Ruthenium-Catalyzed Isomerization of Allylic Alcohols: Oxidation State Determines Resistance Against Diene Inhibition

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The novel complex *mer*-[$RuCl_3$(dmso)(phen)] (**1**) has been prepared and characterized by X-ray diffraction. The ruthenium center is in a distorted octahedral environment with the three chloride ions coordinated in a *mer*-fashion and an *S*-bonded dmso ligand *trans* to one of the phen nitrogen atoms. Electrochemical experiments show two reversible waves in acetonitrile solution, corresponding to the couples $Ru^{III/II}$ (0.11 V) and $Ru^{IV/III}$ (1.73 V). The analogous Ru^{II} complex *cis*,*cis*-[$RuCl_2(dmso)_2$(phen)] (**2**) shows one reversible wave at 1.08 V, corresponding to the $Ru^{III/II}$ couple. Both complexes exhibit high catalytic activity in the isomerization of 3-buten-2-ol to butanone. The initial turnover frequency (TOF) for **1** in diglyme/water at 130 °C is 295 h^{-1} with a first-order k_{ini} of 0.6 h^{-1}, while **2** reaches an initial TOF of 260 h^{-1} and a k_{ini} of 0.5 h^{-1}. A cumulative turnover number (TON) of 1025 has been obtained with **1** as a catalyst precursor. The activity of **1** and **2** has been compared to that of in situ mixtures with both Ru^{III} and Ru^{II} precursors. All Ru^{II} complexes are deactivated before 100% conversion has been attained. $RuCl_3$ is a good catalyst precursor with an initial TOF of 500 h^{-1}. If $RuCl_3$ is mixed in situ with one equivalent of phen, an induction period of 40 min results and the activity thereafter is much lower than without the addition of phen. With 2 equiv. of phen, no reaction is observed in the first 6 h and only a very low activity is obtained after that. An important difference between **1** and **2** becomes apparent when a conjugated diene is added to the reaction mixture; only **1** remains active. The results demonstrate that only Ru^{III} complexes with one phen ligand are active catalyst precursors for the isomerization of allylic alcohols in the presence of conjugated dienes. The consequence of this observation is further demonstrated by applying both catalyst precursors in the direct one-pot conversion of 1,3-butadiene to butanone. In this reaction, complex **1** (TON = 2050, t = 6 h) forms a much more active precursor than complex **2** (TON = 1300, t = 7 h).
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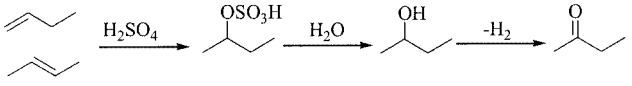
Introduction

Homogeneous catalysis opens new pathways to environmentally benign industrial processes. Many processes in use today produce stoichiometric amounts of inorganic salts. Transition metal catalyzed reactions on the other hand, may offer complete atom-economical routes to important industrial products. For example, butanone (methyl ethyl ketone, MEK) is a megaton-per-year scale solvent traditionally produced from butenes.[1] This process requires the use of stoichiometric amounts of concentrated sulfuric acid as shown in Scheme 1.



Scheme 1. Present-day synthesis of MEK from a mixture of butenes

1,3-Butadiene is an attractive alternative starting material for the preparation of MEK. A viable route would require water as the only other stoichiometric reagent. After acid-catalyzed hydration of butadiene [see (a) in Scheme 2], the 1,2-addition product 3-buten-2-ol can be isomerized to MEK [see (b) in Scheme 2].[2] The equilibrium of Scheme 2 (a) is 97% on the left-hand side, making a one-pot synthesis preferable in order to circumvent an extensive butadiene recycle. For the selective formation of MEK, this calls for catalysts that catalyze the isomerization of the secondary allylic alcohol 3-buten-2-ol but not the primary allylic alcohol 2-buten-1-ol, in the presence of dienes. Despite consid-

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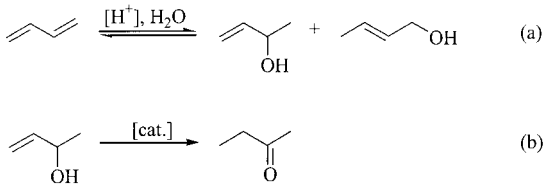
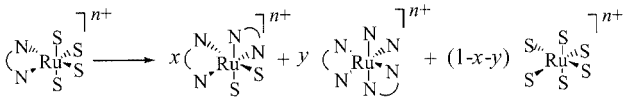
erable efforts this type of catalysts remain scarce.[3] Alternatively, other reagents such as alcohols and amines could be used instead of water to obtain higher conversions, and after isomerization and hydrolysis of the vinyl ether or enamine the carbonyl compound can be obtained.[4,5] In this case an extra, costly purification step will be required to separate MEK from butanal (or to separate the intermediates).



Scheme 2. (a) Acid-catalyzed hydration of 1,3-butadiene (b) followed by isomerization yields MEK in a complete atom-economical process

The feasibility of the one-pot synthesis of MEK from 1,3-butadiene was shown by Drent and co-workers.[6,7] A catalytically active species obtained by in situ mixing of $[Ru(acac)_3]$ (Hacac = 2,4-pentanedione) and between 1 and 2 equiv. of 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) catalyzes the direct conversion of 1,3-butadiene to MEK (in over 95% selectivity) with a maximum of 1200 turnovers in 32 h. Yet, this turnover number (TON) is not sufficiently high to make this route economically successful. An important catalyst deactivation route proved to be ligand redistribution that results in inactive ruthenium complexes with two and three didentate nitrogen-donor ligands (Scheme 3).[7] Indeed, it has been demonstrated recently that reducing the extent of ligand redistribution may increase the initial activity by a factor of almost ten.[8]



Scheme 3. Ligand redistribution of mono(phen)Ru complexes; S = vacant site or labile ligand; N∪N = phen; $2x + 3y = 1$, $n = 2, 3$

Although the catalyst precursor consists of an Ru^{III} complex, both Ru^{III} and Ru^{II} complexes can be identified with mass spectrometry (MS) in a used catalyst. This observation raises the question as to what the oxidation state of the ruthenium atom in the catalytically active species is. In this paper the synthesis and characterization of the Ru^{III} compound *mer*-$[RuCl_3(dmso)(phen)]$ (**1**) and the analogous Ru^{II} complex *cis,cis*-$[RuCl_2(dmso)_2(phen)]$ (**2**) are described. The activities of both complexes in the key step of the catalytic process, the isomerization of 3-buten-2-ol to MEK, are compared in the absence and the presence of isoprene (2-methyl-1,3-butadiene) to reveal the role of the ruthenium oxidation state in the isomerization of allylic alcohols.

