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Journal of Organometallic Chemistry 650 (2002) 1–24

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Review article

Homogeneously catalysed isomerisation of allylic alcohols to carbonyl compounds

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Received 22 August 2001; received in revised form 5 December 2001; accepted 19 December 2001

Abstract

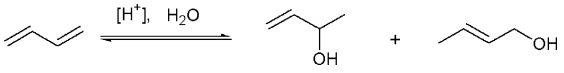
Isomerisation of allylic alcohols forms an elegant shortcut to carbonyl compounds in a completely atom-economical process that offers several useful applications in natural-product synthesis and in bulk chemical processes. This review focuses on the heart of isomerisation catalysis: the catalyst. Combinations of transition metals (from Group 4 to 10), ligands and reaction conditions are compared with respect to yield, turnovers, rate and selectivity. A selected number of clever solutions to synthetic problems are highlighted, such as the synthesis of enols and enolates, chiral carbonyl compounds and silyl substituted ketones. Furthermore, a general overview of the mechanisms proposed for the isomerisation of allylic alcohols is given while some catalyst systems are singled out to discuss mechanistic research. © 2002 Published by Elsevier Science B.V.

Keywords: Allylic alcohols; Carbonyl compounds; Isomerisation; Transition metals; Homogeneous catalysis

1. Introduction

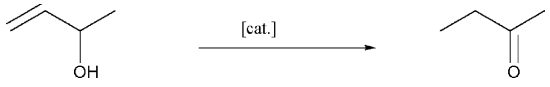
1.1. General

In an industrial scale application, 1,3-butadiene could be the starting material for butanone (methyl ethyl ketone, MEK) and butanal. Both products are nowadays used in a growing market on a Mton per year scale [1,2]. Key intermediates in this synthetic scheme would be allylic alcohols, which can be obtained by acid-catalysed hydration of 1,3-butadiene as is shown in Eq. (1).



(1)

In the second step these allylic alcohols should be isomerised to the carbonyl compounds. The 1,2-addition product, 3-buten-2-ol, would yield MEK (Eq. (2)), while the 1,4-addition product, 2-buten-1-ol, would give butanal (Eq. (3)). A two-reactor process would be economically undesirable, since the equilibrium of Eq. (1) lies heavily on the left-hand side and most of the butadiene would need to be recycled continuously. Thus, the second step should take place in the same reactor as the first step, taking advantage of the thermodynamic gain in the carbonyl formation to drive the equilibrium of Eq. (1) to the right-hand side. However, this means that the transition-metal catalyst should tolerate the presence of dienes and acids during the isomerisation of allylic alcohols.



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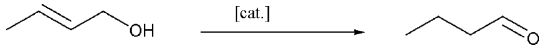

(3)

So far, this has been demonstrated successfully only once [3,4]. In this reaction, discovered by Drent and co-workers, butadiene is converted to MEK by a ruthenium(III) catalyst with a selectivity of over 90% and a total turnover number (TON) of 1200 [3].

As mentioned above, the key reaction in this process is the isomerisation of allylic alcohols to the corresponding carbonyl compounds. Isomerisation of unfunctionalised alkenes has received much attention and it has been the subject of extensive mechanistic and synthetic studies throughout the years [5–12]. In the early days,

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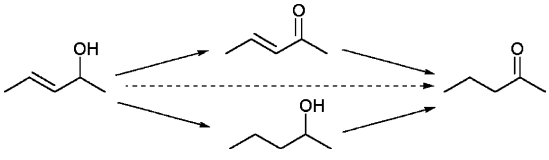
0022-328X/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-328X(02)01150-6

isomerisation of allylic alcohols has been neglected due to the intolerance of many catalysts to the presence of functional groups. Frequently, isomerisation is considered an undesirable side reaction in hydroformylation [13] and hydrogenation [14]. Yet, isomerisation of allylic alcohols forms an elegant shortcut to carbonyl compounds, which otherwise would have to be made in a two-step sequence as shown in Scheme 1 [15]. Thus, this would require separate steps for oxidation of the alcohol and reduction of the double bond. The simple and effective one-step isomerisation of allylic alcohols has been used in smart routes to some natural products [16–19], improving overall yields considerably.

1.2. Scope of the review

Traditionally, isomerisation of allylic alcohols was performed thermally [20,21], by using mineral acids [22,21], bases [21,23] or heterogeneous catalysts [21,24–26]. With the characterisation of organo transition-metal compounds in the late 1950s [27,28], the use of homogeneous catalysts took off. These homogeneous catalysts generally offered a higher reaction rate and improved selectivities [11]. Additionally, the ligands in these catalysts can be varied relatively easily to modify their reactivity.

This review concerns *homogeneously* catalysed isomerisation of allylic alcohols to carbonyl compounds. It covers the period from 1962, the year of the first example known to us, up till present. After a general introduction to the mechanisms involved in isomerisation, it has been attempted to give a concise overview of isomerisation catalysts along the transition-metal series. This paper focuses on the heart of the isomerisation catalysis: the catalyst. The combinations of metals and ligands are compared based on yield, TON, turnover frequency (TOF) and selectivity. Several clever solutions to synthetic problems are highlighted. Some catalyst systems have been studied in-depth and they are singled out to discuss mechanistic research. This review excludes isomerisation of unfunctionalised alkenes, unsaturated amines, ethers and propargyl alcohols, but in some cases, where comparison is illustrative, a few examples are given.



Scheme 1. Isomerisation of allylic alcohols forms an elegant shortcut to carbonyl compounds.

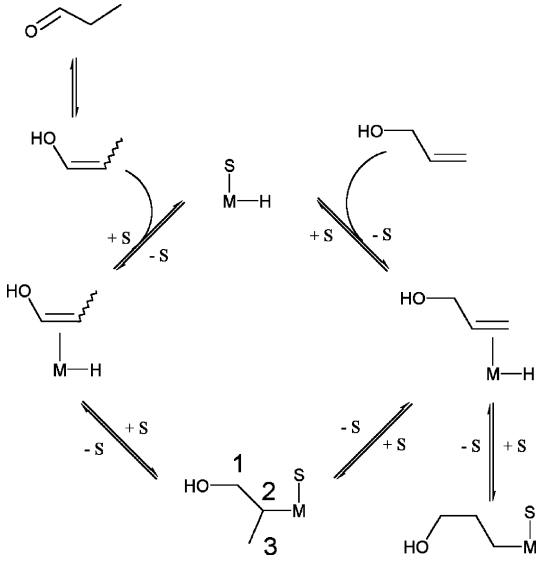
2. Mechanisms in isomerisation of allylic alcohols

Since the reaction steps in homogeneously catalysed isomerisations of alkenes usually are reversible, a thermodynamic mixture of products is formed. Not only regio-isomers result, but also a mixture of *cis* and *trans* compounds. Often, this type of isomerisation constitutes an unwanted side reaction, even more so, since frequently it is faster than the desired reaction. Allylic alcohols on the other hand, almost exclusively yield the carbonyl compound as a single product. This is due to the fact that the energy of a C=O double bond plus a C–C single bond compared to a C=C double bond plus a C–O single bond is lower by 125 kJ mol^{-1} [29]. Only under careful control of the reaction conditions, the corresponding enols can be isolated [30,31]. This feature naturally adds to the versatility and usability of this reaction in a synthetic scheme.

Over the years, two classes of mechanisms have been proposed to explain experimental isomerisation results [11,32–34]: the metal hydride addition–elimination mechanism (also named the alkyl mechanism [32]) and the π-allyl metal hydride mechanism. The main difference between these two mechanisms is that the former is an *inter*molecular mechanism, whereas the latter is *intra*molecular. An elaborate discussion on mechanisms in allylic alcohol isomerisation is given in Ref. [34].

2.1. Metal hydride addition–elimination mechanism

The metal hydride addition–elimination mechanism starts with coordination of the alkene moiety to a metal hydride (Scheme 2) [11,32]. This hydride can be present in the precursor complex as in $[HRh(P(OPh)_3)_4]$ [35] or, alternatively be formed in situ as proposed for



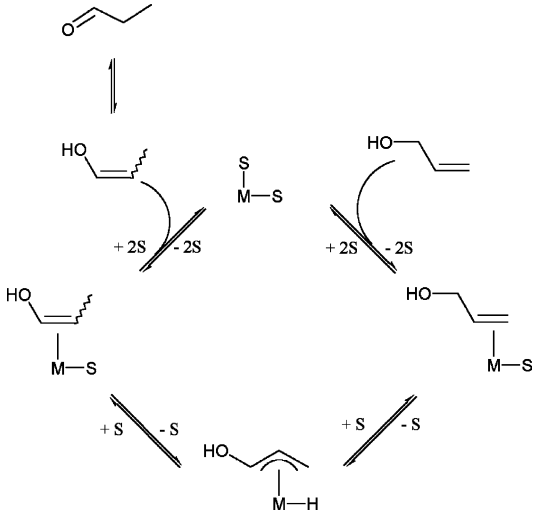
Scheme 2. Metal hydride addition–elimination mechanism. S = 2e-vacant site or labile ligand [11].

$[Ru(H_2O)_6](OTs)_2$ [34]. Insertion of the alkene moiety into the metal–hydride bond will give a metal–alkyl species.

The next step is β-hydrogen elimination, which results in the product alkene coordinated to the metal (or coordinated starting material if a hydrogen from C3 is abstracted as shown in Scheme 2). The final step of dissociation regenerates the starting metal hydride with a vacant site. Alternatively, the last step can be associative replacement, depending both on the metal and the substrate. If an allylic alcohol is used as substrate the initial product is an enol. Dissociation will be facilitated in this case by tautomerisation, which will yield the more stable final product, the carbonyl compound.

2.2. π-Allyl metal hydride mechanism

The π-allyl metal hydride mechanism starts with complexation of the alkene moiety to a metal centre that does not contain a hydride, but must have two vacant sites. Coordination is followed by formal oxidative addition of a C–H single bond to yield a metal–allyl hydride as shown in Scheme 3. The next step is reductive elimination to give the complexed product, which will dissociate to regenerate the starting metal complex. (The latter process can of course again be associative, depending on the metal, and is assisted by tautomerisation in the case of allylic alcohols.) Since during this mechanism the oxidation state at some point has to be raised by two, it is usually invoked for low-valent metal complexes.

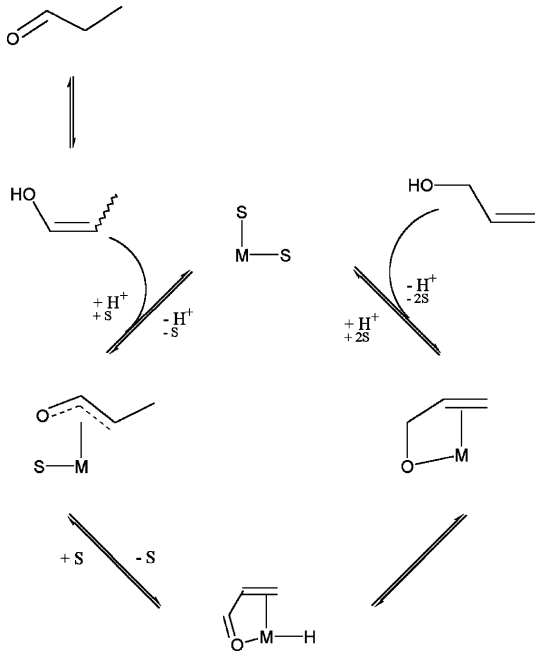


Scheme 3. π-Allyl metal hydride mechanism. S = 2e-vacant site or labile ligand [11].

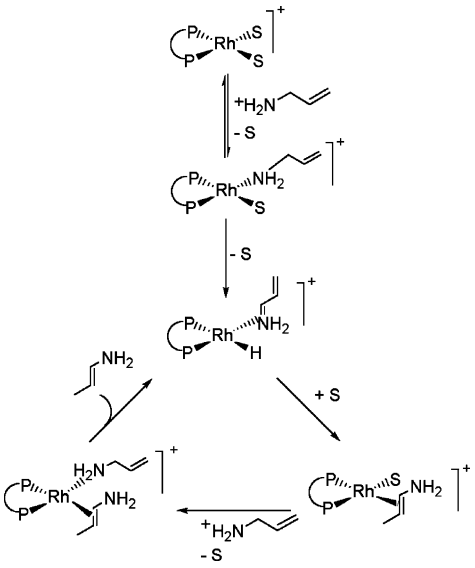
2.3. Alternative mechanisms

Both mechanisms described above have been well established in the case of unfunctionalised alkenes [11,33]. As will be seen in later sections, these two mechanisms have also been generally proposed with allylic alcohol substrates, but unfortunately in many cases without experimental proof. Both mechanisms are taken from older alkene chemistry and do not assign any role to the oxygen moiety. Neither mechanism can explain why some catalysts isomerise allylic alcohols much faster than unfunctionalised alkenes [15,36,37] or sometimes even exclusively [3]. However, a few studies have been performed [15,36–38] that show alternative possibilities, invoking in some stage of the catalytic cycle involvement of the oxygen moiety (Scheme 4).

Especially, an analogous case of isomerisation of several allylic amines was studied in depth by Noyori and co-workers as reviewed by Otsuka [39]. They showed by trapping of intermediates [40], temperature-dependent NMR [41,40] and ab initio calculations [42] that in this case a mechanism is operative that starts with coordination of the nitrogen atom (Scheme 5). Similar mechanisms in which the first step is coordination of the oxygen moiety of an allylic alcohol have so far received very little attention, even though this might be reasonable particularly in cases where bases have been used as co-catalyst. The stepwise pathway as shown in Scheme 4 involves deprotonation and coordination of the alkoxide, β-hydrogen abstraction from the substrate to give an α,β-unsaturated carbonyl compound in an enone metal hydride complex. Migration



Scheme 4. Allylic-alcohol isomerisation mechanism invoking oxygen coordination. S = 2e-vacant site or labile ligand.



Scheme 5. Nitrogen-triggered mechanism of allylic amine isomerisation with a rhodium(I) catalyst [39]. S = 2e-vacant site or labile ligand. P_UP = didentate phosphine ligand.

of the hydride then yields an oxo-allyl species, which upon protonation releases the enol. This intramolecular mechanism can be compared with the mechanism for intermolecular transfer hydrogenation, for which especially ruthenium and rhodium complexes are known to be active catalyst precursors, particularly when a base is added as co-catalyst. However, if the latter mechanism is operative, side products such as the saturated alcohol and the enone should be found (see Scheme 1).

Several other mechanisms have been postulated, but generally these are modified versions of one of the three types mentioned above. Since often a mechanism is proposed without thorough investigations, a detailed description will only be given in the following sections when this is warranted.

3. Isomerisation of allylic alcohols catalysed by transition-metal complexes

In the following sections isomerisation of allylic alcohols to carbonyl compounds is covered, catalysed by complexes containing transition metals of Groups 4–10. The emphasis is given on activity in terms of yields, TONs and rates. On the other hand, mechanistic investigations are highlighted. The overwhelming majority of isomerisation catalysts belong to either Group 8 or 9, illustrating the especially rich chemistry of these groups. Third row elements have received little attention. The metal ions from this row form much stronger bonds with, e.g. alkenes and alkyls than their 3d and 4d counterparts [43], which results in lower reaction rates if reaction occurs at all.

3.1. Groups 4 and 5: titanium to tantalum

The early transition metals are famous for their activity in polymerisation catalysis [44]. Isomerisation of unfunctionalised alkenes has been observed both with heterogeneous [45] and homogenous [46–48] catalytic systems, but for allyl alcohols it has not been reported.

3.2. Group 6: chromium, molybdenum and tungsten

3.2.1. Chromium

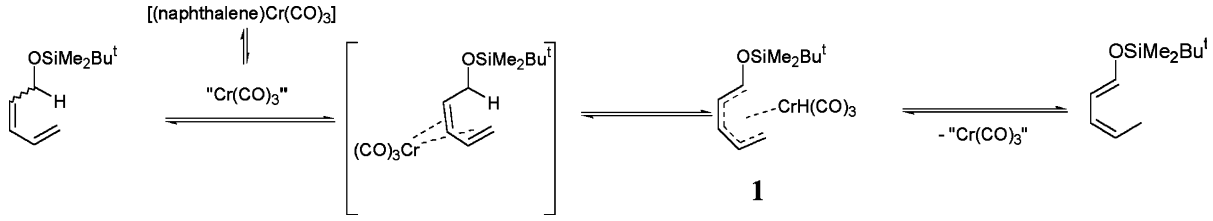
The use of chromium has diminished due to its toxicity and negative impact on the environment. Sodeoka et al. reported in 1990 the stereoselective isomerisation of an allyl silyl dienol ether to its vinyl analogue [49]. The reaction is catalysed by [$Cr(CO)_3$(naphthalene)] and proceeds in high yield at room temperature, but using a relatively high catalyst concentration of 20 mol%. A chromium π-allyl metal hydride mechanism (Scheme 6) is proposed with a U-shaped pentadienyl intermediate (**1**), which can explain the stereoselective formation of *trans*, *cis*-diene product. In fact, compounds which preclude easy formation of this intermediate require much higher temperatures up to 120 °C. The driving force in this reaction is not the formation of a carbonyl compound, but the formation of a fully conjugated system.

