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Remarkable activity of the isomerization catalyst [RuCp(PPh_3)$_2$](OTs) in O-allylation of phenol with allyl alcohol

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ABSTRACT

It was surprisingly found that the highly active allyl alcohol redox isomerization catalyst [RuCp(PPh_3)$_2$](OTs) upon addition of a catalytic amount of a strong acid can change its catalytic action fully to the selective O-allylation of phenols with allyl alcohol. High turnover numbers (75,000 based on phenol; 200,000 based on allyl alcohol) are reached, and the catalyst is very stable in the presence of substrate. Addition of triphenylphosphine to the reaction mixture does not lead to further stabilization of the catalyst; instead, the free phosphine is rapidly allylated, thereby consuming the acid, which deactivates the catalytic system for allylation reactions. This catalyst with monodentate phosphine ligands is superior in both activity and selectivity to similar catalysts with bidentate phosphine ligands. Apart from phenols, also thiophenol can be efficiently allylated to form allyl phenyl sulfide.

1. Introduction

The development of an environmentally benign catalytic route to epoxy resins is highly desirable [1,2]. The bis O-allylation of bisphenol A is regarded as an interesting intermediate pathway in the production of these epoxy resins, in particular, if catalysts could be developed for the catalytic O-allylation reaction. It would, of course, be best if allyl alcohol could be used as the allylating agent in view of the protection of the environment, since only water would be co-produced in ether formation. Prior to our work in this area, only a single example was known where allyl phenyl ethers can be catalytically and selectively produced from a phenol and allyl alcohol [3]; however, a stoichiometric amount of base needs to be added to induce O-allylation of phenols. This addition of base should be avoided, because stoichiometric amounts of saline waste will be co-produced. However, in the absence of such a base, similar systems based on ruthenium [4] or palladium [5] exclusively yield C-allylated phenolic products.

Previously, we have reported the development of ruthenium-based catalytic systems that catalyze both O- and C-allylation of phenols (Scheme 1), without the need of any stoichiometric amount of additives [6]. It has been shown that the O-allylated products are reversibly formed, while C-allylated products are produced irreversibly. Restricted coordination space at the ruthenium center favors the formation of the O-allylated product, which could be achieved by using ligands that have a large bite angle and/or form kinetically stable chelates [7]. It was also observed that [RuCp(dppb)](OTs), (dppb = 1,4-bis(diphenylphosphino)butane), a catalyst known to be active in the isomerization of allyl alcohol into propanal [8], becomes moderately active in allylation reactions in the presence of two equivalents on Ru of a strong acid.

The cationic ruthenium complex, based on a monodentate ligand, triphenylphosphine, i.e. [RuCp(PPh_3)$_2$]$^+$, has been reported to be an extremely active and efficient catalyst for the redox isomerization of allyl alcohols into carbonyl compounds, achieving very high turnover numbers. The catalyst is applicable for a wide range of allylic substrates [9–12]. Similar ruthenium complexes with chelating phosphine ligands proved to be much less active in the isomerization reaction [8] but switch reactivity to allyl ether formation in the presence of isoprene. Surprisingly, we have found that the isomerization catalyst [RuCp(PPh_3)$_2$]$^+$ can be transformed into an extremely active and selective catalyst for allyl phenyl ether formation from a phenol and allyl alcohol.

2. Experimental

2.1. General remarks

All reactions were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled by standard procedures and stored under argon. Triphenylphosphine was commercially available and used as received. $RuCl_3 \cdot 3H_2O$ (Johnson and Matthey) was used as received. [RuCpCl(PPh_3)$_2$]

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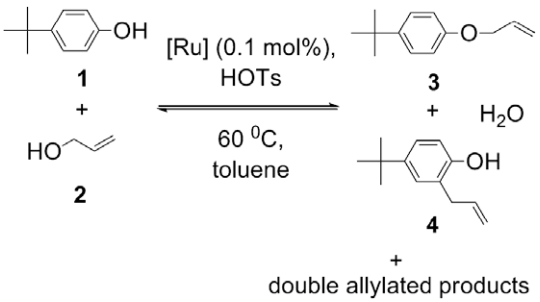


Scheme 1. Reaction of 4-*tert*-butylphenol (**1**) with allyl alcohol (**2**) catalyzed by different $[RuCp(PP)]^+$ complexes.

[13], [RuCpCl(dppp)] [14] (dppp = 1,3-bis[diphenylphosphino]propane) and [RuCpCl(dppb)] [15] were prepared according to literature procedures.