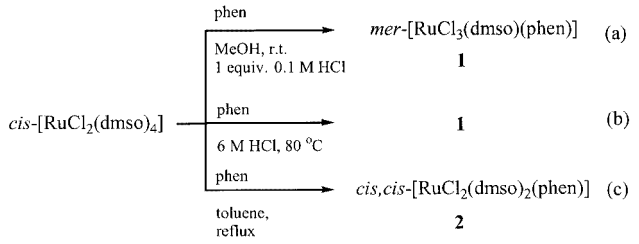
Results and Discussion

Synthesis and Structure of *mer*-$[RuCl_3(dmso)(phen)]$ (1) and *cis,cis*-$[RuCl_2(dmso)_2(phen)]$ (2)

Synthesis of 1 and 2

To obtain a clear view of the influence of the ruthenium oxidation state in the catalytic process, two complexes are required with ligand environments as identical as possible. It was deduced from earlier studies[7,8] that the catalytically active species should contain only one phen ligand. Furthermore, the complexes should contain innocent ligands that are easily replaced during the catalytic cycle. Numerous ruthenium complexes with two or three phen ligands are known,[9,10] but examples of mono(phen) complexes remain scarce.[9–13] It is especially difficult to prevent ligand redistribution during synthesis.[12] The synthesis of mono(phen) complexes was attempted in our laboratory starting from $[Ru(H_2O)_6](OTs)_2$, $[Ru(MeCN)_6](OTf)_2$ [14] and $RuCl_3$. In all cases, it proved impractical to obtain the ruthenium atom in both the 2+ and 3+ oxidation states. The syntheses of $[Ru(acac)_2(phen)]$ and $[Ru(acac)_2(phen)]PF_6$ were successful,[15] but the acac ligand could not be replaced under the reaction conditions.

A literature method to prepare the Ru^{II} complex **2**[12] from *cis*-$[RuCl_2(dmso)_4]$ and phen in $CHCl_3$ gave only low yields in our hands, but changing the solvent to toluene[16] resulted in direct precipitation of the pure product from the reaction mixture [see (c) in Scheme 4]. An additional and vital advantage of this method is the complete absence of bis- and tris(phen)ruthenium complexes. Upon slow concentration of a $CHCl_3$/toluene solution of **2**, red crystals of **1** were obtained; a lead to the synthesis of the analogous Ru^{III} complex **1** was found. $CHCl_3$ is known to contain traces of HCl and recently the syntheses of several complexes with the general formula $[RuCl_3(dmso)L]$, where L is triazole, thiadiazole or diamine, by oxidation with HCl were reported.[17,18] Indeed, it proved feasible to prepare **1** by oxidation of *cis*-$[RuCl_2(dmso)_4]$ with HCl in the presence of phen [see (a) and (b) in Scheme 4]. The formation of an Ru^{III} species from an Ru^{II} precursor can be envisioned to involve simultaneous reduction of the dmso ligand to dimethyl sulfide as proposed by Cingi et al. [see Equation (1)].[17] A general path to the Ru^{II} species that does not invoke ligand participation is discussed below. The room-temperature route [see (a) in Scheme 4] results directly in analytically pure **1**, but the overall yield with the high-temperature route [see (b) in Scheme 4] is higher. It should be noted, however, that at higher reaction temperatures with longer reaction times and using concentrated HCl, other products may precipitate, which are probably oligomeric analogs of **1**.



Scheme 4. Synthesis of **1** (a) (b) and **2** (c) from *cis*-[$RuCl_2(dmso)_4$]

$$2\ cis,cis\text{-}[RuCl_2(dmso)_2(phen)] + 2\ HCl \longrightarrow 2\ mer\text{-}[RuCl_3(dmso)(phen)] + Me_2S + dmso + H_2O \quad (1)$$

Crystal Structure Determination of 1

An ORTEP drawing of **1** is shown in Figure 1. Some selected bond lengths and angles are given in Table 1. The ruthenium center is in a distorted octahedral environment with coordination of one didentate phen ligand, three chloride ions and one *S*-bonded dmso ligand *trans* to one of the phen nitrogen atoms. The S−O bond is in the same plane as the phen ligand. Both ruthenium−nitrogen distances are in the range found for other ruthenium complexes with aromatic nitrogen donor ligands.[13,17] The Ru(1)−S(21) bond is longer than in analogous Ru^{II} complexes,[17] which reflects the smaller degree of π-back donation in this Ru^{III} complex. The S(21)−O(22) bond [1.478(2) Å] is slightly shorter than in free dmso [1.492(1) Å][19] indicating greater S−O double-bond character in the *S*-bonded dmso. The bonds within the phen ligand are similar to those in other (phen)ruthenium complexes.[13]

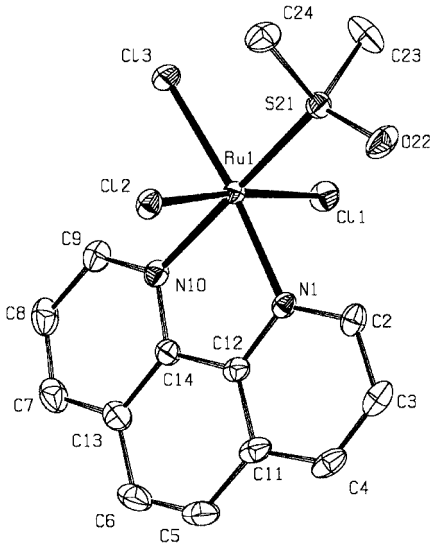


Figure 1. ORTEP plot and numbering scheme of the major component of complex **1**; hydrogen atoms and toluene solvent molecules are omitted for clarity; thermal ellipsoids are drawn at the 50% probability level