3.2.2. Molybdenum

The molybdenum(0) complex *trans*-[$Mo(N_2)_2(dppe)_2$] (dppe = 1,2-bis(diphenylphosphino)ethane) catalyses isomerisation of allylic alcohols [50,51], allylic amines [50] and allylic ethers [50] in refluxing benzene (Table 1). As can be seen from the table, the yields are generally moderate to high, but with TONs just up to 70 during 1–4 h of reaction. The yield with primary allylic alcohol substrates is rather low, due to decarbonylation of the product aldehyde by *trans*-[$Mo(N_2)_2(dppe)_2$] to form *cis*-[$Mo(CO)_2(dppe)_2$], which is inactive [50]. Usually, intermolecular hydrogen transfer is a competing side reaction with cyclic alcohols and this results in α,β-unsaturated ketones and saturated alcohols [51].

The molybdenum(IV) complex [$H_4Mo(dppe)_2$] is also active in isomerisation (entries 2 and 4) [50,51]. This is thought to be due to initial hydrogen transfer of the complex to the allylic alcohol substrate to give a molybdenum(0) active species. The concomitant formation of 2-butanol from 3-buten-2-ol has been demonstrated [51].

Both Tatsumi et al. [50] and Lin and Lu [51] suggest an intramolecular π-allyl metal hydride mechanism. Some support for this mechanism may come from the fact that a π-allyl molybdenum hydride is formed in the reaction of *trans*-[$Mo(N_2)_2(dppe)_2$] with propene [50]. Isomerisation of a mixture of conformationally rigid cyclohexane derivatives *trans*-**2** and *cis*-**2** shows prefer-



Scheme 6. Chromium-catalysed isomerisation of allyl silyl dienol ethers [49].

ential *cis*-isomer consumption [52]. This can be explained by the need for a synperiplanar arrangement between the metal–carbon and the C–H bonds, which is in agreement with the π-allyl metal hydride mechanism.

trans-**2** *cis*-**2**

3.2.3. Tungsten

Tungsten complexes have been used in some cases in isomerisation of unfunctionalised alkenes [7], but to the best of our knowledge not in the isomerisation of allylic alcohols.

3.3. Group 7: manganese, technetium and rhenium

We are not aware of any articles describing isomerisation of allylic alcohols to carbonyl compounds. Some rhenium oxo complexes have been used to catalyse a different type of isomerisation, the 1,3-transposition of the alcohol group [53]. This type of isomerisation falls outside the scope of this review.

3.4. Group 8: iron, ruthenium and osmium

3.4.1. Iron

Iron is among the metals that have been explored in the early days of transition-metal catalysis. In fact, only 10 years after the take off of organometallic chemistry, Emerson and Pettit [54–56] demonstrated the ability of iron pentacarbonyl to isomerise allyl alcohol to propanal. Their original communication did not contain any experimental details. A gap that was filled soon after by Damico and Logan [57].

Unsaturated acyclic secondary allylic alcohols are isomerised to the corresponding ketones in the presence of 10–20 mol% [$Fe(CO)_5$] (see Table 2). The reaction can be carried out neat or in hydrocarbons at 110–125 °C. After 2–6 h, a conversion of around 70% is obtained, with a selectivity of more than 95%. Thus, 1-hepten-4-ol is converted to 4-heptanone in 80% yield after 4 h, whereas a 60% yield is achieved in the isomerisation of 1-decen-3-ol to 3-decanone (entries 1 and 2) [57]. The former result illustrates that also non-allylic alcohols are converted, presumably without metal–olefin dissociation during consecutive isomerisation steps [58].

However, this method gives unsatisfactory results with primary and cyclic unsaturated alcohols. The main problem with primary alcohols is the formation of the aldol dimer of the product aldehyde. Cyclic unsaturated alcohols apparently react too slowly and since the catalyst decomposes under the reaction condi-

Table 1
Molybdenum(0)-catalysed isomerisation of allylic alcohols to carbonyl compounds [a]

Entry	Substrate	Substrate/catalyst precursor	Time (h)	Yield (%)	Reference
1	3-Buten-2-ol	100	1	69	[50]
2 [b]	3-Buten-2-ol	20	1	95	[50]
3	Allyl alcohol	20	1	20	[50]
4 [b]	Allyl alcohol	20	1	27 [c]	[50]
5	3-Penten-2-ol	5	3	98–100	[50]
6	1,7-Octadien-3-ol	5	3	98–100 [d]	[51]
7	2-Cyclopenten-1-ol	5	3	20 [e]	[51]
8	2-Cyclopenten-1-ol	5	3	20 [e]	[51]

[a] Catalyst precursor: 0.1 mmol *trans*-[$Mo(N_2)_2(dppe)_2$], $T = 80$ °C in benzene.
[b] Catalyst precursor: 0.1 mmol [$Mo(dppe)_2H_4$].
[c] 60% of the catalyst precursor is converted to *cis*-[$Mo(CO)_2(dppe)_2$] by decarbonylation of the product aldehyde.
[d] The alkene function at C7 remains unchanged.
[e] The major products arise from intermolecular hydrogen transfer: α,β-unsaturated ketone and saturated alcohol.

Table 2
Isomerisation of unsaturated alcohols to carbonyl compounds catalysed by $[Fe(CO)_5]$

Entry	Substrate	Time (h)	Method [a]	Yield (%)	Reference
1	6-Hepten-4-ol	4	C	80	[57]
2	1-Dodecen-3-ol	6	A	60	[57]
3	2-Methyl-1-hepten-3-ol	6	A	75	[57]
4	1-Octen-3-ol	1	B	70	[57]
5	2-Cyclohexen-1-ol	6	A	20	[57]
6	2-Cyclohexen-1-ol	4	B	40	[57]
7	3-Hexen-1-ol	6	C	8	[57]
8	9-Decen-1-ol	5	A	10	[57]
9	9-Decen-1-ol	5	B	54	[57]
10	2-Methyl-1-octen-3-ol	2	B	95	[59]
11	1-Phenyl-2-(CO_2Me)-2-propen-1-ol	1	B	87	[59]
12	3-Phenyl-2-propen-1-ol	2	B	38	[59]
13	2-Methyl-3-phenyl-2-propen-1-ol	1	B	90	[59]

[a] A: heating in octane at 124 °C, 10–20 mol% $[Fe(CO)_5]$; B: irradiation (200 W high-pressure mercury lamp) in pentane at 20 °C, 1–5 mol% $[Fe(CO)_5]$; C: neat at 110 °C, 10–20 mol% $[Fe(CO)_5]$.

tions, giving mainly precipitated iron metal [60], this results in yields of only 20%.

Both problems can be circumvented partially by adopting different experimental conditions. When a pentane solution of unsaturated alcohol and 3–5 mol% of $[Fe(CO)_5]$ is irradiated with a 200 W high-pressure mercury lamp at room temperature, the yields can be improved to 40–60% (entries 6 and 9) [57]. It was shown recently that in this way both *gem*- (entries 10 and 11) and 1,2-substituted (entries 12 and 13) secondary allylic alcohols can be isomerised within reasonable times at room temperature [59]. Aliphatic, aromatic and electron-withdrawing groups are tolerated, but polyunsaturated allylic alcohols give low yields. Also under these experimental conditions loss of product due to dimerisation is observed after prolonged irradiation [57]. Addition of aldehydes during the reaction affords the aldol products in good yields [61].

A further improvement was made by Iranpoor and co-workers [62,63] by introducing $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$ as catalysts. Both compounds have the advantage over $[Fe(CO)_5]$ that they are solids and therefore more easily handled than the highly poisonous, volatile $[Fe(CO)_5]$. In addition to that, the yields are generally higher, especially with cyclic alcohols (Table 3, entry 1 cf. Table 2, entry 6). In this way some aldehydes now become available in reasonable yields. Thus, decanal is formed in 75% yield from 9-decen-1-ol and 2-propen-1-ol gives propanal in 85%. However, it should be noted that Iranpoor uses 20–80 mol% of catalyst [63]. In the case of $[Fe_3(CO)_{12}]$, e.g. this means that 60–240 mol% of iron is used: considerably more than generally used with $[Fe(CO)_5]$. Some of the improved yields (see Table 3) may be explained in this way. This reasoning is of course only true if in all cases the same species is catalytically active, like $[Fe(CO)_3]$ or $[Fe(CO)_4]$ (vide infra). In fact, when (benzylidene-

Table 3
Comparison of $[Fe_2(CO)_9]$ [62] and $[Fe_3(CO)_{12}]$ [63] as catalyst precursors for the isomerisation of unsaturated alcohols to carbonyl compounds

Entry	Substrate	$[Fe_2(CO)_9]$		$[Fe_3(CO)_{12}]$	
		Time (h)[a]	Yield (%)	Time (h)[b]	Yield (%)
1	2-Cyclohexen-1-ol	1.5	85	2	90
2	6-Hepten-4-ol	1.75	90	1.7	88
3	9-Decen-1-ol	2	75	2	78
4	Allyl alcohol	2	85	1.3	90
5	2-Methyl-3-buten-2-ol	2.5	90	2	88
6		6	85	1	94
7		6	0	2	0
8		5	58	6	60

[a] $T = 40–50$ °C; solvent: benzene; 20–40 mol% $[Fe_2(CO)_9]$. [b] $T = 25–30$ °C, irradiation of substrate in *n*-pentane or *n*-hexane with $\lambda > 560$ nm, 20–40 mol% $[Fe_3(CO)_{12}]$.

acetone)iron tricarbonyl is used [63], which is a well-defined source of $[Fe(CO)_3]$, an even faster reaction is observed and high yields are obtained after only 5–30 min. The greatest advantage in using $[Fe_3(CO)_{12}]$ lies perhaps in the fact that the reaction conditions are much milder: room temperature and a light source with $\lambda > 560$ nm.

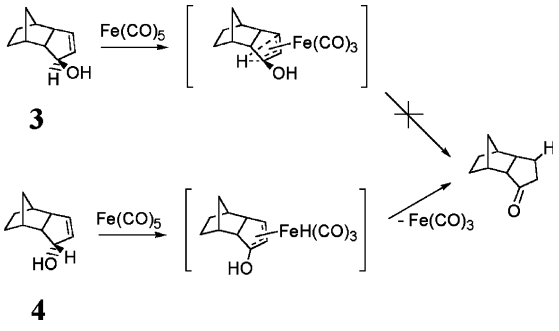
So, the iron carbonyl compounds offer a convenient way to ketones and aldehydes in moderate to high yields. Compared to the traditional acid/base catalysts they offer distinct advantages, mainly due to the mild reaction conditions. Generally, neither polymerisation,

nor structural rearrangements are observed and the catalysts are tolerant towards many functional groups. However, the use of relatively high mol% of catalyst, makes the efficiency in terms of TON (around 20 in the best case) and TOF (typically $< 10\ h^{-1}$) rather poor.

Mechanistically, the isomerisation of unsaturated alcohols by iron carbonyl compounds has been studied in detail. The first mechanistic proposal by Emerson and Pettit [54] was based on the π-allyl metal hydride mechanism. All experimental observations are consistent with this mechanism. The mechanism implies CO dissociation and if the reaction is performed under CO pressure, it is stopped at the alkene–iron species [64]. An infrared study of the thermal and irradiative isomerisation reaction shows only bands of $[Fe(CO)_5]$, $[Fe_2(CO)_9]$ and $[Fe_3(CO)_{12}]$ [60]. In neither case could any intermediate be detected. If the substrate does not contain a hydrogen on the *ipso* carbon as in 2-methyl-3-buten-2-ol, no isomerisation is observed. Upon isomerisation of allyl-1,1-d_2 alcohol by heating with $[Fe(CO)_5]$ deuterium is only observed in the C3-position of the product [65]. It is reasonable to assume that the same mechanism is operative under irradiation conditions.

The alternative, metal hydride addition–elimination mechanism is only possible if the hydride would exclusively add to the C3-position. However, in the isomerisation of 1-butene by $[DFe(CO)_4]$, exclusive addition to the C2-position is found instead [66].

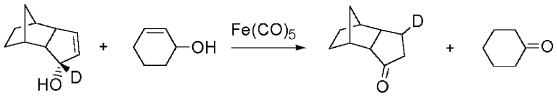
A third mechanism could be envisioned. A suprafacial sigmatropic 1,3-hydrogen shift is allowed by the Woodward–Hoffmann rules [67] if back donation of the iron d-electrons to the alkene moiety results in a molecular orbital (MO) of the correct symmetry to be the highest occupied molecular orbital (HOMO) [68]. This mechanism does not invoke an iron-hydride species. An ingenious experiment was set up by Cowherd and Von Rosenberg [68] to distinguish between this mechanism and the mechanism proposed by Emerson and Pettit. Two epimeric alcohols were synthesised (**3** and **4** in Scheme 7), for which coordination of $[Fe(CO)_3]$ most likely occurs at the least hindered *exo* side. In compound **3** the reaction can only proceed via a suprafacial sigmatropic 1,3-hydrogen shift. Compound **4** can give rise to an iron-hydride species. In fact, the latter compound is isomerised to the corresponding ketone, while the former remains unchanged [68]. This experiment therefore excludes a sigmatropic shift on the opposite side of the metal, but a sigmatropic shift on the same side, without a discrete iron-hydride species cannot be excluded.



Scheme 7. Isomerisation of two epimeric allylic alcohols catalysed by iron pentacarbonyl.

A crossover experiment with the deuterated analogue **4-d** (Eq. (4)) and 2-cyclohexen-1-ol gave only deuterated **5** and unlabeled cyclohexanone [69]. This is in agreement with an intramolecular process, as proposed before. Unfortunately, it was not mentioned if the reaction was monitored at low conversion to rule out preferential reactivity of either substrate. Both substrates differ considerably in structure!

A primary kinetic isotope effect (KIE) for isomerisation is observed both for substrate **4-d** and allyl alcohol, of 1.23 and 1.12, respectively [69]. Since isomerisation of unfunctionalised alkenes with $[Fe(CO)_5]$ does not show a KIE, these results suggest a change in rate-determining step by changing the substrate. The preferred route could be a concerted suprafacial 1,3-hydrogen shift on the same side as the metal.



4-d **5** (4)

3.4.2. Ruthenium

While the iron-catalysed isomerisation solely makes use of iron(0) carbonyl complexes, the ruthenium chemistry is much richer. Ruthenium can form stable complexes in many oxidation states, ranging from zero to eight [70]. This wealth of possibilities is reflected in the vast amount of complexes that has been used in homogeneous catalysis [71]. Together with rhodium (vide infra), ruthenium dominates homogeneously catalysed isomerisation of allylic alcohols. Many significantly different ruthenium complexes are involved, and this section is arranged according to complex type together with their mechanistic implications. At the end a summary will be provided which focuses on synthetic utility.

3.4.2.1. Ruthenium chloride complexes. By far the most available ruthenium compound is $[RuCl_3 \cdot x H_2O]$, which has in fact been used to synthesise all other catalyst precursors. It has itself been used in isomerisation of allylic alcohols [72–74], but care should be taken in interpreting the results, since at the time of the publications, commercially available $[RuCl_3 \cdot x H_2O]$ was an ill-defined compound containing mainly oxo-, hydroxy-,

and polymeric species with an average oxidation state close to four [70]. Refluxing [$RuCl_3 \cdot x H_2O$] in aqueous allyl alcohol results in a mixture of propanal, propenal and propene as a result of inter- and intramolecular hydrogen transfer [72]. A Ru(II) species could be identified upon addition of pyridine to the reaction mixture. The influence of the solvent on product distribution is large. By carrying out the reaction neat in the allylic alcohol [74], the amount of side products is reduced considerably, although yields remain low with primary allylic alcohols. Too strongly coordinating solvents either inhibit all reactivity (DMF) or cause dehydration (DMSO) [74]. If one equivalent of NaOH is added [73], high TONs of around 300 in 5 min could be attained. Some chirality transfer seems to have taken place via a mechanism that involves ruthenium alkoxides. Under the same conditions allylic ethers are not isomerised.

