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Two reactions of allylic alcohols catalysed by ruthenium cyclopentadienyl complexes with didentate phosphine ligands: isomerisation and ether formation

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Abstract

The activity of chloro(η^5-cyclopentadienyl)(didentate phosphine)ruthenium(II) complexes in the catalysis of two types of reaction with allylic alcohols is described. The isomerisation of 3-buten-2-ol to butanone (MEK) and allyl alcohol to propanal proceeds at high rates. A trend in catalytic activity is observed upon variation of the carbon-chain length in the didentate phosphine ligand: dppm < dppe < dppp < dppb. Complexes with rigid didentate phosphine ligands like *cis*-dppv and dppph show no activity. The second type of reaction constitutes the first example of a ruthenium-catalysed ether formation directly from allylic alcohols. Homo-coupled ethers like di-allyl ether (DAE) are easily formed as well as ethers from heterocoupling of allyl alcohol with aromatic and aliphatic alcohols. In fact, the ruthenium complexes achieve much higher turnover frequencies and turnover numbers than reported before in palladium-catalysed ether formation. Complexes with dppe and dppp in the presence of a conjugated diene switch from isomerisation to ether formation, but the new complex [RuClCp(*o*-MeO-dppe)] (Cp = η^5-cyclopentadienyl) (**3**) has proven to be very active in ether formation, even in the absence of a diene. The mechanisms of the reactions have been studied by using both deuterium-labelled substrates and ^{31}P nuclear magnetic resonance (NMR).

Keywords: Ruthenium; Phosphine ligands; Isomerisation; Ether formation; Allylic alcohols

1. Introduction

Conjugated dienes form interesting starting materials for a whole range of products [1–4]. For example, hydration produces allylic alcohols, which may serve as intermediates in ketone and aldehyde synthesis. The isomerisation of allylic alcohols to aldehydes and ketones has been investigated extensively and many transition metal complexes are capable of catalysing the isomerisation reaction [5–9]. Thus far, only one system has proven to be able to catalyse the conversion of butadiene to butanone in a one-pot synthesis [10]. This catalytic system consists of a strong Brønsted acid, a ruthenium(III) salt and 2,2′-bipyridine or 1,10-phenanthroline. One of

Abbreviations: dppm, bis(diphenylphosphino)methane; dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane; dppb, 1,4-bis(diphenylphosphino)butane; dppph, 1,2-bis(diphenylphosphino)benzene; *cis*-dppv, *cis*-1,2-bis(diphenylphosphino)ethene; *o*-MeO-dppe, 1,2-bis(di(*ortho*-methoxyphenyl)phosphino)ethane; dcpe, 1,2-bis(dicyclohexylphosphino)ethane

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the key features of this system is that it can selectively catalyse the isomerisation of allylic alcohols to ketones *in the presence of* alkenes and conjugated dienes, which usually are strong poisons in isomerisation catalysis.

Chloro-(η^5-cyclopentadienyl)bis(triphenylphosphine)ruthenium(II) (**1**) was reported by Trost and Kulawiec [11,12] to isomerise allylic alcohols to ketones and aldehydes without isomerising a simple isolated alkene moiety in the same molecule. This selective isomerisation prompted us to investigate the isomerisation of 3-buten-2-ol to butanone (MEK) catalysed by **1** and analogous complexes with didentate phosphine ligands in the presence or absence of a conjugated diene. Although most complexes showed a very high activity towards isomerisation, in the presence of a conjugated diene, no isomerisation was observed at all. However, some complexes showed an unexpected, but highly interesting activity. The presence of a diene worked as a switch: isomerisation was switched off and ethers were formed instead.

Allylation of nucleophiles is a versatile reaction in organic chemistry to form new carbon–carbon or carbon–heteroatom bonds [13–16], e.g. in the protection of alcohols. Allylic alcohols are usually much cheaper than allylic acetates and allylic halides and in fact most other allyl sources are synthesised from them [17]. Efficient ether formation with allyl alcohol could lead to a halogen-free route to epoxy resins. But, despite increasing interest in the use of allylic alcohols as an 'allyl feed stock'[17–22], catalysed ether formation from allyl alcohol sources remains largely unsuccessful. By far, most reports use a palladium salt as catalyst and have only moderate to low turnover numbers (varying from 20 up to 300). Ruthenium has, to the best of our knowledge, only once successfully been employed to form allylic ethers with glycols from homo-allylic alcohols [23,24].

In this report, it is shown that several ruthenium cyclopentadienyl complexes with didentate phosphine ligands have the possibility of catalysing two reactions of allylic alcohols: isomerisation to form carbonyl compounds, or the formation of allyl ethers with other alcohols. Both a study with deuterated substrates and a ^{31}P nuclear magnetic resonance (NMR) study were used to get more insight in the reaction mechanisms of these two interesting reactions.

2. Experimental

2.1. General

Substrate alcohols, silver *para*-toluenesulfonate (AgOTs), isoprene, phosphines and other reagents were commercially available and used without further purification. Solvents were reagent grade and used as received except for THF, which was distilled over CaH_2 prior to use. 1,2-Bis(di(*ortho*-methoxyphenyl)phosphino)ethane (*o*-MeO-dppe) was kindly supplied by Shell International Chemicals

Both (**1**) [25] and chloro-(1,2-bis(diphenylphosphino)-ethane)(η^5-indenyl)-ruthenium(II) [26] were prepared according to literature procedures. The other chloro-(η^5-cyclopentadienyl)-(didentate phosphine)-ruthenium(II) complexes were prepared from **1** analogous to a published procedure for a substituted dppe complex [27], except for the dcpe complex, which was prepared by a modified procedure [28]. 3-Buten-2-ol-2-*d* was prepared by reduction of methyl vinyl ketone with lithium aluminium deuteride [29].

All syntheses and catalytic reactions were performed in an argon atmosphere using standard Schlenk techniques. Reactions at elevated temperatures and pressures were performed in a 100 ml Hastelloy C22 Premex HPM-T high-pressure autoclave.

Quantitative gas liquid chromatography analyses were carried out on a Chrompack apparatus equipped with a CP Sil 5-CB column (50 m × 0.4 μm) with toluene or anisole as internal standard. Melting points (m.p.) were measured on a Büchi apparatus and are uncorrected. ^{1}H NMR spectra (199.5 MHz) and ^{13}C NMR (49.88

MHz) were performed on a Jeol JNM 200 FT-NMR spectrometer. Proton chemical shifts (δ) are reported in parts per million relative to Me4Si ($\delta = 0$). Carbon chemical shifts (δ) are reported in parts per million referenced to internal solvent carbon atoms. $^{31}P\{^1H\}$ NMR spectra (121.5 MHz) were recorded on a Bruker DPX 300 spectrometer. Chemical shifts (δ) are reported in parts per million relative to external 85% aqueous H_3PO_4 ($\delta = 0$). ^2H NMR spectra (46.07 MHz) were recorded on a Bruker DPX 300 spectrometer. Chemical shifts (δ) are reported in parts per million referenced to internal residual solvent deuterons. Mass spectra were recorded on a Finnigan MAT TSQ-70 equipped with a custom made electrospray interface (ESI).