Table 1. Selected bond lengths and angles for **1**·toluene

Bond lengths [Å]			
Ru(1)−N(1)	2.099(2)	Ru(1)−Cl(3)	2.3477(8)
Ru(1)−N(10)	2.087(2)	Ru(1)−S(21)	2.2971(8)
Ru(1)−Cl(1)	2.3267(8)	S(21)−O(22)	1.478(2)
Ru(1)−Cl(2)	2.3444(8)		
Angles [°]			
N(1)−Ru(1)−N(10)	78.99(8)	N(10)−Ru(1)−S(21)	178.75(7)
N(1)−Ru(1)−Cl(1)	86.27(6)	S(21)−Ru(1)−Cl(1)	90.73(2)
N(1)−Ru(1)−Cl(2)	87.08(6)	S(21)−Ru(1)−Cl(2)	90.87(2)
N(1)−Ru(1)−Cl(3)	172.34(6)	S(21)−Ru(1)−Cl(3)	87.06(2)
N(1)−Ru(1)−S(21)	100.60(6)	Cl(1)−Ru(1)−Cl(2)	173.34(3)
N(10)−Ru(1)−Cl(1)	90.42(6)	Cl(1)−Ru(1)−Cl(3)	93.49(2)
N(10)−Ru(1)−Cl(2)	87.93(7)	Cl(2)−Ru(1)−Cl(3)	93.05(2)
N(10)−Ru(1)−Cl(3)	93.35(6)		

The Cl(1)−Ru(1)−Cl(2) angle is significantly smaller than 180° due to steric repulsion of the dmso methyl groups; the N(1)−Ru1−N(10) bond angle of 78.99(8)° is contracted compared to the ideal octahedral value by the small phen bite angle, which is somewhat smaller than in the complex where dmso is replaced by CO.[13] In this complex the phen ligand itself is boat-shaped to some extent, with angles between pairs of least-squares planes (through each of the three rings) ranging from 4.97(13) to 10.30(12)°. In the crystal packing a high degree of stacking is observed. Only two rings of each phen ligand are stacked with two rings of a phen ligand on an adjacent complex molecule (generated by symmetry operation $1 - x, -y, 1 - z$), avoiding steric repulsion between neighboring dmso groups. Approximately perpendicular to this, the cocrystallized toluene molecules form dimers, totally enclosed by molecules **1**, through stacking interactions.

Cyclic Voltammetry Studies on 1 and 2

The redox properties of both complexes have been investigated with cyclic voltammetry. In an acetonitrile solution, **1** exhibits two reversible one-electron waves (Figure 2). The first peak ($E_{1/2}$ = 0.11 V, ΔE_p = 60 mV) corresponds to the $Ru^{III/II}$ couple, whereas the second peak ($E_{1/2}$ = 1.73 V, ΔE_p = 54 mV) corresponds to the $Ru^{IV/III}$ couple. The nature of both couples has been corroborated by linear sweep voltammetry that shows the expected signs of the currents. The current for both peaks is linearly dependent on $v^{1/2}$ for the scan rates studied (0.05−1 V s^{-1}) indicating reversible diffusion-controlled processes.[20] The potential of the first wave is evidence for the ease of reduction of **1,** which plays an important role in isomerization catalysis (vide infra).

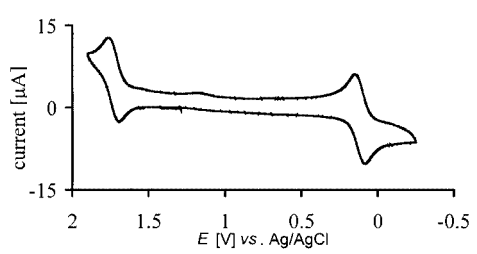


Figure 2. Cyclic voltammogram of **1** in acetonitrile at room temperature; scan rate: 0.1 V s^{-1}

The reversibility of the second peak is remarkable, demonstrating a robust Ru^{IV} complex, this was also observed in the analogous compound *mer*-[$RuCl_3$(dmso)(tmen)] (tmen = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).[18] From this peak it can be concluded that dmso in **1** is primarily a σ-donor and remains *S*-bonded even with the ruthenium atom in the 4+ oxidation state.

Complex **2** shows one reversible one-electron wave ($E_{1/2}$ = 1.08 V, ΔE_p = 56 mV), corresponding to the $Ru^{III/II}$ couple (Figure 3). In this case, the current for this peak is also linearly dependent on $v^{1/2}$ for the scan rates studied (0.05−1 V s^{-1}) and the oxidation state of **2** has been proven with linear sweep voltammetry. In the reductive part of the voltammogram (at potentials < −1.0 V) an irreversible wave is observed that can be attributed to a ligand-based reduction or reduction of the ruthenium center to Ru^0.

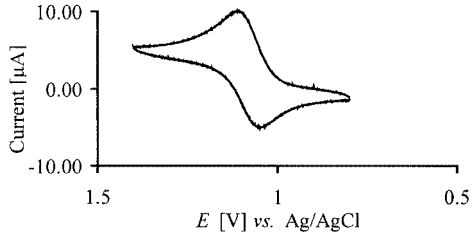
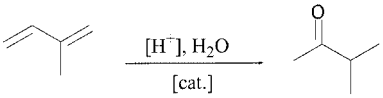


Figure 3. Part of the cyclic voltammogram of **2** in acetonitrile at room temperature showing the $Ru^{III/II}$ wave; scan rate: 0.1 V s^{-1}

Isomerization of 3-Buten-2-ol to MEK

The Influence of a Conjugated Diene

The key step in the direct conversion of 1,3-butadiene to MEK has been identified as the isomerization of 3-buten-2-ol to MEK in the presence of 1,3-butadiene.[3,7] Since 1,3-butadiene is a suspected carcinogenic and due to its high volatility (b.p. −4 °C) it is difficult to handle in standard glassware, so it was decided instead to use isoprene in this study. Isoprene is converted analogously to MIPK [methyl isopropyl ketone, Equation (2)] and can thus function as a reasonable substitute for 1,3-butadiene.[7] The results of isomerization of 3-buten-2-ol to MEK catalyzed by several Ru^{III} (Entries 1−5) and Ru^{II} catalyst precursors (Entries 6−10) both in the absence and presence of isoprene are collected in Table 2.



