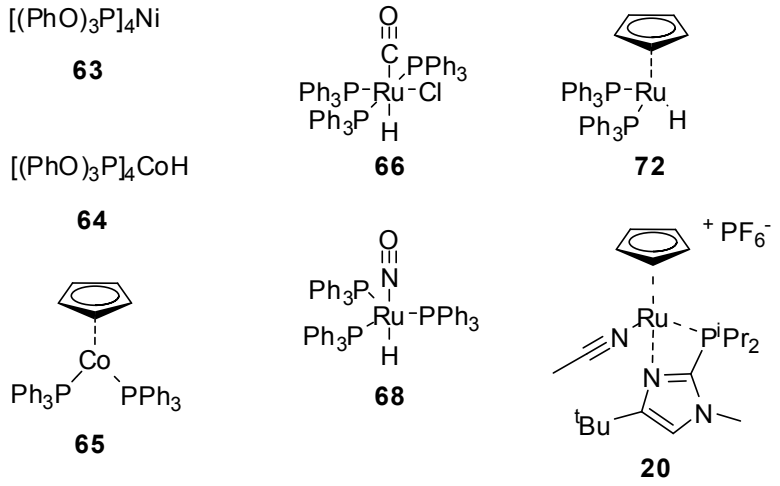


Scheme 55: Possible mechanism of catalyst inactivation

Another plausible reason could be, that the concentration of allylbenzene in equilibrium, which is below the limit of detection of GC-MS, is too low to allow its conversion at useful a rate. Furthermore the allylbenzene had to react with the Grubbs I catalyst, which was also present only in catalytic / substoichiometric amounts with respect to propenylbenzene. Due to these two species existing only in very low concentrations, the probability of a productive interaction was very small. This fact contrasts the case of e.g. the combination of olefin isomerisation and hydroformylation, *vide supra*, in which the active catalyst is the same for both parts of the overall reaction. Therefore it can be expected, that the catalyst resides in close proximity to the substrate of the hydroformylation reaction, which was just generated via isomerisation. This proximity might increase the chance of successful hydroformylation considerable.

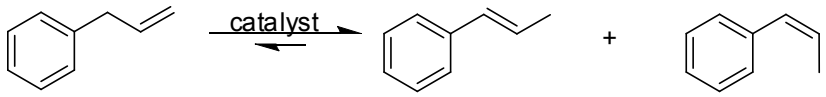
5. Summary

During this work, a couple of different transition metal complexes have been synthesized (Scheme 56).



Scheme 56: Some transition metal complexes, which were prepared

At first the interest was focussed on complexes based on nickel and cobalt, due to the relatively low cost of the starting materials, but these metals were later on abandoned in favour of ruthenium, which gave rise to more active catalysts. The catalytic candidates were tested for their ability to isomerise allylbenzene to its internal conjugated isomers *Z*- and *E*-propenylbenzene, a reaction that was conveniently monitored via GC-MS (Scheme 57).



Scheme 57: Isomerisation of allylbenzene

The required allylbenzene and *E*-propenylbenzene as product reference have also been synthesized.

6. Conclusion

In the course of this work, several metal complexes have been prepared, which have shown the ability to catalyse the (regio)-isomerisation of olefins. The most active and reliable of them were based on ruthenium. In contrast to the different syntheses of these complexes, which were varying from very simple to relative challenging, it turned out to be much more difficult to find useful novel applications of olefin isomerisation. In fact no particular use of the ability to isomerise olefins could be found, which would have offered benefits over already known methods.

7. Outlook

Considering the principle virtues of the isomerisation of olefins, like atom economy, the possibility of converging different starting materials or isomeric intermediates to a single product and the chance for interesting follow-up chemistry even in the same pot, it will be worthwhile to further explore this method. But since it presents a rather special type of reaction, which can unfold its entire potential only under properly chosen circumstances, it will be obligate to create tailored solutions for certain problems. Therefore it seems more realistic to consider it as an option in a well-planned synthesis and a supplementation to the existing olefin-forming and -processing chemistry, rather than as a general method of unlimited scope and utility.

8. Experimental Part

8.1. General Remarks

All reactions, if not explicitly stated otherwise, were carried out without exclusion of atmospheric moisture and oxygen. If reactions are described as inert, the reaction vessel, either a Schlenk flask or a two- or three necked round bottom flask with a stopcock was evacuated at oilpump vacuum ($<10^{-2}$ mbar), heated with a heatgun, cooled to RT in vacuo and finally filled with inert gas. As inert gases either nitrogen or argon were used.

8.1.1. Solvents and Solutions

Solvents if not stated otherwise were used as received, only diethyl ether and tetrahydrofurane (THF) were carefully distilled on a rotary evaporator and stored over KOH.
Saturated aqueous solutions of inorganic salts were prepared by stirring water and adding the salt until a precipitate remained.

8.1.2. Absolute Solvents

Absolute tetrahydrofurane (THF) was obtained via refluxing THF, pre-dried over KOH pellets, over sodium under argon followed by distillation. Benzophenone was used as indicator for the complete removal of water. The thus obtained dry THF was stored over 4 Å molecular sieves (beads) under argon.
Absolute dichloromethane (DCM) was obtained via redistillation of dichloromethane, pre-dried via distillation from phosphorous pentoxide, from calcium hydride under argon. The resulting dry dichloromethane was stored over 4 Å molecular sieves (beads) under argon.
Absolute acetonitrile (MeCN) was obtained via distillation from calcium hydride under argon and was stored over 4 Å moleculare sieves (beads) under argon.
Absolute toluene was obtained via filtration through activated alumina and was stored over 4 Å molecular sieves (beads) under argon.

8.1.3. Thin Layer Chromatography (TLC)

Thin Layer Chromatography (TLC) was performed on TLC plates from Merck, silica 60 F_{254} on aluminium foil 20x20 cm. The detection of the substance was performed with UV light at

254 nm and in some cases additionally with ninhydrin dissolved in ethanol, ceric ammonium molybdate (CAM) or potassium permanganate in dissolved in water.

8.1.4. Flash Chromatography

Preparative flash chromatography was performed on silica gel from Acros Organics with a particle size between 35 and 70 µm. Slight pressure with an air pump was applied to accelerate the flow.