Reduction of $RuCl_3$ in the presence of triphenylphosphine gives the ruthenium(II) complex [$RuCl_2(PPh_3)_3$] [75]. This complex isomerises allylic alcohols more reproducibly than $RuCl_3$, but at relatively low rates (see Table 4 for some representative examples). Especially allylic alcohols with substituted double bonds are isomerised poorly [76–78]. In water, (homo)allylic alcohols undergo a different isomerisation catalysed by [$RuCl_2(PPh_3)_3$]: the 1,3-transposition of the alcohol moiety [79]. Increasing the catalyst concentration or lowering the temperature results in loss of selectivity and a higher percentage of ketone is formed.

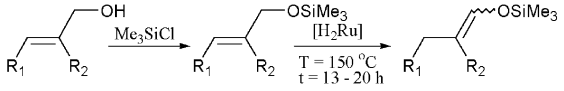
The activity of [$RuCl_2(PPh_3)_3$] in carbonyl compound formation improves by a factor of 50 upon addition of three equivalents of K_2CO_3 [76]. The mechanism is thought to involve a ruthenium–alkoxide intermediate and, just as with $RuCl_3$, the easier formation of this intermediate can explain the positive effect of a base. An additional effect might be caused by creation of a vacant site on the ruthenium centre by removing Cl^- through precipitation of solid KCl.

Addition of one equivalent (to ruthenium) of an organolithium or -magnesium reagent to [$RuCl_2(PPh_3)_3$] yields a catalyst system that catalyses a tandem isomerisation–aldol condensation reaction [80]. Thus, 1-octen-3-ol and benzaldehyde give a mixture of the aldol condensate and 3-octanone. If the reaction is performed in the absence of aldehyde, complete isomerisation to the ketone is observed [81].

[$RuCl_2(PPh_3)_3$] can be incorporated in a polystyryldiphenylphosphine resin [82]. Although its reactivity is reduced by a factor of 2–5.5, it can now be reused more than five times without appreciable loss of activity. The leaching of ruthenium is low in apolar solvents, but becomes significant in protic solvents.

Replacement of one or both the chlorides in [$RuCl_2(PPh_3)_3$] by hydride or hydride and acetate, respectively, results in more active isomerisation catalysts [77,78] (Table 4, entries 5–9). However, both complexes are air-sensitive as solids and in solution. None of the complexes is specific in isomerisation of allylic alcohols. In fact, isolated double bonds are isomerised faster [77]. Replacement of both chlorides by hydrides yields [$H_2Ru(PPh_3)_4$], a catalyst that has been used to isomerise allyl silyl ethers to vinyl silyl ethers as shown in Scheme 8 [83]. Unfortunately, in all cases a mixture of *Z*- and *E*-enol ethers is formed in a ratio close to 1:1.

In the synthesis of ruthenium-dichloride phosphine complexes, triphenylphosphine can be replaced by several chiral phosphines like diop (**6**), bmpp (**7**), *o*-ampp (**8**) and nmdp (**9**). Ru(II) complexes with these ligands have been reported to achieve kinetic resolution of chiral allylic alcohols by selectively reacting away one of the enantiomers to the corresponding carbonyl compound (Eq. (5)) [84], but with extremely low enantiomeric excesses.

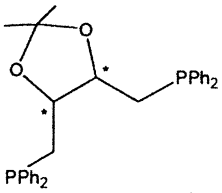


Scheme 8. Isomerisation of allyl silyl ethers to silyl enol ethers. R_1 = H, Me, Ph, vinyl; R_2 = H, Me. In all cases, a *Z*/*E* ratio between 1 and 2 was found [83].

Table 4
Ruthenium(II)-catalysed isomerisation of unsaturated alcohols to carbonyl compounds [a]

Entry	Catalyst precursor	Substrate	Time (h)	*T* (°C)	TON	Reference
1	[$RuCl_2(PPh_3)_3$]	1-Octen-3-ol	3	65	17	[76]
2	[$RuCl_2(PPh_3)_3$]+K_2CO_3	1-Octen-3-ol	0.33	65	94	[76]
3	[$RuCl_2(PPh_3)_3$]+K_2CO_3	2-Cyclohepten-1,4-diol	6.5	65	65	[76]
4	[$RuCl_2(PPh_3)_3$]+K_2CO_3	2-Cycloocten-1,4-diol	3	65	82	[76]
5	[$HRuCl(PPh_3)_3$]	2-Buten-1-ol	1	110	Trace	[77]
6	[$HRuCl(PPh_3)_3$]	3-Buten-2-ol	1	110	450	[77]
7	[$HRuCl(PPh_3)_3$]	2-Cyclohexen-1-ol	1	110	275	[77]
8	[$HRuCl(PPh_3)_3$]	4-Penten-2-ol	1	110	395	[77]
9	[$HRuCl(PPh_3)_3$]	1-hepten-3-ol	1	110	230	[77]

[a] Reactions were performed in an inert atmosphere of N_2, solvent: THF (entries 1–4) or none (entries 5–9).



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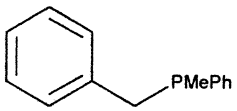

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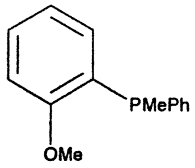

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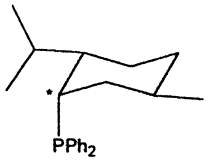

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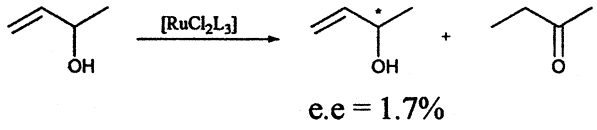
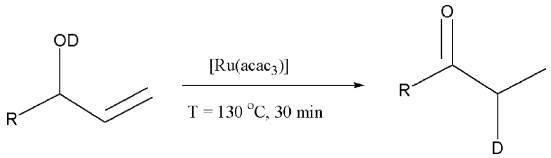


(5)

Reduction of $RuCl_3$ with formic acid yields the ruthenium(0) complex $[Ru(CO)_3(PPh_3)_2]$ [85] that isomerises 1-phenyl-2-propen-1-ol to ethyl phenyl ketone at 40 °C in 3 h (TON = 200) [86]. An intramolecular π-allyl metal hydride mechanism has been proposed based on experiments with deuterium labelled substrate.

3.4.2.2. Ru(acac)$_3$ complexes. $[Ru(acac)_3]$ (acac = acetylacetonato; 2,4-pentanedionato) can be prepared readily from $[RuCl_3 \cdot xH_2O]$ [87] or can be obtained commercially. Alkenes, ethers, esters and allylic alcohols with unsubstituted double bonds are readily isomerised [88–90]. As is shown in Eq. (6), selectively deuterated compounds can be obtained in yields varying from 77% (R = Et) to 92% (R = *i*-Pr). The rate of isomerisation depends on substitution of the alkene at C1. Thus, while 86% (TON = 86) of butanone is formed from 3-buten-2-ol within 15 min at 100 °C [88], 1-phenyl allyl alcohol requires 2 h at a higher temperature [89] to reach complete isomerisation to ethyl phenyl ketone.



(6)

Several experiments have been conducted to elucidate the reaction mechanism of the $[Ru(acac)_3]$-catalysed isomerisation of allylic alcohols. Both the selective deuterium incorporation [88] and the KIE of 2.6 [90] suggest a π-allyl metal hydride mechanism. Neither racemisation of Δ-(+)-$[Ru(acac)_3]$, nor *E*/*Z*-isomerisation of $[Ru(tfacac)_3]$ (tfacac = 1,1,1-trifluoro-2,4-pentanedionato) is observed during isomerisation of alkenes and ethers. Especially the latter result seems to indicate that none of the acac ligands dissociates completely during the catalytic cycle. To avoid a 19e π-allyl species, Krompiec et al. [90] modified the classical π-allyl mechanism to a σ-allyl type mechanism. However, this leads in turn to an unconvincing seven-coordinated ruthenium intermediate. Unfortunately, results obtained with very diverse substrates have been combined into a single mechanistic proposal without considering the possibility of more than one mechanism. In short, the detailed mechanism of $[Ru(acac)_3]$-catalysed isomerisation of allylic alcohols has not been unambiguously ascertained. It was proposed that deactivation of the catalyst takes place via reduction to inactive $[Ru(acac)_2L_2]$ complexes [90], which is facilitated by solvents that coordinate strongly to the ruthenium centre. However, in our laboratory isomerisation did take place with $[Ru(acac)_2L]$ (L = phen, bpy) [91], indicating that at least not all Ru(II)–acac complexes are inactive.

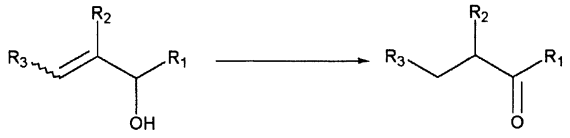
An active isomerisation catalyst is also obtained upon addition of two equivalents of triphenylphosphine and three equivalents of a Brønsted acid to $[Ru(acac)_3]$ [3,4]. An initial TOF of 200 h^{-1} is reached in the isomerisation of 3-buten-2-ol to butanone at 120 °C in diglyme. Apparently, in this case the strongly coordinating phosphine ligands block the first two available vacant sites, since an induction period of 3 h demonstrates the difficulty of complete acac removal even in the presence of three equivalents of acid. Without additional phosphine ligand no induction period is observed (vide supra). The initial TOF is doubled if triphenylphosphine is replaced by phenanthroline [3]. More important than the improved rate is the fact that this catalyst precursor is the only one to isomerise allylic alcohols in the presence of conjugated dienes. With this system a direct conversion of butadiene to butanone is now possible (see Section 1). Internal double bonds are isomerised much less efficiently and in the presence of butadiene only traces of product are observed (Table 5, entries 4 and 5) [3,4].

3.4.2.3. $[Ru(H_2O)_6]^{2+}$. Starting from $RuCl_3$, $[Ru(H_2O)_6](OTs)_2$ (OTs = *p*-toluenesulphonate) can be obtained via a somewhat bothersome route (Eq. (7)) [92].

$$[RuCl_3] \xrightarrow{NaOH} [RuO_2] \xrightarrow{NaIO_4} [RuO_4] \xrightarrow[HOTs]{Pb/H_2SiF_6} [Ru(H_2O)_6](OT)_2 \quad (7)$$

$[Ru(H_2O)_6](OTs)_2$ catalyses the isomerisation of allylic alcohols, acetates and ethers at 45 °C in water [34], THF, as well as in ethanol [93], but with few turnovers (10 in 4–5 h). The complex is readily oxidised to $[Ru(H_2O)_6]^{3+}$ ($E_{1/2} = +0.20$ V) [94] and catalysis has to take place under rigorous exclusion of air. Isomerisa-

Table 5
Allylic alcohol isomerisation catalysed by in situ mixed [Ru(acac)$_3$] and phenanthroline [3] [a]



Entry	R_1	R_2	R_3	Yield (%)	
				No butadiene	5 ml butadiene
1	H	Me	H	92	85
2	Me	Me	H	90	82
3	Me	H	H	98 (400 [b])	91 (200 [b])
4	Me	H	Me	63	7
5	H	H	Me	40	Trace
6	Et	H	H	Not determined	76

[a] Solvent: 25 ml water, 25 ml diglyme; substrate: 5 ml alcohol (circa 1000 mmol); catalyst precursor: 0.5 mmol [Ru(acac)$_3$], 1.0 mmol 1,10-phenanthroline and 1.4 mmol *p*-toluene sulfonic acid; $T = 155^\circ$ C, $t = 5$ h.
[b] Reaction rate in (mol product) (mol Ru)$^{-1}$ h^{-1}.

tion of non-allylic unsaturated alcohols does not proceed fully to the carbonyl stage [94,93]. Thus, 5-hexen-1-ol is isomerised to 4-hexen-1-ol. The same effect is seen in the isomerisation of unsaturated carboxylic acids and may be explained by coordination of both a double bond and an oxygen moiety, yielding a stable complex (Fig. 1a) that is resistant towards further isomerisation [94]. Alternatively, the alcohol can direct the addition of the olefin to the formation of a ruthenium alkyl species that can only give 4-hexen-1-ol or starting material (Fig. 1b).

[Ru(H$_2$O)$_6$](OTs)$_2$ is the most thoroughly studied complex from a mechanistic point of view. Two elegant labelling studies have been performed by McGrath and Grubbs [34].

First, they examined the isomerisation of allyl-1,1-d_2 alcohol, both in water and in D$_2$O. The results, shown in Scheme 9a, indicate a 1,3-hydrogen shift as evidenced by exclusive formation of propanal-1,3-d_2 in water. This can be explained both by the π-allyl metal hydride

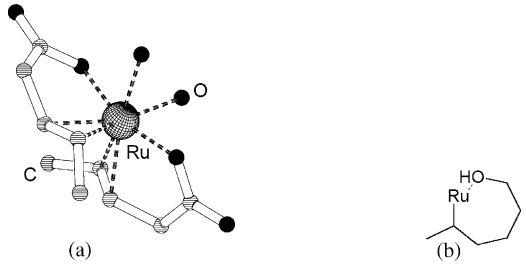
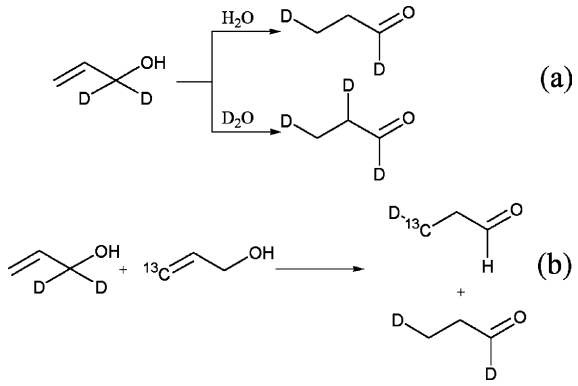


Fig. 1. (a) Molecular structure of [Ru(H$_2$O)$_2$(3-pentenoate)$_2$] [94]. Hydrogen atoms are omitted for clarity. (b) Alcohol directed olefin addition. From the formed ruthenium alkyl species, only 4-hexen-1-ol and starting material can be obtained.

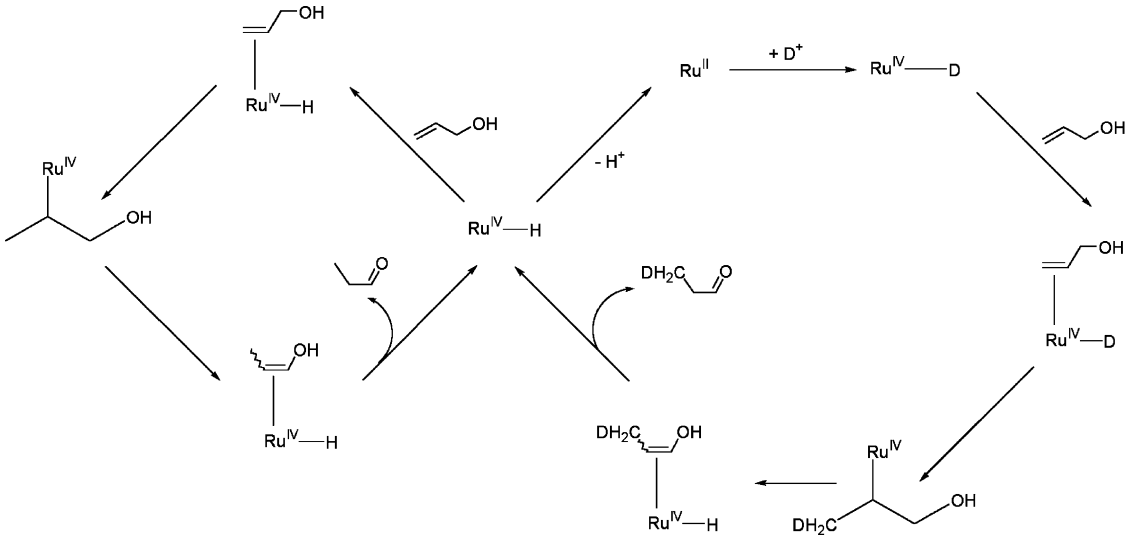


Scheme 9. Isomerisation of allyl-1,1-d_2 alcohol in the absence (a) and presence (b) of allyl-3-^{13}C catalysed by [Ru(H$_2$O)$_6$](OTs)$_2$ [34].

mechanism and by an exclusive Markovnikov addition in the metal hydride addition–elimination mechanism. This latter possibility has been ignored in previous studies. A crossover experiment using allyl-1,1-d_2 alcohol and allyl-3-^{13}C alcohol (Scheme 9b) shows the reaction to be intermolecular, thereby excluding the π-allyl mechanism.

