Hydration of conjugated dienes to produce ketones catalyzed by ruthenium complexes

F. Stunnenberg, F.G.M. Niele and E. Drent*

Koninklijke/Shell Laboratorium, Amsterdam (Shell Research B.V.), Badhuisweg 3, 1031 CM Amsterdam (Netherlands)

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Abstract

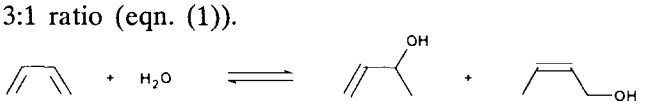
A class of ruthenium catalysts has been developed for the hydration of conjugated dienes to produce ketones directly. One application of interest is the conversion of 1,3-butadiene to methyl ethyl ketone. Whereas the acid component of the catalyst systems is responsible for the intermediate formation of both 3-buten-2-ol and 2-buten-1-ol, the ruthenium component can selectively and directly convert only the former alcohol to methyl ethyl ketone by intramolecular hydrogen transfer. However, the latter alcohol, being in hydration–dehydration equilibrium with 1,3-butadiene, is, indirectly, also converted to the same product. This reaction thus allows methyl ethyl ketone yields above 90% based on 1,3-butadiene. The essential feature of the new catalyst systems is that they are formed by the combination of Brønstedt acids, containing weakly or non-coordinating anions, with a ruthenium(III) source and chelating bipyridyl type ligands. It is suggested that a cationic ruthenium species, coordinated to a single chelating bipyridyl type ligand, fulfills a key role in the catalysis of the most critical step in the overall conversion, i.e. the catalysis of the intramolecular hydrogen transfer of intermediate allylic alcohols under acid catalyzed diene hydration conditions.

Key words: Catalysis; Hydration; Ketones; Ruthenium complexes

1. Introduction

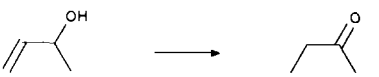
Hydration of conjugated dienes is a potentially useful reaction to produce allylic alcohols which may serve, for instance, as intermediates for the synthesis of ketones and/or aldehydes. Thus, as a large scale industrial application, 1,3-butadiene, abundantly available from naphta crackers C_4 streams could in principle be converted to methyl ethyl ketone (MEK) and n-butanal, respectively, a large scale chemical solvent (600 kt/a (1990)) and chemical intermediate for n-butanol (NBA) and 2-ethylhexanol (EHA) (>2 mil. t/a (1990)).

Such a conversion scheme would thus constitute two consecutive reaction steps in which butadiene is first hydrated, by acid catalysis, to an equilibrium mixture of 3-buten-2-ol and 2-buten-1-ol, approximately in a 3:1 ratio (eqn. (1)).



(1)

After isolation, rearrangement of the former alcohol to MEK could occur by an olefin double bond shift (eqn. (2)).



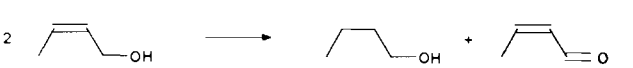
(2)

The latter alcohol could be recycled to the hydration reactor and also be converted to MEK or, alternatively, it could be, similarly to eqn. (2), rearranged to n-butanal (eqn. (3)).

(3)

However, such a conversion scheme is of very limited practical utility. For thermodynamic reasons only a very low equilibrium conversion of butadiene per pass is attainable in the hydration step and excessive separation and recycling costs render such a process uneconomical.

We have endeavored to develop catalyst systems which would allow the direct conversion of dienes to ketones and/or aldehydes in one processing step by combining the hydration and allylic alcohol rearrangement reactions in one reactor (eqn. (4)).



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*Author to whom correspondence should be addressed.

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(4)

Thermodynamically, the overall conversion process of dienes to ketones/aldehydes by water addition is a downhill process with an exothermicity of about 25 kcal/mol, thus allowing a very high diene conversion per pass.

The considerations, which have guided us in the development of suitable catalyst systems for the reaction given in eqn. (4), were the following. The hydration of dienes can be effected by strong Brønsted acids, whereas allylic alcohol rearrangement has been widely studied and shown to proceed efficiently both by heterogeneous and homogeneous transition metal catalysts [1–8]. The exothermicity of the latter rearrangement reaction would pull the unfavourable hydration equilibrium reaction to completion if both reactions could be made to proceed with a combination of the two catalysts in a single reactor. However, the combination with diene hydration poses various stringent requirements upon catalysts for allylic alcohol rearrangement. First, they should tolerate aqueous, acidic reaction conditions and secondly, perhaps more important, they should tolerate relatively high diene concentrations.