(2)

Table 2. Isomerization of 3-buten-2-ol to MEK catalyzed by Ru^{III} and Ru^{II} complexes

Entry[a]	Catalyst precursor	TON	TON with isoprene[b]
1	[$RuCl_3 \cdot xH_2O$]	285	95
2	[$RuCl_3 \cdot xH_2O$] + 1 equiv. phen	390	300
3	**1**	465	440
4	**1**[c]	n.d.	475
5	**1** + 3 equiv. AgOTs	410	n.d.
6	*cis*-[$RuCl_2(dmso)_4$]	325	110
7	*cis*-[$RuCl_2(dmso)_4$] + 1 equiv. phen	275	75
8	**2**	290	150
9	**2** + 2 equiv. AgOTs	295	n.d.
10	**2**[d]	270	n.d.

[a] Reactions were performed in a 25-mL sealed glass vessel at 130°C; substrate: 3-buten-2-ol (5.8 mmol); catalyst: ruthenium complex (0.011 mmol) plus ligand as appropriate; substrate/catalyst: 530; solvent: water/diglyme (1:3 mL); reaction time: 6 h; n.d. = not determined. [b] 10 mmol of isoprene was added prior to addition of the substrate. [c] 15 mmol of isoprene. [d] In Ar with standard Schlenk techniques.

It is clear that both Ru^{III} and Ru^{II} complexes are capable of catalyzing the isomerization of 3-buten-2-ol to MEK, but Ru^{III} precursors consistently show higher conversion. The result of Entry 10 demonstrates that exclusion of air is not essential to obtaining good activity. Comparison of Entries 1 and 6 with 2 and 7, respectively, shows that the phen ligand as such is not a necessary requirement for activity. Both in situ mixing of the components and the use of preformed catalyst precursors gave comparable results. If a higher substrate/**1** ratio is applied, a TON of 1025 in 12 h can be obtained with an average TOF of 85 h^{-1}. The negative influence of an increased ligand-redistribution rate is demonstrated by successive removal of chloride ions by Ag^I salts from either **1** or **2**, which results in the same or only slightly lower catalytic activity (Entries 5 and 9). Presumably, the anticipated higher activity, as a consequence of more vacant coordination sites, is counterbalanced by an increased rate of ligand redistribution. Addition of a fourfold excess of Ag^I gives a color change of the reaction mixture to dark blue and almost complete loss of activity.

While a large number of catalysts are able to catalyze the isomerization of allylic alcohols to carbonyl compounds,[2] almost all of these fail to do so in the presence of dienes. The crucial next step therefore is to compare the catalytic systems *in the presence* of isoprene. From Table 2, it becomes apparent that isoprene indeed has a dramatic effect on the catalysis. Two factors are proven to play a role in resistance against isoprene inhibition. First, although phen is not required for activity in the absence of isoprene, the significant difference in activity of the catalyst precursors in Entries 1 and 2 shows that phen is an essential component for catalytic activity in the presence of isoprene. Second, all Ru^{II} catalyst precursors (Entries 6−9) loose 50% or more of their activity with isoprene in the reaction mixture. The presence of phen here (Entry 7) does not lead to resistance against diene inhibition. Thus, both of the requirements, a 3+ oxidation state and one phen ligand, have to be met. Complex **1** remains active, even if more isoprene is added (Entry 4, > 1300 mol-equiv. to ruthenium). These results unambiguously show, for the first time, the crucial influence of the oxidation state of the ruthenium center in allylic alcohol isomerization in the presence of a diene. Comparison of several catalytic precursors lacking or con-

taining various amounts of dmso ligands (cf. Table 2, Entries 2 and 3, 7 and 8), especially in the presence of isoprene, shows that the influence of the ligands on the difference in activity is marginal.

Isomerization Profile in Time

The difference in isomerization activity of Ru^{III} complex **1** and Ru^{II} complex **2** in the absence of isoprene is smaller than suggested by the overall results given in Table 2. The results plotted in Figure 4 clearly indicate that the reaction does not obey clean first-order kinetics. Therefore, *initial* TOFs and *initial* first-order rate constants (k_{ini}) have been calculated for both complexes.[21] The values obtained for **1** (TOF = 295 h^{-1}; k_{ini} = 0.6 h^{-1}) are similar to those found for **2** (TOF = 260 h^{-1}; k_{ini} = 0.5 h^{-1}). Although initial activity is comparable, **2** is deactivated much faster under the reaction conditions. The influence of isoprene is nicely illustrated (Figure 4). In the initial stages of the reaction, complex **2** still catalyzes the formation of MEK, but both initial TOF (75 h^{-1}) and k_{ini} (0.1 h^{-1}) are significantly lower than they are in the absence of isoprene. This remarkable finding may also explain the relatively low conversion reached by Ru^{II} complexes in the absence of isoprene: under the reaction conditions, some reversion (dehydration) occurs [see (a) in Scheme 2] that yields 1,3-butadiene as evidenced by GLC analysis of the gas cap. The increasing concentration of 1,3-butadiene in time causes a decrease of the number of active catalyst centers until finally catalysis is stopped completely.

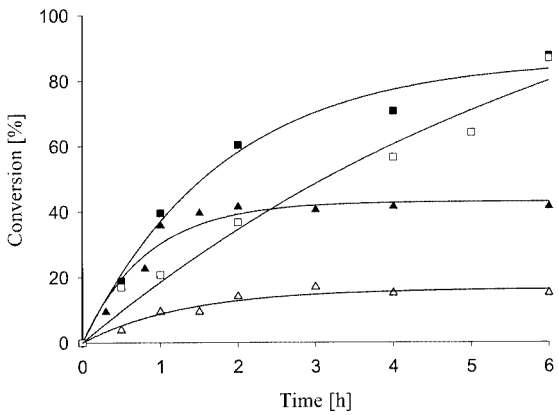


Figure 4. Isomerization of 3-buten-2-ol to MEK catalyzed by complexes **1** (squares) and **2** (triangles) at 130 °C in water/diglyme (1:3 mL) in the absence (filled symbols) and presence (open symbols) of 10 mmol of isoprene; substrate/catalyst precursor = 530