2.2. Synthesis of chloro(η^5-cyclopentadienyl)(o-MeO-dppe)ruthenium(II) (3)

In a two-neck flask equipped with a reflux condenser, chloro-(η^5-cyclopentadienyl)-bis-(triphenylphosphine)-ruthenium(II) (0.18 g, 0.25 mmol) and *o*-MeO-dppe (0.15 g, 0.29 mmol) were dissolved in toluene (20 ml). After 8 h heating to reflux, the resulting orange-brown solution was concentrated to about 1 ml on a rotary evaporator. Precipitation with hexane afforded 0.14 g of a yellow powder (78%). Mass (ESI): m/z 685 ([M−Cl] +). m.p. 200–202°C (dec.). $^{31}P\{^1H\}$ NMR (acetone-d_6) 70.3 ppm.

2.3. Synthesis of allyl-1,1-d_2 alcohol

Allyl-1,1-d_2 alcohol was prepared in a three-step synthesis from acrylic acid analogous to published procedures that start with ethyl acrylate [5,30,31]. Protection of the double bond by a Diels–Alder reaction with anthracene was necessary to prevent extensive polymerisation.

2.3.1. 9,10-Dihydro-9,10-ethano-anthracene-11-carboxylic acid

An autoclave was charged with anthracene (8.94 g, 50.2 mmol) and acrylic acid (5.4 g, 74.9 mmol) dissolved in *p*-xylene (50 ml). The mixture was stirred at 180°C for 24 h and then cooled to room temperature. The resulting white solid was collected by filtration and washed with pentane. A second crop of product was obtained by reducing the volume of the filtrate to about one third. The combined products were dried at reduced pressure to yield 8.1 g (65% based on anthracene). Mass (ESI): 249 ([M–H]–). m.p. 183°C (lit. [30] 187°C). ^1H NMR ($CDCl_3$) 11.0 (br s, 1H, COOH), 7.32–7.22 (m, 4H, ArH), 7.14–7.06 (m, 4H, ArH), 4.66 (d, 1H, ArCHCHCOOH), 4.33 (t, 1H, $ArCHCH_2$), 2.92 (m, 1H, $CH_2CHCOOH$), 2.05 (m, 2H, $CHCH_2CHCOOH$).

2.3.2. 9,10-Dihydroxy-9,10-ethano-11-(hydroxymethyl-d_2)anthracene

To a stirred suspension of lithium aluminium deuteride (0.51 g, 12.1 mmol) in THF (60 ml), 9,10-dihydro-9,10-ethano-anthracene-11-carboxylic acid (3.0 g, 12.0 mmol) was slowly added as a solid. After complete addition, the mixture was heated to reflux for 24 h. The resulting mixture was evaporated to dryness and then taken up in diethyl ether (20 ml). The ether solution was quenched with water (5 ml) and then separated. The ether layer was dried with $MgSO_4$, followed by evaporation on a rotary evaporator. A white solid (2.5 g, 88%) resulted. Residual proton content at the methanol carbon was less than 2% as measured by ^1H NMR. m.p. 108°C (lit. [30] 110°C). ^1H NMR ($CDCl_3$) 7.31–7.22 (m, 4H, ArH), 7.12–7.07 (m, 4H, ArH), 4.43 (d, 1H, $J = 2.6$ Hz, $ArCHCHCD_2OH$), 4.28 (t, 1H, $J = 2.6$ Hz, $ArCHCH_2$), 2.14 (br m, 1H, $CHCHCD_2OH$), 1.92 (dt, 1H, $J = 2.6$ Hz, $J = 12.0$ Hz, $CHHCHCD_2OH$), 1.10 (br s, 1H, OH), 1.08 (dm, 1H, $CHHCHCD_2OH$).

2.3.3. Allyl-1,1-d_2 alcohol

A round-bottom one-neck flask was connected to a round-bottom two-neck flask by a U-shaped tube. The two-neck flask was connected to the Schlenk line. 9,10-Dihydroxy-9,10-ethano-11-(hydroxymethyl-d_2)anthracene

(2.5 g, 10.5 mmol) was heated in the one-neck flask to 300–400°C while the two-neck flask was simultaneously cooled in liquid nitrogen. When no more product distilled over, the two-neck flask was warmed to room temperature and the product was obtained as a colourless liquid (0.5 g, 79%). ^{1}H NMR ($CDCl_3$) 5.93 (dd, 1H, $J = 10.3$ Hz, $J = 17.7$ Hz, $CH_2{=}CH$), 5.21 (dd, 1H, $J = 1.7$ Hz, $J = 17.7$ Hz, $CHH{=}CH$), 5.08 (dd, 1H, $J = 1.7$ Hz, $J = 10.3$ Hz, $CHH{=}CH$), 3.12 (s, 1H, OH). ^{2}H NMR ($CDCl_3$) 4.0 (s). ^{13}C NMR ($CDCl_3$) 137.1 (s, $CH_2{=}CH$), 115.0 (s, $CH_2{=}CH$), 62.8 (quin, CD_2).

2.4. General procedure for isomerisation of allylic alcohols

In a typical experiment, 3-buten-2-ol (46 mmol), a catalyst complex (0.008 mmol), AgOTs (0.010 mmol) and anisole (3.7 mmol) were brought into a two-neck round-bottom flask equipped with a reflux condenser and a septum. Next, the flask was lowered into a pre-heated oil bath of 100°C. After 15 min, a sample was taken with an air-tight syringe, and the sample was analysed by ^{1}H NMR and/or gas–liquid chromatography (GLC). In some cases, several samples were taken at certain time intervals (see text). In cases where isoprene was used, 2 ml (20 mmol) was added to the reaction mixture prior to heating.

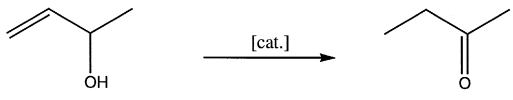
2.5. General procedure for ether formation

Analogous to the isomerisation experiments, a two-neck flask was charged with allyl alcohol (45 mmol), toluene (4 mmol) and catalyst (0.005 mmol). In all cases, a slight excess of AgOTs was added to remove the chloride ion from the ruthenium complex. The reaction mixture was lowered into a pre-heated oil bath at the specified temperature (usually 100°C) and samples were taken at certain time intervals (see text). All samples were analysed with GLC. In cases of coupling of allyl alcohol (12–15 mmol) with other alcohols, the other alcohol (5 mmol) was added before heating. In cases where isoprene was used, 2 ml (20 mmol) was added to the reaction mixture prior to heating.