This leads to a proposed mechanism that is shown in Scheme 10. In the right-hand side of the scheme, free [Ru(H$_2$O)$_6$](OTs)$_2$ is oxidised to a ruthenium(IV) hydride in a rate-limiting step. This is followed by an oxygen-directed exclusive Markovnikov insertion of the alkene. Note that the alkene coordinates *after* the formation of the hydride. The cycle continues with the left-hand side of Scheme 10. As no deuterium incorporation is observed [34], this cycle must be dominant. The isomerisation of allylic alcohols by [Ru(H$_2$O)$_6$](OTs)$_2$ constitutes, therefore, a unique example of catalysis by a metal hydride addition–elimination mechanism with the apparent features of a π-allyl metal hydride mechanism.

3.4.2.4. Ru(II)–cyclopentadienyl complexes. In the beginning of the 1990s, Trost and Kulawiec [15,37] used [RuClCp(PPh$_3$)$_2$] in combination with Et$_3$NHPF$_6$ to isomerise allylic alcohols. Some examples are collected in Table 6. Both unsubstituted and 1,2-disubstituted alkene moieties are isomerised readily (entries 1–4). Isolated double bonds are not isomerised in the presence of allylic alcohols (entry 6). Contrary to Trost's suggestion [37], [RuClCp(PPh$_3$)$_2$] can isomerise unfunctionalised alkenes, although at a much lower rate [36]. Thus, in the absence of allylic alcohols, 1-octene is isomerised to a mixture of 2-, 3- and 4-octene (both *cis* and *trans*) with an initial TOF around 300 h^{-1}. Highly substituted double bonds are at best slowly isomerised. Replacement of the Cp by indenyl (Ind) to give [RuClInd(PPh$_3$)$_2$] yields a more active catalyst [37] (entries 7–9). Thus, while isomerisation of 1-phenyl-1-hepten-3-ol in the presence of [RuClCp(PPh$_3$)$_2$] only gives 23% 1-



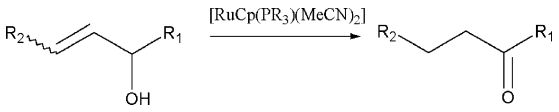
Scheme 10. Mechanism of $[Ru(H_2O)_6](OTs)_2$-catalysed isomerisation of unsaturated alcohols in D_2O. Water ligands are omitted for clarity [34].

phenyl-3-heptanone, 83% yield is obtained with [RuClInd(PPh_3)$_2$] as a catalyst. The higher activity of the indenyl complex compared to the cyclopentadienyl complex is explained by the possibility of the former to release steric strain by η^5-η^3 ring slippage [37] (vide infra).

Trost used a relatively high catalyst concentration of 5 mol% in combination with 10 mol% Et_3NHPF_6. Therefore, although a high selectivity was obtained, the activity was low. The activity has been improved considerably by changing the anion and solvent. Slugovc et al. [95] prepared the complexes [RuCp(PR_3)-($MeCN$)$_2$](PF_6) that isomerise allylic alcohols to carbonyl compounds as shown in Table 7.

Again, unsubstituted and mono-substituted allylic alcohols react more readily. In this case, TOFs of 30 000 h^{-1} can be reached. Depending on the phosphine ligand and temperature, formation of a coupling pro-

Table 7
RuCp-complex catalysed isomerisation of substituted allylic alcohols [95] [a]



Entry	R [b]	R_1	R_2	Time	TON
1	Ph	H	H	10 min	82
2	Me	H	H	15 min	67
3	Cy	H	H	3 min	86
4	Ph	Me	H	3 min	> 98
5	Ph	4-MePh	H	30 min	23
6	Cy	4-MePh	H	5 min	67
7	Ph	H	Ph	17 h	91

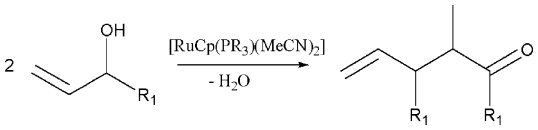
[a] Solvent: $CDCl_3$, $T = 57$ °C, substrate/catalyst precursor = 100.
[b] Cy = cyclohexyl.

Table 6
Isomerisation of allylic alcohols catalysed by [LRuCl(PPh_3)$_2$] [37] [a]

Entry	Substrate	L	Time (h)	Yield (%)	TON
1	3-Phenyl allyl alcohol	Cp	8	90	18
2	1-Cyclohexyl-3-propen-1-ol	Cp	1.5	92	18
3	5-Phenyl-1-penten-3-ol	Cp	2	81	16
4	1-Tetradecen-3-ol	Cp	1	91	18
5	1-Phenyl-1-hepten-3-ol	Cp	9	23	5
6	1,12-Tridecadien-3-ol [b]	Cp	1	87	17
7	1-Phenyl-1-hepten-3-ol	Ind	2	83	17
8	3-Cycloocten-1-ol	Ind	3	47	9
9	1-Methyl-1,3-dodecadiene-5-ol	Ind	3	82	16

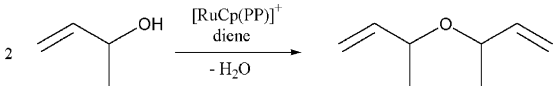
[a] Solvent: dioxane, $T = 100$ °C, catalyst precursor: 5 mol% ruthenium complex and 10 mol% Et_3NHPF_6.
[b] The only product was 12-tridecen-3-one.

duct is observed as a significant side product (Eq. (8)).



(8)

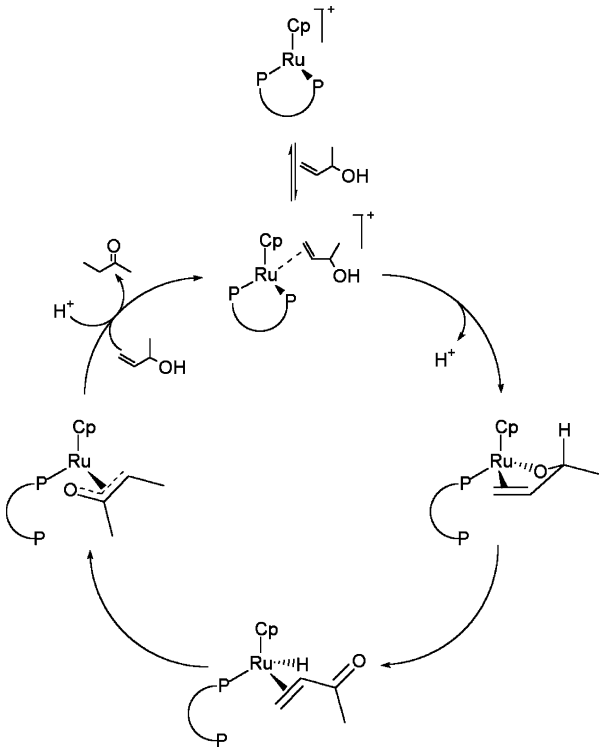
An even higher initial TOF of 200 000 h^{-1} is obtained in the isomerisation of 3-buten-2-ol to MEK if the chloride of $[RuClCp(PPh_3)_2]$ is abstracted with silver(I) tosylate [36]. A considerable increase in rate by abstracting chloride has recently also been found for isomerisation catalysed by $[RuCl_2(PPh_3)_3]$ and $[RhCl(PPh_3)_3]$ [81]. It was shown in our laboratory that didentate phosphines can also be used as ligands for these isomerisation catalysts [36]. A trend in catalytic activity is observed upon variation of the carbon-chain length in the didentate phosphine ligand: dppm < dppe < dppp < dppb (TOF = 18 000) < < $2PPh_3$ [96]. Complexes with rigid didentate ligands like *cis*-dppv and dppph show no activity [96]. On addition of a conjugated diene to the reaction mixtures or by using *o*-MeO-dppe [96] as a ligand, allyl alcohols can be coupled to form allyl ethers with much higher TONs and TOFs than reported before with the well-known palladium catalysts (Eq. (9)) [36].



(9)

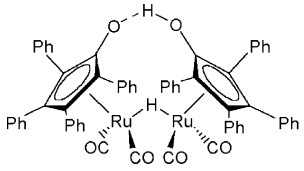
Since allylic alcohols are isomerised much faster than unfunctionalised 1-alkenes, a mechanism that involves coordination of both the alkene and the oxygen moiety has been proposed [37]. A ^{31}P-NMR study indicated that the resting state in the catalytic isomerisation cycle is a ruthenium(II) complex with an allylic alcohol coordinated through the alkene moiety [36]. This slightly adapted mechanism is depicted in Scheme 11. Initial η^2-alkene coordination of the substrate is followed by coordination of the oxygen moiety as an alkoxide; allylic ethers are not isomerised [37]. Next, β-hydrogen elimination takes place. In the case of catalysts containing didentate phosphines, the chelate ring has to open up. This can explain the difference in reactivity among the various didentate phosphine ligands as mentioned above [36]. A small but detectable amount of 3-buten-2-one found in the reaction mixture supports this mechanism. After intramolecular addition of the hydride to the terminal carbon, protonation liberates the carbonyl compound. The intramolecularity of the reaction has been demonstrated by crossover experiments [36,37]. If bulky substrates have to be isomerised, an Ind group can give η^5-η^3 ring slippage. The resulting release in steric hindrance indeed leads to higher reaction rates.

A substituted Cp has been used as ligand by Bäckvall [76] in a dinuclear ruthenium complex (**10**). This complex **10** isomerises allylic alcohols at 65 °C in THF. The built-in base circumvents the need for



Scheme 11. Proposed mechanism for the isomerisation of allylic alcohols with ruthenium(II)Cp didentate phosphine complexes [36].

K_2CO_3. Reported in the same article [76] is the use of $[RuCl_2(p\text{-cymene})]_2$ (**11**), but this complex is much less active even in the presence of a base.



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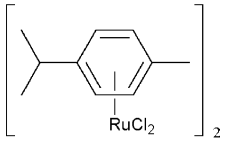


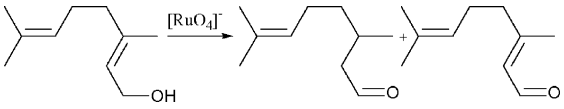
11

3.4.2.5. Ruthenium clusters and other complexes. The cluster $[Ru_3O(OAc)_6(H_2O)_3](OAc)$ (**12**) isomerises selectively allylic alcohols to carbonyl compounds [77,97]. It has been used in a heptane–water two-phase system by Sasson et al. [97]. The activity of cluster **12** is improved by the addition of cationic and anionic surfactants and by increasing the interfacial area mechanically. Each run, a TON of 70 is obtained, with a maximum of four runs without significant loss of activity. In later runs considerable amounts of insoluble ruthenium complexes are formed.

The trinuclear cluster anion $[HRu_3(CO)_{11}]^-$ catalyses the isomerisation of allyl alcohol to propanal [98] with a TON of 1100 in 72 h, after which the catalyst could be recovered in 90% yield. A pseudo-first order rate constant of 0.382 ± 0.005 1 mol^{-1} min^{-1} has been

determined. Other allylic alcohols are also isomerised, but substitution is not tolerated at C2 and considerably lower TONs of around 50 are found in the case of substitution at C1 and/or C3. The mechanism is thought to proceed via an intact ruthenium cluster as evidenced by IR spectroscopy.

The high valent $[Pr_4N][RuO_4]$ has been used as catalyst precursor for the isomerisation of geraniol to citronellal and oxidation of geraniol to geranial (Eq. (10)) [99]. The relative yields depend on the employed solvent and range from 0:100 to 100:0. However, to obtain 100% isomerisation, a sacrificial high molecular weight alcohol like 1-decanol has to be used in all cases. This serves to reduce $[Ru(VII)O_4]^-$ to an active Ru(III) complex, which then catalyses isomerisation via a metal-hydride addition elimination mechanism. An additional role of the sacrificial alcohol is to reduce Ru(V) that is formed by undesired oxidation during the reaction to Ru(III). Allylic alcohols other than geraniol are isomerised also in moderate to high yields and a broad range of substitution at the double bond is tolerated [99]. However, TONs do not exceed 15, making it a rather expensive method.



(10)

Bergens and co-workers [100] reported the stereoselective isomerisation of *rac*-3-buten-2-ol to *Z*-2-buten-1-ol with a HRu(II)(*R*-BINAP) catalyst system (BINAP = 1,1′-diphenylphosphino-2,2′-binaphthyl). The stereoselectivity proved to be better than with the generally used Rh(I)–BINAP catalyst systems (vide infra), which give a mixture of enols and moreover a partial kinetic resolution could be achieved (enantiomeric excess, e.e. = 42% *S*; see Section 3.5.2.3 for a more thorough treatment of chiral catalysis).

Catalytic amounts of the well-known Grubbs' catalyst $([Ru(=CHPh)Cl_2(PCy_3)_2]$ induce exclusively isomerisation of various allylic alcohols to ketones at elevated temperatures, albeit with TONs lower than ten [101]. At room temperature, a stoichiometric amount of Grubbs' catalyst causes fragmentation of the allylic alcohol with loss of a carbon atom. The isomerisation of allyl alcohol to propanal with a very low TON has been reported for other ruthenium carbene complexes, although probably ruthenium-hydride complexes arising from decomposition are responsible for activity in this case [102].

3.4.2.6. Concluding remarks. Ruthenium complexes form versatile catalysts for the isomerisation of allylic alcohols. Generally, activities exceed those of the iron carbonyl complexes. Catalyst amounts of 1 mol% or lower are usually applied. Especially RuCp-complexes give unprecedented high TONs up to 30 000 and rates of 200 000 h^{-1}. However, not in all cases substituted double bonds are tolerated. Substrates with highly substituted double bonds can be isomerised, but with relatively low TONs, making isomerisation rather expensive. Most complexes isomerise all types of unsaturated compounds. Only RuCp-complexes, $[Ru(acac)_3]$ in combination with 1,10-phenanthroline and the $[Ru_3O(OAc)_6]^+$ cluster are selective towards allylic alcohol double bonds.

3.4.3. Osmium

In contrast to the other two members of this group, osmium has hardly received any attention in isomerisation catalysis. This can quite readily be explained by the strong complexes it forms with all kinds of double bonds, thereby making catalysis slow or impossible. For example, the mononuclear complex $[HOsBr(CO)(PPh_3)_3]$ catalyses a variety of reactions, including alkene isomerisation [43]. However, isomerisation of allyl alcohol stops at one equivalent with respect to osmium. Probably a strong interaction between the complex and propanal prevents further coordination of the substrate.

The application of the trinuclear osmium-hydrido compound $[H_2Os_3(CO)_{10}]$ is more successful. Several allylic alcohols are isomerised to ketones or aldehydes at approximately the same rate as unfunctionalised alkenes, while some ethers are converted much faster (see Table 8) [103]. TONs to carbonyl compounds of 5400 can be reached. A metal hydride addition–elimination mechanism is proposed in which association and dissociation of substrates is allowed by varying a Os–Os bond order and therefore no CO groups have to dissociate. The mechanism was probed using $[D_2Os_3(CO)_{10}]$, which was indeed completely converted to $[H_2Os_3(CO)_{10}]$. Allyl-1,1-d_2 alcohol gave exclusive deuterium incorporation at the methylene group, which is consistent with the proposed mechanism. The influence of CO on the rate of isomerisation has not been established. The rate-determining step is proposed to be initial alkene coordination or insertion of the alkene in

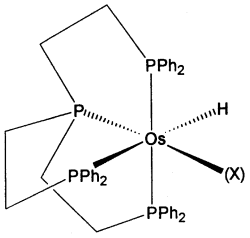
Table 8
Rate constants of $[H_2Os_3(CO)_{10}]$-catalysed isomerisation of functionalised alkenes [103] [a]

Entry	Substrate	$k \times 10^3$ (l mol^{-1} s^{-1}) [b]
1	1-Hexene	7.7 ± 0.4
2	Phenylallyl ether	43 ± 2
3	Allyl alcohol	10.7 ± 0.4
4	3-Buten-2-ol	10.5 ± 0.4
5	2-Buten-1-ol	0.16 ± 0.01
6	2-Methylallyl alcohol	≪ 0.1

[a] Solvent: $CDCl_3$, $T = 32.5$ °C.
[b] The rates of the reaction with various catalyst concentrations have been determined. A plot of these rates vs. catalyst concentration gives a straight line with slope k.

an Os–H bond. This is illustrated by comparison of entries 4–6 in Table 8: substitution at the vinylic position leads to a marked reduction in rate, whereas substitution at the allylic position does not.