^{1}H NMR spectra (300 MHz) and ^{31}P{1H} NMR spectra (121.4 MHz) were measured on a Bruker DPX-300. Chemical shifts are reported in ppm. Proton chemical shifts are relative to TMS, and phosphorus chemical shifts are relative to 85% aqueous H_3PO_4. The spectra were taken at room temperature.

2.2. Synthesis of [RuCpCl(dpppe)] (dpppe = bis(diphenylphosphinophenyl) ether)

A solution of $RuCpCl(PPh_3)_2$ (72 mg, 0.1 mmol) and the bidentate dpppe phosphine ligand (0.1 mmol) in 5 ml toluene was stirred for 16 h at 90 °C. The solution was cooled to room temperature and flushed over a column of silica gel (3 g, d = 1 cm) with 15 ml of toluene to remove the triphenylphosphine. Finally, the orange product was eluted with ethyl acetate until the eluens was colorless. The solution was then concentrated in *vacuo* to approximately 1 ml, and the product precipitated with petroleum ether and [RuCpCl(dpppe)] was obtained as a yellow solid in a yield of 69 mg (93%). Anal. Calcd for $C_{41}H_{33}ClOP_2Ru{\cdot}0.25$(hexane): C, 67.01; H, 4.83. Found: C, 66.62; H, 4.92. ^{1}H NMR ($CDCl_3$): δ 7.50 (m, 2H, ArH), 7.36 (m, 8H, ArH), 7.26–7.13 (m, 8H, ArH), 7.01 (m, 4H, ArH), 6.92–6.90 (m, 2H, ArH), 6.84–6.71 (m, 4H, ArH), 4.10 (s, 5H, Cp). ^{31}P NMR ($CDCl_3$): δ 44.6 (s).

2.3. General procedure for catalytic reactions

Into the reaction vessel were charged 2.5 mmol of 4-*tert*-butylphenol (or another nucleophilic substrate if indicated), 2.5 μmol of the ruthenium-chloride catalyst precursor complex, 5.0 μmol of AgOTs (to displace chloride anions with tosyl through formation of AgCl) and 0.05 mmol of HOTs and flushed with argon. Degassed and dried toluene was added (2.5 ml), and the mixture was stirred for 5 min. Allyl alcohol was added (5 mmol), and the reaction was stirred at 60 °C. Samples were taken at certain time intervals with an airtight syringe and analyzed by gas chromatography [6].

The spectroscopic data of allyl phenyl ether [16], allyl 2,4,6-trimethylphenyl ether [17] and allyl phenyl sulfide [18] corresponded with the data reported in literature.

2.4. High turnover number experiments

The catalyst amount ($[RuCpCl(PPh_3)_2]$ and AgOTs) was kept constant while increasing the amounts of the reactants (4-*tert*-butylphenol and allyl alcohol), acid (HOTs) and solvent (toluene) by a factor 20. A similar reaction was conducted, but the amount of ruthenium complex was reduced to 0.25 μmol. After 72 h, a turnover number of 75,000 was reached.

2.5. GLC method

Quantitative gas liquid chromatography analyses were carried out on a Varian CP-3800 apparatus equipped with a VF-1 ms (25 m × 0.25 mm) column with decane as internal standard. The temperature gradient used was as follows: isothermal for 5 min at 40 °C, heating 10 °C/min to 250 °C and finally isothermal for 5 min at 250 °C.

2.6. Phosphonium salt formation

Into the reaction vessel were charged 2.5 μmol of $[RuCpCl(PPh_3)_2]$, 5 μmol of AgOTs, 0.05 mmol of triphenylphosphine and 0.05 mmol of HOTs and flushed with argon. Degassed and dried toluene was added (2.5 ml), and the mixture was stirred for 5 min. Allyl alcohol was added (5 mmol), and the reaction was stirred at 60 °C for 5 min. Reaction was cooled to room temperature, and the mixture was concentrated *in vacuo* to yield a colorless oil in 24 mg (100%). ^{1}H NMR ($CDCl_3$): δ 7.76–7.62 (m, 17H, ArH), 7.06 (d, 2H, J = 7 Hz, ArH), 5.73–5.59 (m, 1H, H-allyl), 5.40 (dd, 1H, J = 6 Hz, 30 Hz, =CHH), 5.35 (dd, 1H, J = 6 Hz, 24 Hz, =CHH), 4.38 (dd, 2H, J = 9 Hz, 12 Hz, CH_2), 2.30 (s, 3H, Me). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 21.6 (s).

2.7. Kinetic data on experiments with extra triphenylphosphine addition

The general procedure for catalytic reactions was followed, but with addition of the indicated amount of triphenylphosphine to the mixture prior to flushing with argon.