8.1.5. Gas Chromatography

Gas chromatographic separation were performed using an Agilent Technologies 7890A GC system fitted with an Agilent Technologies 7683B Series injector and an Agilent Technologies 7683 Series autosampler. The column was a polar HP-5MS capillary column (length: 30 m, internal diameter: 0.25 mm, layer thickness: 0.25 µm). Helium 5.0 was used as carrier gas. The ionisation was affected via an EI-ionisation source at a potential of 70 eV, the separation of the resulting ions occurred by the means of a mass selective detector type Agilent Technologies 5975C inert MSD with triple axis detector.

The samples were prepared as dry solutions in either dichloromethane or ethyl acetate with a concentration of ≤1 mg/mL. They were injected in split-mode. All separations were carried out using the method MK_STANDARD, which employed a split ratio of 1:20 and a temperature gradient which starts at 50 °C, holds this temperature for 1 min, heats up to 300 °C with a heating rate of 40 °C/min and stays for 1 min at 300 °C.

8.1.6. Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE III with autosampler: 300.36 MHz-^{1}H-NMR, 75.53 MHz-^{13}C-NMR. In ^{1}H- and ^{13}C NMR spectra, the residual proton signal of the deuterated solvent served as standard. Deuterated acetone, benzene, chloroform and dimethyl sulfoxide were used as solvents. Signals are abbreviated as follows: s (singulet), bs (broad singulet), d (doublet), bd (broad doublet), dd (doublet of a doublet), t (triplet), q (quartet) und m (multipltt). The chemical shifts were recorded in ppm (parts per million).

8.1.7. Infrared Spectroscopy (IR)

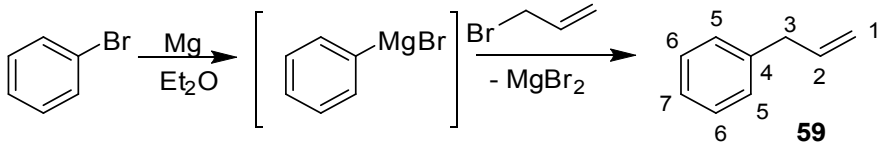
Infrared spectra were recorded on a Bruker Tensor 37 spectrometer in attenuated total reflection (ATR) mode. The samples were applied neat, the spectra were corrected via subtraction of background spectra.

8.1.8. Melting points

The reported melting points were determined using a melting point apparaturs type „Mel-Temp®“ fitted with a microscope attachment. The measured melting points were have not been corrected.

8.2. Syntheses

8.2.1. Synthesis of Allylbenzene (59)



In a 250 mL three-necked round-bottomed flask fitted with a magnetic stir bar, a connector to a protecting gas-vacuum manifold and a 50 mL dropping funnel was evacuated, flame-dried and filled with N_2 twice. The flask was charged with 4.90 g magnesium turnings (0.20 mol, 1 eq), these were stirred dry under N_2 for 15 min. Then the flask was fitted with a reflux condenser carrying a N_2 in- and outlet and the magnesium was covered with 25 mL diethyl ether. The dropping funnel was charged with 21.0 mL pure bromobenzene (31.4 g, 0.20 mol 1 eq) and 2 mL thereof were added at once. When the reaction started, the reaction mixture in the flask was diluted with 25 mL diethyl ether and the remaining bromobenzene was diluted with 25 mL diethyl ether, the resulting solution was added dropwise, to maintain the reaction mixture at steady reflux. When the addition was complete, the reaction mixture was heated under reflux on a 45 °C warm oilbath for 30 min. Then the oilbath was removed and 17.0 mL allyl bromide (23.8 g, 0.20 mol) were placed in the dropping funnel and added slowly. During the addition, the colour of the reaction mixture changed from brown to greenish-gray and a colourless precipitate formed. When the addition was complete, the reaction mixture was heated again under reflux for 1.5 h. Then the reaction mixture was cooled to 20 °C and 40 mL water and 5 mL concentrated HCl were added sequentially. When the precipitate was

completely dissolved, the phases were separated and the aqueous phase was extracted with diethyl ether (2x 25 mL). The pooled organic phases were dried over Na_2SO_4, filtrated with suction and the diethyl ether was removed carefully on a rotary evaporator at 50 °C and ≤ 900 mbar, to give a yellow oil (27.3 g). This crude product was fractionated at 100 ± 5 mbar through a Vigreux column (1.5 x 10 cm). The pure product was collected at 82 – 83 °C.

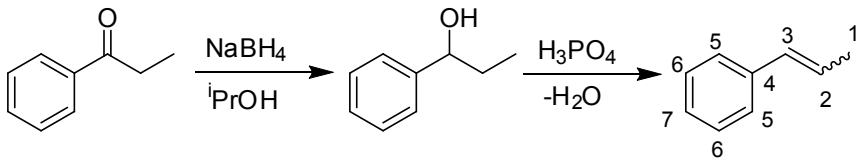
Yield: 17.9 g (0.15 mol, 75 %)

bp: 82-83 °C/100 mbar

^{1}H NMR (300.36 MHz, $CDCl_3$): δ= 7.37 – 7.13 (m, 5H, aromatic protons 5-7.), 5.99 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H, H-2), 5.14 – 5.04 (m, 2H, H-1), 3.41 (d, *J* = 6.6 Hz, 2H, H-3).

^{13}C NMR (75.53 MHz, $CDCl_3$): δ 140.21 (C-4), 137.61 (C-7), 128.73 (C-6), 128.56 (C-5), 126.20 (C-2), 115.92 (C-1), 40.39 (C-3).

