ChemPubSoc Europe

DOI: 10.1002/chem.201403236

CHEMISTRY A European Journal Full Paper

Homogenous Catalysis

Alkene Isomerisation Catalysed by a Ruthenium PNN Pincer Complex**

Sébastien Perdriau,[a] Mu-Chieh Chang,[a] Edwin Otten,*[a] Hero J. Heeres,*[b] and Johannes G. de Vries*[a, c]

Abstract: The [Ru(CO)H(PNN)] pincer complex based on a dearomatised PNN ligand (PNN: 2-di-*tert*-butylphosphinomethyl-6-diethylaminomethylpyridine) was examined for its ability to isomerise alkenes. The isomerisation reaction proceeded under mild conditions after activation of the complex with alcohols. Variable-temperature (VT) NMR experiments to investigate the role of the alcohol in the mechanism lend credence to the hypothesis that the first step involves the formation of a rearomatised alkoxide complex. In this complex, the hemilabile diethylamino side-arm can dissociate, allowing alkene binding *cis* to the hydride, enabling insertion of the alkene into the metal–hydride bond, whereas in the parent complex only *trans* binding is possible. During this study, a new uncommon Ru^0 coordination complex was also characterised. The scope of the alkene isomerisation reaction was examined.

Introduction

Although isomerisation is often observed as an unwanted side reaction,[1–3] it is also put to good use, in particular in tandem reactions, such as isomerising hydroformylation, carbonylation or hydrocyanation. Examples include the Evonik/Oxeno isomerising hydroformylation of a mixture of butenes to *n*-pentanal,[4] and the Dupont process for the production of adiponitrile through isomerising hydrocyanation of 3-pentenenitrile.[5] High yields and selectivities have been obtained for catalysis involving alkene isomerisation in tandem with hydroformylation/reduction to alcohols,[6] methoxycarbonylation,[7] metathesis,[8] conjugate addition,[9] hydroboration,[10] cyclisation[11] and trialkylsilylation.[12] Other examples are the isomerisation of allyl benzenes such as estragol or safrole, which are of great interest for the fragrance industry.[13,14] A wide range of isomerisation catalysts have been developed based on various metals such as Pd,[15–17] Ru,[18–22] Ti,[23–25] V,[26] Fe,[27–29] Rh,[30–32] Mo,[33] Ni,[34–36] etc., but also metal-free systems such as frustrated Lewis pairs.[37] One of the most active catalysts is the ruthenium-based "alkene zipper" developed by Grotjahn and co-workers.[38,39]

Recently, researchers have focused on the selectivity of the alkene isomerisation. Beller and Grotjahn have developed catalysts which allow a selective one-position shift of the double bond with high selectivity for *E* isomers,[27,40] whereas other groups focused on the synthesis of the less thermodynamically favoured *Z* isomers.[41]

Two different mechanisms are generally believed to be operative for alkene isomerisation. The alkyl mechanism starts with an organometallic hydride species. Coordination of the alkene to the metal centre followed by insertion into the M–H bond gives two possible metal alkyl intermediates. β-H elimination will then generate either the same alkene or its double-bond shifted isomer. The π-allyl mechanism initiates with coordination of the double bond to a low-valent metal centre. A π-allyl complex is generated together with an M–H bond by oxidative addition of the C–H bond in the allylic position. A reductive elimination can take place in two directions and will provide either the olefin isomer or the starting olefin.[42]

Among the catalysts developed for this reaction, only a few belong to the family of the pincer complexes[43–47] and, to our surprise, the reactivity of PNN (PNN: 2-di-*tert*-butylphosphinomethyl-6-diethylaminomethylpyridine) ruthenium complexes with alkenes has not been explored. In particular, the pyridine-based PNN ruthenium pincer complexes are of great interest, due to the unique participation of the ligand in the reaction (non-innocent ligand).[48] This involves dearomatisation/aromatisation of the pyridine ring of the ligand without a change in

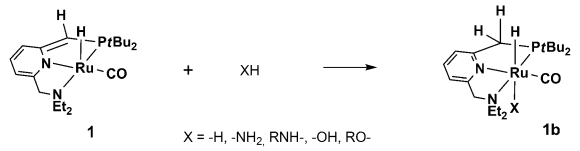
[a] S. Perdriau, M.-C. Chang, Dr. E. Otten, Prof. Dr. J. G. de Vries
Stratingh Institute for Chemistry
University of Groningen, Nijenborgh 4
9747 AG Groningen (The Netherlands)
Fax: (+31) 50-3634296
E-mail: edwin.otten@rug.nl

[b] Prof. Dr. H. J. Heeres
Department of Chemical Engineering
University of Groningen, Nijenborgh 4
9747 AG Groningen (The Netherlands)
E-mail: h.j.heeres@rug.nl

[c] Prof. Dr. J. G. de Vries
Leibniz Institut für Katalyse e.V.
An der Universität Rostock
Albert-Einstein-Strasse 29a
18059 Rostock (Germany)
E-mail: johannes.devries@Catalysis.de

[**] PNN = 2-*di*-tert-*butylphosphinomethyl-6-diethylaminomethylpyridine*

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201403236.



Scheme 1. Activation of the PNN ruthenium catalyst.

the metal oxidation state. This mechanism permits the facile activation of a variety of X–H bonds (Scheme 1).