It appeared that many of the commonly known catalysts, highly efficient in olefinic bond migration for alkenes in general and allylic alcohols in particular, failed to show catalyst activity in the presence of dienes. This is perhaps not surprising in view of the generally high binding strength of conjugated dienes relative to monoalkenes.

We now report on a class of efficient ruthenium/bipyridyl catalyst systems, which do possess a good activity for intramolecular hydrogen transfer of allylic alcohols, even in the presence of a conjugated diene. In addition, they are tolerant towards water (in fact, they can operate in pure water) and protic acids containing weakly or non-coordinating anions. These catalysts, thus, for the first time, allow the one step hydration of dienes to ketones, in particular the hydration of 1,3-butadiene to MEK, in high yield [9]. One peculiar and surprising property of the catalysts is that whereas both 3-buten-2-ol and 2-buten-1-ol are intermediately formed, only the former undergoes intramolecular hydrogen transfer. The latter alcohol, being in hydration–dehydration equilibrium (eqn. (1)) with butadiene, is also converted to MEK.

2. Results

2.1. The hydration of 1,3-butadiene to MEK

Tables 1–3 summarize the results of batch autoclave experiments. The catalysts originally tested for the hydration of 1,3-butadiene were palladium, rhodium, ruthenium and iridium systems similar to known catalysts for olefinic bond isomerization and, in particular, those capable of rapid isomerization of allylic alcohols and for the intermolecular hydrogen transfer between alcohols and alkenes [10–13]. Although some of these systems produced MEK in direct 1,3-butadiene hydration experiments, the yield was low.

Table 1 shows the first superior results with catalyst systems formed by the combination of a ruthenium(III) salt with 1,10-phenanthroline (phen) and a Brønsted acid such as *p*-toluenesulfonic acid (HOTs). With ruthenium(acac)$_3$ or ruthenium(acetate)$_3$ as the ruthenium source the reaction proceeded with good rate and selectivity.

At temperatures below 150 °C, for instance at 125 °C, the reaction profile was characterized by an induction period of several hours. However, when the catalyst

TABLE 1. Hydration of butadiene[a]: effect of metal precursor

Exp. No.	Metal precursor	Rate[b] (mol/mol/h)	Selectivity to MEK (%)
I	$Ru(acac)_3$	100	90
A		85[c]	90[c]
B		50[f]	94[f]
II	$Ru(acetate)_3$	60	90
III	$RuCl_3$	35	60
IV	$RuCl_3$ + 3 equiv. AgOTs[d]	60	90
V	RuO_2	trace	
VI	$Ru^{(0)}$	trace	
VII	$Ru(phen)_3Cl_2$ + 2 equiv. AgOTs[e]	trace	
VIII	*cis*-$Ru(bipy)_2Cl_2$ + 2 equiv. AgOTs[e]	trace	
IX	$Ru_2Cl(acetate)_4$ + 1 equiv. AgOTs	85	90

[a]Conditions: batch experiments, 250 ml Hastelloy C autoclave. Intake: 10 ml butadiene, 25 ml H_2O, 25 ml diglyme. Catalyst formed by combination of metal precursor, 1,10-phenanthroline and *p*-toluene sulfonic acid (HOTs) 1:2:14 (mol/mol/mol), T = 155 °C, 5 h. [b]Rate averaged over 5 h. [c]Water as only solvent. [d]AgOTs = silver tosylate. [e]No phenanthroline added. [f]Activated at 155 °C for 1 h, thereafter at 125 °C reaction temperature.

system was 'activated' in the presence of butadiene at 155 °C for 1 h, the reaction still proceeded thereafter at good rate (50 mol (mol Ru)$^{-1}$ h^{-1}) and selectivity (94%) at 125 °C.

Water could be used as the only reaction solvent or in combination with water-mixable solvents like diglyme.

As the only significant byproducts 4-vinylcyclohexene (butadiene Diels–Alder dimer), 1- and 2-butenes and 4-acetylcyclohexene (Diels–Alder adduct of 1,3-butadiene and methyl vinyl ketone) were observed, each in yields not exceeding a few percent. No butanal and butenal could be observed as byproducts!

A considerable drop in activity and selectivity, with mainly 4-vinylhexene as byproduct, was observed when ruthenium(chloride)$_3$ was used as catalyst precursor. However, restoration of catalyst activity and selectivity occurred when chloride anions were replaced with an equivalent quantity of tosylate (OTs^-) anions by adding silver tosylate.

No active catalysts could be generated with zero-, di- or tetra-valent ruthenium precursor compounds, whereas an active catalyst resulted again when ruthenium$_2$chloride(acetate)$_4$, a mixed di-/tri-valent ruthenium compound, was used.

Neither could active catalysts be generated with a variety of iridium, palladium, iron or cobalt compounds.