The initial rate of isomerization in the presence of isoprene is also lower with **1** as the catalyst precursor (TOF = 140 h^{-1}, k_{ini} = 0.3 h^{-1}), but deactivation in time does not occur and a high conversion can be attained in 6 h. Previous studies with $Ru(acac)_3$ and phen or bpy likewise showed a decrease in the reaction rate in the presence of 1,3-butadiene, but this system also remained active.[7]

The results of a time-dependent investigation using catalysts formed from [$RuCl_3 \cdot xH_2O$] and varying amounts of phen at 100 °C are shown in Figure 5. In the absence of phen, the isomerization is first order in 3-buten-2-ol with an initial TOF of 500 h^{-1} after a negligible induction period. When 1 equiv. of phen is added, the induction time increases to 40 min. Moreover, the initial TOF drops to 105 h^{-1}. In the original catalytic system with $Ru(acac)_3$, addition of either 1 or 2 equiv. of phen resulted in equal reactivity.[7] In sharp contrast to this, the activity of $RuCl_3$ with 2 equiv. of phen is virtually zero. After more than 16 h of reaction time, a small amount of MEK (60 turnovers) is obtained, but this must have been formed after an induction period of at least 5 h (Figure 5). The variation in lengths of the induction periods most likely originates from a kinetic difference in displacement of the various ligands involved. If isomerization is to occur with [$RuCl_3 \cdot xH_2O$] as the catalyst precursor, water has to be replaced by the substrate, which appears to be reasonably fast. Upon addition of 1 equiv. of phen, [$RuCl_3(H_2O)$(phen)] is formed. In this case, dissociation of one or more chloride ions has to take place prior to catalysis, which is considerably slower.[22] An induction period is not often observed in transition metal catalyzed isomerization of allylic alcohols and it seems to point at a cooperative effect; dissociation of the second and subsequent chloride ions is faster after dissociation of the first chloride ion. A similar effect has also been observed in isomerization of 3-buten-2-ol to MEK catalyzed by [$Ru(MeCN)_6$].[14] Increasing the polarity of the reaction mixture, by doubling the water content, should facilitate dissociation. Indeed, the induction period is reduced to 20 min, while the initial TOF is raised to 215 h^{-1}. At the higher reaction temperatures used with complexes **1** and **2** (Figure 4), chloride dissociation is much faster and only a small induction period is observed. If 2 equiv. of phen are added to $RuCl_3$, [$Ru(phen)_2Cl_2$]Cl is formed. In an analogous isomerization reaction catalyzed by $RuCl_3$ with 2 equiv. of 2,2′-bipyridine, only [$RuCl_2(bpy)_2$]Cl and related dinuclear species are observed with electrospray MS,[15] while complexes with only one bpy ligand are not found under these

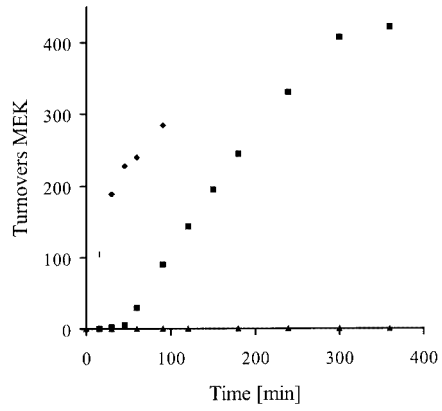


Figure 5. Isomerization of 3-buten-2-ol to MEK with $RuCl_3$ (◆) and $RuCl_3$ plus 1 (■) and 2 (▲) equiv. of phen at 100 °C in water/diglyme (1:3)

conditions. Given the slow dissociation of chloride ions from Ru^{III},[22] catalytic activity is now difficult to achieve.

Direct Conversion of 1,3-Butadiene to MEK

In the presence of *p*-toluenesulfonic acid, the preformed complex **1** is active in the direct conversion of 1,3-butadiene to MEK (Scheme 2). A TON of 2050 is reached in 6 h with a selectivity for MEK of over 95% in water/diglyme at 145 °C. Remarkably, in view of the isomerization results above, **2** also catalyzes the formation of MEK from 1,3-butadiene. The TON of 1300 in 7 h, however, is considerably lower than the TON reached with **1** as the catalyst precursor. The activity of **2** may be ascribed to the in situ oxidation of Ru^{II} to Ru^{III} by the acid present in the reaction mixture for the hydration of 1,3-butadiene. As schematically shown in Equation (3), oxidative addition of a proton initially leads to an Ru^{IV} hydride species. After protonation of the hydride yielding dihydrogen, the resulting Ru^{IV} species may comproportionate with a second Ru^{II} complex to give two Ru^{III} complexes. On the other hand, complex **1** can be reduced, under these reaction conditions, to the inactive Ru^{II} species according to Equation (4). Coordination of a substrate alkoxide followed by β-hydrogen elimination gives an Ru^{III} hydride and an aldehyde. After reductive elimination of 1 equiv. of HCl, the resulting Ru^{I} species may comproportionate with a starting Ru^{III} complex to give two Ru^{II} species.

$$\mathrm{Ru(II)} + \mathrm{HCl} \longrightarrow \mathrm{HRu(IV)Cl} \xrightarrow[-H_2]{\mathrm{HCl}} \mathrm{Ru(IV)Cl_2} \xrightarrow{\mathrm{Ru(II)}} 2\ \mathrm{Ru(III)Cl} \quad (3)$$

$$\mathrm{Cl_3Ru(III)} + {}^{-}\mathrm{OCH_2R} \xrightarrow[-Cl^-]{} \mathrm{Cl_2Ru(III)OCH_2R} \xrightarrow[-O{=}CHR]{}$$