Complex **13**, but not its iron and ruthenium analogues, catalyses the isomerisation of 4-phenyl-2-buten-3-ol at 30 °C with a TON of 10 in 3 h [104]. The reaction only proceeds well in non-coordinating solvents under argon. Bianchini et al. suggest a metal hydride addition–elimination mechanism to be operative.



(X) = H_2 or N_2

13

3.5. Group 9: cobalt, rhodium and iridium

3.5.1. Cobalt

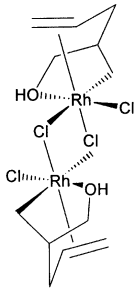
Shortly after the report on isomerisation of allyl alcohol by iron pentacarbonyl [54], Goetz and Orchin published their work on $[HCo(CO)_4]$ [105]. This compound isomerises both unfunctionalised and functionalised alkenes, but yields are extremely low due to competing hydroformylation (the reaction was carried out in a CO atmosphere), a reaction for which $[HCo(CO)_4]$ is of course well known [106]. Thus, only 3.7% of MEK was formed from 3-buten-2-ol together with 94% of hydroformylated product. The highest reported yield was a mere 21% of propanal from allyl alcohol [105]. Up to 50% conversion, was reported by Falbe et al. [107], but again side reactions such as condensation and polymerisation kept the yields of carbonyl compounds low. Remarkably, this is the prototype of isomerisation of allylic alcohols that is mentioned in some textbooks [27,32].

The mechanism is proposed [105] to be of the metal hydride addition–elimination type with exclusive Markovnikov addition as evidenced by the formation of CH_2DCH_2CHO from isomerisation of allyl alcohol with $[DCo(CO)_4]$. Originally, $[HCo(CO)_4]$ was reported to be the catalytically active species [105], but nowadays more support exists [27] for a mechanism in which dissociation of one CO molecule gives the coordinatively unsaturated $[HCo(CO)_3]$.

3.5.2. Rhodium

3.5.2.1. General. The majority of rhodium complexes used in isomerisation catalysis contains rhodium in the oxidation state +1. Yet, the variety in ligands is large as is the diversity in catalysed reactions. Rhodium complexes have been considered in depth both from a mechanistic and from a synthetic point of view. Traditionally, rhodium-based complexes have been used in asymmetric synthesis and this is reflected in the use of chiral phosphine ligands in the isomerisation of prochiral allylic alcohols. Together with ruthenium, rhodium is the dominant metal in isomerisation catalysis of allylic alcohols. Whereas ruthenium complexes have been used mostly in straightforward isomerisation to ketones and aldehydes, rhodium complexes have also been employed in enol and enolate synthesis, the formation of silylated carbonyl compounds and biphasic catalysis. Many different complexes have been used to catalyse the same type of reaction; this section will therefore be ordered according to reaction type rather than by complex. A small part of the older literature has been reviewed before [5,108], but the material covered is included in the present paper.

The starting point of many syntheses of rhodium complexes is $[RhCl_3 \cdot 3H_2O]$, which constitutes a rare example of a rhodium(III) complex to catalyse isomerisation of allylic alcohols. In methanol, $RhCl_3$ reacts with allyl alcohol upon heating to give a mixture of propene, propanal (and its allyl alcohol diacetal), propenal and traces of ethene [109] just as was the case with ruthenium (vide supra). Simultaneously, $RhCl_3$ is converted to $[Rh_2Cl_6]$ and finally to the dimer **14**, which is thought to be formed by 1,2-insertion of an intermediate σ-allyl rhodium species into a coordinated allyl alcohol. In neat allylic alcohols, selective formation of ketones can be observed, but only terminal double bonds are isomerised with appreciable rate [78].



14

3.5.2.2. Biphasic catalysis. Selective isomerisation of 1-octen-3-ol to 3-octanone can be achieved with $RhCl_3$ in a benzene–water two-phase system at ambient tempera-

ture [110]. An ammonium salt has to be used as phase-transfer catalyst to obtain conversion and the reaction then takes place in the organic phase. If pure $RhCl_3$ is used in a homogeneous organic solution, the rate decreases by a factor of 10–20 compared to the biphasic system and the catalyst shows transfer hydrogenation as a pH-dependent side reaction. The rate of the reaction varies slightly with the solvent employed, with the highest rate obtained in cyclohexane (6.1×10^{-2} M min^{-1}). A total TON of around 50 is reached in 1 h at room temperature; increasing the temperature leads to improved TONs.

$RhCl_3$, $Rh_2(SO_4)_3$ or $[Rh(COD)Cl]_2$ in combination with water-soluble ligands such as TPPTS (the sodium salt of sulphonated triphenylphosphine) and DPPPS (the sodium salt of sulphonated dppp (1,3-bis(diphenylphosphino)propane)) affords active catalysts for the isomerisation of 1-hexene-3-ol to 3-hexanone [111]. During the reaction, which showed TOFs up to 2520 h^{-1}, only Rh(I) species could be detected regardless of the starting Rh-salt. After four consecutive runs, still no appreciable deactivation occurred and a TON of 3300 could be obtained. As with most catalyst systems, secondary allylic alcohols with a terminal double bond moiety gave the best results, while reduced solubility in the water phase caused a drop in reaction rate with heavier allylic alcohols.

Several other rhodium(I) complexes have been used in two-phase systems. Alper and Hachem [112] reported in 1980 the isomerisation of several allylic alcohols to ketones catalysed by $[RhCl(CO)_2]_2$ and NaOH in dichloromethane. The use of a phase-transfer catalyst is not required, but results in cleaner reactions. Thus, 1-hexen-3-ol is converted to 3-hexanone at room temperature in 6–10 h with a TON of 50 in the presence of $[RhCl(CO)_2]_2$, NaOH and $PhCH_2NEt_3Cl$. The mechanism is suggested to be of the π-allyl type, whereby hydroxide replaces chloride in the precursor complex [112]. In this report deprotonation of the alcohol to give an alkoxide, which may increase reaction rate via a slightly different mechanism as was proposed by Bäckvall for ruthenium complexes [76], has not been considered.

In an *n*-octane–water system, the complex [Rh(I)-(sulphos)(COD)] (**15**) (sulphos = *p*-$^-O_3S(C_6H_4)CH_2C$-$(CH_2PPh_2)_3$; COD = 1,5-cyclooctadiene) catalyses the isomerisation of a variety of allylic alcohols (for a selection, see Table 9) [113]. Substitution is tolerated at C2, but not at the terminal carbon. Entry 5 illustrates that catalyst **15** is also able to isomerise homoallylic alcohols.

By recycling the catalyst in three consecutive runs, a total TON of 1310 could be attained. In each run, deactivation of the catalyst took place by the formation of an inactive $[Rh(sulphos)(CO)_2]$ complex. A mechanism of the π-allyl metal-hydride type is proposed, in which the COD ligand initially is replaced by water [113]. If the same catalyst is used in a homogeneous system, a considerable amount of dehydration is observed.

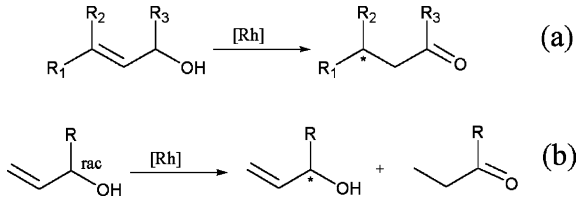
Apart from the sulphos ligand, other water-soluble phosphine ligands have been employed [114]. Of a series of $[RhCl(COD)(PAr_3)]$ complexes with *o*-, *m*- and *p*-substituted carboxyphenyl diphenylphosphines of general formula $P(Ph)_n(PhCOOH)_{3-n}$, the fastest by far was the complex with $P(Ph)_2$(*o*-PhCOOH) as ligand, reaching a k_{obs} of $160.0 \pm 4.0 \times 10^{-2}$ s^{-1} in the isomerisation of 1-octen-3-ol in water–toluene at 104 °C. The high activity of $[RhCl(COD)(P(Ph)_2$(*o*-PhCOOH))] was ascribed to the existence of an equilibrium between $[RhCl(COD)(P(Ph)_2$(*o*-PhCOOH))] and its oxidative-addition product $[RhClH(COD)(P(Ph)_2$(*o*-$PhCOO^-$))]. The latter complex already contains the hydride necessary for isomerisation, which can also be supplied by the toluene solvent. The rate of the reaction was zeroth order in catalyst and first order in substrate and primary KIE of 1.9 was found. These results are best interpreted in terms of the metal hydride addition–elimination mechanism, although the coexistence of the π-allyl mechanism cannot be ruled out.

3.5.2.3. Asymmetric synthesis. Many Rh(I)-complexes are renowned for their use in asymmetric catalysis. Commercial applications exist in asymmetric hydrogenation [115] and production of enamines [39]. Two types of asymmetric isomerisation of allylic alcohols can be discerned (Scheme 12). If the double bond is asymmetrically substituted, isomerisation gives a new chiral centre at the C3 position as indicated in Scheme 12a. To obtain chiral induction, the catalyst should be able to

Table 9
Homogeneous and *n*-octane–water two-phase isomerisation of allylic alcohols catalysed by [(sulphos)Rh(COD)] [113] [a]

Entry	Substrate	Yield (%) in 1,2-dichloroethane	Yield (%) in *n*-octane–water
1	Allyl alcohol	95	100
2	2-Methylallyl alcohol	38	73
3	3-Buten-2-ol	98	100
4	1-Methyl-3-buten-2-ol	0	0
5	3-Buten-1-ol	89	33

[a] Substrate/catalyst precursor = 100, $T = 100$ °C, $t = 1$ h.



Scheme 12. Asymmetric isomerisation of allylic alcohols. (a) Isomerisation of a prochiral allylic alcohol ($R_1 \neq R_2$) and (b) kinetic resolution of a racemic mixture of allylic alcohols.

discriminate between the two enantiotopic faces of the double bond in the addition of the hydride. Kinetic resolution is shown in Scheme 12b. Of a racemic mixture of allylic alcohols one enantiomer is converted to the corresponding carbonyl compound. The other enantiomer can be obtained purely (in a maximum chemical yield of 50%) if the catalyst can selectively abstract one of both hydrogen atoms. Both types of asymmetric isomerisation have been demonstrated, but especially the latter type has met with difficulty. In Table 10, some pertinent examples of asymmetric isomerisation have been collected.

Table 10
Examples of asymmetric isomerisation of allylic alcohols

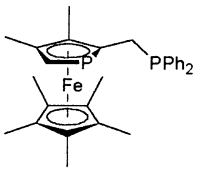
Entry	Type[a]	Catalyst precursor	Substrate	Time	T (°C)	TON	e.e. (%)	Reference
1	A	[HRh(CO)(PPh_3)$_3$] + DIOP	2-methyl-2-buten-1-ol	55 h	75	295	4[b]	[116]
2	A	[HRh(CO)(PPh_3)$_3$] + DIOP	3-methyl-2-penten-1-ol	400 h	75	205	2	[116]
3	A	[Rh(*R*-BINAP)(COD)]$^+$	geraniol	24 h	60	200	37	[41]
4	A	[Rh(*R*-BINAP)(COD)]$^+$		24 h	60	200	53	[41]
5	A	[Rh(COD)$_2$]$^+$ + **16**		48 h	70	10	64	[117]
6	A	[Rh(COD)$_2$]$^+$ + **16**		48 h	70	18	83	[117]
7	A	[Rh(COD)$_2$]$^+$ + **16**		48 h	70	15	86	[117]
8	A	[Rh(*S*-BINAP)(COD)]$^+$		15 h	25	20	43.3	[118]
9[c]	A	[Rh(*S*-BINAP)(COD)]$^+$		16 h	83	17	97.5	[118]
10	B	[Rh(*R*-BINAP)(MeOH)$_2$]$^+$		14 d	0	200	91	[19]

[a] A: creation of a new chiral centre at C3. B: kinetic resolution.

[b] A chiral centre is created at C2.

[c] TES, triethlsilyl.

The first report on asymmetric isomerisation using rhodium complexes dates from the mid 1970s [116]. The isomerisation of asymmetrically substituted allylic alcohols catalysed by [Rh(CO)(PPh_3)$_3$] in combination with diop (**7**) is described. At 75 °C in trifluoroethanol a disappointingly low e.e. of 4% is obtained [116].



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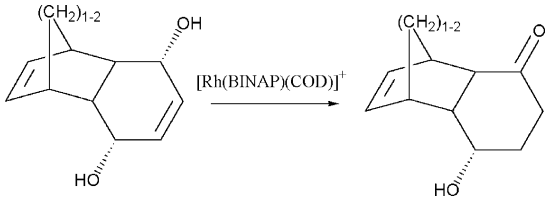
Recently, e.e. values up to 86% have been reported by Fu and co-workers [117]. A combination of 5 mol% [Rh(COD)$_2$](BF_4) and 5 mol% of a planar chiral phosphaferrocene ligand (**16**) catalyses the isomerisation of several allylic alcohols with low activity (TONs around 15). The enantioselectivity is influenced both by the solvent (THF appears to be the best) and the counter ion. *Z*-Allylic alcohols result in higher e.e. values than do their *E*-isomers.

The BINAP ligand (BINAP = 1,1′-diphenylphosphino-2,2′-binaphthyl), successfully employed in many asymmetric catalysts [119], has also been used in Rh(I)-catalysed isomerisation of allylic alcohols. Tani [41] reported the isomerisation of asymmetrically substituted allylic alcohols catalysed by [Rh(*R*-(+)-BINAP)(COD)]$^+$ with e.e. values up to 53% in THF at 60 °C. These e.e. values are much lower than reported for the same catalyst system with allylic amines [41]. An increase in e.e. to 60% with geraniol as substrate could be attained by using triflate as counter-ion [120]. Replacement of COD with nbd (norbornadiene) resulted in much slower reactions, indicating its stronger bonding to rhodium. TONs vary from 100 to 200. Although extensive mechanistic investigations were performed on the isomerisation of allylic amines (see also Section 1 and Ref. [41]), no details were given for the isomerisation of allylic alcohols.

The BINAP ligand has been patented for its use in isomerisation catalysis and thus, new ligands have been explored. The MeO-biphep ligand (6,6′-dimethoxy-2,2′-bis(diarylphosphino)-1,1′-biphenyl) is only slightly less active and selective (with an e.e. around 51%) [120]. An asymmetric 1,2-substituted ferrocene ligand (josiphos) resulted in e.e. values around only 20%.

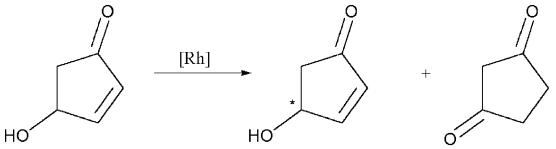
Stereoselective isomerisation of *meso*-1,4-diols with [Rh(*S*-(−)-BINAP)(COD)](ClO_4) yields hydroxyketones with high e.e. values as shown in Eq. (11) [118]. See also Table 10 (entries 8 and 9) for some examples. The best results are obtained with vinyl silyl ethers, which can be easily converted to the corresponding ketones. It is noteworthy that the free diols give opposite

absolute configuration in the product to the (silyl)ethers [118]. Deuterium-labelling experiments suggest a mechanism involving a suprafacial 1,3-hydrogen shift.



(11)

Kinetic resolution of hydroxycyclopentenones has been achieved with [Rh(*R*-BINAP)(MeOH)$_2$](ClO$_4$) [19]. In THF at 0 °C, a k_{fast}/k_{slow} of 5 was obtained, making this a convenient method to obtain *R*-**17** (Eq. 12). Recrystallisation yields the product in 27% chemical yield and an e.e. of >99%, although only after 14 days of reaction.