2.2. The effect of ligand type

The results in Table 2 indicate that active ruthenium catalysts can only be generated when ligands capable of bis-nitrogen coordination (of the bi-pyridyl-type) are combined with ruthenium(acac)$_3$ and HOTs. A low catalyst activity was observed in the absence of ligand or with phosphine ligands. A low activity was also observed with monodentate pyridyl ligands.

2.3. The effect of acid type

Table 3 shows the effect of the acid component of the catalyst system on catalyst performance. Replacing HOTs by other strong acids (sulfuric acid, phosphoric acid, trifluoroacetic acid or trifluoromethanesulfonic acid) resulted in similar catalyst performance. In the case of HCl, also a strong acid, no activity for 1,3-butadiene hydration to MEK was observed, suggesting that besides acidity, the coordinating properties of the conjugate base towards the ruthenium center play a decisive role in the catalytic performance.

2.4. The effect of catalyst composition

The effect of acid (HOTs)/ruthenium ratio on the rate of MEK formation is shown in Fig. 1. To obtain good catalyst performance it is necessary to use an excess of acid over an above the 3 mol (mol Ru)$^{-1}$, required for the removal of acac anions as acetylacetone from the ruthenium coordination sphere. The reaction order for MEK formation with respect to acid concentration was close to zero at acid/ruthenium ratios above 8.

The ratio of ligand to ruthenium plays a decisive role in the formation of the active catalyst as is indicated in Fig. 2. Active catalyst systems were only formed for a ligand(phen)/ruthenium ratio between 1 and 2. Remarkably, within this range the reaction order for MEK formation is close to zero with respect to this ratio. At ratios, even marginally larger than 2, MEK formation becomes strongly inhibited.

2.5. Semi-continuous experiments

In addition to batch experiments, semi-continuously fed stirred tank reactor experiments were carried out with 1,3-butadiene to obtain information on catalyst

TABLE 2. Hydration of butadiene[a]: effect of ligand type

Exp. No.	Ligand	Rate (mol/mol/h)	MEK yield (%)
I	No ligand	8	14
II	1,10-Phenanthroline	100	90
III	2,2'-Bipyridine	100	90
IV	4,7-Dimethyl-1,10-phenanthroline[b]	85	90
V	4,7-Diphenyl-1,10-phenanthroline[b]	65	85
VI	2,9-Dimethyl-1,10-phenanthroline[b]	30	40
VII	4,4'-Dimethyl-2,2'-bipyridine[b]	75	90
VIII	Terpyridine	51	53
IX	2-Diphenylphosphinepyridine	20	30
X	2-Methoxypyridine	10	15
XI	Triphenylphosphine[c]	0	
XII	1,2-Bis(diphenylphosphino)ethane	0	
XIII	1,3-Bis(diphenylphosphino)propane	0	

[a]Conditions: batch experiments, 250 ml Hastelloy C autoclave. Intake: 10 ml butadiene, 25 ml H_2O, 25 ml diglyme. Metal precursor 0.5 mmol Ru(acac)$_3$, L/Ru = 1 (mol/mol), acid = *p*-toluene sulfonic acid (HOTs), acid/Ru = 14 (mol/mol), T = 155 °C, 5 h. [b]5 ml butadiene. [c]2 equiv. used per mol Ru.

TABLE 3. Hydration of butadiene[a]: effect of acid type

Acid	Rate (mol/mol/h)	Selectivity to MEK (%)
HOTs	70	90
H_2SO_4	50	86
H_3PO_4	60	85
CF_3COOH	90	70
HCl	0	
CF_3SO_3H	70	70

[a]Conditions: batch experiments, 250 ml Hastelloy C autoclave. Intake: 5 ml butadiene, 25 ml H_2O, 25 ml diglyme. Catalyst: 0.5 mmol Ru(acac)$_3$, 1,10-phenanthroline and acid 1:1:14 (mol/mol/mol), $T = 155$ °C, 5 h.

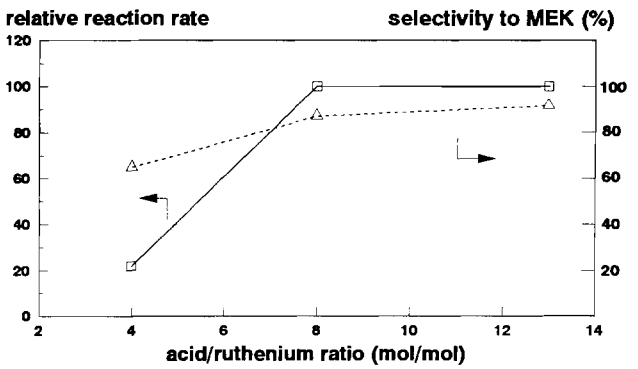


Fig. 1. Reaction rate and selectivity as a function of acid/Ru ratio for hydration of butadiene to MEK. Phen/Ru = 2, $T = 155$ °C, 25/25 ml H_2O/diglyme, 10 ml BD.