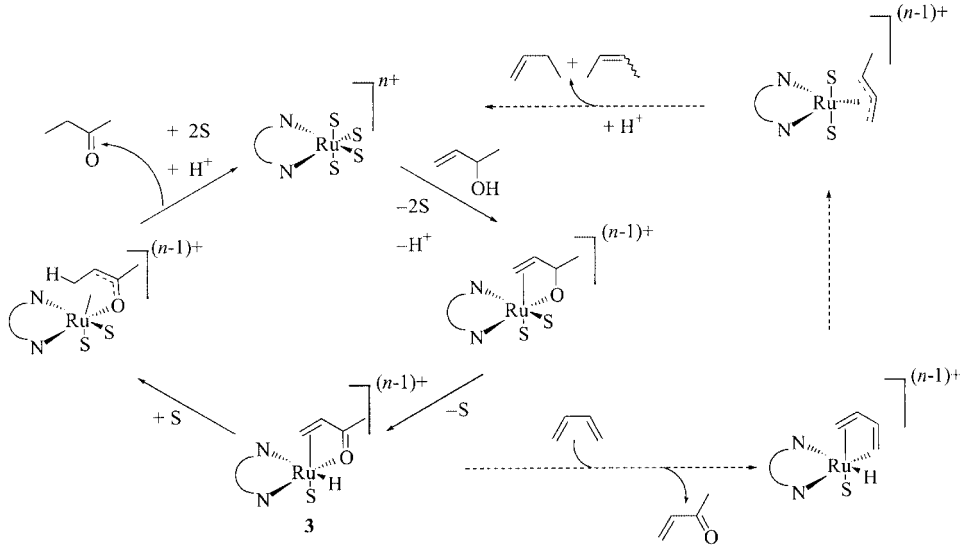
$$\mathrm{HCl_2Ru(III)} \xrightarrow[-HCl]{} \mathrm{ClRu(I)} \xrightarrow{\mathrm{Cl_3Ru(III)}} 2\ \mathrm{Cl_2Ru(II)} \quad (4)$$

Analysis of reaction mixtures containing either catalyst precursors **1** or **2** with electrospray MS clearly shows the presence of Ru^{II} and Ru^{III} species in both cases. Since both catalyst precursors exhibit a significantly different activity, apparently an equilibrium has not been reached during the early stages of the reaction. The formation of Ru^{II} complexes, even to a significant extent in the presence of (oxidizing) acid, is unfortunate and should receive further attention in attempts to maximize catalytic activity. However, simply increasing the acid concentration to keep the ruthenium centers in the 3+ oxidation state results in an increased amount of side reactions such as 1,3-butadiene polymerization.

The direct conversion of 1,3-butadiene was previously shown to also be catalyzed by an in situ mixture of $RuCl_3$ and one phen ligand.[8] In fact, the performance of this system with an initial TOF of 960 h^{-1} and a cumulative TON of 2700 in 5 h is significantly better than the $Ru(acac)_3$/phen system.[7] In connection with the present study it is interesting to recall that electrospray MS spectra showed the presence of species with ruthenium in the oxidation state 3+ or 2+.[8] It can now be concluded that the latter species are inactive under the actual 1,3-butadiene hydration/isomerization reaction conditions used.

Mechanistic Rationale of Diene Inhibition

Two general mechanisms have been proposed for isomerization of allylic alcohols: the intramolecular π-allylmetal hydride mechanism and the intermolecular metal hydride addition/elimination mechanism.[2] Neither mechanism assigns a specific role to the oxygen moiety during the catalytic cycle. However, complexes **1** and **2** are inactive in the isomerization of unsubstituted alkenes such as 1-octene. So, a third, fundamentally different mechanism that invokes coordination of the oxygen moiety was proposed that is shown in Scheme 5.[3,23]



Scheme 5. Mechanism of isomerization of 3-buten-2-ol invoking oxygen coordination; indicated with dotted arrows is a possible deactivation/regeneration route involving a π-allyl species; S = labile ligand or $2e^-$ vacant site; $N_{\cup}N$ = phen, n = 2, 3

The first step is the coordination of 3-buten-2-olate to the ruthenium center after deprotonation of the substrate. This coordination can either be directly didentate as shown in Scheme 5, or occur in two consecutive steps with initial coordination of the double bond.[3] β-Hydrogen abstraction yields the (enone)ruthenium hydride species **3**. After readdition of the hydride ion to give an (oxaallyl)ruthenium complex, protonation affords MEK and regenerates the starting complex.

Two possibilities of catalyst deactivation by conjugated dienes can be envisioned. The simplest mode of action is preferential coordination; if isoprene coordinates much stronger to the ruthenium center than 3-buten-2-ol, no isomerization can take place. Although at this point we cannot completely exclude formation of a stable (isoprene)ruthenium complex with either **1** or **2**, NMR studies with ruthenium(II) complexes in our laboratory indicated a stronger initial coordination of 3-buten-2-ol.[15]

Intermediate **3** forms a second possible handle for diene inhibition as dienes are known to form stable π-allyl complexes after reaction with ruthenium hydrides.[24] Throughout a normal catalytic cycle with extremely fast intramolecular hydrogen transfer no long-lived ("free") hydride is present. However, if methyl vinyl ketone (MVK) dissociates from **3**, the resulting ruthenium hydride may react with isoprene to form a (presumably inactive) (methylallyl)ruthenium complex. Whereas pure 1-octene is not isomerized in the presence of **1** or **2**, *trans*-2-octene (ca. 10 turnovers with either **1** or **2** as catalyst precursor) can be detected by GLC during the isomerization of 3-buten-2-ol in the presence of 1-octene, a strong support for the presence of free hydrides. Hydrides resulting from direct oxidative addition of acids to the ruthenium atom in **1** or **2** (vide supra) appear to be short-lived as 1-octene isomerization is not observed upon addition of HOTs in the absence of allylic alcohols.

The behavior of both catalyst precursors **1** and **2** is similar with the GLC detection of approximately 30 turnovers of MVK with respect to ruthenium. It should be noted that in both cases a mixture of Ru^{III} and Ru^{II} species is produced and it cannot be determined which of the two is responsible for MVK formation. The higher selectivity to MEK with catalyst precursor **1** suggests a lower rate of MVK dissociation in this case. The amount of MVK formed is more than stoichiometric and there must therefore be a way to regenerate the original catalytically active species from a ruthenium hydride or a (π-allyl)ruthenium species. A tentative route for a ruthenium hydride involves reaction of the hydride with the protic allylic alcohol to generate dihydrogen gas. Alternatively, protonation of an allylruthenium species will yield alkenes. A GLC gas-cap analysis of $RuCl_3$/phen-catalyzed isomerization of 3-buten-2-ol in the presence of isoprene demonstrates the presence of a mixture of C_5 alkenes, which is nicely explained by the protonation of π-allyl species.