8.2.2. Synthesis of Propenylbenzene (62)



61 **62**

A 50 mL round-bottomed flask with a magnetic stir bar was charged with 2.7 mL propiophenone (2.7 g, 20 mmol) which was dissolved in 22 mL isopropanol. 390 mg finely ground sodium borohydride (10.3 mmol, 0.51 eq) was added to the clear colourless solution. The flask was fitted with a calcium chloride drying tube and the suspension was stirred for 15 h. The progress of the reaction was monitored via TLC with cyclohexane and ethyl acetate 4:1 (propiophenone: R_f 0.81, product: R_f 0.61). After 15 h there was still starting material present, another 190 mg sodium borohydride (5.0 mmol) was added and the reaction mixture was stirred for another 7 h. Then TLC indicated complete conversion of the starting material. 10 mL 20 % aqueous HCl and 10 mL water were added sequentially. The resulting clear solution was extracted with ethyl acetate (3x25 mL). The combined extracts were dried over Na_2SO_4 and carefully evaporated with a rotary evaporator at 40 °C and ≤800 mbar to yield 2.60 g of a colourless oil. GC-MS indicated > 99 % pure 1-phenylpropane-1-ol (**61**). This crude product was used in the next step without further purification.

A 25 mL round-bottomed flask with a magnetic stir bar was charged with 3 mL 85 % phosphoric acid and 10 mg 2,6-ditertbutyl-4-methylphenol (0.045 mmol, 0.002 eq). The crude 1-phenylpropane-1-ol from the first step was added, the flask was fitted with a ca. 1 x 10 cm air condenser and the content was heated for 13 h in a 130 °C hot oilbath. Then the flask was

cooled to 20 °C and TLC analysis (cyclohexene/ethyl acetate 9:1, $KMnO_4$-solution staining, (1-phenylpropane-1-ol: R_f 0.45, propenylbenzene: R_f 0.91) indicated complete conversion. The biphasic reaction mixture was poured onto 10 mL water and extracted with diethyl ether (3x 10 mL). The combined organic phases were dried over Na_2SO_4, filtrated and the diethyl ether was carefully removed on a rotary evaporator at 40 °C and ≤900 mbar. The remaining orange oil (1.80 g) was subjected to Kugelrohr-destillation at 30 mbar with an oven temperature of 100–180 °C, to yield a colourless oil.

Yield: 0.67 g (5.7 mmol, 28 % over both steps), *E/Z* ratio: 94.4 : 5.6 [GC-MS]

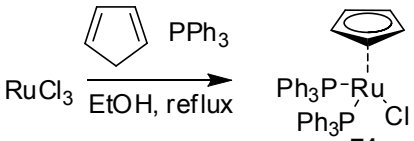
R_f (cyclohexene:ethyl acetate 9:1): 0.91

^{1}H NMR (300.36 MHz, $CDCl_3$) δ 7.34– 7.12 (m, 5H, aromatic protons 5-7), 6.40 (dd, *J* = 12.5, 11.5 Hz, 1H, H-3), 6.29 – 6.13 (m, 1H, H-2), 1.86 (dd, *J* = 6.4, 1.3 Hz, 3H, H-1).

^{13}C NMR (75.53 MHz, $CDCl_3$): δ 138.08 (C-4), 131.17 (C-3), 128.60 (C-6), 126.87 (C-7), 125.95 (C-5), 125.82 (C-2), 18.61 (C-1).

8.2.3. Synthesis of Cyclopentadienyl(bistriphenylphosphine)-ruthenium(II)chloride (71)

Literature: L. Ballester, A. Outlkez, M. F. Perpitiin *J. Chem. Ed*, **1989**, *66*, 777-781.



71

A 250 mL two-necked round-bottomed flask with a magnetic stir bar and a connection to a vacuum/protecting gas manifold was charged with 40 mL ethanol. The ethanol was degassed by bubbling N_2 through it for 10 min and maintained afterward under a N_2 atmosphere. 1.20 g triphenylphosphine (4.6 mmol, 4 eq) were added. The flask was fitted with a reflux condenser carrying a gas in- and outlet and the suspension was heated under reflux in a 100 °C hot oilbath. When the PPh_3 was completely dissolved, a solution of 300 mg hydrated ruthenium(III)chloride (ca. 1.12 mmol) in 20 mL warm ethanol was added in one portion to the refluxing solution. After 5 min a solution of 2.0 mL freshly destilled cyclopentadiene (1.6 g, 24 mmol, 22 eq), in 5 mL ethanol was added in one portion and the deep red solution was refluxed for 70 min. Then the oilbath was removed and the solution was cooled to 20 °C. No precipitation occurred at this point, the still clear solution was concentrated to a volume of 50 mL on a rotary evaporator a 45 °C and ≤ 250mbar. Then the solution was cooled again to 20

°C and orange crystals precipitated. This precipitate was collected by filtration on a fritted glass funnel and washed with ethanol (2x 3 mL). The orange solid was dissolved in 5 mL dichloromethane, transferred into another round-bottomed flask and re-precipitated by the addition of 25 mL pentane. After standing overnight at 20 °C to complete the precipitation, the precipitate was filtered off again and the remaining solid was dried in vacuo. The ethanol- and dichloromethane/pentane filtrates were combined and concentrated to a volume of 20 mL, to give a second crop of product, which was treated in the same way as describe above.

Yield: 754 mg (1.04 mmol, 92 %)

mp: 135 – 138 °C (dec.) mp lit.: 135 °C (dec.)

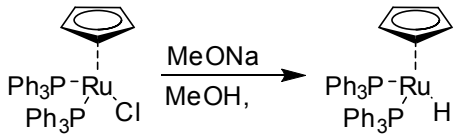
^{1}H NMR (300.36 MHz, $CDCl_3$) δ= 7.37 (dd, *J* = 9.2, 7.6 Hz, 12H, triphenylphosphine-o-protons), 7.22 (d, *J* = 6.9 Hz, 6H, triphenylphosphine-p-protons), 7.13 (t, *J* = 7.2 Hz, 12H, triphenylphosphine-m-protons), 4.10 (s, 5H, Cp-protons).

^{13}C NMR (75.53 MHz, $CDCl_3$) δ= 138.50 (d, *J* = 51.4 Hz, triphenylphosphine-ipso-carbons), 133.96 (t, *J* = 5.1 Hz, triphenylphosphine-o-carbons), 128.84 (triphenylphosphine-p-carbons), 127.63 (t, *J* = 4.6, triphenylphosphine-m-carbons), 81.57 (Cp-carbons).

IR (cm^{-1}): 1479, 1432, 1269, 1088, 997, 835, 804, 741, 728, 693, 619.