With this unique feature, a wide range of catalytic reactions has been performed, such as dehydrogenative coupling of alcohols into esters or of amines and alcohols into amides, ester hydrogenation, etc.[49–52] The presence of a Ru–H bond in the PNN Ru complex **1** and the robustness of this class of compounds prompted us to explore its use as an olefin isomerisation catalyst, the results of which are presented here.

Results and Discussion

Preliminary results

Initial alkene isomerisation studies using complex **1** were performed with 1-octene in [D_6]benzene plus catalyst (2 mol%). Low activity was observed at room temperature (3% conversion after 16 h, entry 1, Table 1). Higher reaction temperatures (65 °C) improved the conversion somewhat to 22% after 8 h (entry 2). A higher catalyst loading did not improve the rate of the reaction and only 42% conversion was reached after 2.5 days. Also, the use of a more polar solvent ([D_8]THF) did not bring significant improvement either at room temperature or higher (entries 4 and 5). Similar results were obtained with estragol as substrate, even though a slightly better conversion (52%) was observed after an overnight reaction at room temperature (entry 7). Substantial progress was achieved with the addition of an equivalent of isopropanol to the substrate. An overnight reaction in [D_8]THF led to almost full conversion of both 1-octene and estragol even at room temperature (entries 6 and 8).

A GC/MS-FID (flame ionisation detector) analysis of the mixture from the reaction with 1-octene after 4.5 days in [D_8]THF indicates a good selectivity for 2-octene (77%), present as a *cis*/*trans* mixture (Figure 1). Other octene isomers were observed as well in smaller quantities (11% total for 3- and 4-octene). Octane (11%) was present in the mixture as the only side-product. Since this type of catalyst is known to dehydrogenate alcohols, we suggest that transfer hydrogenation from isopropanol is taking place as a side reaction during the process to yield the saturated product. We were intrigued by the dramatic influence of isopropanol on the isomerisation rate, and decided to study the interaction of **1** with isopropanol in more detail.

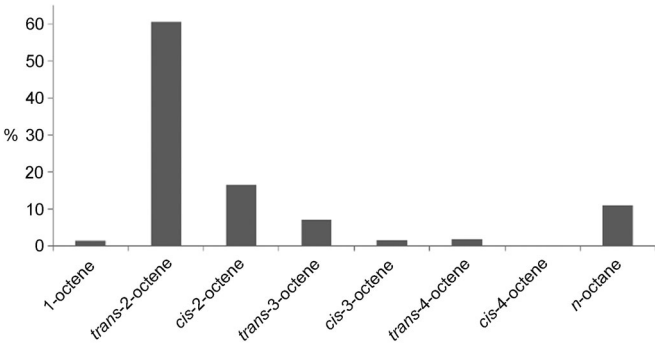


Figure 1. Isomeric composition of 1-octene isomerisation (Table 1, entry 6).

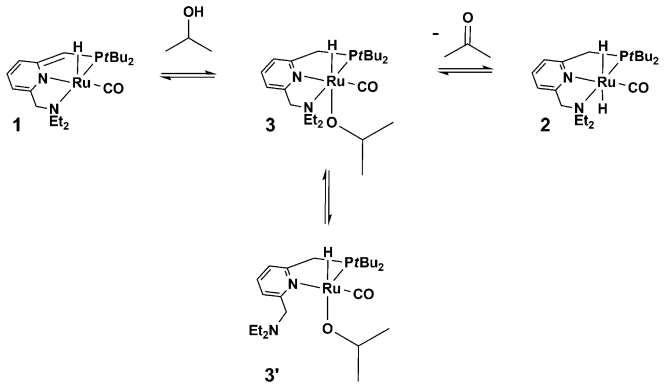
Table 1. Isomerisation reactions.

Entry	Substrate	Catalyst loading [mol%]	Solvent	Temp. [°C]	Time [h]	Conversion [%]
1	1-octene	2	C_6D_6	RT	16	3
2	"	"	"	65	4	17
					8	22
3	"	10	"	RT	2	traces of isomers
					60	42
4	"	"	[D_8]THF	RT	3	traces of isomers
					21	11
5	"	"	"	40	4	15
					21	27
6	"	"	[D_8]THF + 1equiv *i*PrOH[a]	RT	2	48
					19	93
					96	> 99
7	estragol	"	[D_8]THF	RT	3	15
					21	52
8	"	"	[D_8]THF + 1equiv *i*PrOH[a]	RT	2	61
					19	86

[a] *i*PrOH/substrate, 1/1 molar ratio.

The role of isopropanol: a VT-NMR study

The role of isopropanol was studied by performing variable-temperature NMR (VT-NMR) on complex **1** and isopropanol. A first series of NMR spectra of **1** were recorded in [D_8]toluene solution in the absence of isopropanol between 25 °C and −50 °C. In this temperature range, no significant change of the characteristic NMR resonances of **1** were observed, except for a broadening of all signals and a slight up-field shift of the signals corresponding to the CH_2 protons of the NEt_2 group. When one equivalent of isopropanol was added to this solution and an ^{1}H NMR spectrum was recorded at room temperature, a mixture of the starting material **1** (Ru–H, $\delta = -26.7$ ppm) and free isopropanol was observed together with a small amount of the known dihydride **2** (Scheme 2, $\delta = -4.4$ ppm) which stems from isopropanol dehydrogenation[49] (confirmed by the presence of acetone). By cooling down the reaction mixture, a new hydride appears (Ru–*H*, $\delta = -15.9$ ppm), which becomes the major complex below −50 °C (**3**, Figure 2A). NOESY NMR measurements at −70 °C (Figure 2B) show cross-peaks diagnostic for exchange between free isopropanol and the new ruthenium complex **3**, indicating