Thus, the reaction of a diene with a free ruthenium hydride may explain the deactivation of the catalyst, but at this point no conclusion can be drawn as to why Ru^{III} complexes are much more resistant to this deactivation route and various explanations may be offered. Perhaps ruthenium(III) hydrides are less easily formed, as dissociation of MVK, coordinated through both the oxygen moiety and the double bond, from the higher charged Ru^{III} center may be relatively slower than from Ru^{II}. Alternatively, the removal of a π-allyl species by protonation might be faster with (allyl)Ru^{III} species. We currently favor the former explanation as more plausible, but molecular modeling aided by well-designed experiments should further clarify the peculiar difference in reactivity between Ru^{III} and Ru^{II} complexes.

Conclusion

In conclusion, the novel ruthenium(III) complex **1** has been synthesized and characterized by X-ray diffraction. The comparison with its Ru^{II} analog **2** revealed an important difference in catalytic activity in isomerization of allylic alcohols. Whereas both complexes show high activity in the isomerization of 3-buten-2-ol to MEK, only **1** remains active in the presence of the conjugated diene isoprene. Comparison with other catalyst precursors demonstrated that not only an Ru^{III} oxidation state is required for activity in the presence of isoprene, but also that one phen ligand has to be present in the complex. This is the first time that the role of the oxidation state has been pinpointed, implying that a second major deactivation route is discovered in the ruthenium-catalyzed direct conversion of 1,3-butadiene to MEK, next to ligand redistribution. In fact, while **1** gives high turnovers of MEK (up to 2050), **2** is less active (TON = 1300). The activity of **2** is most likely caused by in situ oxidation to **1** by the acid present in the reaction mixture. The reduction potential of **1** (0.11 V, $Ru^{III/II}$) and the oxidation potential of **2** (1.08 V, $Ru^{III/II}$) indicate that under the applied reaction conditions a delicate balance between both Ru^{III} and Ru^{II} complexes will be present in solution, which is confirmed by MS. Further studies are aimed at complexes with higher redox potentials with ligands that may provide stabilization of Ru^{III}.

Experimental Section

General Remarks: *cis*-$[RuCl_2(dmso)_4]$[12] was prepared according to a literature procedure. $[RuCl_3 \cdot xH_2O]$ (Aldrich), 3-buten-2-ol (Aldrich), isoprene (Acros) and other reagents and solvents were commercially available and used as received, except 1-octene, from which peroxides were removed by flash chromatography on alumina immediately prior to use. Quantitative gas liquid chromatography (GLC) analyses were carried out with a Chrompack apparatus equipped with a CP wax 58 (FFAP) CB column (25 m × 1.2 μm) with toluene as internal standard. Melting points were measured with a Büchi apparatus and are uncorrected. Matrix Assisted Laser Desorption Ionization (MALDI) Time of Flight (TOF) mass spectra were recorded with a Finnigan MAT Vision 2000 spectrometer. The analytes were mixed with a 2,5-dihydroxybenzoic acid (DHB) or a α-cyano-4-hydroxycinnamic acid (α-CHCA) matrix. Elemental analyses were performed with a Perkin−Elmer series II 2400 CHNS/O analyzer. IR spectra were

obtained with a Perkin−Elmer Paragon 1000 FT-IR spectrophotometer equipped with a golden gate ATR device, using the reflectance technique (4000−300 cm^{-1}). ^1H NMR spectra (300.1 MHz) were measured with a Bruker 300 DPX. Chemical shifts (δ) are reported in ppm. Proton chemical shifts are relative to TMS.

***mer*-[RuCl$_3$(dmso)(phen)] (1):** A bright yellow solution of [RuCl$_2$(dmso)$_4$] (1.0 g, 2.1 mmol) and phen (0.39 g, 2.2 mmol) in 6 M HCl was heated at 80 °C for 2.5 h, after which time the resulting orange-red mixture was filtered. The filtrate was concentrated in a rotary evaporator. Flash chromatography of the red-brown solid on Al_2O_3 with CH_2Cl_2/MeOH (10:1) as eluent gave **1** as a dark red solid. Yield: 0.71 g, 74%. Alternatively, **1** can be prepared in situ from *cis*-[RuCl$_2$(dmso)$_4$] and phen at room temperature in MeOH with 1 equiv. of 0.1 M HCl (yield: 30%). Crystals suitable for X-ray analysis can be obtained from slow concentration of an MeOH solution at room temperature. M.p. 182 °C (decomp.). Paramagnetic ^1H NMR ($CDCl_3$): δ = −17.3 (br. s, 6 H, dmso), −8.9 (br. s, 1 H, phen), 2.2 (br. s, 1 H, phen), 8.2 (br. s, 1 H, phen), 8.5 (br. s, 1 H, phen), 11.5 (br. s, 1 H, phen) ppm. Other phen peaks were too broad to be observed. MALDI-TOF MS: *m*/*z* = 497 [M − 2 Cl − dmso + (α-CHCA−H)]$^+$. IR: $\tilde{\nu}$ = 3055 (νC−H), 2923 (νC−H), 1429−1411 (δC−H), 1342−1309 (δC−H), 1106 (νS−O), 1094 (νS−O), 328 (νRu−Cl). $C_{14}H_{14}Cl_3N_2ORuS$ (465.5): calcd. C 36.1, H 3.0, N 6.0, S 6.9; found C 36.9, H 2.9, N 6.0, S 7.0.