3. Results and discussion

3.1. Isomerisation of 3-buten-2-ol

In view of our interest in the formation of butanone (methyl ethyl ketone, MEK) from butadiene (vide supra) [10], we started our investigations with the isomerisation of 3-buten-2-ol (Eq. 1). Trost and Kulawiec [11,12] showed that **1** selectively isomerises allylic alcohols in the presence of unfunctionalised alkene moieties. The reported yields are high, but a catalyst concentration of 1 mol% is used. However, with 3-buten-2-ol, **1** is capable of reaching a turnover frequency (TOF) of over 200,000 h^{-1}, which is higher than reported before by three orders of magnitude. This dramatic increase in rate may be attributed to three factors. First of all, 3-buten-2-ol is much smaller than the substrates used by Trost. Secondly, the use of silver tosylate (this manuscript) instead of Et_3NHPF_6 (Trost) is more effective in the removal of the chloride ion, which in our case leads quantitatively to the formation of the cationic ruthenium species. Finally, the use of a potentially coordinating solvent like dioxane may possibly retard the reaction. In our case, no additional solvent is used.



(1)

To modify the reactivity and perhaps gain selectivity, a series of ruthenium cyclopentadienyl complexes with didentate phosphine ligands has been prepared. The results of the isomerisation reaction of 3-buten-2-ol to MEK catalysed with these complexes are reported in

Table 1
Isomerisation of 3-buten-2-ol to MEK catalysed by [RuClCpL] complexes[a]

Entry	L	TOF (h^{-1})
1	$2PPh_3$ (**1**)[b]	> 200,000
2	dppm[c]	2000
3	dppm	530
4	dppe (**2**)	1675
5	dppp (**5**)	5500
6	dppb (**6**)	18,000
7	dcpe	20,000
8	dppph	0
9	*cis*-dppv	0

[a]Reactions were carried out at 100°C in neat 3-buten-2-ol (45 mmol) with anisole as IS and 0.008 mmol of catalyst. In all cases, a slight excess of AgOTs was added to remove the chloride ion. Activities were determined after 158 min by ^{1}H NMR, shown as moles of MEK formed per mole catalyst per hour. No products other than MEK were observed.
[b]Activity after 2 min.
[c]Activity after 5 min.

Table 1. In all cases, only the selective formation of MEK (> 95%) was observed. All complexes with didentate phosphine ligands are clearly less active than **1**. Upon increasing the carbon-chain length between the phosphorus-donor atoms, the reactivity of the ruthenium complexes increases. The mechanism of isomerisation of allylic alcohols by **1**, as proposed by Trost and Kulawiec [11], involves the dissociation of one triphenylphosphine ligand. The increased reactivity with increasing chain length in the phosphine ligand reflects the greater ease of ring opening of larger chelate rings. Indeed, complexes with didentate phosphine ligands that are extremely rigid, such as with a phenylene or ethene bridge, show no catalytic activity at all (entries **8** and **9**). The complex with the ligand dppm is active in the early stages of the reaction, but it almost completely loses activity within 15 min (cf. entries **2** and **3**). This may be due to the fact that the ruthenium dppm complex has a considerable ring strain energy in the order of 13 kcal/mol [32] and the ligand may therefore dissociate completely.

3.2. Formation of di-allylic ethers from 3-buten-2-ol and allyl alcohol

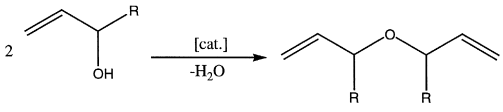
In the following experiments, the isomerisation of 3-buten-2-ol in the presence of isoprene was examined to mimic the reaction conditions for the target reaction [10]. Unfortunately, most of the complexes showed no catalytic activity under these conditions. Although no isomerisation was observed, complex **2** showed an interesting reaction (Eq. 2), which we explored in further detail. The formation of an ether from allylic alcohols under such relative mild conditions is rare, but has been reported [17–22]. All reported catalysts, however, are less active than complex **2**, which reaches a TOF of 1050 h^{-1} (Table 2). A total of 3300 turnovers can be reached after a few hours, which is, to our knowledge, the highest activity reported so far. Previous results with ruthenium bipyridine-catalysed isomerisation of 3-buten-2-ol [10] showed that conjugated dienes have an in-

Table 2
Formation of BMAE and MEK from 3-buten-2-ol[a]

Entry	Complex	TOF (h^{-1}) BMAE[b]	TOF (h^{-1}) MEK
1	[RuClCp(dppe)] (**2**)	0	1675
2	2 + isoprene (2 ml)	1050	25
3	[RuClCp(*o*-MeO-dppe)] (**3**)	200	340
4	3 + isoprene (2 ml)	0	0
5	[RuCl(Ind)(dppe)] (**4**)[c]	150	400
6	4 + isoprene (2 ml)	110	0

[a]Reactions were carried out at 100°C in neat 3-buten-2-ol (45 mmol) with toluene as IS and 0.005 mmol of catalyst. In all cases, a slight excess of AgOTs was added to remove the chloride ion. Activities were determined after 2 h by GLC, shown as moles of product formed per mole catalyst per hour.
[b]BMAE is formed in a 1:1 mixture of DL-BMAE and *rac*-BMAE as observed by GLC analysis.
[c]Ind: η^5-indenyl.

hibitory effect on the MEK formation rate. In the present study with phosphine ligands, isoprene completely stops isomerisation and ether formation is started instead. This makes isoprene an ideal 'on–off switch' between both reactions. The effect is best observed with **2**. Without isoprene, only MEK is formed (entry **1**). When isoprene is added, the same catalyst switches to bis(methylallyl)ether (BMAE) formation with only traces of MEK (entry **2**).



(2)

BMAE: R = Me
DAE: R = H

For the isomerisation of allylic alcohols, Trost and Kulawiec [11] reported an increase in catalytic activity when the cyclopentadienyl ligand is replaced by the indenyl ligand. In our case (entry **5**, Table 2), complex **4** gives a lower activity for isomerisation and clearly gives lower selectivity than **2**. The formation of BMAE is only slightly slower in the presence of isoprene with **4**, but again, the formation of MEK has completely stopped (cf. entries **5** and **6**).

To probe the steric requirements of the reaction, *o*-MeO-dppe, a more sterically demanding ligand successfully employed in our laboratory in hydrogenation reactions [33], was tested using complex **3**. The formation of the ether BMAE is now already observed in the absence of isoprene, but the steric effect is demonstrated by the fact that the overall TOF is lower than that observed with complex **2**.