91 % e.e.
R-**17**

(12)

3.5.2.4. Preparation of enols and enolates. The complex [Rh(BINAP)(solvent)$_2$](ClO$_4$) has been used by Bergens and Bosnich [30] in a non-chiral manner to produce enols of simple allylic alcohols. BINAP can be replaced by dppe or dcpe (dcpe = 1,2-bis(dicyclohexylphosphino)ethane) as didentate ligand to give active catalysts. In the latter case, however, the intermediate enols are not stable. Upon mixing a solution of [Rh(dcpe)(acetone)$_2$](ClO$_4$) in acetone with allyl alcohol, propanal is obtained instantaneously. Some examples of enol formation of substituted allylic alcohols are given in Table 11.

[Rh(dppe)(solvent)$_2$]$^+$ catalyses the isomerisation of allyl alcohol in dry acetone at ambient temperature. As shown in Fig. 2, after 15 min allyl alcohol is completely consumed to give essentially a mixture of *Z*- and *E*-enol. The difference in the rate of formation between *E*- and *Z*-enol originates from the difference in rate in initial abstraction of hydrogen, rather than from a possible π–σ–π interconversion of the π-allyl intermediate [30]. The catalyst not only catalyses isomerisation, but also the tautomerisation to propanal. Depending on the substrate, an enol concentration of around 0.6 M can be reached, after which sudden and instantaneous tautomerisation occurs. Deactivation of the catalyst towards tautomerisation was only partially successful with CO, forming the inactive complex [Rh(CO)$_2$(dppe)]$^+$.

Table 11
Formation of enols from allylic alcohols, catalysed by [Rh(dppe)(solvent)$_2$]$^+$ [30] [a]

Entry	Substrate	Time (min) [b]	Enol (%) (*Z*/*E*) [c]
1	Allyl alcohol	14	89 (1/1.1)
2	3-Buten-2-ol	9	83 (5.3/1)
3	2-Methylallyl alcohol	16	96 (n.a.) [d]
4	3-Phenylallyl alcohol	167	48 (1/1.7) [e]

[a] Solvent: acetone, $T = 25$ °C, substrate/catalyst precursor = 100.
[b] Time needed for complete conversion of the substrate.
[c] Ratio *Z*/*E* at the end of the reaction.
[d] n.a. = not applicable.
[e] Catalyst precursor: [Rh(BINAP)(THF)$_2$]$^+$, solvent: THF, substrate/catalyst precursor = 46.

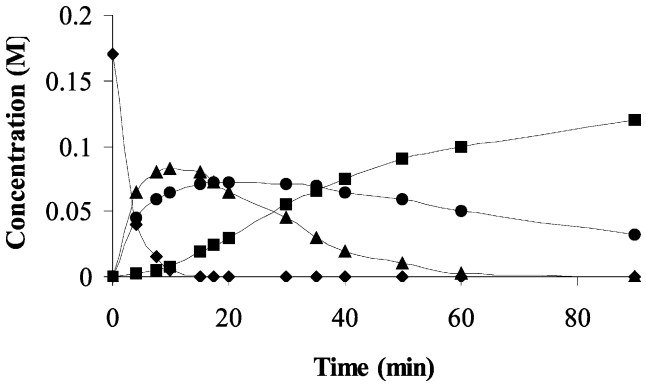


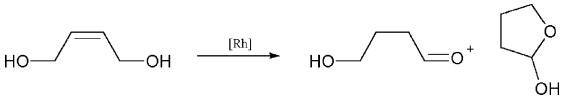
Fig. 2. Formation of enols from allyl alcohol catalysed by [Rh(dppe)(acetone)$_2$]$^+$. Concentration is determined by ^{1}H-NMR in acetone-d_6 at room temperature [30]. Shown are the concentrations of allyl alcohol (◆), propanal (■), *Z*-enol (●) and *E*-enol (▲).

The mechanism of isomerisation is thought to be of the π-allyl metal hydride type [30]. No intermediates could be detected with low-temperature ^{1}H-NMR, but deuterium labelling clearly shows selective formation of 1,3-dideuterated propanal from allyl-1,1-d_2 alcohol. Coordination of the oxygen atom during the catalytic cycle has not been invoked. However, to explain the inhibiting effect of a homo-allyl alcohol, a didentate coordination of the alcohol through its oxygen and double bond moieties is proposed [30], which was corroborated by ^{1}H-NMR spectroscopy.

Much work has been done in the generation and stabilisation of simple enols by Chin and co-workers. Fast isomerisation of 2-methyl-2-propen-1-ol by [Rh(CO)(PPh$_3$)$_3$](ClO$_4$) gives a 0.72 M solution of 2-methyl-1-propen-1-ol in CDCl$_3$ [121]. Other allylic alcohols like allyl alcohol and 3-buten-2-ol are isomerised too slowly relative to tautomerisation, which exhibits first-order kinetics [121,122], and yield carbonyl compounds only [121]. Isomerisation of methyl allyl alcohol in the absence of solvent gives 95% enol and 5% methyl propanal [122]. If the O-deuterated analogue is used, even pure enol can be obtained. Tautomerisation is as expected faster in protic solvents like water ($k = 4.6 \pm 0.3 \times 10^{-4}$) and methanol than in aprotic solvents like benzene ($k = 2.2 \pm 0.3 \times 10^{-5}$) [122]. The initially

proposed [121] unexpectedly fast tautomerisation in $CDCl_3$ and alleged stabilisation of the enol by the catalyst [121,123], later proved [124] to be due to DCl impurity in the solvent.

Several catalysts of the type $[Rh(CO)(L)_n](ClO_4)$ (L = PPh_3, $AsPh_3$; $n = 2$, 3) catalyse the isomerisation of allylic alcohols to the corresponding carbonyl compounds under different experimental conditions, without the intermediate formation of stable enols [123,125–127]. Thus, at 30 °C in $CDCl_3$ in a dihydrogen atmosphere, butanone and 2-butanol are formed from 3-buten-2-ol in 30 min catalysed by $[Rh(CO)(PPh_3)_2](ClO_4)$. The latter product must arise from concomitant hydrogenation of 3-buten-2-ol, since no alcohol formation is detected in the reaction of $[Rh(CO)(PPh_3)_2](ClO_4)$ with butanone [126]. The isomerisation reaction is thought to proceed via $[Rh(H)_2(CO)(PPh_3)_2]^+$ [126]. Substitution of the allylic alcohol on either C1 or C3 reduces the rate of the reaction, whereas substitution at C2 increases the rate [125,126]. Triphenylphosphine dissociation in $[Rh(CO)(PPh_3)_3](ClO_4)$ is significant and in solution actually the concentration of $[Rh(CO)(PPh_3)_2]^+$ is higher than that of $[Rh(CO)(PPh_3)_3]^+$ [125]. The difference in rate of isomerisation in a reaction catalysed by $[Rh(CO)(PPh_3)_2](ClO_4)$ or $[Rh(CO)(PPh_3)_3](ClO_4)$ was explained by a faster reductive elimination step with the latter to form the coordinated enol [125]. If these catalytic systems are applied to 1,4-endiols, 4-hydroxyaldehydes are formed, ultimately resulting in the cyclised hydroxy-substituted THF (Eq. (13)) [128]. 4-Hydroxybutanal can also be synthesised by hydroformylation of allyl alcohol, catalysed by $[HRh(CO)(PPh_3)_3]$ [129]. In this case competitive isomerisation at temperatures higher than 60 °C yields propanal.



(13)

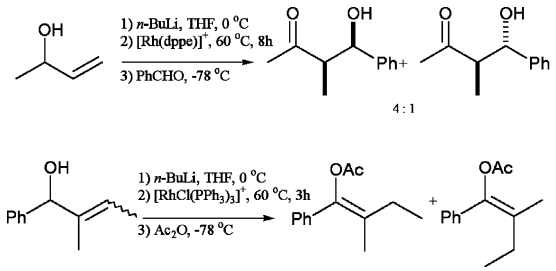
If enols are generated in situ with Wilkinson's catalyst ($[Rh(PPh_3)_3Cl]$) in combination with one equivalent of an organolithium or -magnesium compound (e.g. *n*-BuLi, PhLi, MeMgBr), they can be trapped with aldehydes to form the aldol condensates in moderate yield [80]. This method circumvents the need for stoichiometric amounts of base. In all cases, a considerable amount of ketone is observed as side product. The ketone is formed quantitatively in less than 1 h (but with a relatively high catalyst concentration of 5 mol%) if no additional aldehyde is present [81]. In the absence of an organolithium compound, Wilkinson's catalyst is reported to isomerise allylic alcohols at best with low rate and a low TON [78,130].

While enols sooner or later tautomerise to the corresponding carbonyl compounds, metal enolates are stable and are indeed one of the most valuable intermediates in synthetic organic synthesis. Motherwell and co-workers [131,132] demonstrated the ability of $[Rh(dppe)(THF)_2]^+$ and $[RhCl(PPh_3)_3]$ to catalyse the isomerisation of allylic alcoholates specifically to lithium *Z*-enolates. However, the *Z*-enolates are in equilibrium with their *E*-isomers during the reaction.

Several electrophiles can trap the formed enolates as is illustrated in Scheme 13. A difference between both catalysts only becomes apparent in the isomerisation of highly substituted double bonds (Scheme 13b), with Wilkinson's catalyst being the most active [132].

Isomerisation catalysed by $[Rh(dppe)(THF)_2]^+$ shows specific 1,3-hydrogen migration indicative of a π-allyl mechanism as proved by isomerisation of deuterated substrates [132]. Wilkinson's catalyst gives a small amount of 2-deuterioketone, which signifies that at least in part a metal hydride addition–elimination mechanism is operative. The selective formation of *Z*-enolates requires a *cisoid* alkoxide conformation and this is ascribed to possible coordination of the oxygen moiety to the rhodium centre.

3.5.2.5. Aldehydes and ketones. Some rhodium phosphite complexes are moderately active in the isomerisation of allyl alcohol to propanal at ambient temperature in benzene, chloroform or toluene [35,38,133]. $[HRh(P(OPh)_3)_4]$ gives propanal in a maximum TON of 40 at ambient temperature and of 80 at 50 °C [35]. Especially the *ortho*-metallated complex was proved to be active $[Rh(P(OPh)_3)_2(P(OPh_2)(OC_6H_4))]$ (**18**) [35,38,133]. A maximum TON of 1000 could be reached and an initial TOF of 2400 h^{-1} [35]. The activity of **18** can be blocked by addition of CO or excess phosphite. Unsubstituted alcohols react fast, but, e.g. 2-methyl-2-propen-1-ol remains unchanged [133]. Complex **18** is selective in catalysing isomerisation of allylic alcohols. Non-allylic alcohols, allylic amines and unfunctionalised alkenes are not isomerised [133]. If the isomerisation of allyl alcohol with **18** is monitored with ^{31}P-NMR, no Rh–C bond breaking in **18** is observed, nor dissociation of a phosphite ligand [38]. The products of isomerisation of allyl-1,1-d_2 alcohol and allyl alcohol-*OD* suggest a π-allyl mechanism [38]. The selectivity in allylic alcohol



Scheme 13. Tandem isomerisation and trapping of allylic alkoxides [132].

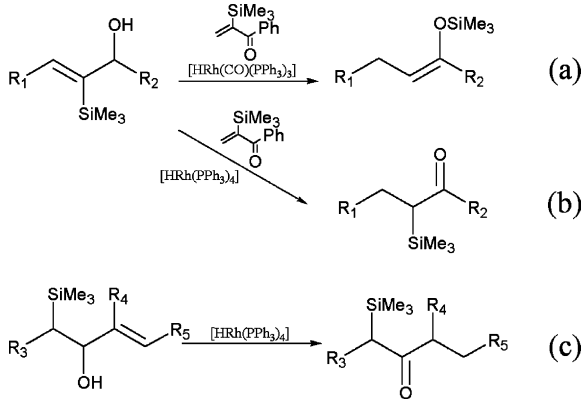
isomerisation led the authors to assume a simultaneous coordination of both the alkene and the alcohol moieties.

Some rhodium(I) acetylacetonato complexes of the type [Rh(acac)(CO)(PR_3)] in which PR_3 is a monodentate phosphine ligand (e.g. tris(*o*-methoxyphenyl)phosphine, tris(2-pyridyl)phosphine or 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane) catalyse the isomerisation of allyl alcohol to propanal in a H_2 atmosphere [134]. The highest yield is obtained with complexes that exhibit a lower ν(CO). This isomerisation is most likely catalysed via the addition–elimination mechanism by hydrido rhodium complexes that result from homolytic splitting of H_2.

The rhodium(0) carbonyl clusters [$Rh_6(CO)_{16}$] and [$Rh_6(CO)_{15}$(MeCN)] catalyse the isomerisation of allyl alcohol to propanal at room temperature [137]. [$Rh_6(CO)_{16}$] requires prior activation by either UV-radiation or the presence of Me_3NO. The maximum TONs around 200 are considerably lower than for isomerisation of 1-hexene, caused by rapid deactivation of the catalyst.

Trimethylsilyl (TMS) substituted ketones and enol ethers can be prepared as shown in Scheme 14. [$HRh(CO)(PPh_3)_3$]-catalysed isomerisation of TMS substituted allylic alcohols at 105 °C yields the silyl enol ether [135], whereas [$HRh(PPh_3)_4$] catalyses the formation of 2-TMS substituted ketones [138]. In both cases, 2-TMS-1-phenyl-2-propen-1-one is required as co-catalyst [135,136,138]. The function of the co-catalyst has not been conclusively elucidated, but it seems to facilitate the interaction between the bulky substrates and the rhodium centre. Some examples are given in Table 12. In entry 5, the only product is 2-TMS-7-octen-3-one and this demonstrates the discrimination in asymmetrically substituted allylic alcohols.

Since trimethylsilylmethyl ketones cannot be prepared via this reaction scheme, a route starting from a different class of allylic alcohols (Scheme 14c) has been developed [139,136]. The use of a co-catalyst can



Scheme 14. Rhodium hydride-catalysed synthesis of silyl enol ethers (a) and α-TMS ketones (b and c).

be avoided in this way [139,136]. An advantage of all these methods is the possibility of a non-aqueous work-up, which spares the relatively labile Si–C bond.

3.5.2.6. Concluding remarks. In conclusion, rhodium complexes offer versatile tools for isomerisation of a wide range of allylic alcohols, including highly substituted ones. Yet, TONs generally do not exceed 100 and since rhodium is an expensive metal, it could often be replaced with cheaper metals with the same results. However, rhodium-based catalysts open up new routes to important building blocks such as enols and enolates. Especially the use of chiral ligands (e.g. BINAP and diop) gives access to chiral natural products in a selective manner (i.e. high e.e. values), which cannot be achieved easily with any other metal.

3.5.3. Iridium

Compared to other third-row transition-metal complexes, iridium complexes have been used quite often as catalysts in the isomerisation of allylic alcohols. As with rhodium, especially iridium(I) complexes have been employed. A small part of the older literature has been reviewed before [5,108], but the material covered is included in the present paper.

Baudry et al. [140] reported the synthesis of propanal from allyl alcohol, catalysed by [Ir(COD)($PMePh_2$)$_2$](PF_6) and [Ir(COD)(PCy_3)(py)](PF_6) (Cy = cyclohexyl; py = pyridine) (see Table 13). The latter complex is more active, but often gives irreproducible results. This problem is solved by using [Ir(COD)(PPh_3)(PhCN)](ClO_4) [31]. The reactions are conducted in a H_2 atmosphere at ambient temperature. Unsubstituted allylic alcohols can be converted with TONs around 1000 [140]. If the double bond is substituted, higher temperatures are required and yields are considerably lower. Side reactions such as acetalisation or dimerisation are not observed. Enol ethers [141] and silyl enol ethers [142,143] can be obtained similarly by several [Ir(COD)(PR_3)$_2$]$^+$ complexes. Specifically *E*-silyl enol ethers can be prepared in acetone, whereas in CH_2Cl_2–acetone mixtures a preference exists for the formation of *Z*-isomers [143].

The iridium pentahydride complex [IrH_5(*i*-Pr_3P)$_2$] also catalyses the isomerisation of several allylic alcohols (Table 13) [144,145]. Higher temperatures around 100 °C are necessary to obtain the active species [IrH_3(*i*-Pr_3P)$_2$] by liberation of a molecule of H_2 [144]. [IrH_5(*i*-Pr_3P)$_2$] is not specific for allylic alcohols. 1,4-Enediols yield initially 4-hydroxybutanals, which after cyclisation and subsequent dehydrogenation give the corresponding lactones [146]. Propargyl alcohols can be isomerised to α,β-unsaturated ketones by refluxing in toluene with [IrH_5(*i*-Pr_3P)$_2$] [147].