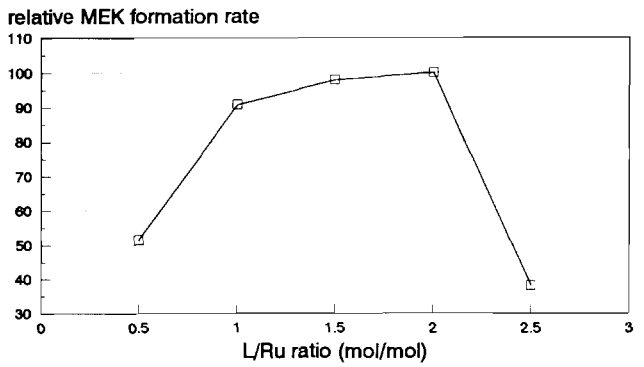


Fig. 2. MEK formation rate as function of ligand/Ru ratio. Ligand = 1,10-phen, $T = 155$ °C, catalyst composition: Ru(acac)$_3$/1,10-phen/acid, acid/Ru = 14.

stability. For these experiments a catalyst system was used formed by combining ruthenium(acac)$_3$, phen and HOTs in a molar ratio of 1:2:14. The reactor was initially loaded with sufficient water/diglyme (1:2 vol./vol.) to allow complete conversion of 1,3-butadiene admitted stepwise into the reactor by injecting portions of 10 ml at selected intervals. During the first hour the catalyst was activated (in the presence of 1,3 butadiene) at 155 °C; thereafter the reaction was carried out at a constant temperature of 125 °C. From these experiments it appeared that in a period of 20 h the MEK formation rate was halved with respect to the 'fresh' catalyst. A cumulative turnover of 1200 mol MEK (mol Ru)$^{-1}$ could be achieved in a period of 30 h.

In a similar experiment at a constant temperature of 155 °C the higher reaction rate was compensated for by a faster catalyst deactivation rate, which resulted in a similar cumulative turnover number.

It was found that higher acid/ruthenium ratios (for instance equal to 40) resulted in improved catalyst stability; however, this went at the cost of selectivity due to consecutive acid catalyzed aldol condensation of the product ketone.

2.6. Scope of the hydration of conjugated dienes

In the above-mentioned experiments the catalytic phenomena were illustrated for the hydration of 1,3-butadiene. Similar results were obtained for other 1,3-alkadienes, such as 1,3-octadiene and isoprene. Thus, in the latter case methyl isopropyl ketone (MIPK) was produced with the ruthenium(acac)$_3$/phen/HOTs (1:2:14) catalyst system in 80–85% yield by feeding continuously isoprene at a rate of 2 ml (h)$^{-1}$ into a reactor containing diglyme/water (50:15) for 15 h at 150 °C. During this period an average rate of MIPK formation of 25 mol (mol Ru)$^{-1}$ h^{-1} at 95% conversion was observed.

Substrates containing the conjugated alkadiene moiety at internal positions in the molecule were less suited for hydration to ketones with the above reported catalyst systems. This also holds for cyclic conjugated dienes, such as 1,3-cyclohexadiene and cyclopentadiene. Only small quantities of cyclic ketone could be observed as product.

2.7. Isomerization of allylic alcohols

The isomerization of unsaturated alcohols in the absence of conjugated dienes has been studied by other workers and shown to proceed efficiently, for example, with ruthenium–phosphine complexes of various type [7, 8, 14–16]. We confirmed that, indeed an active catalyst for the isomerization of 3-buten-2-ol to MEK was formed *in situ* by the combination ruthenium(acac)$_3$/triphenylphosphine (1:2): at 120 °C, MEK was formed with a rate of 200 mol (mol Ru)$^{-1}$ h^{-1} in diglyme as solvent. The reaction started after an induction period of about 3 h.

As shown above, we were, however, unable to form active catalysts by combining ruthenium(acac)$_3$ with phosphines and HOTs for the direct hydration of 1,3-butadiene to MEK.

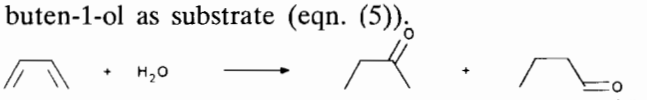
In addition, it was shown that with ruthenium(acac)$_3$/phen/HOTs catalyst systems no butanal was observed as hydration product, implying that 2-buten-1-ol could not be isomerized by these catalysts.