2.8. Procedure for "second batch" experiments

The general procedure for catalytic reactions was followed, but after 3 h, a second batch of substrates was added (2.5 mmol of 4-*tert*-butylphenol and 5.0 mmol of allyl alcohol). Samples were taken at one and 3 h after addition of the first batch and at one and 3 h after addition of the second batch (4 h total reaction time).

3. Results and discussion

In an earlier study, we have shown that the catalytic allyl ether formation is enhanced by addition of two equivalents of acid on ruthenium [6]. However, under those conditions (at 100 °C), the use of $[RuCp(PPh_3)_2](OTs)$ results in only low conversion of phenol, and propanal is still produced as the major product. It was found that at lower reaction temperatures and higher acid concentrations, the production of propanal can be effectively prevented and the catalyst becomes extremely active and selective in the O-allylation of phenols (Table 1).

As expected, in the absence of acid, no reactivity for allylation is observed (entry 1). Gradually increasing the acid concentration results in higher yields of the desired allyl ether, but still propanal is the major product (entries 2–4). In a reaction mixture with 20 mM of HOTs (2 mol% on phenol), the production of propanal is completely blocked and a high conversion of **1** is achieved. The selectivity for O-allyl ether **3** is very high for this acid concentration, and the catalyst remains selective also after longer reaction times (6 h). When the concentration of HOTs is increased beyond 20 mM, the selectivity drops significantly, with only marginal increase in the conversion of **1**. Therefore, 20 mM HOTs at 60 °C was used in the further experiments. Without the ruthenium complex but with the acid only, no allylation or allyl alcohol isomerization is observed, thus clearly providing evidence for ruthenium complex catalyzed reactions that can be tuned by the acid.

Table 1
Conversion of **1** and selectivity for **3** using [RuCp(PPh_3)$_2$](OTs) as catalyst at 60 °C with the addition of different amounts of HOTs.[a]

Entry	mM HOTs	Conversion of **1** (%)		Selectivity for **3** (%)[b]	Yield of propanal (%)[c]
		1 h	6 h	6 h	6 h
1	0	0	0	–	100
2	1	6	7	100	79
3	2	8	9	100	62
4	4	28	31	100	38
5	10	32	39	95	11
6	20	40	70	86	0
7	50	43	75	86	0
8	100	45	74	58	0
9	200	26	69	40	0

[a] Reaction conditions: ratio 1/2/[RuCpCl(PPh_3)$_2$]/AgOTs = 1000/2000/1/2; toluene; 60 °C. 1 mM [RuCpCl(PPh_3)$_2$].
[b] Based on **1** converted.
[c] Based on **2**.

It has also to be noted that dehydrative condensation of allyl alcohol to give diallyl ether tends to precede the allylation of the phenol. Thus, diallyl ether mainly functions as the actual phenol allylation agent, and it has been shown that diallyl ether performs as an equally suitable allylation agent as allyl alcohol [6]. As half the water is being co-produced overall, diallyl ether would in fact be the allylation agent of choice in commercial applications, allowing high phenol conversion, in particular at high diallylether/phenol substrate ratios.

Under these conditions, high turnover numbers could be obtained by decreasing the Ru catalyst concentration (to 0.05 mM) and as many as 14,300 turnovers were achieved in a single batch experiment (after 24 h, 72% conversion of **1** with 87% selectivity for O-allylation), demonstrating the stability of the catalyst (Fig. 1). After a small induction time caused by relatively slow formation of [RuCp(PPh_3)$_2$](OTs) from [RuCp(PPh_3)$_2$Cl] and AgOTs in the diluted reaction medium, a linear increase in turnover number vs. time is observed. After about 24 h (72% conversion of **1**), the conversion is halted.

In order to see if even higher turnover numbers can be achieved, a similar reaction was performed, but with a phenol over catalyst ratio of 200,000. When this reaction was left for longer time (72 h), a turnover of 75,000 is reached, based on **1**. In this time, all the allyl alcohol is converted to either diallyl ether or allyl phenyl ether, the TON based on allyl alcohol is even higher than 200,000.

The allyl phenyl ether formation is an equilibrium condensation reaction, and the substrate conversions at thermodynamic equilibrium will be determined by the amount of water that is soluble in the reaction medium (mainly toluene) at reaction temperature. *In situ* removal of water from the reaction medium, for instance by means of a Dean–Stark trap, could lead to increased substrate conversion [6]. A Dean–Stark water trap, however, is not efficient at the reaction temperature used in these experiments. On the other hand, at the low reaction temperature applied of 60 °C, the solubility of water in the reaction medium is very low and the water produced forms a separate phase, thus shifting the dehydrative equilibrium in the toluene phase automatically toward high substrate conversion.