[Ir(CO)(PPh_3)$_2$(ClO_4)] catalyses the isomerisation of 3-buten-2-ol to butanone faster than the analogous

Table 12
Synthesis of trimethylsilyl substituted ketones or silyl enol ethers [a]

Entry	Catalyst precursor [b]	Substrate [c]	Product	Time (h)	TON (selectivity %)	Reference
1	$[HRh(CO)(PPh_3)_3]$	$R_1 = H$; $R_2 = Me$	Ether	65	2 (38)	[135]
2	$[HRh(CO)(PPh_3)_3]$	$R_1 = H$; $R_2 = Ph$	Ether	20	16 (78)	[135]
3	$[HRh(CO)(PPh_3)_3]$	$R_1 = n$-Bu; $R_2 = n$-Pe	Ether	113	18 (92)	[135]
4	$[HRh(PPh_3)_4]$	$R_1 = H$; $R_2 = n$-Pe	Ketone	1	12 (60)	[136]
5	$[HRh(PPh_3)_4]$	$R_1 = H$; $R_2 =$ 1-pentenyl	Ketone	0.5	16 (92)	[136]
6	$[HRh(PPh_3)_4]$ [d]	$R_3 = R_4 = R_5 = H$	Ketone	0.67	19 (95)	[136]
7	$[HRh(PPh_3)_4]$ [d]	$R_3 = Me$; $R_4 = H$; $R_5 = n$-Pr	Ketone	0.67	20 (99)	[136]

[a] Solvent: benzene or 1,4-dioxane, $T = 105$ °C, substrate/catalyst precursor = 20.
[b] Co-catalyst: one equivalent (to Rh-complex) phenyl(1-trimethylsilylvinyl) ketone.
[c] See Scheme 14 for designation of R.
[d] No co-catalyst added.

rhodium complex [127]. However, the complex $[Ir(CO)(PPh_3)_3](ClO_4)$ is a much less active catalyst due to the slow dissociation of PPh_3 [127]. The reaction is performed in a H_2 atmosphere and usually a mixture of isomerisation and hydrogenation products (saturated alcohols) is obtained. At H_2 pressures higher than 5 bar, only the hydrogenation products are observed [148]. A metal hydride addition–elimination mechanism is proposed [148] in which $[Ir(H)_2(CO)(PPh_3)_2]^+$ is the actual active species.

Both iridium(III) complexes $[IrCl_3]$ and $K_3[IrCl_6]$ have been reported to catalyse the isomerisation of 1-octen-3-ol in a two-phase benzene–water system [110] with rates of 0.28 and 0.20 mmol min^{-1} ml^{-1}, respectively, which are comparable to the rate reported for $RhCl_3$.

3.6. Group 10: nickel, palladium and platinum

3.6.1. Nickel

Three of the four articles on nickel-catalysed isomerisation of allylic alcohols date from the 1970s [149–151]. Since then, quite some research has been directed towards isomerisation of unfunctionalised alkenes, but it was not until 1998 that allylic alcohols received again attention [152]. Apart from a briefly mentioned Ni(0) 1-thioethyl-2-diphenylphosphinoethane complex without any details [149], all Ni-based catalyst systems consist of a nickel(0)–didentate phosphine or phosphite catalyst precursor combined with an acid co-catalyst.

$[Ni(dppb)_2]$ (dppb = 1,4-bis(diphenylphosphino)butane) combined with HCN in a 1:4 ratio in benzene converts allyl alcohol to propanal in 100% yield (125 turnovers under the employed conditions) in 25 min [151]. Replacement of HCN by CF_3COOH (TFA) did not result in any conversion. Oxidative addition of HCN to the Ni(0) precursor gives a Ni(II) complex. Yet, the active complex is proposed to be a Ni(I) complex ($[Ni_2(CN)_2(dppb)_3]$ gives indeed comparable results to the in situ system), which consequently should originate from comproportionation.

Another nickel(0) precursor system, 1,2-bis(di(*o*-tolyl)phosphito)ethanenickel(0) reported by Lochow and Miller [150], catalyses the isomerisation of several unsaturated alcohols, both allylic and non-allylic, in combination with slightly less than one equivalent of HCl. This system only isomerises alcohols with unsubstituted double bonds, while it deactivates within 2 h with substituted substrates. However, in all cases, TONs do not exceed 20 and sometimes reaction times are as long as 5 days.

After more than 20 years, the Ni-systems were revisited in 1998 by Bricout et al. [152]. They chose again the original $[Ni(dppb)_2]$ catalyst precursor, this

Table 13
Iridium(I)-catalysed isomerisation of allylic alcohols [a]

Entry	Catalyst precursor	Substrate	Time (h)	T (°C)	TON	Reference
1	$[Ir(COD)(PMePh_2)_2]^+$	Allyl alcohol	0.5	20	1000	[140]
2	$[Ir(COD)(PMePh_2)_2]^+$	2-Methylallyl alcohol	0.5	20	1000	[140]
3	$[Ir(CO)(PPh_3)_2(ClO_4)]$	2-Methylallyl alcohol	7	30	30	[127]
4	$[Ir(COD)(PMePh_2)_2]^+$	3-Buten-2-ol	1	20	1000	[140]
5	$[Ir(CO)(PPh_3)_2(ClO_4)]$	3-Buten-2-ol	0.5	30	30	[127]
6	$[IrH_5(i\text{-}Pr_3P)_2]$	3-Buten-2-ol	12	100	400	[144]
7	$[Ir(COD)(PMePh_2)_2]^+$	2-Buten-1-ol	10	65	1000	[140]
8	$[Ir(COD)(PMePh_2)_2]^+$	2-Cyclohexen-1-ol	2	65	70	[140]
9	$[IrH_5(i\text{-}Pr_3P)_2]$	2-Cyclohexen-1-ol	16	120	425	[144]

[a] Solvent: $CDCl_3$ (entries 3 and 5) or THF, substrate/catalyst precursor = 1000.

time prepared in situ from $[Ni(COD)_2]$. Geraniol and prenol were isomerised to geranial and prenal, respectively. Peculiarly, this time the use of two equivalents of TFA proved best suitable when compared to acetic acid and HCl. Lower TFA concentrations gave slower reactions, whereas higher concentrations gave more acid-catalysed side reactions.

All reactions suffered from a serious limitation in the fact that the catalyst deactivated completely after ca. 60 turnovers. This was ascribed to coordination of the product aldehyde, which renders the catalyst inactive. This was confirmed by removing the product by reacting it with butane-1,2-diol [152]. An attempt to remove the aldehyde by using a two-phase system with the tetrasulphonated dppb analogue was not successful.

Concluding, the nickel-catalysed isomerisation of allylic alcohols in its modern form allows for 60 turnovers in ca. 2 h. Highly substituted double bonds can be converted, which is often a problem with other systems. It remains difficult to minimise acid-catalysed side reactions.

An interesting analogous reaction was studied during the past decade by Motherwell and Sandham [153], namely the isomerisation of lithium allylic alkoxides to give lithium enolates. Most of this work was done with rhodium-based catalysts [131,132], including a mechanistic investigation recently (vide supra) [132]. It should be noted here, however, that $[NiCl_2(PCy_3)_2]$ (Cy = cyclohexyl) generally gives much higher regioselectivity and is more capable of isomerising highly substituted double bonds.

3.6.2. Palladium

Palladium complexes generally are not efficient isomerisation catalysts [154]. Consequently, not much effort has been put in this line of research. Some work has been done on the isomerisation of allylic ethers [155], allylic esters [156] and recently unfunctionalised alkenes [157–159]. Three types of allylic alcohol isomerisation have been reported. The first type is the 1,3-transposition of the alcohol moiety, which falls outside the scope of this review. The second type is the isomerisation of alkyne-1,4-diols to 1,4-diketones [160]. This reaction breaks down into two parts. The first part is the isomerisation of a propargyl alcohol, which has a profoundly different mechanism from alkene isomerisation via a palladium allene species. This reaction results in an 4-oxo allyl alcohol, which can be isomerised subsequently in the second part of the reaction, by the same palladium catalyst, to a ketone through a metal hydride addition–elimination mechanism.

The best system for this reaction was found to be $[Pd_2(dba)_3]\cdot CHCl_3$ (dba = dibenzylideneacetone) in combination with two equivalents of n-Bu_3P [160], but also in the absence of phosphine ligand significant isomerisation took place. The yield of the reaction is very much dependent on the solvent, with acetonitrile as the best choice. Heating for 70 h is required in most cases, while a TON of only 20 is reached. Synthetically, however, this reaction is quite versatile.

The isomerisation of allylic alcohols to aldehydes and ketones has been described scarcely [161]. As a side reaction in $[PdCl_2(py)_2]$-catalysed hydrogenation of 2-propen-1-ol, 33% selectivity towards propanal is observed [162]. The selectivity can be increased to 74% by heterogenising the palladium onto a styrene–divinylbenzene copolymer with iminodithiol ligands. However, in this case, reaction rates drop considerably.

3.6.3. Platinum

A few platinum hydride complexes catalyse the isomerisation of unfunctionalised alkenes [163], but with allyl alcohols a stoichiometric reaction is reported [164]. Instead of simply isomerising allyl alcohol to propanal, only 50% conversion is obtained, while the other half of the substrate captures the catalyst in a platinum allyl species.

4. Conclusions

Isomerisation of allylic alcohols offers a versatile and elegant route to various substituted aldehydes and ketones. Present-day catalysts tolerate many labile functional groups and this adds considerably to the usability in synthetic schemes. However, only very few catalysts isomerise highly substituted double bonds and generally TONs are low. In the majority of cases, catalysts are not selective towards allylic alcohols and other types of substrates are easily converted as well. A wide range of solvents has been employed varying from hydrocarbons to water. Reaction conditions are generally mild and often ambient temperature and pressure suffice. In cases where the nature of the allylic alcohol does not allow for one type of catalyst, another catalyst is likely to be found.

Although many transition metals have been employed in the isomerisation of allylic alcohols, this field is dominated by ruthenium and rhodium. Most systems catalyse the isomerisation with relatively low TONs up to around 100. Some ruthenium, rhodium and iridium complexes reach higher TONs of ca. 1000. However, the only real exceptions are the RuCp-complexes, which can reach TONs up to 30 000. Mostly, the transition metals have been combined with phosphine and phosphite ligands of a diverse nature. Several rhodium- and especially iron–CO complexes have been applied, while in exceptional cases nitrogen-donor ligands are used.

As important organic building blocks, enols and enolates have been prepared efficiently by isomerisation of allylic alcohols, catalysed by rhodium, iridium and nickel complexes. Chiral carbonyl compounds can be

synthesised by rhodium-catalysed isomerisation, which is applied in the preparation of natural products. Several factors govern catalyst choice. Apart from efficiency in terms of TON and TOF, selectivity and price are to be considered. It depends mainly on the substrate where the balance lies. The more expensive metals rhodium and ruthenium give higher yields and in many cases this outweighs their somewhat higher price even on a laboratory scale. For small-scale syntheses, commercially available catalysts, such as $[Fe_3(CO)_{12}]$, $RuCl_3$ or $Ru(acac)_3$, will do the job conveniently.

Three types of mechanisms have been proposed for isomerisation of allylic alcohols. The metal hydride addition–elimination mechanism is usually invoked for metal-hydride catalyst precursors. In a few cases, a hydride is generated in situ. With low valent metal complexes that can easily accommodate a π-allyl group, the π-allyl metal hydride mechanism has been proposed. Experimental evidence for this mechanism comes usually from results of isomerisation of deuterated substrates. It should be stressed that this is not conclusive proof; only crossover experiments to determine inter- or intramolecularity can exclude either mechanism, but these experiments have only been performed in exceptional cases. The third type of mechanism involves coordination of the oxygen moiety to the metal centre during the catalytic cycle. Unfortunately, this mechanism has been largely neglected, apart from a few instances where allylic alcohols were isomerised selectively in the presence of other alkene moieties or where unsubstituted alkenes are not isomerised at all. In particular, often a base is used as a co-catalyst, which should raise the idea of the participation of an alkoxide in the reaction mechanism.

Acknowledgements

This research was supported by the Technology Foundation STW, Applied Science Division of NWO and the Technology Programme of the Ministry of Economic Affairs.

References

[1] C.D. Frohning, C.W. Kohlpaintner, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, VCH, Weinheim, 1996, p. 61.
[2] Ullmann's Encyclopedia of Industrial Chemistry, sixth ed., Wiley–VCH, Weinheim, 2000.
[3] F. Stunnenberg, F.G.M. Niele, E. Drent, Inorg. Chim. Acta 222 (1994) 225.
[4] E. Drent, Eur. Patent, 457387, 1991.
[5] P.A. Chaloner, Handbook of Coordination Catalysis in Organic Chemistry, Butterworths, London, 1986, p. 403.
[6] M. Orchin, Adv. Catal. 16 (1966) 1.
[7] T. Szymanska-Buzar, Coord. Chem. Rev. 159 (1997) 205.
[8] J.A. Belmont, J. Soto, R.E. King, A.J. Donaldson, J.D. Hewes, M.F. Hawthorne, J. Am. Chem. Soc. 111 (1989) 7475.
[9] W.V. Steele, R.D. Chirico, J. Phys. Chem. Ref. Data 22 (1993) 377.
[10] M.P. Doyle, G.A. Devora, A.O. Nefedov, K.G. High, Organometallics 11 (1992) 549.
[11] G.W. Parshall, S.D. Ittel, Homogeneous Catalysis, Wiley-Interscience, New York, 1992, p. 9.
[12] J.A. Moulijn, R.A. Sheldon, H. Van Bekkum, P.W.N.M. Van Leeuwen, in: J.A. Moulijn, P.W.N.M. Van Leeuwen, R.A. Van Santen (Eds.), Catalysis: An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis, Elsevier, Amsterdam, 1995, p. 45.
[13] A.M. Trzeciak, J.J. Ziolkowski, Coord. Chem. Rev. 192 (1999) 883.
[14] H. Brunner, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 1, VCH, Weinheim, 1996, p. 201.
[15] B.M. Trost, R.J. Kulawiec, Tetrahedron Lett. 32 (1991) 3039.
[16] C. Malanga, R. Menicagli, M. Dell'Innocenti, L. Lardicci, Tetrahedron Lett. (1987) 239.
[17] A.I. Meyers, J.R. Flisak, R.A. Aitken, J. Am. Chem. Soc. 111 (1987) 5446.
[18] D.P. Curran, P.B. Jacobs, R.L. Elliot, B.H. Kim, J. Am. Chem. Soc. 111 (1987) 5280.
[19] M. Kitamura, K. Manabe, R. Noyori, Tetrahedron Lett. 28 (1987) 4719.
[20] A.H. Andrist, L.E. Slivon, J.E. Graas, J. Org. Chem. 43 (1978) 634.
[21] L.A. Yanovskaya, K. Shakhidaystov, Russ. Chem. Rev. 39 (1970) 859.
[22] R.H. DeWolfe, W.G. Young, in: S. Patai (Ed.), The Chemistry of Alkenes, Interscience, London, 1964, p. 681.
[23] D.R. Dimmel, S.B. Gharpure, J. Am. Chem. Soc. 93 (1971) 3991.
[24] G. Eadon, M.Y. Shiekh, J. Am. Chem. Soc. 96 (1974) 2288.
[25] M. Craus, Coll. Czech. Chem. Commun. 37 (1972) 460.
[26] T. Martinek, A. Molnar, T. Katona, M. Bartok, A. Lovas, J. Mol. Catal. A: Chem 112 (1996) 85.
[27] C. Elschenbroich, A. Salzer, Organometallics: A Concise Introduction, VCH, New York, 1989.
[28] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, Wiley, New York, 1988.
[29] F.A. Carey, R.J. Sundberg, Advanced Organic Chemistry. Part A: Structure and Mechanisms, Plenum Press, New York, 1991, p. 12.
[30] S.H. Bergens, B. Bosnich, J. Am. Chem. Soc. 113 (1991) 958.
[31] C.S. Chin, B. Lee, S. Kim, J. Chun, J. Chem. Soc., Dalton Trans. (1991) 443.
[32] W.A. Herrmann, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, vol. 2, VCH, Weinheim, 1996, p. 980.
[33] F.J. McQuillin, D.G. Parker, G.R. Stephenson, Transition Metal Organometallics for Organic Synthesis, Cambridge University Press, Cambridge, 1991, p. 27.
[34] D.V. McGrath, R.H. Grubbs, Organometallics 13 (1994) 224.
[35] A.M. Trzeciak, J.J. Ziolkowski, J. Mol. Catal. 43 (1987) 15.
[36] R.C. Van der Drift, M. Vailati, E. Bouwman, E. Drent, J. Mol. Catal. A: Chem 159 (2000) 163.
[37] B.M. Trost, R.J. Kulawiec, J. Am. Chem. Soc. 115 (1993) 2027.
[38] A.M. Trzeciak, J.J. Ziolkowski, Gazz. Chim. Ital. 124 (1994) 403.
[39] S. Otsuka, Acta Chem. Scand. 50 (1996) 353.
[40] S. Inoue, H. Takaya, K. Tani, S. Otsuka, T. Sato, R. Noyori, J. Am. Chem. Soc. 112 (1990) 4897.
[41] K. Tani, Pure Appl. Chem. 57 (1985) 1845.
[42] M. Yamakawa, Organometallics 11 (1992) 3167.

