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Rhodium-catalysed isomerisation of allylic alcohols in water at ambient temperature†

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An environmentally benign method for the transformation of allylic alcohols into carbonyl compounds is described. Using $[Rh(COD(CH_3CN)_2]BF_4$ (**2**) in combination with 1,3,5-triaza-7-phosphaadamantane (PTA, **1**) as the catalytic system in water results in a very fast redox isomerisation of a variety of secondary allylic alcohols at ambient temperature. Also, some primary allylic alcohols can be isomerised into the corresponding aldehydes. The active complex, which in some cases can be used in catalyst loadings as low as 0.5 mol%, is formed *in situ* from commercially available reagents. Based on deuterium labelling studies, a tentative mechanism involving metal-enone intermediates is presented.

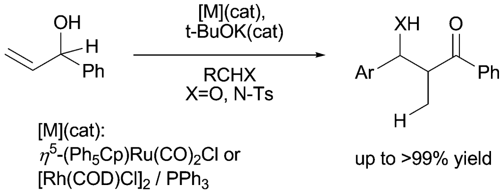
Introduction

The design of chemical transformations with low environmental impact is recognized by both industry and academic research as increasingly important. In this context, the development of atom-efficient transformations and reactions occurring at ambient temperature, as well as the use of non-toxic, non-hazardous solvents is highly desirable.[1,2] As an inexpensive, and unarguably readily available and renewable feedstock, water is attracting attention as a replacement for traditionally used organic solvents. The number of examples of highly selective and efficient transition metal promoted reactions performed in water is growing, not only due to environmentally beneficial reasons, but also due to the reactivity that sometimes can be achieved with such a highly polar, protic and coordinating solvent.[3]

The transition-metal-catalysed redox-isomerisation of allylic alcohols is an atom-economical route to ketones and aldehydes. Various transition metal complexes catalyse the transformation, which has been extensively studied in organic solvents.[4,5,6a,e] Several catalytic systems working in aqueous media or biphasic organic-water solvent systems have also been reported, and in particular, complexes of Ru,[6] Rh,[7] and Ni[8] have been used. A common strategy for reactions occurring in water is to immobilize the metal in the aqueous phase by using water soluble phosphines. This approach facilitates separation of the organic products from the aqueous phase containing the catalyst by simple phase separation or extraction. Some frequently used water soluble ligands are sulfonated phosphines [*e.g.* triphenylphosphine-3,3′,3″-trisulfonic acid trisodium salt (TPPTS) or sodium 3-(diphenylphosphino)benzenesulfonate (TPPMS)][9] and phosphatriazaadamantane (PTA).[10]

Despite numerous reports in the literature, examples of the transformation occurring under very mild reaction conditions where water is used as the only solvent are rare. Very efficient isomerisations of allylic alcohols occurring at temperatures above 60 °C using bis-allyl Ru[IV] dimer $[\{Ru(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(\mu\text{-}Cl)Cl\}_2]$ and mononuclear $[Ru(\eta^3{:}\eta^2{:}\eta^3\text{-}C_{12}H_{18})Cl_2]$ have been reported by Cadierno, Sordo, Gimeno *et al.* Catalyst activities could be retained even at very low loadings, leading to TOFs up to 50 000 h^{-1} and TONs of 10^6 for the isomerisation of 3-buten-2-ol into butane-2-one in water.[6a,e] However, when applied to 1,1- or 1,2-disubstituted allylic alcohols, higher catalyst loadings (5–10 mol%) were required. Rh-complexes in combination with aryl sulfonated phosphines (*e.g.* TPPMS, TPPTS)[7a–c] and/or phase transfer catalysts[7d,e] have also been used for isomerisations of allylic alcohols in biphasic systems. In addition, size-selective isomerisation of small allylic alcohols at room temperature using a supramolecular guest-host approach has been demonstrated in water using Gd-encapsulated Rh complexes.[11] The few examples in the literature of catalysts that promote the transformation at ambient temperature in water either require high catalyst loadings or highly basic conditions.[6h,7e,11]

During the last year we have been involved in the development of aldol and Mannich-type tandem isomerisations/C–C bond formations of allylic alcohols with aldehydes and *N*-tosylimines (Scheme 1).[12] The reactions are catalysed by ruthenium and rhodium complexes in combination with a catalytic amount of base.



Scheme 1

In the absence of aldehydes or *N*-tosylimines, our catalytic systems catalyse the isomerisation of allylic alcohols to their

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† Electronic supplementary information (ESI) available: General methods, characterisation data and deuterium labelling experiment. See DOI: 10.1039/c004964f

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corresponding carbonyl compounds in excellent yields and under very mild reaction conditions.[12] One of the keys to the success of the isomerisation under our reaction conditions is the efficient activation of the metal halides by ^{t}BuOK, which promotes a catalytic cycle *via* metal alkoxide intermediates. We envisioned that transition metal alkoxide complexes could also be formed from transition metal hydroxo or aqua complexes as the catalyst precursor. Rhodium hydroxo or aqua complexes can be easily formed when water is used as the solvent.[13,14,15]

Here, we report a very fast isomerisation of allylic alcohols catalysed by a cationic water soluble Rh(I) complex formed *in situ* from commercially available 1,3,5-triaza-7-phosphaadamantane (PTA, **1**) and [Rh(COD)(CH$_3$CN)$_2$]BF$_4$ (**2**) using water as the only solvent at ambient temperature.