Complex **3** turned out to be a more active catalyst than complex **2** when we turned our attention to allyl alcohol itself. The results are reported in Table 3. Although the TOF is somewhat lower than with the ether formation of 3-buten-2-ol, selectivity is virtually complete. Complex **3** produces di-allyl ether (DAE) with a TOF of 615 h^{-1}. Addition of isoprene leads in all cases only to a slower reaction. As with the isomerisation of 3-buten-2-ol, a trend is visible with carbon-chain length between the phosphorous donor atoms. This time, however, increasing the chain length of the diphosphine bridge decreases activity. Apparently, in the mechanism for ether formation, ring opening is not required in or before the rate-determining step. Ring opening seems to be necessary in some stage of the reaction, because the complex with *cis*-dppv does not show ether formation (nor isomerisation, Table 1, entry **9**). If the ring is opened too easily, isomerisation becomes predominant again as can be seen with complex **6**.

The homocoupling of alcohols is limited to allylic alcohols with a terminal double bond. Both an allylic alcohol with an internal double bond, 2-buten-1-ol and a homo-allylic alcohol, 3-buten-1-ol, remain unchanged even after prolonged heating.

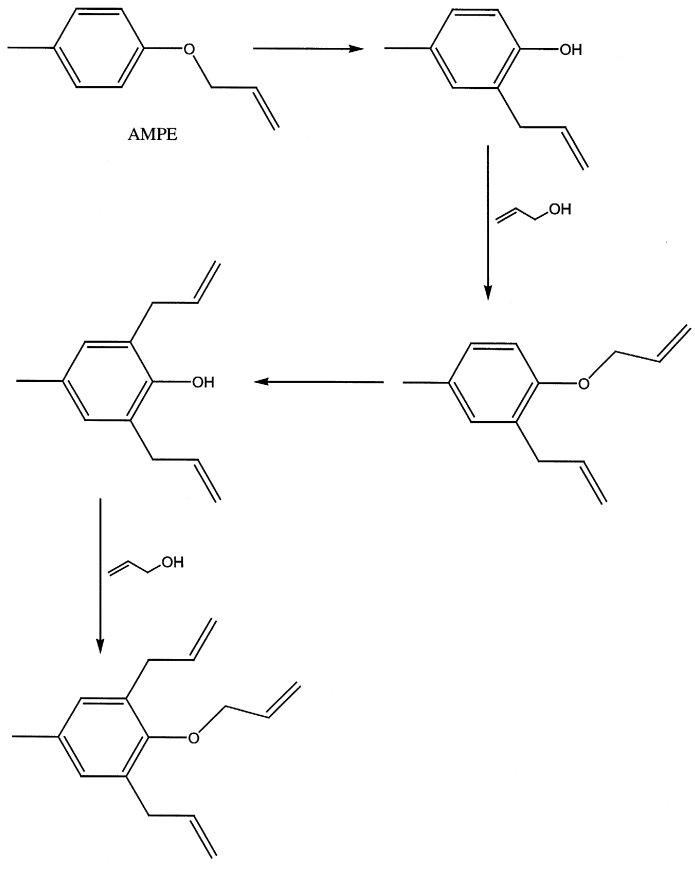
Table 3
Formation of DAE and propanal from allyl alcohol[a]

Entry	Complex	TOF (h^{-1}) DAE	TOF (h^{-1}) propanal
1	[RuClCp(dppe)] (**2**)	150	0
2	2 + isoprene (2 ml)	0	0
3	[RuClCp(dppp)] (**5**)	94	0
4	[RuClCp(dppb)] (**6**)	trace	815
5	[RuClCp(*o*-MeO-dppe)] (**3**)	615	0
6	3 + isoprene (2 ml)	225	0
7	[RuCl(Ind)(dppe)] (**4**)	0	150
8	4 + isoprene (2 ml)	0	0

[a] Reactions were carried out at 100°C in neat allyl alcohol (45 mmol) with toluene as IS and 0.005 mmol of catalyst. In all cases, a slight excess of AgOTs was added to remove the chloride ion. Activities were determined after 2 h by GLC, shown as moles of product formed per mole catalyst per hour.

3.3. Coupling of allyl alcohol with other alcohols

The best catalyst for coupling of allyl alcohol to DAE proved to be **3**. Therefore, **3** was used to extend this reaction to other nucleophiles. Thus, when *p*-cresol is added to the reaction mixture, not only DAE is formed, but a considerable amount of allyl (*p*-methylphenyl) ether (AMPE) is also formed. Under the reaction conditions, at 100°C, AMPE partially undergoes a Claisen rearrangement to form a mixture of several ring allylated cresols and ethers (Eq. 3). In Fig. 1, it is shown that formation of DAE in the initial stages of the reaction is much faster than the formation of the cross-coupling product AMPE. Apparently, the amount of DAE decreases with time, but this is most likely due to losses during sampling. No reaction is observed when DAE is heated with *p*-cresol in the presence of **3**. Reaction of *p*-cresol does not start until around 40 min. In the period until 1 h, AMPE is selectively formed. Heating for a longer period does not increase the yield of AMPE, but increases the amount of ring allylated products. A direct ring attack to form *o*-allyl cresol and other ring allylated products cannot be excluded. However, since both toluene and anisole fail to react with allyl alcohol under the reaction conditions, this seems less likely.



(3)

Other aromatic and aliphatic alcohols can be coupled with allyl alcohol (Table 4). The reaction conditions required for heterocoupling are more severe than for homocoupling. Whereas

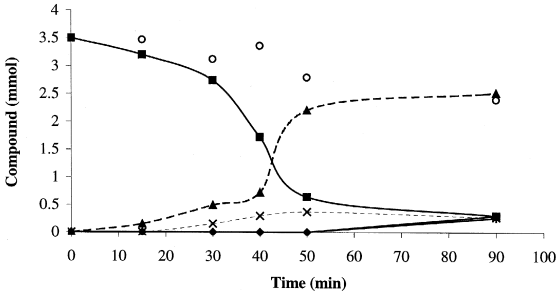


Fig. 1. Coupling of allyl alcohol with *p*-cresol catalysed by **3**. (*p*-Cresol (3.5 mmol) was reacted with allyl alcohol (15 mmol) at 100°C with toluene as IS and 0.014 mmol of **3**). (▲) Allyl (*p*-methylphenyl) ether (AMPE). (■) *p*-Cresol. (○) DAE. (X) *o*-Allyl (*p*-cresol). (♦) (*o*-Allyl *p*-methylphenyl) allyl ether.(+) 2,6-Di-allyl cresol.

the reaction proceeds smoothly at 100°C, no reaction is observed at 80°C or less (entry **5**). DAE is formed even at 50°C, albeit at a much lower rate. Aromatic alcohols are good nucleophiles in this reaction and substituents are tolerated. Both *p*-methoxy phenol and 2,4,6-trimethyl phenol react to give a TOF of 700 h^{-1} (to the mono allyl aryl ether) and 55 h^{-1}, respectively. The latter only gives one product, since Claisen rearrangements are not possible in this case.