It is clear that isomerization of allylic alcohol intermediates *in the presence of conjugated dienes* is the critical factor for the success of converting conjugated dienes directly to ketones or aldehydes.

We therefore paid attention to the isomerization of allylic alcohols by ruthenium(acac)$_3$/phen/HOTs catalyst systems in model experiments, with a special interest in the relationship between the catalyst's activity/selectivity and allylic alcohol structure, both in the presence and absence of 1,3-butadiene. To prevent extensive alcohol dehydration to diene, an acid/Ru ratio of slightly less than 3 was applied in these experiments.

The results in Table 4, first indicate that allylic alcohols (both primary and secondary alcohols) with a *terminal* olefin moiety could be isomerized efficiently to the corresponding aldehyde or ketone both in the absence and presence of added 1,3-butadiene. Yet, with 3-buten-2-ol as substrate, isomerization proceeded at least by a factor of 2 slower in the presence of added 1,3-butadiene, which indicates that 1,3-butadiene is competing for coordination sites around ruthenium with the allylic alcohol.

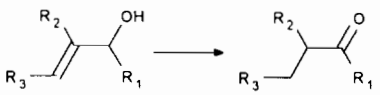
Secondly, allylic alcohols with an *internal* olefinic moiety could be much less efficiently isomerized to the corresponding aldehyde and ketone, while in the presence of added 1,3-butadiene, hardly any isomerization took place. With these substrates, it is also interesting to note that in the absence of butadiene, *inter*molecular hydrogen transfer to produce the corresponding saturated alcohol and unsaturated ketone or aldehyde, is a significant side-reaction; for example, about 20% of the product was observed as crotonaldehyde with 2-buten-1-ol as substrate (eqn. (5)).



(5)

It is also noteworthy that in attempted isomerization experiments with 2-buten-1-ol in the absence of added butadiene, but with acidic catalysts (acid/Ru > 3), MEK was obtained as the main product. Under these conditions the equilibrium reaction given in eqn. (1) is concurrently established via dehydration of 2-buten-1-ol and subsequent selective isomerization of 3-buten-2-ol then yields MEK.

TABLE 4. Isomerization of allylic alcohols[a]: influence of substrate structure and presence of butadiene



substrate product

Substrate			Product yield (%)	
R_1	R_2	R_3	with butadiene	without butadiene
H	Me	H	85	92
Me	Me	H	82	90
Me	H	H	91 (200)[b]	98 (>400)[b]
Me	H	Me	7	63
H	H	Me	trace	40
Et	H	H	76	n.m.[c]

[a]Conditions: batch experiments, 250 ml Hastelloy C autoclave. Intake: 25 ml H_2O, 25 ml diglyme, 5 ml unsaturated alcohol. Catalyst: 0.5 mmol Ru(acac)$_3$, 1 mmol 1,10-phenanthroline and 1.4 mmol HOTs, T = 155 °C, 5 h. In experiments with butadiene 5 ml is added. [b]Reaction rate: mol MEK mol Ru^{-1} h^{-1}. [c]n.m. = not measured.

2.8. Attempts to characterize reaction mixtures by liquid chromatography/mass spectroscopy/UV–Vis spectroscopy

We undertook a liquid chromatography/mass spectroscopy (LC/MS) and UV–Vis spectroscopy study 'to throw light' on which ruthenium species could be present in the reaction medium at various stages of the reaction. It could be established that in aqueous reaction media containing ruthenium(acac)$_3$/phen/HOTs catalyst systems (conditions given in Table 1), activation of the catalyst system was accompanied with displacement of the anionic acac ligands by tosylate anions to generate cationic ruthenium(III) species and, initially, free acac, which degraded with the concomitant formation of acetone and acetic acid on further heating.

When the activation was carried out in the presence of 1,3-butadiene and water, the predominant formation of cationic ruthenium(II) complexes, Ru(II)(phen)$_3$-(OTs)$_2$ (**I**) and Ru(II)(phen)$_2$OTs)$_2$ (**II**), identified by comparison with authentic samples, became apparent. In fact, with catalyst systems containing phen/Ru = 1 and 2, respectively 20% and more than 40% of ruthenium was present as complex **I** after activation at 155 °C for 1 h.

A clearcut identification of three other ruthenium species present in the mixtures could not be established; some of the species did not contain phen as coordinating ligand, in particular when a ligand/Ru = 1 was applied. The other species might contain a single phen ligand coordinated to ruthenium.