Scheme 2. Reactivity of the PNN ruthenium complex **1** with isopropanol.

that this species contains an isopropoxide group (CH, $\delta =$ 4.70 ppm; diastereotopic Me, $\delta = 1.95/1.75$ ppm), which has also been confirmed by COSY NMR measurement at $-70\,^{\circ}C$ (Figure 2C). Thus, the NMR data indicate the new species **3** to be the complex [Ru(CO)(H)(O*i*Pr)(PNN)], in which the ligand is rearomatised by proton transfer from isopropanol (Scheme 2). Compound **1** and related Ru complexes have been shown to react with X–H bonds (X = H, OH, NHR)[49,52] through metal–ligand cooperation. Reaction of **1** with isopropanol to form **3**, in which the NEt_2 group is presumably hemilabile, has been suggested by Milstein and co-workers to be a key step in the (catalytic) reactivity of **1**.[49] This has recently been confirmed by detailed DFT calculations, which shows that a complex similar to **3** but with a 2-methoxyethoxide rather than an isopropoxide ligand is only 2.3 kcal mol^{-1} uphill from **1** plus 2-methoxyethanol due to an unfavourable entropic contribution.[53] Compound **3** should be favoured at low temperature according to these calculations, in agreement with the experimental observations. Our data show that formation of **3** is reversible and warming the NMR tube to room temperature results in the quantitative regeneration of **1**. The limited temperature range in which **3** can be studied prevents a detailed characterisation of the fluxional behaviour of the NEt_2 arm. However, as indicated by ^1H NMR at $-30\,^{\circ}C$ (Figure 2A), **1** and **3** are present in a 1 to 1 ratio. A more detailed analysis of the NOESY NMR spectra at $-30\,^{\circ}C$ shows cross-peaks diagnostic for exchange between the two diastereotopic $N(CH_2CH_3)_2$ signals of **1** ($\delta =$ 0.65 and 0.80 ppm), while a single broad signal is observed in the case of **3** ($\delta = 0.96$ ppm). This suggests that indeed this arm is less strongly bound (hemilabile) in **3** (see the Supporting Information).

Equilibria similar to that between **1**/isopropanol and **3** have been demonstrated for N–H activation of amines by [RuH(CO)(PNP)] (PNP = 2,6-bis-(di-*tert*-butylphosphinomethyl)pyridine).[54] In this case, the observation at room temperature by NMR spectroscopy of the starting material with free amine, the coordination complex or the activation of the amine N–H bond was highly dependent on the electronic properties of the substrate. We thus decided to react compound **1** with one equivalent of the more acidic *o*-allyl phenol. Instant formation of a new species (**7**) with a hydride resonance at $\delta = -15.7$ ppm

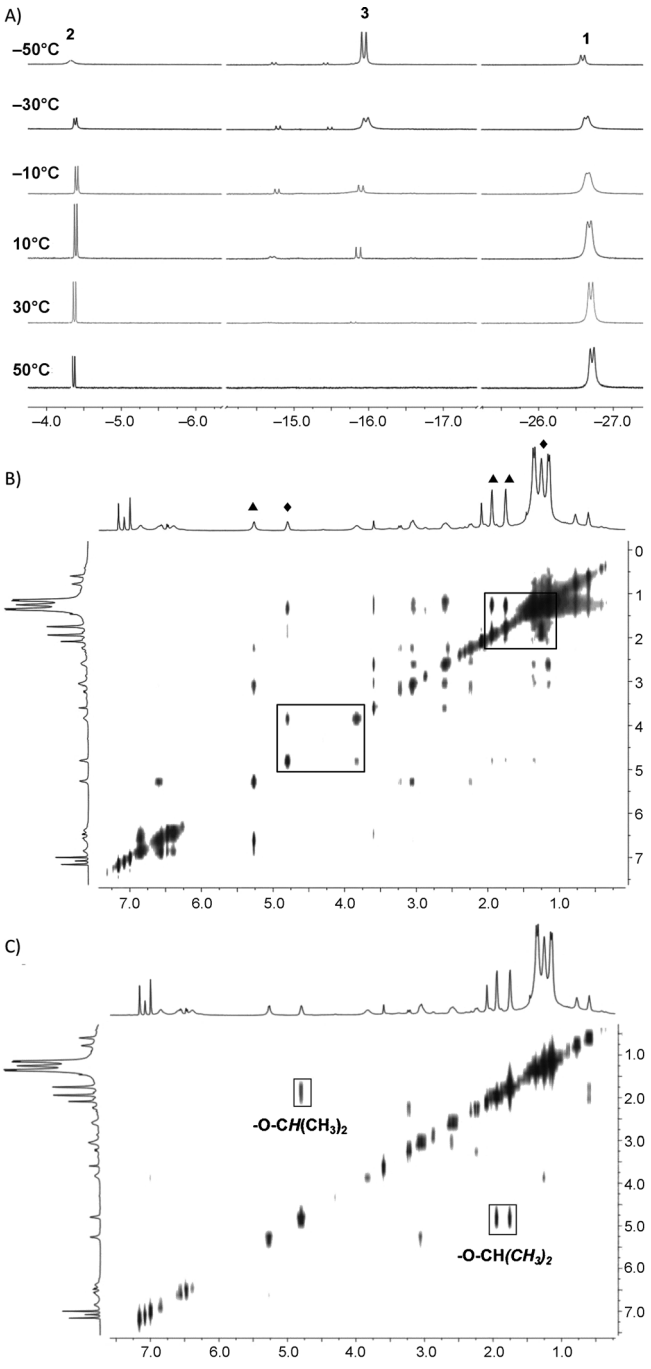
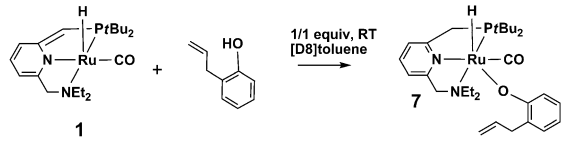