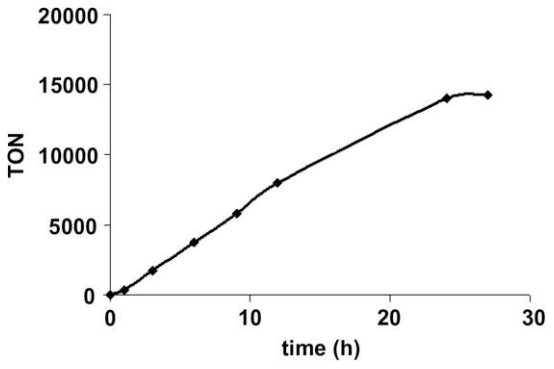


Fig. 1. Total turnover number (TON) of phenol to allylated products in time (maximum TON = 20,000). Reaction conditions: ratio 4-*tert*-butylphenol/allyl alcohol/[RuCpCl(PPh_3)$_2$]/AgOTs/HOTs = 20,000/40,000/1/2/400; toluene; 60 °C.

3.1. Monodentate phosphine vs. bidentate phosphine ligands

The [RuCp(PPh_3)$_2$](OTs) catalyst was compared to catalysts containing bidentate ligands under the optimal conditions. The results are shown in Table 2.

Compared to any of the catalysts with a bidentate ligand (entries 2–4), the activity of [RuCp(PPh_3)$_2$](OTs) is very high (entry 1). Its selectivity is only slightly lower than that of the complexes with large bite angle bidentate ligands (entry 2–3). [RuCp(dppp)](OTs), with the smallest bite angle ligand in this table, shows very low selectivity for O-allylation under the acidic conditions applied (entry 4).

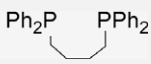
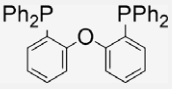
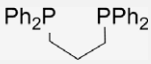
3.2. Reactivity of triphenylphosphine

The mechanism for the isomerization of allyl alcohols into carbonyl compounds requires that a phosphine ligand dissociates from the Ru(II) complex and this readily can occur in [RuCp(PPh_3)$_2$](OTs) [9]. However, it appears that in the presence of a catalytic amount of acid, the allyl alcohol isomerization reaction is efficiently blocked. We surmised that phosphine dissociation can still play a role in the catalytic allylation cycle and the stability of the catalyst. For this reason, triphenylphosphine was added in different amounts (2, 5, 10 and 20 eq on [Ru]) to the reaction mixture to test its effect on the stability and the lifetime of the catalyst (Table 3).

The initial catalytic allylation rate of the catalyst after 15 min is not affected when 2 (entry 2) or 5 eq (entry 3) of PPh_3 is added compared to the rate of the reaction in the absence of PPh_3 (entry 1). Upon addition of 10 eq of PPh_3, the initial rate of allylation is unchanged (entry 4), but after 30 min, conversion of **1** is halted at 40% and a large amount of propanal is formed. Addition of 20 eq of triphenylphosphine or more completely inhibits the catalytic activity for allylation and only propanal is formed. The fate of free triphenylphosphine under reaction conditions was investigated, and it was found that the reaction shown in Scheme 2 takes place: allyl alcohol reacts with triphenylphosphine and the acid under the agency of the catalyst to form an allyl phosphonium salt and water. In the absence of catalyst, this quaternization is not observed. A similar reaction has been reported by Basset et al. for a palladium complex [19]. The formation of propanal, when 20 equivalents of PPh_3 are added to the reaction, can thus be explained by the fact that the acid is consumed quantitatively by the additional PPh_3. It is intriguing to see that whereas free triphenylphosphine is rapidly converted to an allyl phosphonium salt, even in the presence of a large excess of phenol, the two equivalents of coordinated triphenylphosphine are apparently not, since the catalyst remains stable for many hours and yielding high TON's.

When, however, a second batch of substrates is added to the catalyst after 23 h (at 84% conversion of **1**), no further conversion is observed, but when this second batch of substrates is added after 3 h, continued conversion proceeds smoothly, even without a reduction of the reaction rate (Fig. 2; Table 4). In Fig. 2, it is shown

Table 2
Conversion of **1** and selectivity for **3** for the allylation of 4-*tert*-butylphenol using different $[RuCp(PP)]^+$ complexes as catalysts.[a]

Entry	PP	Conversion of **1** (%)		Selectivity for **3** (%)	
		1 h	6 h	1 h	6 h
1	2 PPh_3	40	70	93	86
2	dppb 	7	52	100	100
3	dpppe 	<1	42	100	100
4	dppp 	1	32	100	25

[a] Reaction conditions: ratio 1/2/[RuCpCl(PP)]/AgOTs/HOTs = 1000/2000/1/2/20; toluene; 60 °C.