***cis*,*cis*-[RuCl$_2$(dmso)$_2$(phen)] (2):** This complex was prepared analogous to the method described in ref.[16] from *cis*-[RuCl$_2$(dmso)$_4$] (0.20 g, 0.41 mmol) and phen (0.07 g, 0.4 mmol). Yield: 0.18 g, 86%; m.p. > 300 °C (decomp.). ^1H NMR ($CDCl_3$): δ = 2.44 (s, dmso), 3.12 (s, dmso), 3.59 (s, dmso), 3.62 (s, dmso), 7.76 (dd, 1 H, ArH^3 or ArH^8, ^3J = 5.1, ^3J = 8.1 Hz), 7.87 (dd, 1 H, ArH^3 or ArH^8, ^3J = 5.1, ^3J = 8.1 Hz), 7.92 (d, 1 H, ArH^5 or ArH^6, ^3J = 9.0 Hz), 7.98 (d, 1 H, ArH^5 or ArH^6, ^3J = 9.0 Hz), 8.37 (d, 1 H, ArH^4 or ArH^7, ^3J = 8.1 Hz), 8.47 (d, 1 H, ArH^4 or ArH^7, ^3J = 8.1 Hz), 9.98 (d, 1 H, ArH^2 or ArH^9, ^3J = 5.1 Hz), 10.07 (d, 1 H, ArH^2 or ArH^9, ^3J = 5.1 Hz) ppm. MALDI-TOF MS: *m*/*z* = 435 [M − 2Cl + (DHB−H)]$^+$. IR (cm^{-1}): $\tilde{\nu}$ = 3049 (νC−H), 2924 (νC−H), 1418 (δC−H), 1302 (δC−H), 1082 (νS−O), 930 (νS−O), 328 (νRu−Cl). $C_{16}H_{20}Cl_2N_2O_2RuS_2$·0.1toluene (517.3): calcd. C 38.7, H 4.0, N 5.4, S 12.4; found C 38.4, H 3.9, N 5.7, S 11.5.

Cyclic Voltammetry Experiments: The electrochemistry measurements were performed with an Autolab PGstat 10 potentiostat controlled by GPES4 software. A three-electrode system was used, consisting of a platinum (Pt) working electrode, a platinum (Pt) auxiliary electrode and an Ag/AgCl reference electrode. The experiments were carried out in acetonitrile at room temperature under argon with tetrabutylammonium hexafluorophosphate as electrolyte (0.1 M). Under these conditions the ferrocenium/ferrocene couple was located at +0.436 V with a peak separation of 0.099 V. All potentials are reported relative to Ag/AgCl. Linear voltammograms were obtained with a rotating (500 rpm) platinum disc as working electrode at a scan rate of 0.005 V s^{-1}.

Isomerization Experiments: Catalytic reactions were performed in a closed glass vessel under air. The reaction vessel was charged with ruthenium precursor (0.011 mmol), ligand as appropriate (0.011 mmol, see text) and substrate (5.8 mmol). In some experiments an Ag^I salt (silver tosylate and silver triflate gave identical results) was added in the required stoichiometric amount. After addition of the solvent mixture water/diglyme (1:3 mL) and internal standard (toluene, 0.3 mL), the vessel was closed and the mixture was stirred in a pre-heated oil bath at 130 °C for 6 h. After cooling to room temperature, the mixture was analyzed by GLC. Several time-dependent measurements were performed at 100 °C under argon by using standard Schlenk techniques (see Figure captions). In isoprene inhibition experiments the amount of isoprene [typically 1.0 mL (10 mmol)] was added prior to the addition of the substrate. All reported values for TONs and TOFs are the arithmetic means of two or more reproducible experiments. Experiments are considered reproducible when the deviation of the obtained results are less than 15% of the arithmetic mean.

Direct Conversion of 1,3-Butadiene to MEK: In a typical experiment, a high-pressure autoclave was filled with 0.09 mmol of **1** or **2** and 3.5 mmol of *p*-toluenesulfonic acid (for the acid-catalyzed hydration of 1,3-butadiene). After addition of 100 mL of diglyme/water (70/30) solvent mixture, the autoclave was closed and purged three times with dinitrogen. Next, 1,3-butadiene (10 mL) was added as a liquid using an ISCO high-pressure pump and the autoclave was heated to 145 °C. After 10 h, the autoclave was cooled to room temperature and the contents were analyzed with GLC.

X-ray Crystallographic Study of 1: Crystals of **1** suitable for X-ray analysis were obtained by slow concentration of a $CHCl_3$/toluene solution of **2** at room temperature. Pertinent data for **1**: $C_{14}H_{14}Cl_3N_2ORuS{\cdot}C_7H_8$, M_r = 557.90, red, block-shaped crystal (0.2 × 0.3 × 0.3 mm), triclinic, space group $P\bar{1}$ with a = 7.7503(10), b = 12.046(2), c = 12.872(3) Å, α = 73.972(10), β = 80.949(10), γ = 79.691(10)°, V = 1128.9(4) Å^3, Z = 2, D_c = 1.641 g cm^{-3}, μ(Mo-K_α) = 1.157 mm^{-1}. 20526 Reflections were measured (5133 independent, R_{int} = 0.0442, 1.6° < θ < 27.48°, T = 150 K, Mo-K_α radiation, graphite monochromator, λ = 0.71073 Å) with a Nonius Kappa CCD diffractometer with a rotating anode; no absorption correction was applied. The structure was solved by automated direct methods.[25] The structure displays relatively high residual density peaks in the area around Ru (peak height up to 2.7 e Å^{-3} at 0.78 Å from Ru). The peaks appear to be related to the heavy atoms positions (Ru, Cl and S) by a noncrystallographic twofold rotation, approximately parallel to the local twofold rotation axis of the phenanthroline ligand. The rotation images of some heavy atoms coincide with existing atom sites. Similar peaks were observed in data sets collected on two other crystals. There are no signs of twinning. Rough models, describing these peaks as the result of orientational disorder of the Ru complex, indicated a disorder fraction of approximately 3%. In view of the low occupation factor of the minor component, the disorder model was abandoned. Hydrogen atoms were introduced on calculated positions and included riding on their carrier atoms. Non-hydrogen atoms were described with anisotropic displacement parameters. The isotropic displacement parameters of the hydrogen atoms were coupled to the equivalent isotropic displacement parameters of their carrier atoms. Full-matrix least-squares refinement[26] of 265 parameters on F^2 resulted in a final $R1$ value of 0.0306 [for 4914 reflections with $I > \sigma(I)$], $wR2$ = 0.0729, GoF = 1.044. The final residual density was in the range of −1.09 to 2.66 e Å^{-3}. Geometric calculations and molecular graphics were performed with the PLATON package.[27] CCDC-176535 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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