8.2.4. Synthesis of Cyclopentadienyl(bistriphenylphosphine)-ruthenium(II)hydride (72)

Literature: L. Ballester, A. Outlkez, M. F. Perpitiin *J. Chem. Ed*, **1989**, *66*, 777-781.



71 **72**

A 20 mL Schlenk tube with a magnetic stir bar was charged with 10 mL methanol. The methanol was degassed by bubbling N_2 through it for 10 min and maintained afterward under a N_2 atmosphere. 46 mg sodium (2 mmol, 36 eq) was dissolved in the methanol. After the dissolution was complete, 40 mg cyclopentadienyl(bistriphenylphosphine)-ruthenium(II)chloride (0.055 mmol, 1 eq) were added to the well stirred sodium methoxide solution. The orange solid dissolved slowly to give a yellow solution. After 30 min at 20 °C, the reaction mixture was heated in a 50 °C warm oilbath for another 15 min. Then the oilbath was removed and a yellow solid precipitated from the almost colourless solution. When the reaction mixture was cooled to 20 °C, the precipitate was collected via filtration through a

fritted glass funnel, washed with 5 mL cold methanol and 5 mL pentane and the solid was dried in vacuo.

Yield: 16 mg (0.023 mmol, 42 %)

mp: 145 °C (dec.) mp lit.: 140-145 °C (dec.)

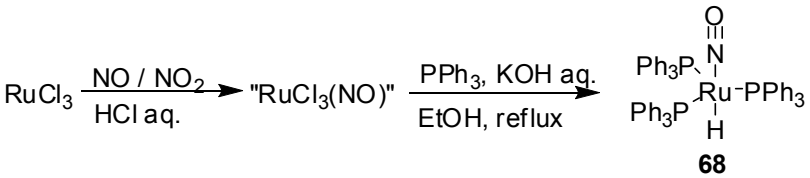
^{1}H NMR (300.36 MHz, C_6D_6) δ 7.53 (dd, *J* = 7.5, 5.3 Hz, 12H, triphenylphosphine-m-protons), 6.93 (d, *J* = 3.8 Hz, 18H, triphenylphosphine-o and-p-protons), 4.50 (s, 5H, Cp-protons), -11.10 (t, *J* = 33.8 Hz, 1H, Ru-**H**).

^{13}C NMR (75.53 MHz, C_6D_6) δ 141.92 (triphenylphosphine-ipso-carbons), 134.16 (t, *J* = 5.6 Hz, triphenylphosphine-o-carbons), 128.28 (triphenylphosphine-p-carbons), 127.31 (t, *J* = 4.5 Hz triphenylphosphine-m-carbons), 82.08 (Cp-carbons).

IR (cm^{-1}): 1969, 1584, 1477, 1431, 1086, 803, 743, 693.

8.2.5. Synthesis of Nitrosyl(tristriphenylphosphine)rutheniumhydride (68)

Literature: J. S. Bradley, G. Wilkinson, *Inorg. Synth.* **1977**, *17*, 73-74.



68

A NO-gas generator is set up, consisting of a 250 mL round-bottomed flask fitted with a 100 mL pressure equalizing dropping funnel carrying a gas valve connected to a three-way gas wash bottle. The round-bottomed flask is charged with 37 g $NaNO_2$ (0.54 mol, 300 eq), which was suspended in 50 mL water. The dropping funnel was charged with 90 mL concentrated hydrochloric acid (39.6 g, 1.09 mol, 608 eq). The gas wash bottle was fitted with an inlet for compressed air and a connection to a gas introduction tube reaching into a 50 mL two-necked round-bottomed flask with a magnetic stir bar and a reflux condenser fitted with a tube leading to the vent. This 50 mL two-necked round-bottomed flask was charged with 467 mg hydrated ruthenium(III)chloride (1.78 mmol, 1 eq), which was dissolved in water 20 mL. The resulting solution was heated under reflux in a 120 °C hot oilbath. When it started to boil, the addition of hydrochloric acid to the sodium nitrite solution/suspension was started, to generate NO. The thus produced almost colourless NO was treated periodically with pressurized air, to yield a mixture of NO and NO_2. This brownish mixture was passed through the vigorously boiling $RuCl_3$ solution, until the colour of the solution had changed from dark brown to deep purple. Then the gas generation was stopped and the $RuCl_3$(NO) solution was flushed

thoroughly with pressurized air, to expel remaining nitrous oxides. When no more brown gases are evolved, the reflux condenser was switched for a distillation bridge, 5 mL concentrated hydrochloric acid were added to the purple solution and it was concentrated at ambient pressure to a syrupy consistence. The resulting dark violet semi-solid substance was dissolved in 15 mL ethanol.

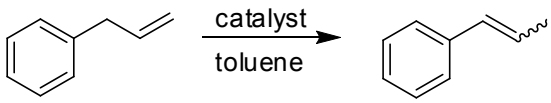
In parallel, a 100 mL two-necked round-bottomed flask with a magnetic stir bar was charged with 35 mL ethanol. The ethanol was degassed by bubbling N_2 through it for 15 min and maintained afterwards under N_2 atmosphere. 2.04 g triphenylphosphine (7.8 mmol, 4.4 eq) and 0.36 g potassium hydroxide (6.4 mmol, 3.6 eq) were added to the ethanol, the two-necked round-bottomed flask was fitted with a reflux condenser carrying a gas in- and outlet and the resulting suspension was heated under reflux in a 100 °C hot oilbath. When everything had dissolved, the side neck of the flask was fitted with a 25 mL dropping funnel, and the $RuCl_3(NO)$ solution was added to the boiling PPh_3/KOH solution very slowly. The reaction mixture was reddish-brown in the beginning, but turned green later (presumably due to too fast addition of the $RuCl_3(NO)$ solution). The reaction mixture was refluxed for 12 h and was still green afterwards. Then 0.56 g triphenylphosphine (2.1 mmol, 1.2 eq) was added without change in colour and 0.12 g potassium hydroxide (2.1 mmol, 1.2 eq) was added, which caused the reaction mixture within 5 min to turn reddish-brown. The reaction mixture was refluxed for further 1 h and then cooled to 20 °C. A brown precipitate began to settle and was left for 1 h to complete the crystallisation. It was collected by filtration through a sintered glass funnel and washed with hot ethanol (2x 10 mL), water (2x 10 mL) and cold ethanol (2x 10 mL). The remaining brown solid was dried in vacuo.