Aliphatic alcohols can be coupled to allyl alcohol as well, although much slower (entries **13** and **14**). If the reaction is carried out with methanol as a solvent, a complete conversion to methyl allyl ether takes place, with no formation of DAE. Coupling with 3-buten-1-ol (entry **11**) fails because it co-ordinates strongly to the ruthenium centre and thereby inhibits further reaction. In this case also, no formation of DAE is observed.

3.4. Mechanistic considerations

From the results mentioned above, it is clear that ruthenium cyclopentadienyl complexes with didentate phosphine ligands are, in principle, capable of catalysing both isomerisation and ether formation of allylic alcohols. Which reaction is catalysed predominantly depends both on the phosphine ligand and on the substrate. Trost and Kulawiec [11] have proposed an intramolecular mechanism for the isomerisation of allylic alcohols by **1**. We performed a cross-over experiment to prove the proposed intramolecularity. Deuterated 3-buten-2-ol was prepared by

Table 4
Coupling of allyl alcohol with nucleophiles catalysed by [RuClCp(*o*-MeO-dppe)] (**3**)[a]

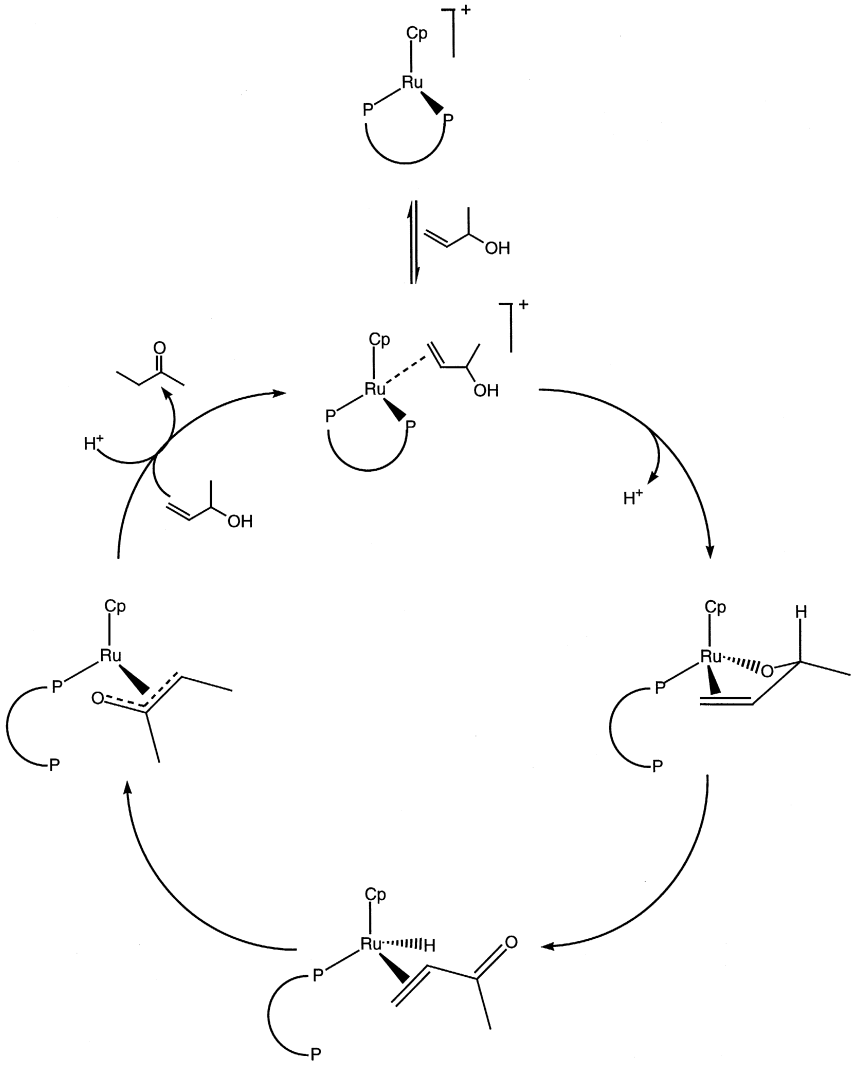
Entry	Nucleophile	Product	TOF (h^{-1})
1	–[b]	DAE	19
2	toluene	allyl toluene	0
3	anisole	allyl anisole	0
4	phenol	allyl phenyl ether	144
5	phenol[c]	allyl phenyl ether	0
6	*p*-cresol	allyl (*p*-methylphenyl) ether	254
7	*p*-MeO-phenol	allyl (*p*-methoxyphenyl) ether	700
8	2,4,6-trimethylphenol	allyl (2,4,6-trimethylphenyl) ether	41
9	2-naphthol	allyl 2-napthyl ether	875
10	3-buten-1-ol	allyl 3-butenyl ether	0
11	MeOH	allyl methyl ether	0
12	MeOH (5 ml)	allyl methyl ether	100
13	EtOH	allyl ethyl ether	63

[a] Reactions were carried out at 100°C with 12–15 mmol allyl alcohol and 5 mmol nucleophile. Toluene was used as IS and 0.005 mmol of catalyst was applied. In all cases, a slight excess of AgOTs was added to remove the chloride ion. Activities were determined after 45 min by GLC, shown as moles of product formed per mole catalyst per hour. In all cases, DAE was formed in considerable amounts as well. (The selectivity towards the cross-coupled ether is time-dependent. For an example, see Fig. 1. Selectivities for other nucleophiles are comparable.)

[b] $T = 50$°C.

[c] $T = 80$°C.

reduction of methyl vinyl ketone with lithium aluminium deuteride [29]. This was stirred together with allyl alcohol at room temperature in the presence of **1**. If the hydrogen shift during the isomerisation is intramolecular, two products are expected to be formed: butanone-4-*d* and propanal (Eq. 4). An intermolecular hydrogen shift would give rise to four products. Next to the already mentioned butanone-4-*d* and propanal, also butanone and propanal-3-*d* would be formed. In this case, some unsaturated carbonyl compounds, e.g. methyl vinyl ketone, are expected to be formed as well, which originate from the initial formation of a ruthenium(IV) hydride. To avoid difficulty in observing aldehyde molecular ion peaks by mass spectrometry, the reaction mixture was analysed by NMR techniques. ^{13}C NMR proved to be best suitable, because in ^{1}H NMR, all peaks overlapped. During the reaction, two product peaks appeared, assigned to butanone-C_4 (7.24 ppm) and propanal-C_3 (5.69 ppm) after independent synthesis. Only the peak at 7.24 ppm was a 1:1:1 triplet indicative of monodeuteration at that car-



Scheme 1. Proposed mechanism for the isomerisation of allylic alcohols with ruthenium(II) Cp didentate phosphine complexes. (Cp: η^5-cyclopentadienyl).

bon atom. No deuteration was observed at any other carbon atom. This proves the proposed intramolecularity of the isomerisation of allylic alcohols catalysed by **1**.