Figure 2. Reaction of PNN complex with *i*PrOH: A) VT-NMR spectrum of the hydride region; B) NOESY spectrum at $-70\,^{\circ}C$, ◆: *i*PrOH, ▲: Ru-O*i*Pr; C) COSY spectrum at $-70\,^{\circ}C$.

was observed similar to the isopropoxide complex **3** (Scheme 3). This product possesses an aromatic pyridine ring as well as diastereotopic $-P(tBu)_2$ and $-N(CH_2CH_3)_2$ groups, indicative of a C_1 symmetric compound. It also shows a single peak in the $^{31}P\{^1H\}$ NMR spectrum ($\delta = 114$ ppm). X-ray characterisation of **7** indicated the presence of a phenoxide ligand *trans* to the hydride (Figure 3).

Coordination of the $-NEt_2$ group rather than the olefin was observed in both solution and solid state. A comparison with



Scheme 3. Reactivity of the PNN ruthenium complex **1** with *o*-allylphenol.

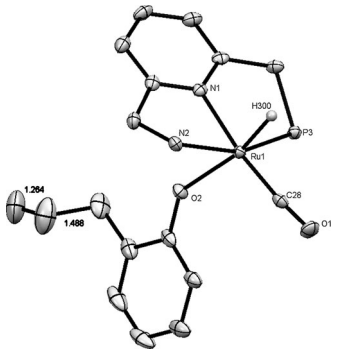
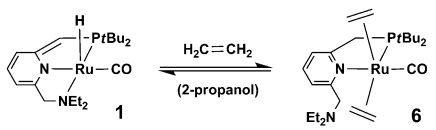


Figure 3. X-ray structure of complex **7**. Hydrogen atoms, $-NEt_2$ and $-PtBu_2$ groups have been omitted for clarity. Selected bond distances [Å]: Ru1–P3, 2.261; Ru1–N1, 2.108; Ru1–N2, 2.256; Ru1–H300, 1.523; Ru1–O2, 2.200; Ru1–C28, 1.821; C28–O1, 1.168.

the known hydroxide complex[50] shows only two main differences: a shorter Ru1–O2 bond length and an elongated Ru1–N2 in the case of the phenoxide.

A second NMR experiment with the PNN ruthenium complex **1** was performed in the presence of ethylene in an attempt to characterise alkene coordination complexes such as the putative intermediate **5**. For this purpose, equimolar amounts of isopropanol and **1** were mixed in [D_8]toluene together with ethylene (4 bar). However, NMR spectroscopy showed no evidence for the formation of the expected Ru^{II} complex with a coordinated olefin group. Instead, leaving the reaction mixture overnight at $-20\,^{\circ}C$ led to the quantitative formation of a new Ru species **6** (Scheme 4). The $^{31}P\{^1H\}$ NMR spectrum shows a single peak at $\delta = 75.8$ ppm. The ligand backbone was confirmed to be aromatic with equivalent alkyl groups for both the $-N(CH_2CH_3)_2$ and $-P(tBu)_2$ side arms, which suggests that **6** possesses C_s symmetry. Surprisingly, no hydride resonance could be located, and the ^1H NMR spectrum shows new signals attributed to coordinated ethylene, the integration of which corresponds to two ethylene molecules per pincer ligand. These resonances are shifted upfield from free ethylene ($\delta = 3.10$, 2.87 and 1.50 ppm) and appear in a 1:2:1 ratio. A HSQC NMR experiment indicated the signal at $\delta =$ 2.87 ppm to correlate with two different carbon atoms ($\delta = 41$ and 44 ppm), proving that all hydrogens of the coordinated ethylene are inequivalent (Supporting Information). Based on this, we formulate **6** as the 18e organometallic compound [Ru(C_2H_4)$_2$(CO)(PNN)], in which the ruthenium metal centre is in the zero oxidation state, two ethylene molecules are coordinated *trans* to each other, and the diethylamino arm is off the metal centre.



Scheme 4. Proposed $CH_2{=}CH_2$ adduct complex of **1**.

Although not very common, ruthenium(0) PNP pincer complexes have already been synthesised[55] and were suggested to be intermediates in a water splitting reaction with the catalyst used in the present study.[50]

The stability of complex **6** was tested by warming the NMR tube to room temperature. This resulted in the regeneration of the starting material **1** even though the process seems slow. The position of the equilibrium reaction (Scheme 4) is highly dependent on the ethylene pressure. Whereas no quantitative reaction was obtained with only 1 bar of ethylene, removal of pressure leads to a full reversible formation of the starting catalyst **1**.