Yield: 1.14 g (1.24 mmol, 69 %)

mp: 143-145 °C

IR ($cm^{-}1$): 1967, 1767, 1645, 1478, 1432,1086, 742, 693.

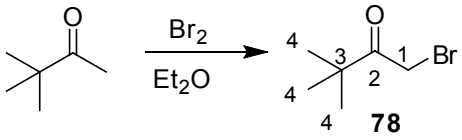
8.2.6. Isomerisation of Allylbenzene to Propenylbenzene



A flame-dried 20 mL Schlenk tube with a magnetic stir bar was charged with 66.2 µl allylbenzene (59.1 mg, 0.5 mmol, 1 eq), which was dissolved in 2 mL degassed toluene. The catalyst **63**, **65** or **69** was added 0.1 – 2 mol% and the homogeneous reaction mixture was stirred in a 50 °C warm oilbath. The progress of the reaction was monitored via GC-MS.

8.2.7. Synthesis of α-Bromopinacolone (78)

Literature: N. L. Dunn, M. Ha, A. T. Radosevich *J. Am. Chem. Soc*. **2012**, *134*, 11330-11333.



A 250 mL three-necked round-bottomed flask equipped with a magnetic stir bar, an internal thermometer, a rubber septum and a connector to an exhaust tube that led to the vent, was charged with 16.0 mL pinacolone (12.8 g, 128 mmol, 1 eq), which was diluted with 16 mL diethyl ether. 7.3 mL bromine (23 g, 144 mmol, 1.125 eq) was drawn into a hypodermic syringe and a few drops were added through the septum to the reaction mixture. When the orange colour had faded, the reaction flask was immersed into an ice bath and the remaining bromine was added slowly at such a rate, to keep the internal temperature below 20 °C. When the addition was complete, the pale orange solution was stirred for another 30 min and 40 mL water was added. 12 g $NaHCO_3$ (143 mmol, 1.12 eq) were added in small portions to the biphasic mixture. When the CO_2 evolution had ceased, the phases were separated and the organic phase was washed with brine (15 mL), saturated $NaHCO_3$ solution (2x15 mL) and again brine (15 mL). Then the organic phase was dried over $MgSO_4$ and the diethyl ether was removed carefully on a rotary evaporator at 40 °C and ≤900 mbar, to yield a pale yellow oil with pungent odour. This crude product consisted of a ≈ 8:1 mixture of mono- and dibrominated pinacolone [GC-MS]. It was distilled through a 1x10 cm Vigreux column at 30 mbar. The desired product had a boiling range of 127 – 130 °C.

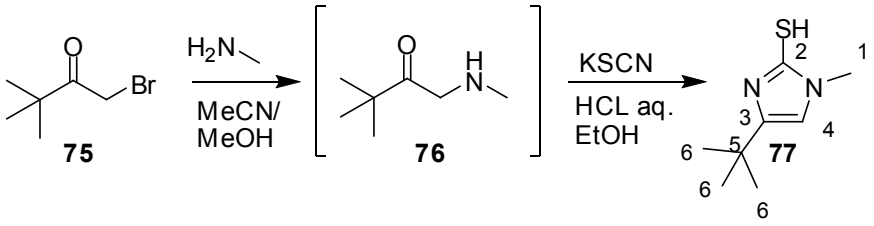
Yield: 17.5 g (98 mmol, 76 %)

bp: 127-130 °C/30 mbar

^{1}H NMR (300.36 MHz, $CDCl_3$): δ 4.17 (s, 2H, H-1), 1.22 (s, 9H, H-4).

^{13}C NMR (75.53 MHz, $CDCl_3$): δ 206.19 (C-2), 44.36 (C-3), 31.80 (C-1), 26.85 (C-4).

8.2.8. Synthesis of 4-tert-butyl-1-methyl-1*H*-imidazole-2-thiol (80)



A 25 mL two-necked round-bottomed flask with a magnetic stir bar and a 10 mL dropping funnel was charged with 4 mL of a 5 M methylamine solution in methanol (20 mmol, 2 eq), which was diluted with 5 mL acetonitrile. The dropping funnel was charged with a solution of 1.36 mL α-bromopinacolone (1.79 g, 10 mmol, 1 eq) in 5 mL acetonitrile. The round-bottomed flask was immersed in an icebath and the α-bromopinacolone solution was added slowly. When the addition was finished, the reaction mixture was stirred for 4 h in the icebath, then it was diluted with 100 mL diethyl ether, which caused a copious colourless solid to precipitate. This was removed via filtration through a fritted glass funnel and the filtrate was concentrated on a rotary evaporator at 40 °C and ≤ 900 mbar to yield 1.5 g yellow oil with amine-like odour. This was dissolved in 50 mL ethanol and transferred into a 100 mL round-bottomed flask with a magnetic stir bar. 5.23 g potassium thiocyanate (54 mmol, 5.4 eq) were added and the pH value of the resulting suspension was adjusted to 2 with 5 % hydrochloric acid. The round-bottomed flask was fitted with a reflux condenser and the reaction mixture was heated under reflux in a 100 °C hot oilbath for 16 h. Then the oilbath was removed and the orange reaction mixture was cooled to 20 °C. 10 mL of a saturated $NaHCO_3$ solution and 10 mL water were added and the resulting solution was extracted with dichloromethane (3x 25 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated to dryness on a rotary evaporator at 40 °c and ≤700 mbar to yield a yellow solid, which was dried in vacuo. This crude product (2.1 g) was recrystallised from 25 mL hot toluene to yield a colourless solid 360 mg. The mother liquor was concentrated to 10 mL to give a second crop of 215 mg pale yellow solid.