It did not appear possible to correlate observed catalyst activity with the intensity of individual LC peaks measured (*ex situ*) in reaction samples at ambient LC/MS conditions. Likewise LC/MS traces taken from samples in the course of long duration experiments showed only that slight changes occurred on aging, whereas the observed catalytic activity can vary substantially, even by a factor of 5–10. It was apparent that in all samples, complexes **I** and **II** are by far the dominant ruthenium species.

3. Discussion

Clearly, under sufficiently acidic reaction conditions (Fig. 1) the isomerization of the intermediately generated allylic alcohols presents the overall rate-determining obstacle in the direct hydration of butadiene to form MEK. It is therefore appropriate to concentrate on a discussion of the ruthenium component(s) present in the acidic ruthenium catalyst system, which could be responsible for the observed catalytic phenomena associated with the isomerization of the allylic alcohols.

The essential characteristics of the active ruthenium catalyst systems are the following.

(i) They are only formed by combination of a ruthenium(III) source with neutral chelating bipyridyl ligands and acids containing weakly or non-coordinating anionic ligands (Tables 1–3). The molar quantity of ligand with respect to ruthenium should be within narrow limits, i.e. between 1 and 2 (Fig. 2).

(ii) They are active catalysts for terminal allylic alcohol isomerization in the presence of 1,3-dienes (Table 4).

(iii) However, in the presence of dienes, they cannot effectively isomerize allylic alcohols containing an internal olefinic moiety (Table 4), including cyclic allylic alcohols (Section 2.6.).

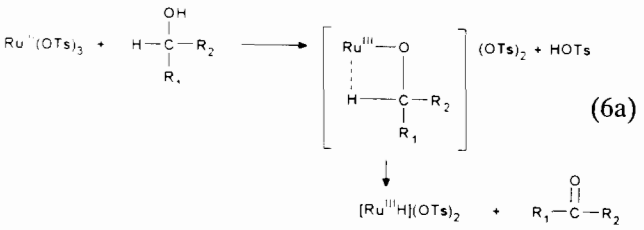
Any suggestion with respect to the active catalyst species should thus give a reasonable account of these characteristics.

3.1. About the nature of the active ruthenium catalyst species

Although we do not have direct, e.g. spectroscopic or organometallic, evidence concerning the nature of the real catalytically active ruthenium complex, we consider it worthwhile to comment on the available catalytic and chromatographic data and how these can be related to the essential characteristics of the active catalyst complex.

The organometallic chemistry of ruthenium is especially rich and complicated and this is also true for ruthenium/1,10-phenanthroline or 2,2′-bipyridyl complexes [17–19]. A variety of complexes, containing ruthenium in various valencies and with variable ligand coordination numbers, is possible.

The reduction of ruthenium(III) to ruthenium(II) (chlorides) in the presence of phosphines in alcoholic medium is well documented [17, 20]. It is reasonable to assume a similar reduction of ruthenium(III) tosylates to take place under our reaction conditions, where initially formed allylic alcohols may serve as the reductant to form hydrido–ruthenium(III) species (eqn. (6a)) (neutral ligand(s) omitted for clarity).



(6a)

We suggest these hydrido–ruthenium species exist in a deprotonation–protonation equilibrium (eqn. (6b)).

$$[Ru^{III}H](OTs)_2 \rightleftharpoons Ru^{I}OTs + HOTs \qquad (6b)$$

Ruthenium(I) species may be withdrawn from this equilibrium by disproportionation with ruthenium(III) to yield the observed ruthenium(II) complexes **I** and **II** (eqn. (6c)).

$$Ru^{I}OTs + Ru^{III}(OTs)_3 \longrightarrow 2Ru^{II}(OTs)_2 \qquad (6c)$$

Clearly, from the LC/MS experiments no direct evidence can be extracted with respect to the nature of the real catalytically active ruthenium species present under our reaction conditions. Complex **I**, observed as a main component in active catalyst systems, can, however, not be the real active catalyst species, since no correlation between its concentration and catalyst activity could be established. This is also supported by the results given in Table 1 (exp. VII) and the results depicted in Fig. 2, where it is shown that catalyst activity falls off very rapidly by increasing the phen/Ru ratio above 2. Moreover, the results of Table 1 (exp. VIII) prove that complex **II** also cannot be identified with the active catalyst species. Thus, it is clear that the real active catalyst species must represent only a minor fraction of the total amount of ruthenium complexes present in the reaction medium.

The presence of relatively large quantities of ruthenium species with high ligand coordination numbers, two and three, leaves only a limited amount of ligand available for coordination to the remaining ruthenium species; for example, an applied ligand/Ru ratio of 2 and more than 40% of ruthenium present as **I** leaves an average coordination of less than 1.3 for the remaining ruthenium species. With an applied ligand/Ru ratio of 1 this number becomes only 0.5.