[43] R.A. Sanchez-Delgado, A. Andriollo, E. Gonzalez, N. Valencia, V. Leon, J. Espidel, J. Chem. Soc., Dalton Trans. (1985) 1859.
[44] W. Kaminsky, Catal. Today 62 (2000) 23.
[45] K. Endo, T. Otsu, Makromol. Chem.-Macro. Chem. Phys. 192 (1991) 261.
[46] P. Jengo, G. Aprile, M. DiSerio, D. Gazzoli, E. Santacesaria, Appl. Catal. A: General 178 (1999) 97.
[47] C. Averbuj, M.S. Eisen, J. Am. Chem. Soc. 121 (1999) 8755.
[48] J. Nieman, Thesis Groningen University, 1982.
[49] M. Sodeoka, H. Yamada, M. Shibasaki, J. Am. Chem. Soc. 112 (1990) 4906.
[50] T. Tatsumi, K. Hashimoto, H. Tominaga, Y. Mizuta, K. Hata, M. Hidai, Y. Uchida, J. Organomet. Chem. 252 (1983) 105.
[51] Y. Lin, X. Lu, J. Organomet. Chem. 251 (1983) 321.
[52] J.-C. Fiaud, L. Aribi-Zouioueche, J. Chem. Soc., Chem. Commun. (1986) 390.
[53] S. Bellemin-Laponnaz, J.P. Le Ny, J.A. Osborn, Tetrahedron Lett. 41 (2000) 1549.
[54] G.F. Emerson, R. Pettit, J. Am. Chem. Soc. 84 (1962) 4591.
[55] R. Pettit, Ann. N. Y. Acad. Sci. 125 (1965) 89.
[56] G.F. Emerson, R. Pettit, Adv. Organomet. Chem. 1 (1964) 1.
[57] R. Damico, T.J. Logan, J. Org. Chem. 32 (1967) 2356.
[58] E. Weissberger, Bull. Soc. Chim. Belg. 89 (1980) 281.
[59] H. Cherkaoui, M. Soufiaoui, R. Grée, Tetrahedron 57 (2001) 2379.
[60] R. Damico, J. Org. Chem. 33 (1968) 1550.
[61] C. Crévisy, M. Wietrich, V. Le Boulaire, R. Uma, R. Grée, Tetrahedron Lett. 42 (2001) 395.
[62] N. Iranpoor, H. Imanieh, E.J. Forbes, Synth. Commun. 19 (1989) 2955.
[63] N. Iranpoor, E. Mottaghinejad, J. Organomet. Chem. 423 (1992) 399.
[64] J. Dieter, K.M. Nicholas, J. Organomet. Chem. 212 (1981) 107.
[65] W.T. Hendrix, F.G. Cowherd, J.L. Von Rosenberg, J. Chem. Soc., Chem. Commun. (1968) 97.
[66] R. Cramer, R.V. Lindsey Jun, J. Am. Chem. Soc. 88 (1966) 3534.
[67] F.A. Carey, R.J. Sundberg, Advanced Organic Chemistry. Part A: Structure and Mechanisms, Plenum Press, New York, 1991, p. 596.
[68] F.G. Cowherd, J.L. Von Rosenberg, J. Am. Chem. Soc. 91 (1969) 2157.
[69] J.U. Strauss, P.W. Ford, Tetrahedron Lett. (1975) 2917.
[70] E.A. Seddon, K.R. Seddon, The Chemistry of Ruthenium, vol. 19, Elsevier, Amsterdam, 1984.
[71] T. Naota, H. Tokaya, S.-I. Murakashi, Chem. Rev. 98 (1998) 2599.
[72] J.K. Nicholson, B.L. Shaw, Proc. Chem. Soc. (1963) 282.
[73] W. Smadja, G. Ville, C. Georgoulis, J. Chem. Soc., Chem. Commun. (1980) 594.
[74] M. Dedieu, Y.-L. Pascal, J. Mol. Catal. 9 (1980) 71.
[75] P.S. Hallman, T.A. Stephenson, G. Wilkinson, Inorg. Synth. XII (1970) 237.
[76] J.-E. Bäckvall, U. Andreasson, Tetrahedron Lett. 34 (1993) 5459.
[77] Y. Sasson, G.L. Rempel, Tetrahedron Lett. (1974) 4133.
[78] K. Felföldi, M. Bartók, J. Organomet. Chem. 297 (1985) C37.
[79] D. Wang, D. Chen, J.X. Haberman, C.-J. Li, Tetrahedron 54 (1998) 5129.
[80] R. Uma, M. Davies, C. Crévisy, R. Grée, Tetrahedron Lett. 42 (2001) 3069.
[81] R. Uma, M.K. Davies, C. Crévisy, R. Grée, Eur. J. Org. Chem. (2001) 3141.
[82] A. Zoran, Y. Sasson, J. Org. Chem. 46 (1981) 255.
[83] H. Suzuki, Y. Koyama, Y. Moro-Oka, T. Ikawa, Tetrahedron Lett. (1979) 1415.
[84] K. Ohkubo, T. Ohgushi, T. Kusaga, K. Yoshinaga, Inorg. Nucl. Chem. Lett. 13 (1977) 631.
[85] N. Ahmad, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. XV (1974) 50.
[86] S. Krompiec, J. Suwinski, J. Grobelny, Pol. J. Chem. 70 (1996) 813.
[87] A. Johnson, G.W. Everett, Jr., J. Am. Chem. Soc. 94 (1972) 1419.
[88] C. Georgoulis, J.M. Valery, G. Ville, Synth. Commun. 14 (1984) 1043.
[89] S. Krompiec, J. Suwinski, Pol. J. Chem. 64 (1990) 505.
[90] S. Krompiec, J. Suwinski, R. Grobelny, J. Mol. Catal. 89 (1994) 303.
[91] R.C. Van der Drift, E. Bouwman, E. Drent, unpublished results.
[92] P. Bernard, M. Biner, A. Ludi, Polyhedron 9 (1990) 1095.
[93] T. Karlen, A. Ludi, Helv. Chim. Acta 75 (1992) 1604.
[94] D.V. McGrath, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 113 (1991) 3611.
[95] C. Slugovc, E. Ruba, R. Schmid, K. Kirchner, Organometallics 18 (1999) 4230.
[96] In this section, the following abbreviations for phosphane ligands have been used: dppm = 1,1-bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane; *cis*-dppv = *cis*-1,2-bis(di-phenylphosphino)-ethene; dpppph = 1,2-bis(diphenylphosphino)benzene; *o*-MeO-dppe = 1,2-bis(*o*-methoxyphenylphosphino)ethane.
[97] Y. Sasson, A. Zoran, J. Blum, J. Mol. Catal. 6 (1979) 289.
[98] M. Langenbahn, K. Bernauer, G. Suss-Fink, J. Organomet. Chem. 379 (1989) 165.
[99] I.E. Marko, A. Gautier, M. Tsukazaki, A. Llobet, E. Plantalech-Mir, C.J. Urch, S.M. Brown, Angew. Chem., Int. Ed. Engl. 38 (1999) 1960.
[100] J.A. Wiles, C.E. Lee, R. McDonald, S.H. Bergens, Organometallics 15 (1996) 3782.
[101] M.K. Gurjar, P. Yakambram, Tetrahedron Lett. 42 (2001) 3633.
[102] Z.W. Wu, S.T. Nguyen, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 117 (1995) 5503.
[103] A.J. Deeming, S. Hasso, J. Organomet. Chem. 114 (1976) 313.
[104] C. Bianchini, E. Farnetti, M. Graziani, M. Peruzzini, A. Polo, Organometallics 12 (1993) 3753.
[105] R.W. Goetz, M. Orchin, J. Am. Chem. Soc. 85 (1963) 1549.
[106] C. Elschenbroich, A. Salzer, Organometallics: A Concise Introduction, VCH, New York, 1989.
[107] J. Falbe, H.-J. Schulze-Steinen, F. Korte, Chem. Ber. 98 (1965) 886.
[108] R.S. Dickson, Homogeneous Catalysis with Compounds of Rhodium and Iridium, D. Reidel, Dordrecht, 1985.
[109] A. Bright, J.F. Malone, J.K. Nicholson, J. Powell, B.L. Shaw, J. Chem. Soc., Chem. Commun. (1971) 712.
[110] Y. Sasson, A. Zoran, J. Blum, J. Mol. Catal. 11 (1981) 293.
[111] C. De Bellefon, S. Caravieilhes, E.G. Kuntz, C. R. Acad. Sci. Paris, IIc Chem. 3 (2000) 607.
[112] H. Alper, K. Hachem, J. Org. Chem. 45 (1980) 2269.
[113] C. Bianchini, A. Meli, W. Oberhauser, New J. Chem. 25 (2001) 11.
[114] H. Schumann, V. Ravindar, L. Meltser, W. Baidossi, Y. Sasson, J. Blum, J. Mol. Catal. A: Chem 118 (1997) 55.
[115] J.A. Moulijn, R.A. Sheldon, H. Van Bekkum, P.W.N.M. Van Leeuwen, in: J.A. Moulijn, P.W.N.M. Van Leeuwen, R.A. Van Santen (Eds.), Catalysis: An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis, Elsevier, Amsterdam, 1995, p. 237.
[116] C. Botteghi, G. Giacomelli, Gazz. Chim. Ital. 106 (1976) 1131.
[117] K. Tanaka, S. Qiao, M. Tobisu, M.M.-C. Lo, G.C. Fu, J. Am. Chem. Soc. 122 (2000) 9870.
[118] K. Hiroya, Y. Kurihara, K. Ogasawara, Angew. Chem., Int. Ed. Engl. 34 (1995) 2287.

[119] J.A. Moulijn, R.A. Sheldon, H. Van Bekkum, P.W.N.M. Van Leeuwen, in: J.A. Moulijn, P.W.N.M. Van Leeuwen, R.A. Van Santen (Eds.), Catalysis: An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis, Elsevier, Amsterdam, 1995, p. 244.
[120] C. Chapuis, M. Barthe, J.-Y. De Saint Laumer, Helv. Chim. Acta 84 (2001) 230.
[121] J. Park, C.S. Chin, J. Chem. Soc., Chem. Commun. (1987) 1213.
[122] C.S. Chin, S.Y. Lee, J. Park, S. Kim, J. Am. Chem. Soc. 110 (1988) 8244.
[123] C.S. Chin, J. Park, S.Y. Lee, C. Kim, J. Organomet. Chem. 352 (1988) 379.
[124] C.S. Chin, S.Y. Lee, B. Lee, Bull. Korean Chem. Soc. 11 (1990) 176.
[125] C.S. Chin, J. Park, C. Kim, Bull. Korean Chem. Soc. 10 (1989) 102.
[126] C.S. Chin, J. Park, C. Kim, Bull. Korean Chem. Soc. 10 (1989) 360.
[127] C.S. Chin, J. Park, C. Kim, S.Y. Lee, J.H. Shin, J.B. Kim, Catal. Lett. 1 (1988) 203.
[128] C.S. Chin, B. Lee, K. Hong, Bull. Korean Chem. Soc. 11 (1990) 162.
[129] C.U. Pittman, W.D. Honnick, J. Org. Chem. 45 (1980) 2132.
[130] G.-J. Boons, A. Burton, S. Isles, Chem. Commun. (1996) 141.
[131] G.L. Edwards, W.B. Motherwell, D.M. Powell, D.A. Sandham, J. Chem. Soc., Chem. Commun. (1991) 1399.
[132] L.J. Gazzard, W.B. Motherwell, D.A. Sandham, J. Chem. Soc., Perkin Trans. I (1999) 979.
[133] A.M. Trzeciak, J.J. Ziolkowski, Rhodium Express (1993) 7.
[134] F.P. Pruchnik, P. Smolenski, K. Wajda-Hermanowicz, J. Organomet. Chem. 570 (1998) 63.
[135] I. Matsuda, S. Sato, Y. Izumi, Tetrahedron Lett. 24 (1983) 2787.
[136] S. Sato, I. Matsuda, Y. Izumi, J. Organomet. Chem. 344 (1988) 71.
[137] S.P. Tunik, A.V. Vlasov, A.B. Nikol'skii, V.V. Krivykh, M.I. Rybinska, Organomet. Chem. USSR 4 (1991) 286.
[138] S. Sato, I. Matsuda, Y. Izumi, Tetrahedron Lett. 24 (1983) 3855.
[139] S. Sato, H. Okada, I. Matsuda, Y. Izumi, Tetrahedron Lett. 25 (1984) 769.
[140] D. Baudry, M. Ephritikhine, H. Felkin, Nouv. J. Chim. 2 (1978) 355.
[141] D. Baudry, M. Ephritikhine, H. Felkin, J. Chem. Soc., Chem. Commun. (1978) 694.
[142] T. Ohmura, Y. Shirai, Y. Yamamoto, N. Miyaura, Chem. Commun. (1998) 1337.
[143] T. Ohmura, Y. Yamamoto, N. Miyaura, Organometallics 18 (1999) 413.
[144] X. Lu, Y. Lin, D. Ma, Pure Appl. Chem. 60 (1988) 1299.
[145] Y. Lin, D. Ma, X. Lu, Acta Chim. Sin. 46 (1988) 93.
[146] Y. Lin, X. Zhu, Y. Zhou, J. Organomet. Chem. 429 (1992) 269.
[147] D. Ma, X. Lu, Tetrahedron Lett. 30 (1989) 2109.
[148] C.S. Chin, J.H. Shin, J.B. Kim, J. Organomet. Chem. 356 (1988) 381.
[149] P. Rigo, M. Bressan, M. Basato, Inorg. Chem. 18 (1979) 860.
[150] C.F. Lochow, R.G. Miller, J. Org. Chem. 41 (1976) 3020.
[151] B. Corain, G. Puosi, J. Catal. 30 (1973) 403.
[152] H. Bricout, E. Monflier, J.-F. Carpentier, A. Mortreux, Eur. J. Inorg. Chem. (1998) 1739.
[153] W.B. Motherwell, D.A. Sandham, Tetrahedron Lett. 33 (1992) 6187.
[154] R.F. Heck, Palladium Reagents in Organic Synthesis, Academic Press, London, 1985.
[155] P. Golborn, F. Scheinmann, J. Chem. Soc., Perkin Trans. I (1973) 870.
[156] X.T. Wang, L.K. Woo, J. Mol. Catal. A: Chem 130 (1998) 171.
[157] H.G. Tang, D.C. Sherrington, J. Mol. Catal. 94 (1994) 7.
[158] D.B. Dahl, C. Davies, R. Hyden, M.L. Kirova, W.H. Lloyd, J. Mol. Catal. A: Chem 123 (1997) 91.
[159] K.J. Cavell, K.Y. Chan, E.J. Peacock, M.J. Ridd, N.W. Davies, Aust. J. Chem. 44 (1991) 171.
[160] X. Lu, J. Ji, D. Ma, W. Shen, J. Org. Chem. 56 (1991) 5774.
[161] J.W. Francis, Thesis Loyola University, 1990.
[162] A.K. Zharmagambetova, R.K. Ashkeeva, E.E. Ergozhin, B.A. Utkelov, Dokl. Akad. Nauk 321 (1991) 1014.
[163] H.C. Clark, H. Kurosawa, Inorg. Chem. 12 (1973) 1566.
[164] H.C. Clark, H. Kurosawa, J. Chem. Soc., Chem. Commun. (1972) 150.