Yield: 575 mg (3.38 mmol, 34 %)

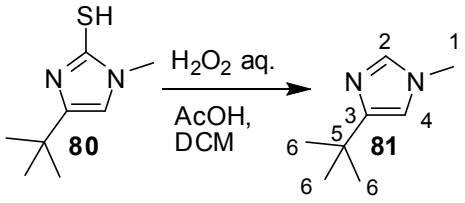
mp: 185-187 °C

^{1}H NMR (300.36 MHz, $CDCl_3$) δ 6.29 (d, *J* = 2.3 Hz, 1H, H-4), 3.54 (s, 3H, H-1), 1.26 (s, 9H, H-6).

^{13}C NMR (75.53 MHz, $CDCl_3$) δ 138.89 (C-3), 112.91 (C-4), 34.24 (C-1), 30.59 (C-5), 29.55 (C-6).

8.2.9. Synthesis of 4-tert-butyl-1-methyl-1*H*-imidazole (81):

Literature: D. B. Grotjahn, E. J. Kragulj, C. D. Zeinalipour-Yazdi, V. Miranda-Soto, D. A. Lev, A. L. Cooksy, *J. Am. Chem. Soc*. **2008**, *130*, 10860–10861.



A 50 mL round-bottomed flask with a magnetic stir bar was charged with 360 mg 4-tert-butyl-1-methyl-1*H*-imidazole-2-thiol (2.1 mmol, 1 eq), which was dissolved in 7 mL dichloromethane and 5 mL glacial acetic acid. The flask with the resulting colourless solution was immersed in an ice bath and 857 µl 30 % aqueous hydrogen peroxide (257 mg, 7.6 mmol, 3.6 eq) was added dropwise to the solution. The reaction mixture turned to yellow and became colourless again. It was stirred for 2 h in the ice bath, then 20 mL 5 M NaOH solution was added, the phases were separated and the aqueous phase was extracted with dichloromethane (4x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered and carefully concentrated to a volume of ca. 2 mL at 40 °C and ≤700 mbar on a rotary evaporator. The remaining yellow liquid was dissolved in 10 mL pentane and the pentane was then evaporated at 40 °C and ≤800 mbar. This procedure was repeated two more times. After the last evaporation, a yellow oil was obtained.

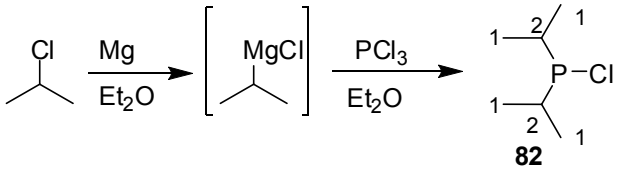
Yield: 213 mg (1.54 mmol, 73 %)

^{1}H NMR (300.36 MHz, $CDCl_3$): δ 7.34 (s, 1H, H-2), 6.57 (s, 1H, H-4), 3.62 (s, 3H, H-1), 1.28 (s, 9H, H-6).

^{13}C NMR (75.53 MHz, $CDCl_3$): δ 137.05 (C-2), 132.68 (C-3), 113.86 (C-4), 33.28 (C-1), 31.82 (C-5), 30.33 (C-6).

8.2.10. Synthesis of Chlorodiisopropylphosphine (82):

Literature: W. Voskuil, J. F. Arens, *Org. Synth*. **1968**, *48*, 47 – 50.



82

A 500 mL three-necked round-bottomed flask with a magnetic stir bar, a 250 mL pressure equalizing dropping funnel and a connection to a protecting gas/vacuum manifold was flame-dried and filled with N_2 twice. 13.34 g magnesium turnings (0.55 mol, 2.2 eq) were added and the flask was fitted with a reflux condenser carrying a gas-inlet and outlet. The magnesium was covered with 50 mL diethyl ether and the dropping funnel was charged with 47.0 mL isopropyl chloride (40.4 g, 0.51 mol, 2.04 eq) of which ca. 5 mL were added neat in one portion to the magnesium turnings. When the reaction had started, the remaining isopropyl chloride was diluted with 100 mL diethyl ether, and added at such a rate to maintain a permanent reflux. When the addition was complete, the grey reaction mixture was heated for 1 h under reflux in a 50 °C warm oilbath. After this period, the oilbath was removed and the GRIGNARD-solution was cooled to 20 °C. It was filtered into a flame-dried 250 mL round-bottomed flask fitted with a Schlenk-adapter via a cannula and stored overnight at -28 °C. The isopropyl magnesium chloride solution was titrated with 1 M 2-butanol in toluene against 1,10-phenantholine as indicator three times (see W. Voskuil, J. F. Arens, *Org. Synth*. **1968**, *48*, 47 – 50.) and estimated to be 3.6 M.

A 500 mL three-necked round-bottomed flask was fitted with a 250 mL dropping funnel on the right neck and a Schlenk-adapter on the left neck and flame-dried. Then a mechanical overhead stirrer was introduced through the central neck and 22.0 mL distilled phosphorous(III)chloride (0.25 mol, 1 eq) were added to the round-bottomed flask and dissolved in 150 mL absolute diethyl ether. The dropping funnel was charged with 140 mL isopropyl magnesium chloride solution (0.50 mol, 2 eq). A low temperature internal thermometer was introduced through the Schlenk-adapter, deep enough to dip into the solution, but not to get damaged by the mechanical stirrer. The PCl_3 solution was cooled to -35 °C (internal temperature) and maintained between -35 and -25 °C by the means of an acetone/dry ice bath. Then the Grignard-solution was added slowly under vigorous stirring and soon a copious colourless solid began to precipitate. When the addition was complete, the dropping funnel was replaced by a reflux condenser and the reaction mixture was heated

under reflux for 30 min in a 60 °C hot oilbath. Then the oilbath was removed and the reaction mixture was cooled to 20 °C. The suspension was filtered into a flame-dried 1000 mL three-necked round-bottomed flask and the retained solid was rinsed with absolute diethyl ether (3x100 mL). The combined filtrates were transferred in portions of ca. 50 mL into an inert distillation apparatus consisting of a 100 mL two-necked round-bottomed flask, a distillation bridge with a ca. 1x10 cm Vigreux column and a 500 mL round-bottomed receiving flask. The diethyl ether was distilled off at atmospheric pressure under N_2, the remaining yellow liquid was distilled at 30 mbar. Two fractions boiling at 39-43 °C and 45–46 °C respectively were collected in Schlenk tubes, the latter was the desired product.