When the reaction of the PNN ruthenium complex **1** with ethylene was performed in the absence of isopropanol, the catalyst remained mostly unchanged. Only traces of **6** were observed, which underlines the important role of isopropanol for the reactivity with alkenes. The formation pathway of **6** without isopropanol is still unclear. It is possible that ethylene plays the role of a hydride transfer agent. Another explanation would be a simple rearrangement of **1**, as has recently been observed with bispyridine PNN ruthenium complexes.[56]

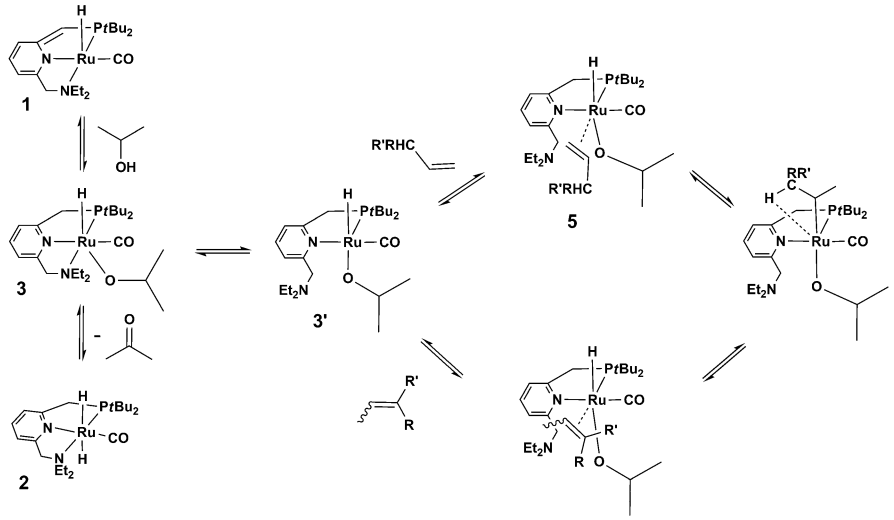
Based on literature precedents and the NMR studies reported here, we propose a mechanism for 1-octene isomerisation with compound **1**, as shown in Scheme 5. It involves the initial activation of isopropanol, allowing the formation of a vacant coordination site *cis* to the hydride. After coordination of the alkene, the isomerisation proceeds via the formation of a ruthenium-alkyl complex.

Isomerisation of 1-octene followed over time

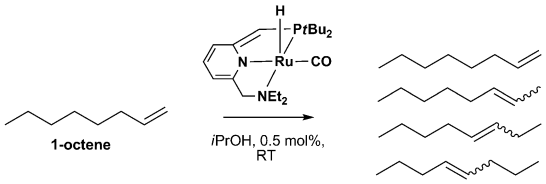
The composition of the 1-octene isomerisation reaction mixture was followed over time to gain insight in the relative rates of the reactions (Scheme 6). The reaction was performed in isopropanol at room temperature with a catalyst loading of 0.5 mol%. Samples taken at different time intervals were analysed by GC/MS-FID after calibration of the different octene isomers and using cyclooctane as external standard. The results are presented in Figure 4.

We observe that 98% of 1-octene is already converted after 5 h. At this point in time 2-octene is the main product of the reaction, reaching almost 88%. 3-Octene is slowly emerging, whereas only traces of 4-octene are detected. Samples taken after one, two and 21 days of reaction show that the composition is slowly approaching the calculated equilibrium composition.

A comparison between the calculated[30] and the experimental isomeric octene distribution reveals that after 21 days the thermodynamic equilibrium is indeed approached, although not fully reached (Table 2). This might be due to catalyst deac-



Scheme 5. Proposed mechanism for octene isomerisation catalysed by **1** in the presence of isopropanol.



Scheme 6. Isomerisation of 1-octene catalysed by **1** in the presence of isopropanol.

tivation but possibly also to kinetic effects due to the large reactivity differences between the terminal and internal alkenes. The isomerisation reaction from a terminal alkene to a 2-alkene is in general much faster than the isomerisation of an internal alkene which is in accordance with the results obtained. It is also not very surprising that the internal alkenes are mostly present in their *trans* form, this being the thermodynamically more stable isomer. Finally, formation of octane was also observed under these conditions. However, the formation of this side product stayed below 10%, even after two days.

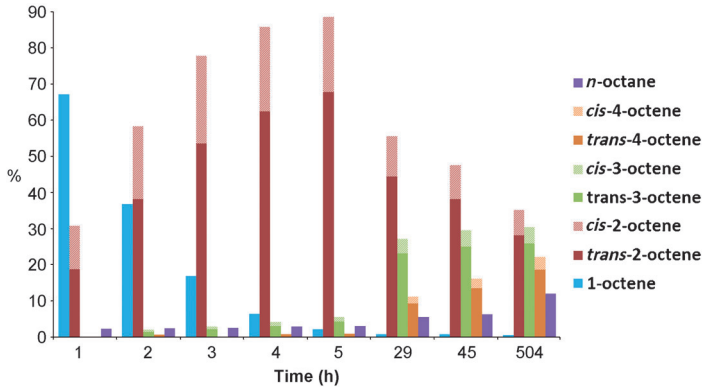


Figure 4. Isomerisation of 1-octene catalysed by **1** followed over time.

Catalyst loading

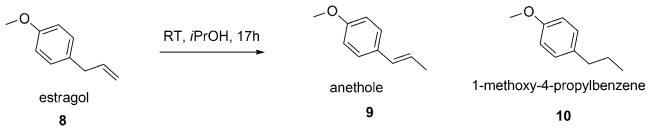
A study of the influence of the catalyst loading on the selectivity of the reaction was performed using estragol. The latter was chosen instead of 1-octene as it simplifies the analyses considerably, because only two isomerisation products are formed (*cis*- and *trans*-anethole), along with the saturated side product **10**, 1-methoxy-4-propylbenzene (see Scheme 7 and Figure 5).