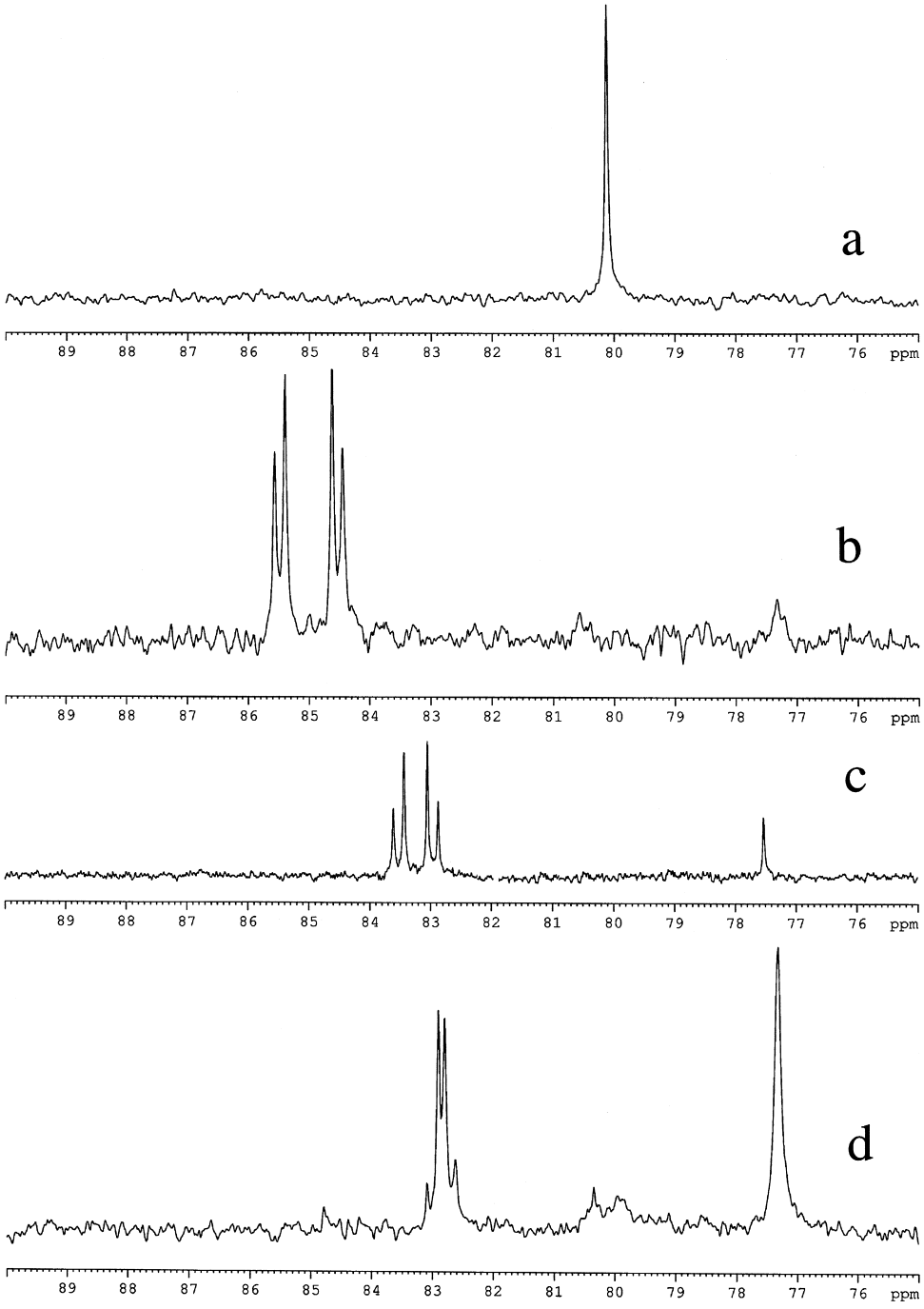
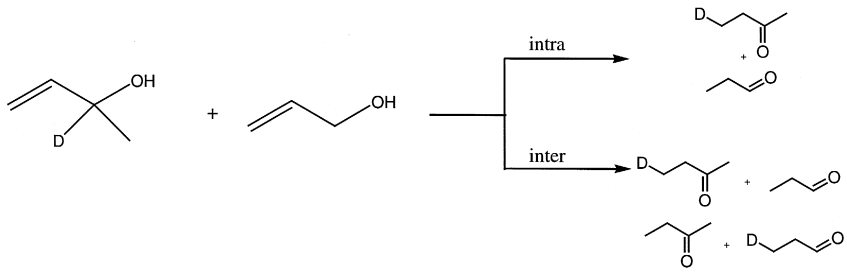
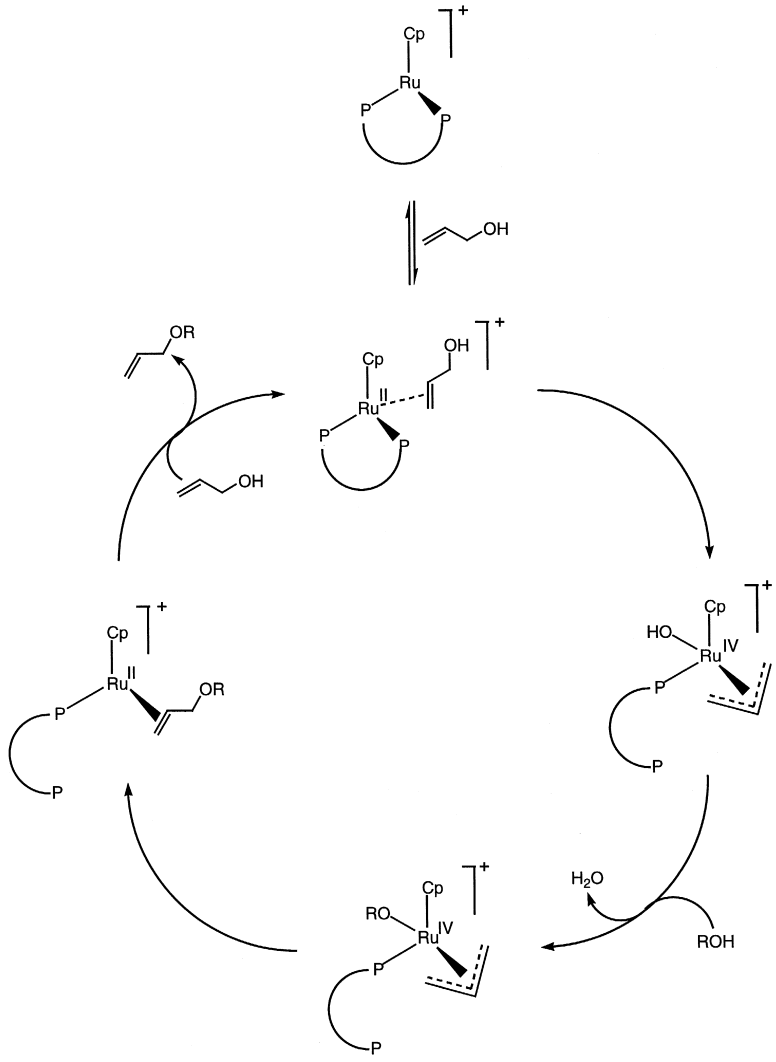