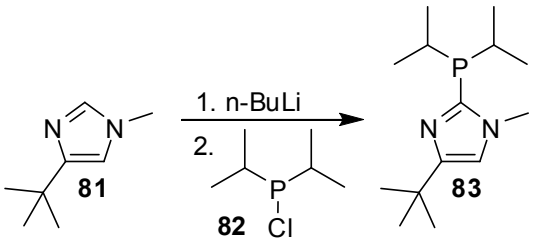
Yield: 9.38 g (61 mmol, 25 %)

bp: 45-46 °C/30 mbar

^{1}H NMR (300.36 MHz, $CDCl_3$) δ 2.04 – 1.86 (m, 2H, H-2), 1.14 (dd, *J* = 13.7, 7.0 Hz, 12H, H-1).

^{13}C NMR (75.53 MHz, $CDCl_3$) δ 28.98 (d, *J* = 30.1 Hz, C-2), 17.66 (d, *J* = 14.2 Hz, C-1).

8.2.11. Synthesis of 4-tert-butyl-2-(diisopropylphosphino)-1-methyl-1*H*-imidazole (83)



An inert 20 mL Schlenk tube with a magnetic stir bar under N_2 atmosphere was charged with 136 mg 4-tert-butyl-1-methyl-1*H*-imidazole (0.98 mmol, 1 eq) which was dissolved in 4 mL absolute diethyl ether. The resulting pale yellow solution was cooled in an acetone/dry ice bath to -78 °C. 0.51 mL of a 2.06 M solution of n-butyl-lithium in hexane (1.05 mmol, 1.07 eq) was added dropwise and the reaction mixture was stirred 1 h at –78 °C. Then 170 µl chlorodiisopropylphosphine (1.06 mmol, 162 mg, 1.06 mmol, 1.08 eq) were added, whereupon a colourless solid precipitated. The reaction mixture was stirred at -78 °C for 1 h. Then the cooling bath was removed and the reaction mixture was allowed to warm to 20 °C. The turbid mixture was filtered inert through a pad of celite into a second inert Schlenk tube. The first Schlenk tube and the celite were rinsed with absolute diethyl ether (2x 3 mL) and the

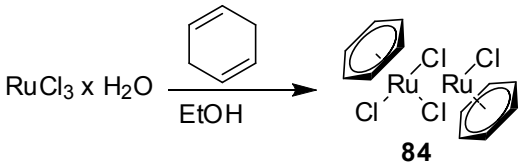
combined filtrates were concentrated to dryness in vacuo at 20 °C and ≤0.1 mbar. The remaining colourless very viscous oil was further dried in vacuo.

Yield: 253 mg (1 mmol, 100 %)

GC-MS (tR= 5.77 min): m/z = 253.9 (2.7 %, M), 212.1 (14,4 %, M – ^{i}Pr), 211.1 (100 %, M – ^{i}Pr), 197.1 (6.3 %, M – ^{t}Bu).

8.2.12. Synthesis of Benzene-ruthenium(II)chloride dimer (84):

Literature: M. A. Bennett, A. K. Smith, *J. Chem. Soc. Dalton Trans*. **1974**, *2*, 233 – 241.



84

A 250 mL three-necked round-bottomed flask with a magnetic stir bar was charged with 732 mg hydrated ruthenium(III)chloride (2.8 mmol, 1 eq), which was dissolved in 70 mL ethanol. The resulting dark brown solution was degassed by bubbling N_2 through it for 15 min. Then the central neck was fitted with a reflux condenser carrying a N_2 in- and outlet. 5.0 mL 1,4-cyclohexadiene (4.3 g, 54 mmol, 19 eq) were added, and the reaction mixture was heated under reflux in a 100 °C oilbath for 4 h. During this period, the colour of the solution changed from brown to red. Then the oilbath was removed and the reaction mixture was cooled to 20 °C and concentrated to dryness on a rotary evaporator at 40 °C and ≤150 mbar. The remaining brown solid was triturated with 20 mL methanol, collected by filtration on a fritted glass funnel and dried in vacuo.

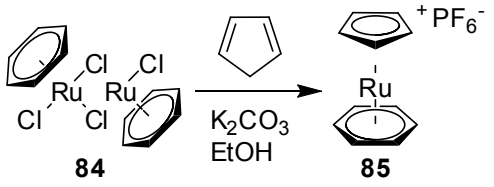
Yield: 523 mg (1.05 mmol, 75 %)

Mp: 265 °C (dec.)

IR (cm-1): 3077, 3035, 2130, 1418, 1148, 976, 843.

8.2.13. Synthesis of Benzene cyclopentadiene ruthenium hexafluorophosphate (85)

Literature: B. M. Trost, C. M. Older, *Organometallics* **2002,** *21,* 2544-2546.



A flame-dried 80 mL Schlenk tube with a magnetic stir bar was charged with 1.00 g potassium carbonate (7.2 mmol, 7 eq) and was evacuated and again flame-dried. Then 518 mg benzene ruthenium(II)chloride dimer (1.04 mmol, 1 eq) were added and both components were suspended in 25 mL absolute ethanol. 2.0 mL freshly distilled cyclopentadiene (1.6 g, 24 mmol, 23 eq) were added and the brown reaction mixture was heated in an 70 °C hot oilbath for 5 h. Then the oilbath was removed. The reaction mixture, which consisted at this point of a reddish-brown solution and a greenish precipitate, was filtrated inert through a pad of celite into a flame-dried 100 mL round-bottomed flask fitted with a Schlenk-adapter. The Schlenk tube and the celite were rinsed with absolute ethanol (2x 10 mL) and the combined filtrates were concentrated to a volume of ca. 10 mL at 20 °C and ≤ 0.1 mbar. To the remaining solution a solution of 700 mg ammonium hexafluorophosphate (4.3 mmol, 4.1 eq) in 7.0 mL degassed water was added. This caused a pale brown solid to precipitate. The resulting suspension was cooled to 4 °C for 15 h to complete the precipitation. Then the supernatant brown liquid was removed via filtration through a cannula fitted with a paper filter and the remaining solid was dried in vacuo. Then it was dissolved in 12 mL degassed acetone to give a slightly brown clear solution, from which the product was again precipitated via the addition of 40 mL degassed diethyl ether. The flask was cooled to 4 °C for 5 h to complete the precipitation. Then the supernatant liquid was again removed via filtration through a cannula fitted with a paper filter, the colourless precipitate was triturated with 20 mL degassed pentane and dried in vacuo.