Table 3
Rate constants for conversion of **1** with different amounts of added PPh_3.[a]

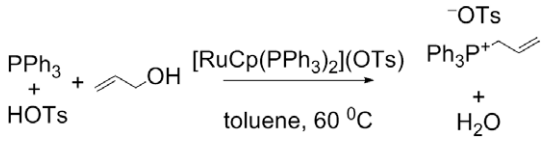
Entry	Added PPh_3 (eq on [Ru]) [b]	Time (min)	Conversion of **1** (%)	Rate constant k (h^{-1})[c]
1	0	15	21	0.94
2	2	15	25	1.15
3	5	15	24	1.09
4	10	15	24	1.09

[a] Reaction conditions: ratio 4-*tert*-butylphenol/allyl alcohol/$[RuCpCl(PPh_3)_2]$/AgOTs/HOTs = 1000/2000/1/2/20; toluene; 60 °C.
[b] After addition of 20 equivalents of PPh_3 or more, the catalyst shows no activity for allylation, only propanal is formed quantitatively.
[c] $k = -\ln\{1 - \text{conversion}\ (\%)/100]/t\}$ for $t = 15$ min.

Table 4
Rate constants for first and second batch of 4-*tert*-butylphenol and allyl alcohol.[a]

Entry	Time (h)	Conversion of **1** (mmol)	Rate constant k (h^{-1})[b,c]
1	1	1.0	0.51
2	4	3.3[d]	0.73

[a] Reaction conditions: ratio 4-*tert*-butylphenol/allyl alcohol/$[RuCpCl(PPh_3)_2]$/AgOTs/HOTs = 1000/2000/1/2/20; toluene; 60 °C. 2.5 mmol 4-*tert*-butylphenol per batch.
[b] $k = -\ln\{1 - \text{conversion}\ (\%)/100]/t\}$ for $t = 1$ h.
[c] $k = -\ln\{1 - \text{conversion}\ (\%)/100]/t\}$ for $t = 4$ h (1 h after addition of second batch).
[d] Cumulative conversion.



Scheme 2. Formation of allyl phosphonium salt with stoichiometric consumption of acid and phosphine.

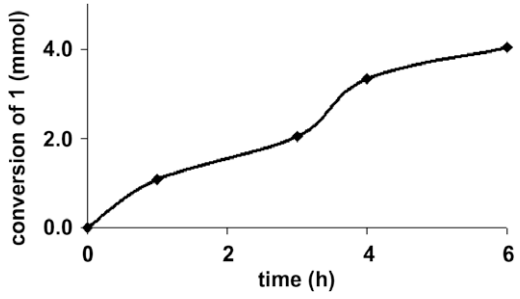


Fig. 2. Conversion of **1** (4-*tert*-butylphenol) in time in the allylation reaction using allyl alcohol as the allylating agent. A second batch of the substrates was added after 3 h. Reaction conditions: ratio 4-*tert*-butylphenol/allyl alcohol/$[RuCpCl(PPh_3)_2]$/AgOTs/HOTs = 1000/2000/1/2/20; toluene; 60 °C. 2.5 mmol 4-*tert*-butylphenol/5 mmol allyl alcohol per batch.

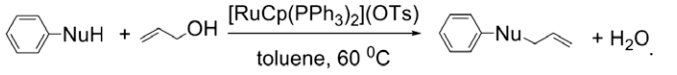
that the second batch of substrate, added after 3 h of reaction time, is converted with a similar rate as the initial batch. The quantitative data are reported in Table 4; the rate constant determined after 1-h reaction time after the addition of the second batch (entry 2) seems to be even slightly higher than that of the initial batch (entry 1). However, reaction conditions at the start of the reaction and after 3 h will not be exactly the same. Importantly, these data do indicate that in these 3 h of reaction time, the catalyst is not significantly degraded. Apparently, the catalyst is stable at a high substrate over catalyst ratio as also observed from the high TON in the experiment with a very low catalyst concentration. However, when the reaction is near completion at relatively low substrate to catalyst ratio, the catalyst deactivates. This deactivation is accompanied with a color change of the reaction mixture from light yellow to brown.