It is thought that under the applied conditions and with the applied ligand/Ru ratio between 1 and 2, there is insufficient ligand available to convert ruthenium tosylate totally into complex **I** and **II** but sufficient to allow the co-existence of intermediate ruthenium species with a low ligand coordination number in the reactions given by eqns. (6).

A recent study by McGrath and Grubbs [21a] concerning the mechanism of isomerization of allylic ethers and allylic alcohols (in the absence of diene) is

noteworthy. They report that isomerization of allyl alcohol is catalyzed under mild conditions (20–45 °C) by free cationic $Ru(II)(H_2O)_6(OTs)_2$ complexes in aqueous solution (catalyst turnover number of 10–20 in 12–48 h). An intermolecular metal hydride addition–elimination mechanism has been proposed.

However, our results obtained under 1,3-butadiene hydration conditions (Table 2, cf. exps. I and II) indicate that it is highly unlikely that free ruthenium species, unligated by phen or bipyridyl ligands, are responsible for the observed hydration–isomerization catalysis in the presence of these ligands, such as applied in our study.

We suggest, therefore, that the catalytically active ruthenium complex is one in which only a single phen or bipyridyl ligand is complexed to cationic ruthenium species. The formal valency of this ruthenium species cannot easily be established. Since only active catalysts could be generated from Ru(III) precursor complexes, we consider it likely that the actual catalyst species is a 'trapped' intermediate (e.g. by ligand, diene and/or allylic alcohols) in the course of the *in situ* reduction process given in eqns. (6).

3.2. Allylic alcohol isomerization in the presence of 1,3-butadiene

We suggest that in the presence of 1,3-butadiene, the traditional olefinic bond shift mechanism, via intermolecular metal hydride addition–elimination, for allylic alcohol isomerization is not very likely. It is expected that intermediate ruthenium hydride complexes would be readily trapped by insertion of 1,3-butadiene in the ruthenium–hydride bond to give relatively stable ruthenium π-allyl species.

It is interesting to mention an experiment in which 1-hexene (5 ml) was additionally present in the reactor during a 1,3-butadiene hydration experiment (similar to exp. I at 140 °C, Table 1.). Although MEK was formed with good rate and selectivity, isomerization of 1-hexene to internal hexenes did not take place, thus confirming that the active catalyst species for isomerization of 3-buten-2-ol under actual 1,3-butadiene hydration conditions, is not capable of isomerizing simple alkenes.

A similar observation was made by Trost and Kulawiec in their study of the isomerization of allylic alcohols (in the absence of conjugated dienes) by $(Cp)(PPh_3)_2RuCl$ [22]. An *intramolecular hydrogen-transfer* mechanism, involving the coordination of the allylic alcohol as a *bidentate* ligand via the alcohol and olefin functionality, has been proposed by them. We suggest that the same mechanism is operative under 1,3-butadiene hydration conditions in our study.

It is thought that bidentate coordination of certain allylic alcohols, such as 3-buten-2-ol, can effectively compete with the coordination of 1,3-butadiene.

β-Hydride elimination from the coordinated alkoxide leads to an enone hydride complex. Subsequent rearrangement to an oxa-allyl species is thought to occur through addition of the ruthenium hydride to the coordinated olefin moiety, after which protonation liberates the product.

Such a mechanism is consistent with the observation that 3-buten-2-ol is selectively isomerized while isolated olefin functionalities remain untouched. Further evidence includes the observed discrimination between 3-buten-2-ol and allylic alcohols containing an internal olefinic moiety, such as 2-buten-1-ol. Bidentate coordination of allylic alcohols with an *internal* olefin functionality is expected to be a relatively unlikely especially in the presence of 1,3-butadiene. Similarly, chelation by cyclic allylic alcohols is also deemed unlikely.

However, a too strong chelation by the alcohol and olefin functionalities is also undesirable. We have observed that 3-buten-1-ol, added in 1,3-butadiene hydration experiments, significantly inhibits MEK formation. For example, the addition of 50 mmol of 3-buten-1-ol in exp. I of Table 1, leads to a rate decrease of MEK formation by a factor 10, without significant isomerization of 3-buten-1-ol. Clearly, the more stable complex with 3-buten-1-ol [21b] makes the formation of the chelate complex with 3-buten-2-ol a less likely event.

The observation of only small amounts of methyl vinyl ketone (observed as adduct with 1,3-butadiene) together with butenes, obtainable via *inter*molecular hydrogen-transfer from 3-buten-2-ol to 1,3-butadiene, is also consistent with a by far predominant *intra*molecular hydrogen-transfer pathway of MEK formation.

We briefly comment on the effects of anions and ligand type.