Comparing the results after 17 h, we find that although the amount of product increases at higher catalyst loading, the same is true for the formation of the saturated side product **10**. Thus, a maximum yield of anethole is reached with 5 mol% catalyst loading.

Table 2. Calculated versus experimental product distribution.[a]

Octene isomers	$\Delta_r H^\circ$	$\Delta\Delta_r H^\circ$	Calc. [%]	Exptl. [%] (excl. octane) 45 h	504 h
1-octene	−125	10	0.5	0.8 (0.8)	0.6 (0.6)
trans-2-octene	−115.5	0.5	24.6	38.1 (40.6)	28.0 (31.8)
cis-2-octene	−119.4	4.4	5.1	9.4 (10.1)	7.1 (8.0)
trans-3-octene	−115.8	0.8	21.8	25.0 (26.7)	25.8 (29.3)
cis-3-octene	−117.8	2.8	9.7	4.5 (4.8)	4.5 (5.1)
trans-4-octene	−115	0	30.1	13.4 (14.3)	18.5 (21.0)
cis-4-octene	−118.2	3.2	8.3	2.6 (2.8)	3.6 (4.0)
octane	–	–	–	6.3	11.9

[a] $\Delta_r H^\circ$ = hydrogenation enthalpies [kJ mol^{-1}]; $\Delta\Delta_r H^\circ$ = relative formation enthalpies [kJ mol^{-1}]; Calc. [%] = $\exp(-\Delta\Delta_r H^\circ/RT)/[\Sigma(\exp(-\Delta\Delta_r H^\circ/RT))]$*100.



Scheme 7. Estragol isomerisation.

Alcohol screening

Although the addition of isopropanol clearly increases the rate of the reaction, it also leads to the formation of saturated product through transfer hydrogenation (Figure 1). For this reason we tested the use of other alcohols (ethanol, *t*-amylalcohol) for 1-octene isomerisation. With ethanol, the reaction performs well with a 1-octene conversion of 83% (Figure 6) after 15 h, which is about 15% lower than in isopropanol. Ethanol is also capable of transfer hy-

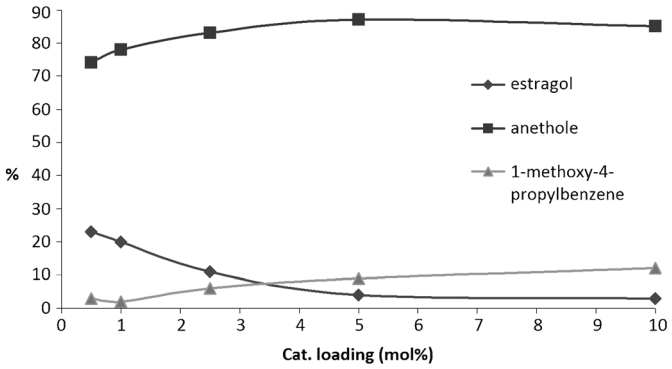


Figure 5. Estragol isomerisation as a function of catalyst loading (◆ estragol, ■ anethole, ▲ 1-methoxy-4-propylbenzene) after 17 h.

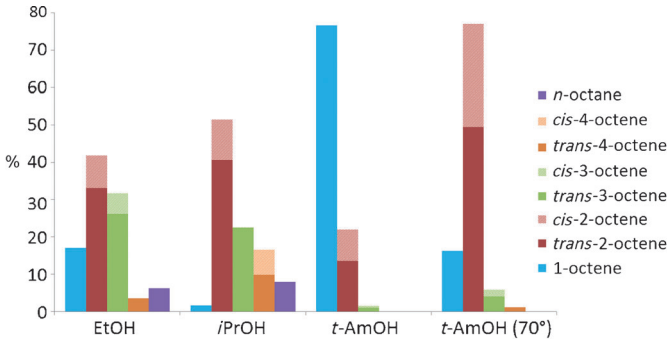


Figure 6. Alcohol effect on octene isomerisation.

drogenation and octane is observed in amounts up to 6%. The isomeric composition of the reaction mixtures in EtOH and *i*PrOH are comparable after an overnight reaction, though less 4-octene is obtained with ethanol. This suggests that not only the 1-octene to 2-octene isomerisation but also the subsequent 2-octene to 3- and 4-octene in ethanol are slower than in isopropanol.

It is clear that the undesired transfer hydrogenation reaction to saturated alkanes is directly linked to the presence of a hydrogen atom on the carbon in the alpha position of the alcohol. Thus, the use of a tertiary alcohol should solve this issue. With this in mind, a reaction was performed using *tert*-amyl alcohol as solvent. A reaction at room temperature for a 16 h reaction time resulted in very low conversion (23%) with essentially only 2-octene as product. At higher temperatures (70 °C), 84% conversion was obtained. In addition, no octane was detected, which confirmed our hypothesis. Furthermore, the selectivity for 2-octene was high, which indicates that the C=C internal bonds are not prone to isomerisation in the presence of a tertiary alcohol. The higher temperature needed with *tert*-amyl alcohol may be caused by steric factors that influence alkene coordination, particularly when the double bond is internal. This is supported by the very small amount of 3 and 4-octene isomers found, even at 70 °C.