Fig. 2. ^{31}P NMR monitoring of $[RuCp(dppe)]^+$ in reaction with several alkene moieties. All spectra were taken at room temperature in $CDCl_3$ directly after mixing of the $[RuCp(dppe)]^+$ solution with the substrate. (a) [RuClCp(dppe)]. (b) $[RuCp(dppe)]^+$ after reaction with allyl alcohol. (c) $[RuCp(dppe)]^+$ after reaction with 1-octene. The peak at 77.5 ppm is from uncomplexed $[RuCp(dppe)]^+$. (d) $[RuCp(dppe)]^+$ after reaction with 2-buten-1-ol. The peak at 77.5 ppm is from uncomplexed $[RuCp(dppe)]^+$.



(4)

In analogy to the mechanism for catalysis by **1** [11], we propose a mechanism as depicted in Scheme 1. Removal of the chloride ion from [RuCpCl(dppe)] by a silver(I) salt gives a vacant

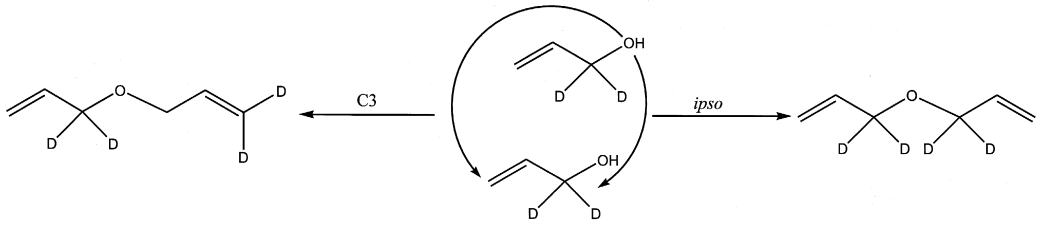


Scheme 2. Proposed mechanism for formation of DAE catalysed by ruthenium(II) Cp didentate phosphine complexes (Cp: η^5-cyclopentadienyl).

site on the ruthenium centre. The behaviour of the resulting $[RuCp(dppe)]^+$ towards allyl alcohol was examined with ^{31}P NMR (Fig. 2). The appearance of two doublets at approximately the same δ-value (Fig. 2b) suggests an asymmetric co-ordination of allyl alcohol, with both phosphorous atoms co-ordinated to the ruthenium. Both allylic and homo-allylic alcohols give the same pattern in the ^{31}P NMR spectrum around the same δ-value, as does 1-octene (Fig. 2c). Allylic alcohols with an internal double bond react much slower. Reaction of $[RuCp(dppe)]^+$ with 2-buten-1-ol leaves most of the cations uncomplexed (Fig. 2d). These results show that initial co-ordination of the allylic alcohol to the ruthenium centre with its alkene moiety is most likely.

The results in the isomerisation with didentate phosphine ligands, as shown in Table 1, further suggest that the chelate ring has to open up in order to create a vacant site at the ruthenium centre. If the ring cannot be opened easily, as is the case with *cis*-dppv, no catalysis takes place. The ring might be opened under the influence of co-ordination of the oxygen moiety. (Contrary to a previous report [11], unfunctionalised alkenes are also isomerised by **1** and complexes with didentate phosphine ligands, although at a much lower rate. Still, chelating co-ordination of both the oxygen and the alkene moiety can explain the selectivity towards allylic alcohols when both allylic alcohols and unfunctionalised alkenes are present.) Co-ordination of an allylic alcohol through both the oxygen moiety and the alkene moiety is then followed by hydrogen abstraction from C_1. The resulting hydride is intramolecularly added to the C_3 position to give an oxo-allyl species. Finally, protonation liberates the product and regenerates the ruthenium complex. Since a considerable difference in activity is observed between, e.g. complexes **2** and **6**, it is suggested that the ring closes again at the end of the cycle, as is shown in the last step of Scheme 1.

To account for the formation of an ether, a mechanism that includes an oxidative addition of the allylic alcohol, followed by attack of an alcohol and liberation of the product seems plausible (cf. Scheme 2). This mechanism has indeed been generally accepted for palladium catalysts [20]. Two pathways can be envisioned for the attack of the alcohol. The first pathway is direct attack of the alcohol on the ruthenium-allyl species. The second pathway (shown in Scheme 2) consists of exchange of the alcohol with the hydroxide resulting in a ruthenium alkoxide accompanied by release of a water molecule. Reductive elimination then yields the product ether. At present, no discrimination can be made between both pathways. Some support for the direct attack pathway has recently been published [34]. Oxidative addition of allyl bromide on $[RuCp(PPh_3)(MeCN)_2]^+$ followed by stoichiometric addition of triethylamine resulted in $[RuBrCp(PPh_3)(CH_2{=}CHCH_2NEt_3)]^+$: the product resulting from direct attack on the allyl moiety. In the reaction of 3-buten-2-ol catalysed by **2**, only the branched ether is formed (in a 1:1 mixture of DL-BMAE and *meso*-BMAE). This can be explained by assuming that rotation of the methyl allyl moiety is not possible (or rotation is slower than reductive elimination). Di-



Scheme 3. Formation of two possible regio isomers in the ether formation of allyl-1,1-d_2 alcohol.

rect attack could be sterically and/or electronically directed towards the *ipso* position.