3.3. Scope of the allylation reaction

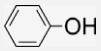
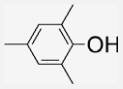
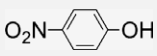
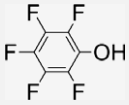
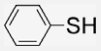
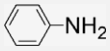
In order to explore the scope of the reaction, several other phenols were reacted with allyl alcohol (Table 5). Phenol itself also shows high reactivity toward allyl alcohol in the presence of the catalytic system (entry 1), with very high selectivity for the O-allylated product. The reaction with 2,4,6-trimethylphenol is logically completely selective toward O-allylation, but considerably slower (entry 2). Highly acidic phenols like *p*-nitrophenol (p*K*a = 7.08; entry 3) or pentafluorophenol (p*K*a = 5.49; entry 4) are not reactive for allylation. The increased acidity does not deactivate the catalyst, since diallyl ether formation is observed in both cases and therefore we attribute the decreased reactivity for O-allylation to the low nucleophilicity of the corresponding phenolates.

Nucleophilic substrates with other donor atoms than oxygen also proved to be reactive toward allylation. Thiophenol (entry 5) is efficiently S-allylated with complete selectivity toward the allyl

Table 5
Conversion of **5** and selectivity for **6** for the allylation of several nucleophilic substrates with allyl alcohol.[a]



5 **2** **6**

Entry	5=	Conversion after 3 h (%)	Selectivity for **6** (%)
1		71	99
2		8	100
3		0[b]	–
4		0[b]	–
5		94	100
6		0	–
7		0[c]	–

[a] Reaction conditions: ratio 5/allyl alcohol/[RuCpCl(PPh$_3$)$_2$]/AgOTs/HOTs = 1000/2000/1/2/20; toluene; 60 °C, 3 h.
[b] Diallyl ether is formed.
[c] Propanal is formed.

phenyl sulfide. Aniline, however, does not show any reactivity for allylation, and even diallyl ether formation (entry 6) does not take place in this instance. Apparently, aniline's N-coordination to Ru inhibits the catalyst completely. When a non-nucleophilic N-containing substrate like indole is used (entry 7), allylation is not observed, but propanal is quantitatively formed. This indicates the neutralization of acid by the indole functionality.

Substituted higher allyl alcohols can also be used as allylating agent; however, these are considerably less reactive, and the subsequent cross-allylation with phenols proceeds with lower selectivity for O-allylation. Due to the complicated product development with such allylic alcohols, their reactions will be discussed in a future publication [20].

3.4. Mechanistic implications

The mechanistic implications of our findings are summarized in Scheme 3. Allyl alcohol can coordinate to Ru(II) either with its olefin moiety (**A**) or via its alcoholate functionality (**B**) [12]. Even in the absence of added protons, the alcoholate coordination mode is present only in very small amounts since this species escapes observation with NMR spectroscopy at room temperature. For isomerization toward the aldehyde to occur, it has been proposed that a phosphine ligand dissociates with consecutive coordination of the olefin moiety, forming species **C** [12]. After subsequent β-hydrogen elimination, a Ru(II)(enone)-hydride forms, which after reinsertion of the enone moiety into Ru(II)–H gives a Ru(II)–oxa-allyl species. Protonation then results in the formation of the aldehyde [12].