Substrate scope and limitations

The scope of the isomerisation reaction was determined by testing a number of substrates (Table 3). All reactions were performed in isopropanol as this resulted in the highest rates (vide supra). Product compositions were determined by GC and, in addition, isolated yields are reported as well. Reactions with vinyl cyclohexane (entry 1 a–d) showed that the isomerisation of a terminal double bond to an internal tri-substituted double bond is possible with **1** even at room temperature with reasonable conversion. C=C double-bond isomerisation into the ring was not observed. Saturated side product accounted for 16% in the product composition. Although increasing the temperature is beneficial for the conversion, it also decreases the selectivity. Performing the reaction neat with only 1.2 mol/mol of isopropanol led to a lower conversion with an increased amount of saturated ethyl cyclohexane. It is likely that all the alcohol has been consumed in the transfer hydrogenation reaction.

4-Methyl-1-pentene was converted selectively into 4-methyl-2-pentene (Table 3, entry 2). None of the other isomers or the saturated product were detected.

No isomerisation of citronellene (Table 3, entries 3 a, b) occurred at room temperature. Although reactivity was observed at 50 °C, large amounts of saturated product were also formed. This issue could be solved by using *tert*-amyl alcohol. Full isomerisation of the terminal double bond was observed whereas the internal double bond was not reactive under the conditions employed. The small percentage of saturated compound found can be explained by secondary alcohol impurities present in the *tert*-amyl alcohol.

Surprisingly high temperatures were required to convert 1,7-octadiene (Table 3, entries 4 a, b). The main products were 1,6 and 2,6-octadiene with very little octene and no saturated octane detected.

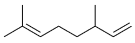
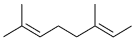
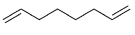
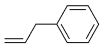
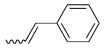
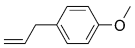
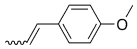
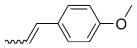
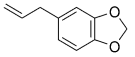
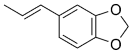
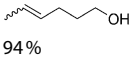
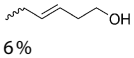
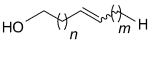
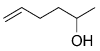
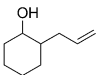
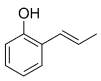
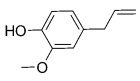
Isomerisation of 1,5-cyclooctadiene (COD) (Table 3, entries 5 a, b), proceeded sluggishly, yielding mainly 1,4-COD at room temperature, whereas cyclooctene was the major product when the reaction was performed at 70 °C.

Allyl benzene as well as alkyloxy substituted estragol and safrole (Table 3, entries 6–8 b) were easily isomerised at room temperature with good selectivities. The thermodynamically most stable *trans* isomer was always obtained as the main product.

Whereas diethylallylamine was not reactive at room temperature in isopropanol, or neat at 70 °C, full conversion was observed at 70 °C in the presence of a few equivalents of isopropanol (Table 3, entry 9). This again illustrates the important role of isopropanol.

The isomerisation of unsaturated linear alcohols using **1** was also tested. Interestingly, the reaction of 5-hexen-1-ol resulted in a highly selective isomerisation to 4-hexene-1-ol (94%) (Table 3, entry 10). Knowing that the alcohol function in these substrates can also be activated by the catalyst, both coordination of the -OH group and the double bond may take place. A similar type of coordination complex has already been observed by Bäckvall and co-workers.[57] The stability of this possible intermediate may be influenced by the chain length, thus restricting the extent of the isomerisation. The fact that isomerisation of 9-decen-1-ol leads to a mixture of isomers seems to prove this hypothesis (Table 3, entry 11).

Table 3. Substrate scope.

Entry	Substrate	Conditions	Solvent	Product composition[a]		Conv. [%]	Isolated yield[b] [%]
1a		RT	*i*PrOH		84% (16%)	61	–
b		50 °C	*i*PrOH		70% (30%)	87	68
c		70 °C, 6 h 1.2 equiv *i*PrOH/cat.	neat		77% (23%)	22	–
2		RT	[D_8]-*i*PrOD		>99%	100	91
3a		RT	*i*PrOH		–	0	–
b		50 °C	*i*PrOH		45% (55%)	49	94
c		70 °C	*t*-AmOH		95% (5%)	100	–
4a		RT	*i*PrOH	isomers		7	–
b		70 °C	*i*PrOH	isomers 94%+octene 6%		77	63
5a		RT	*i*PrOH	 29%	 71%	17	–
b		70 °C	*i*PrOH	33%	2% (65%)[c]	79	71
6		RT	*i*PrOH		98% (*E*/*Z*:90/10) (2%)	80	70
7a		RT	*i*PrOH		92% (*E*/*Z*:87/13) (8%)	77	85
b		70 °C	*t*-AmOH		100% (*E*/*Z*:98/2)	100	91
8a		RT	*i*PrOH		88% (2%)	57	76
b		70 °C	*t*-AmOH		99% (1%)	100	87
9a		RT	*i*PrOH		–	0	–
b		70 °C, 2.5 equiv *i*PrOH/cat.	neat		>99%[d]	100	91
c		70 °C	neat		–	0	–
10		RT	*i*PrOH	 94%	 6%	97	83
11		RT	*i*PrOH	 *n*+*m*=7		100	79
12a		RT	*i*PrOH		100%	88	34
b		70 °C	*t*-AmOH		–	0	–
13a		RT	*i*PrOH		100%	>99	89
b		70 °C	*t*-AmOH		–	0	–
14a		RT	*i*PrOH		–	0	–
b		130 °C	[D_8]toluene		100%	100	75
15a		RT	*i*PrOH		–	0	–
b		50 °C	*i*PrOH		–	0	–

[a] Number in parentheses indicates the saturated product from hydrogenation; [b] Isolated product consists of a mixture of the different products and starting material; [c] Cyclooctene; [d] Traces of saturated product are observed in GC-MS/FID.