Yield: 542 mg (1.4 mmol, 67 %)

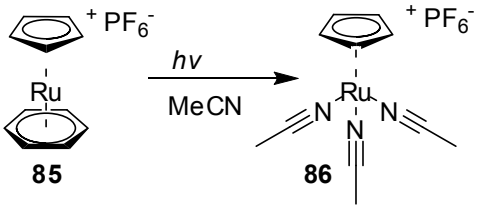
mp: 273 °C (dec.)

^{1}H NMR (300.36 MHz, d6 acetone) δ = 6.35 (s, 6H, benzene-protons), 5.54 (s, 5H, Cp-protons).

^{13}C NMR (75.53 MHz, d6 acetone) δ 87.05 (benzene-carbons), 81.21 (Cp-carbons).

8.2.14. Synthesis of Cyclopentadienyl(trisacetonitrile)ruthenium(II)-hexafluorophosphate (86)

Literature: B. M. Trost, C. M. Older, *Organometallics* **2002,** *21,* 2544-2546.



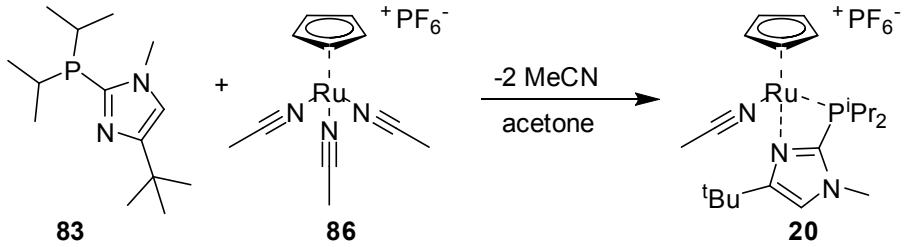
A flame-dried 750 mL Schlenk tube with a magnetic stir bar was charged with 195 mg benzene cyclopentadiene ruthenium hexafluorophosphate (0.5 mmol), which was dissolved in 50 mL absolute acetonitrile. The colourless solution was degassed by bubbling N_2 through it for 45 min. Then a 5 W low pressure mercury UV lamp (type JBL AquaCristal UV-C 5W) was immersed into the solution. The Schlenk tube was put into a large aluminium can to shield off the UV light, and the reaction mixture was irradiated for 8 h. During this time the reaction mixture turned yellow and finally green, maybe due to traces of oxygen, the course of the reaction was followed via ^{1}H-NMR spectroscopy. After the indicated period, the solution was transferred via a cannula into a flame-dried 100 mL round-bottomed flask and concentrated to dryness at 20 °C and ≤0.1 mbar to give a green solid.

Yield: 213 mg (0.49 mmol, 98 %)

mp: 170-177 °C

^{1}H NMR (300.36 MHz, d6 acetone) δ = 4.32 (s, 5H, Cp-protons), 2.52 (s, 9H, acetonitrile-protons).

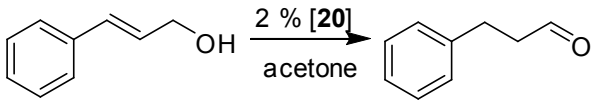
8.2.15. Synthesis of Grotjahn's Catalyst 20



A flame-dried 20 mL Schlenk tube with a magnetic stir bar was charged with ligand **83** 21.0 mg (82 µmol, 1.04 eq) which was dissolved in 2 mL degassed acetone. An inert 5 mL round-bottomed flask fitted with a Schlenk-adapter and a magnetic stir bar was charged with 34.3 mg $CpRu(MeCN)_3^+$ PF_6^- (**86**) (79 µmol, 1 eq) and the pale yellow solution of the ligand was

added to it. The resulting brown solution was stirred for 19 h. This solution was used for catalytic experiments, under the assumption of complete conversion, without further purification.

8.2.16. Isomerisation of cinnamyl alcohol to 3-phenylpropanal



A flame-dried 20 mL Schlenk tube with a magnetic stir bar was charged with 27 mg cinnamyl alcohol (0.2 mmol, 1 eq), which was dissolved in 2 mL degassed acetone. To this solution 100 µl of the above prepared solution of **20**, (≈ 4 µmol, 0.02 eq) was added and the reaction mixture was stirred at 20 °C. The progress of the isomerisation was monitored via GC-MS, no other product than 3-phenylpropanal was formed.

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10. Abreviations

10.1. Analytical Abreviations

APT	Attached Proton Test
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass Spectrometry
NMR	Nuclear Magnetic Resonance)
bd	broad doublet
bs	broad singlet
d	doublet
dd	doublet of doublets
m	multiplet
q	quartet
s	singlet
t	triplet
δ	chemical shift (parts per million)
e.e.	enantiomeric excess
Hz	Hertz
J	coupling constant
MHz	Megahertz
min	minute
nm	nanometer
R_f	retention faktor
TLC	Thil Layer Chromatography
t_R	retention time
UV	ultraviolett
v/v	ratio of volume to volume
w/w	ratio of mass to mass

10.2. Chemical Abreviations

CAM	ceric ammonium molybdate
DCM	dichloromethane
DIPEA	diisopropylethylamine
DMAP	(4-dimethylamino)pyridine

DMF	*N,N*-dimethylformamide
EtOAc	ethyl acetate
EtOH	ethanol
MeOH	methanol
THF	tetrahydrofuran
TMS	trimethylsilyl

10.3. Further Abreviations

Å	Ångström
bp	boiling point
cm	centimeter
d	day
eq	equivalent
g	gram
°C	centigrade
h	hours
M	molar
µL	mikroliter
mbar	millibar
mg	milligram
mL	milliliter
mmol	millimol
mp	melting point
%	percent
ppm	parts per million
rpm	rounds per minute
RT	room temperature

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