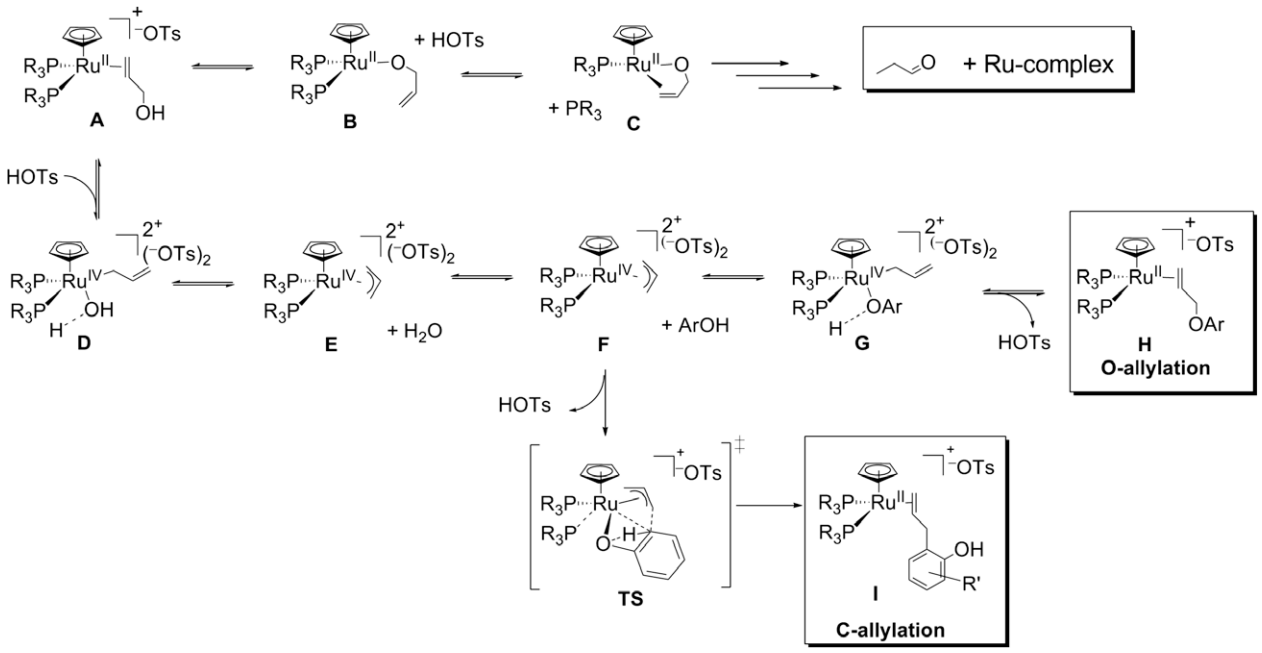
Addition of protons will affect the catalytic performance of the Ru complexes twofold. First, added protons in mM quantities will dramatically suppress formation of the alcoholate species **B** by orders of magnitude due to a strong shift to the left of the alcoholate forming equilibrium (**A** ⇆ **B** + HOTs). This will thus strongly inhibit the catalytic isomerization pathway.

Secondly, whereas the concentration of the major species in solution olefin-bound allyl alcohol (**A**) is not expected to be influenced by protons, a possible subsequent oxidative addition onto Ru(II) of the C–O bond in allyl alcohol will be strongly enhanced by protons, similar to that observed with other RuCp(PP)–cationic complexes [6,7]. The significantly lower barrier for oxidative addition of species **A** caused by acid is rationalized by protonation of the OH moiety, thus transforming the poor hydroxyl leaving group into water as a good leaving group. This results initially in σ-allyl species **D**, which subsequently rearranges to π-allyl intermediate **E**. As oxidative addition is thought to be rate determining for allylation, one can thus rationalize that added protons dramatically increase the rate of allylation at the cost of allyl alcohol isomerization.

After exchange of water with a phenol to form species **F**, either the microscopic analogous reverse reaction of (acid-promoted) oxidative addition, i.e. reductive elimination of the allyl ether takes place via a species **G**, eventually forming allyl ether bound species **H**, or alternatively C-allylation of the phenol occurs, forming eventually Ru-bound C-allylated phenol product **I**. It is thought that for C-allylation to occur, some mode of phosphine dissociation in species **F** has to take place to allow for the formation of transition state **TS**, in which an intramolecular electrophilic attack at *ortho*-C–H positions of the O-coordinated phenol by the allyl moiety may occur.

As is observed from the experiments, the selectivity for O-allylation (pathway **F** → **G** → **H**) is very high under the optimal reaction conditions. Previously, it was concluded that restriction of coordination space around the ruthenium(IV) intermediate favors O-allylation and inhibits C-allylation [6,7]. Complexes with relatively large bite angle diphosphine ligands indeed have restricted coordination space around the Ru(IV) and thus favor the formation of O-allylated product. Although in the present RuCp(PP) complexes, containing two monodentate phosphine ligands, the P–Ru–P coordination angle can formally not be regarded as a bite angle in the sense of bidentate diphosphine ligands, it is yet instructive to consider the P–Ru–P coordination angle as such and to compare this angle with the bite angle of bidentate phosphine ligands in corresponding complexes. Indeed, the precursor of the active catalyst, [RuCpCl(PPh$_3$)$_2$], has a P–Ru–P angle of 107° [13], and under the conditions used here, it shows high selectivity for O-allylation similar to that of the complexes [RuCp(dppb)](OTs) and [RuCp(dpppe)](OTs) with large bite angle ligands (Table 2). Since it is assumed that phosphine dissociation is relatively easy in [RuCp(dppb)](OTs) and especially [RuCp(PPh$_3$)$_2$](OTs) in the Ru(II) oxidation state, it seems counterintuitive that these complexes hardly form C-allylated products and are very selective for O-allylation. However, it must be noted that selectivity in the allylation reaction (i.e. O- vs. C-allylation) is determined in the Ru(IV) state; phosphine dissociation is expected to be much less favored here, because of the highly electrophilic character of the Ru(IV) center. Furthermore, it must be taken into account that these complexes are active at lower reaction temperatures, which also influences the rate of dissociation. We thus propose that in species **F** (Scheme 3), the phenol molecule will approach the highly electrophilic Ru(IV) center and enter its coordination sphere to give species **G**, thereby forcing the π-allyl fragment to σ-allyl to maintain an 18-electron species; the proton of the phenol will become extremely acidic in **G** because of the very high Lewis acidity of the Ru(IV) center. Thus, the phenol will be deprotonated, which is followed by a relatively fast reductive elimination induced by the large P–Ru–P angle to give **H**.