When unsaturated ketones were subjected to the isomerisation reaction, full conversion of the starting material was obtained (Table 3, entries 12–13). However, the product was not the expected C=C double-bond isomer but rather the unsaturated alcohol, resulting from transfer hydrogenation of the ketone function. Moreover, and to our surprise, no isomerisation of the double bond was detected. When *tert*-amyl alcohol was used in an attempt to avoid transfer hydrogenation, no conversion at all was obtained with full recovery of the starting material. The chain length between the alcohol function and the double bond is the same as in the product of the 5-hexen-1-ol isomerisation, which strengthens the hypothesis of the formation of the stable intermediate where both the alcohol and alkene may be coordinated to the metal centre.

Finally, room temperature isomerisation of allyl phenols (Table 3, entries 14a–15b) was performed and shown to be unsuccessful. As in the case of *o*-allyl phenol (vide supra), a stable alkoxide complex may be formed. However, isomerisation activity was observed when performing a stoichiometric reaction of the catalyst with these phenolic substrates. After one day, 50% conversion into the conjugated isomer was observed and this was close to full conversion after two days. After the addition of a second equivalent of phenol, the isomerisation process proceeds and is complete after 3.5 days at room temperature. Thus, although isomerisation seems possible in the presence of phenols, the reaction rates are very low. This was further supported by the isomerisation of *o*-allyl phenol at 130 °C in toluene. After 16 h, full conversion to 2-(prop-1-en-1-yl)-phenol was observed.

Conclusion

The [Ru(CO)H(PNN)] catalyst developed by Milstein was examined for its ability to isomerise alkenes. Isomerisation was found to be slow but could be accelerated by alcohols, in particular, using isopropanol as an additive. Transfer hydrogenation also occurs to some extent upon the use of this alcohol. This side reaction could be suppressed by the use of tertiary alcohols such as *tert*-amylalcohol, but at the cost of catalyst activity. VT NMR experiments and a model reaction with ethene lend credence to the hypothesis that reaction with isopropanol leads to formation of a [Ru(CO)H(OR)(PNN)] complex by metal/ligand cooperation. In this complex the diethylamino sidearm can dissociate, allowing binding of the alkene in the *cis* position relative to the hydride, followed by insertion of the alkene. In the parent complex, the alkene can only bind *trans* to the hydride, which explains why the isomerisation reaction is slow in the absence of alcohols. A new bis ethylene adduct Ru^0 complex was discovered during the VT-NMR study. A range of substrates was examined, allowing determination of the scope and limitations of the synthetic methodology. Whereas a single shift of a terminal to a linear 2-alkene proceeds smoothly at room temperature, isomerisation of a terminal alkene to a tri-substituted internal alkene requires a higher temperature, leading to lower selectivity. Isomerisation of internal alkenes is much slower and tri-substituted internal alkenes do not react at all. Functional groups like alcohols, ethers, phenyl groups or di-alkyl amines do not influence the isomerisation, whereas with phenols stable complex formation reduces the catalyst activity.

When comparing this catalyst system with other published catalysts we see that most other catalysts operate at higher temperatures, usually around 70 °C. We have achieved alkene isomerisation at room temperature, which is rare. Also, the catalyst is selective enough to allow the isomerisation reaction to stop at the first internal alkene with good selectivity, which most catalysts cannot do at higher temperatures.

Experimental Section

Typical isomerisation reaction

All reactions were carried out under a protective nitrogen atmosphere using a glove box and Schlenk techniques.

A vial (4 mL) was loaded with a solution of the catalyst (0.044 mmol) in isopropanol (2 mL) and cyclooctane (20 μL) was added as internal standard followed by the substrate (1.8 mmol). The vial was sealed with a screw cap and septum after addition of a stir bar and the reaction mixture was stirred at room temperature for 16 h. Conversion was determined using GC-MS/FID. The reaction was quenched by exposure to air. The product was isolated after evaporation of isopropanol and passing the residue over a short silica column with gradient elution from pentane to 1:5 AcOEt/pentane. The product obtained was further analysed by NMR techniques.

VT-NMR experiments

In an oven-dried Young's NMR tube, a solution of **1** (0.022 mmol) was dissolved in [D_8]toluene and isopropanol (1 equiv) was added. The reaction mixture was degassed using three freeze–pump–thaw cycles. The required amount of ethylene to reach 1 or 4 bars ethylene in the NMR Young's tube was collected in a calibrated gas bulb. The tube was plunged into liquid nitrogen and the ethylene was further condensed into it. The tube was then carefully sealed and slowly warmed up to room temperature. The desired temperature was reached stepwise. The tube was arbitrarily left for 10–15 min. for establishment of equilibrium before NMR experiments were recorded.

CCDC-999441 (**7**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The authors thank the Smart Mix Program of the Dutch Ministry of Economic Affairs and the Dutch Ministry of Education, Culture and Science, Royal DSM NV, Merck & Co and Avantium for funding of this work within the framework of the CatchBio Program. Paul Alsters, Lavinia Panella and Bernard Kaptein (all DSM) are thanked for stimulating discussions. We thank Pieter van der Meulen for helping to set-up the VT-NMR experiments.

Keywords: alkene · isomerisation · alcohols · pincer complex · ruthenium

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Received: April 24, 2014
Published online on September 26, 2014