To probe the nature of the reaction with allyl alcohol, allyl-1,1-d_2 alcohol was prepared. As shown in Scheme 3, exclusive attack on the *ipso* position would only lead to deuteration on aliphatic carbons, whereas attack on both sides would lead to a mixture of deuterated aliphatic and vinylic carbons. Indeed, attack on both sides takes place, which can be deduced from the appearance of a doublet at 3.95 ppm in the ^{1}H NMR and two doublets at 5.4 ppm in the ^{2}H NMR (Fig. 3). The ratio between both products is dependent on the nature of the catalyst. The difference in ratio can be explained by both steric and electronic reasons [35], although in this case, steric reasons will probably dominate. Again, two rationales can be given: via the direct attack route or the reductive elimination route. The sterically more crowded **3** gives predominant attack on the C_3 position (aliphatic to vinylic = 1:3), which is probably the most eas-

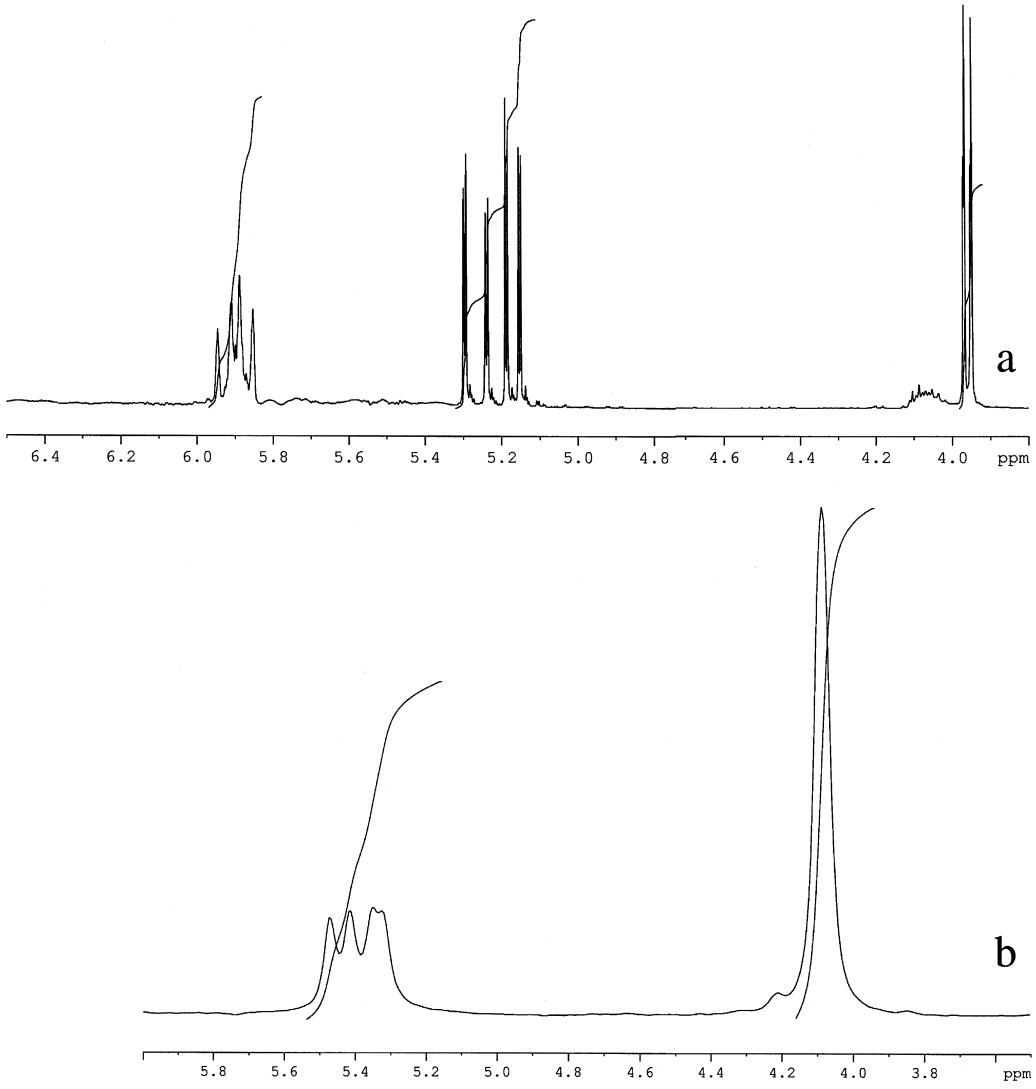


Fig. 3. Formation of DAE from allyl-1,1-d_2-alcohol catalysed by **3**. (a) ^{1}H NMR spectrum in $CDCl_3$. Note the appearance of a doublet at 3.95 ppm due to attack at C_3. (b) ^{2}H NMR spectrum in $CDCl_3$. Note the appearance of two doublets at 5.4 ppm due to attack at C_3.

ily accessible for the attacking nucleophile. In the less bulky catalysts **2** and **5**, both sides become more and more accessible and the ratio drops to 1:2 and 1:1, respectively. The latter ratio is expected when a symmetrical η^3-allyl ligand is well accessible from both sides. In case the pathway, as shown in Scheme 2, is operative, the co-ordinated allyl must be able to rotate freely. Apparently, rotation is more restricted in complex **3** than in **2** and **5**; in the latter complex apparently, the allyl moiety can rotate freely. These results exclude a mechanism in which direct S_{N_2} attack on the alcohol takes place with the ruthenium complexes merely acting as a Lewis acid.

The role of isoprene is not yet fully understood. Co-ordination of isoprene to the ruthenium centre may prevent the *didentate* co-ordination of the allylic alcohol (by both the alkene and oxygen moieties; see Scheme 1), and thereby inhibit the isomerisation reaction. However, oxidative addition may still be possible from the *monodentate* co-ordination with the alkene moiety of the allylic alcohol (Scheme 2).

Both mechanisms and the influence of conjugated dienes on switching from one reaction to the other are currently under investigation.

4. Conclusions

One type of ruthenium(II) complex, viz. chloro cyclopentadienyl (didentate phosphine)-ruthenium(II), can catalyse two types of reaction of allylic alcohols: isomerisation and ether formation. Conjugated dienes can act as a switch between both reactions. [Chloro-cyclopentadienyl)-bis(triphenylphosphine)-ruthenium(II)] is most active in the isomerisation of allylic alcohols to carbonyl compounds. Replacing triphenylphosphine by didentate phosphine ligands lowers the activity. The increased reactivity of those complexes with increasing chain length reflects the greater ease of ring opening of larger chelate rings.

Ether formation of allylic alcohols to di-allylic ethers is much faster with this type of ruthenium(II) complex than reported before with palladium and nickel catalysts. The new complex [RuClCp(*o*-MeO-dppe)] forms ethers even in the absence of isoprene and is the most active of the tested complexes in the coupling of allyl alcohol to aromatic and aliphatic alcohols.

The mechanism of isomerisation is intramolecular and starts with the co-ordination of allyl alcohol to the ruthenium centre through its alkene moiety. It is proposed that the mechanism of ether formation involves the intermediacy of a ruthenium allyl species. Attack of a nucleophile on that allyl species is probably sterically directed, as *ipso* attack predominates with *o*-MeO-dppe as a ligand, whereas a 1:1 mixture of products resulting from both *ipso* attack and C_3 attack is observed with the sterically less hindered dppp ligand. If the allyl group is substituted on C_1 as is the case in the reaction of 3-buten-2-ol, attack is sterically and/or electronically directed towards the *ipso* position.

Acknowledgements

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