It is intriguing to note the striking difference between a Ru(II)- and Ru(IV)–alcoholate species concerning the proposed role and



Scheme 3. Catalytic intermediates for isomerization of allyl alcohol into propanal (**A**–**C**; absence of acid; Ref. [8]) and O- and C-allylation with allyl alcohol as allylating agent (**A**, **D**–**I**; in the presence of acid).

influence of excess of protons (HOTs) on the catalysis and reflecting their vast difference in Lewis acidity. Whereas with Ru(II) species, formation of Ru(II)–alcoholate **B** is strongly suppressed by the addition of acid, no negative effect of acid on the formation of Ru(IV)–phenolate species **G** is invoked.

Allyl phosphonium salt formation of an excess of PPh_3 as observed (Scheme 2), via the allylation reaction of PPh_3, has mechanistic similarity to the allylation of phenol. However, the fact that coordinated phosphines are not susceptible for allylation to form allyl phosphonium salts seems to indicate that the free phosphine attacks the Ru(IV)–bound allyl group from outside the coordination sphere. If phenol, similar to PPh_3, also were to attack the Ru(IV)-bound π-allyl from outside the coordination sphere one, would expect a strong negative order in added acid, as the phenolate concentration outside the coordination sphere will of course be dramatically reduced by protonation. A similar mechanistic detail is proposed for the Tsuji–Trost reaction with palladium, where it is proposed that hard nucleophiles will first coordinate to the metal center, followed by reductive elimination, while soft nucleophiles such as a phosphine will attack from outside the coordination sphere [21].

Finally, the observation that a complex containing two monodentate ligands has a much higher activity for the allylation reaction than complexes with bidentate phosphine ligands seems to indicate that for the rate-determining oxidative addition of allyl alcohol, some mode of dissociation of a phosphine may occur. However, this must be a mode in which the PPh_3 ligand does not fully leave the coordination sphere, since it was shown that free PPh_3 reacts rapidly to form the allyl phosphonium salt, which would lead to rapid deactivation of the catalyst due to PPh_3 consumption. It is thought that the monodentate phosphine ligands with a more flexible coordination configuration probably can easily move aside to accommodate the space needed for approach of the C–O moiety of allyl alcohol and subsequent oxidative addition. A more facile approach of the C–O moiety to the Ru(II) center with monodentate ligands compared to bidentate ligands is thus believed to be at the basis of the high activity for allylation with the $[Ru(II)Cp(PPh_3)_2]^+$ complex.

4. Conclusions

In summary, we have found that the allyl alcohol isomerization catalyst $[RuCp(PPh_3)_2](OTs)$ can be forced into new reactivity with allyl alcohol. In the presence of acid and at relatively mild temperatures, the catalyst is highly active and selective for the O-allylation of phenols with allyl alcohol, outperforming the catalysts with bidentate phosphine ligands previously reported. Very high turnover numbers can be achieved, indicative of a highly stable catalyst.

The observations lead to refinement of some mechanistic details proposed earlier for Ru-catalyzed allylation, in particular with respect to catalyst activity and selectivity for O- vs. C-allylation of phenols. In the presence of excess of monodentate phosphine ligand and acid, rapid allylation of phosphine, yielding allyl phosphonium salts, also takes place. The observations imply similarities, but also distinct differences between the allylation of phenol and that of a phosphine such as PPh_3. The main difference lies in the product-forming steps, i.e. the formation of allyl phenyl ether and allyl phosphonium salt, respectively. The formation of allyl phenyl ether requires pre-coordination of phenol at the strongly Lewis acidic Ru(IV)–allyl center, before reductive elimination of the allyl ether takes place, while the allyl phosphonium salt is formed by attack of the free phosphine from outside the Ru(IV) coordination sphere on the allyl fragment at Ru(IV), followed by protonation.

Although we have rationalized several observations, it is clear that further mechanistic and theoretical studies (DFT) are required to fully understand the organometallic elementary steps underlying the catalysis. This is subject of future publications.

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