The requirement of weakly coordinating anions in the ruthenium complexes, as opposed to the more coordinating chloride anions, for obtaining a good catalyst activity, is thought to derive from the easier access of allylic alcohol substrate molecules. Another factor related to this may be the increased electrophilicity of the cationic ruthenium center facilitating the required electrophilic bi-functional attack of both the alcohol and olefin functionality of the allylic alcohol.

The chelating property of the bipyridyl ligand is thought to be important for keeping the substrate coordination sites around the ruthenium center simultaneously accessible for both the alcohol and olefin moieties of the allylic alcohol. At the same time a vacant coordination site should be available to facilitate the elementary steps of β-hydrogen elimination (from the alkoxide functionality) and ruthenium hydride ad-

dition (to the olefin functionality). It is thought that this requirement is best fulfilled at low ligand coordination numbers. This is consistent with our observation that bis- and tris-bipyridyl ligated ruthenium species are inactive as catalysts for the hydration of 1,3-butadiene to MEK.

The fact that phosphines, including chelating phosphines, are unsuitable as the neutral ligands may be related to the steric and electronic properties of these ligands. The increased steric bulk of phosphines relative to bipyridyl ligands makes the coordination sites at the ruthenium center less easily accessible. At the same time, the reduced electrophilicity of the ruthenium center in phosphine complexes relative to that of the corresponding bipyridyl complexes could make the simultaneous electrophilic bi-functional attack of the alcohol and olefin moieties a less probable event.

However, in the absence of 1,3-butadiene, phosphines are suitable ligands in the ruthenium catalyzed isomerization of allylic alcohols [7, 8, 14–16]. This is an indication of an alternative mechanism, i.e. via the traditional olefinic bond-shift, under diene-free conditions.

4. Conclusions

The combination of Brønsted acids containing weakly or non-coordinating anions with cationic ruthenium complexes, described above, shows the unprecedented ability to catalyze the direct hydration of certain conjugated dienes to produce ketones in high selectivity, in particular, methyl ethyl ketone from 1,3-butadiene.

We suggest that a cationic (bipyridyl)ruthenium species, present in the reaction medium as a minority ruthenium species, fulfills a key role in the catalysis of the most critical step in the overall conversion, i.e. the intramolecular hydrogen transfer of intermediate allylic alcohols in the presence of conjugated dienes, water and strong acids.

It is though that an efficient bi-pronged electrophilic attack of the allylic alcohol, via its alcohol and olefinic moiety, forming a metallocycle intermediate, constitutes the most characteristic feature of the catalysis. For certain allylic alcohols of a particular structure, such as 3-buten-2-ol, this enables the catalysis of intramolecular hydrogen transfer to take place efficiently under acid-catalyzed 1,3-butadiene hydration conditions.

Although the observed catalytic phenomena have been made plausible it is clear that further detailed studies of the elementary steps are required to elucidate the precise nature of the catalyst species.

5. Experimental

5.1. Analytical equipment

Routine gas–liquid chromatographic (GLC) analysis was performed on a Perkin-Elmer 8500 gas chromatograph equipped with a FID. The columns are a 50 m fused silica CP-sil 5 CB and a 50 m fused silica FFAP.

UV–Vis experiments were carried out on a Shimadzu UV-240 spectrophotometer.

For the LC/MS experiments the samples were separated on a Nucleosil C18 column using a Waters 600 MS LC system and a Waters 490 MS UV detector. For the MS detection a dual-beam thermospray method was used. The MS analysis was performed on a Finnigan 4500 TSQ mass spectrometer using a 0.95 s scan time and an interscan delay of 0.05 s.

Field desorption experiments were performed on a JEOL HV 110 mass spectrometer.

5.2. Materials

All ruthenium compounds were obtained from Johnson Matthey. *p*-Tsa was obtained from Merck. The nitrogen ligands were obtained from Aldrich or Janssen Chimica. Allylic alcohols mentioned in Table 4 were obtained from Aldrich. Butadiene (purity greater than 99%) was obtained from Intermar (Breda, Netherlands).

5.3. Autoclave experiments

Batch and semi-batch experiments were carried out in 250 ml Hastelloy C autoclaves. BD and isoprene were pumped into the autoclaves as liquid using ISCO high pressure pumps. The following general procedure was used. The autoclave was charged with the catalyst precursors and the acid in predetermined ratios and solvent was added. Next the autoclave was closed, purged 3 times with nitrogen. The diene was added and the autoclave was heated to the appropriate temperature. A more detailed description regarding concentrations and temperatures is given with the Tables.

Semi-continuous experiments were performed by charging a fixed amount of butadiene into the autoclave at given time intervals. The reaction rate constants were calculated from the pressure decrease versus time.

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