Results and Discussion

We investigated the ability of two different rhodium sources (5 mol% Rh), [Rh(COD)Cl]$_2$ (**3**) and [Rh(COD)(CH$_3$CN)$_2$]BF$_4$ (**2**), and two water soluble phosphines, sodium (4-methoxy-3-sulfonatephenyl)-diphenylphosphine (**4**, abbreviated as MeO–TPPMS) and 1,3,5-triaza-7-phosphaadamantane (**1**, PTA) (Fig. 1), as catalysts in the isomerisation of allylic alcohol **5a** into ketone **6a** (Scheme 2). The results are shown in Table 1.

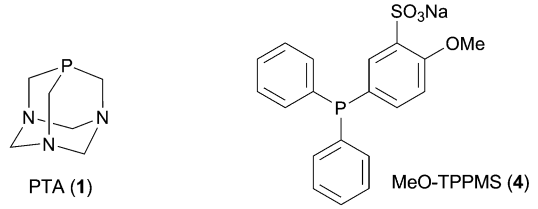
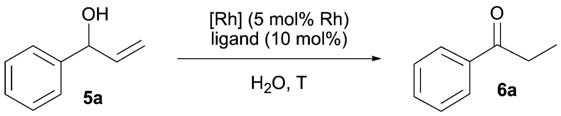


Fig. 1



Scheme 2

Both the cationic Rh(I) complex **2** and Rh(I)–Cl **3** in combination with the sulfonated ligand (**4**) afforded complete conversion of α-vinylbenzyl alcohol **5a** into propiophenone **6a**, although the transformations were efficient only at high temperature (80 °C) (entries 1 and 6 *vs.* 2 and 7). Addition of base (NaOH) in order to facilitate displacement of the chloride ligand of **3** afforded a very low yield of **6a** at room temperature (entry 3). However, when employing **3** in combination with ligand **1**, addition of a base was a requirement for selective formation of **6a** (entry 4 *vs.* 5). Finally, we were pleased to find that the combination of [Rh(COD)(CH$_3$CN)$_2$]BF$_4$ (**2**) and PTA (**1**) displayed dramatically higher reaction rates than the other metal/ligand combinations. The reaction was finished in only 5 min at ambient temperature using 2 mol% Rh and was fully selective for the formation of **6a** (entry 8). In the absence of ligand, rearrangement of **5a** into cinnamyl alcohol emerged as the dominant pathway with either Rh source (Table 1, entries 9–10). Lower conversions were obtained when switching to THF as the solvent (entry 11).[16] We also investigated the optimal amount of water, however, no apparent difference in rate was observed between catalyst concentrations of 8 mM to 1 mM, although the reaction times are highly dependent on vigorous stirring.[17]

With the best catalytic system [Rh (**2**, 2 mol%), PTA (**1**, 4 mol%), Table 1, entry 8], we investigated the possibility of lowering the catalyst loading. Results are shown in Table 2. Excellent yields were also obtained after 15 min at room temperature when using 1 mol% of Rh catalyst (Table 2, entry 2). At 60 °C using 0.5 mol% Rh, the reaction was complete within 5 min (entry 3) corresponding to a TOF[18] of 2400 h^{-1}. Lower catalyst loadings (0.25 mol% of Rh) resulted in lower conversions (entry 4). By lowering the Rh/phosphine ratio (Rh/PTA = 1/1), the rate of the reaction notably decreased (entry 5 *vs.* 2).

The pH of the aqueous solution may affect the rate of isomerisation due to structural changes in the catalyst or catalytic intermediates, and due to variations in substrate solubility. Base-accelerated isomerisations of allylic alcohols have been rationalized by the formation of metal alkoxides rather than alcohol complexes, although halogen abstraction from a catalyst precursor has often played a major role in the acceleration.[19] In the case of aqueous reaction media, both

Table 1 Rh-catalysed redox-isomerisation of allylic alcohol **5a**.[a]

Entry	[Rh]	Ligand	Base[b]	*T*/°C	Time	Conversion[c] (%)	Selectivity[c] (%)	**6a**[c] (%)
1	[Rh(COD)Cl]$_2$ (**3**)	MeO–TPPMS (**4**)	—	80	17 h	100	>99	>99
2	**3**	**4**	—	40	18 h	10	>99	10
3	**3**	**4**	NaOH	rt	18 h	33	>99	33
4	**3**	PTA (**1**)	—	80	17 h	100	48	48
5	**3**	**1**	NaOH	80	18 h	100	>99	>99
6	[Rh(COD)(CH$_3$CN)$_2$]BF$_4$ (**2**)	**4**	—	80	19 h	100	>99	>99
7	**2**	**4**	—	rt	18 h	10	>99	10
8[d]	**2**	**1**	—	rt	5 min	100	>99	>99
9	**3**	—	—	80	18 h	90	16	14
10	**2**	—	—	80	18 h	100	8	8
11[e]	**2**	**1**	—	60	1 h	36	>99	36

[a] All reactions were carried out in a sealed tube under a nitrogen atmosphere. Unless otherwise stated, a solution of [Rh(COD)(CH$_3$CN)$_2$]BF$_4$ (**2**, 5 mol%) and PTA (**1**, 10 mol%) in degassed, deionised H$_2$O (1 mL) was added to **5a** (0.4 mmol) and the mixture was stirred at the appropriate temperature for the time indicated. The tube was opened (if heated, the mixture was poured onto ice) and instantly extracted with diethyl ether. [b] 10 mol%. [c] Determined by ^{1}H-NMR spectroscopy. [d] 2 mol% Rh and 4 mol% PTA were used. [e] THF was used as solvent, 2 mol% Rh, 4 mol% PTA.

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Table 2 Catalyst loading screening in the isomerisation of **5a** to **6a** catalysed by $[Rh(COD)(CH_3CN)_2]BF_4$ (**2**) and PTA (**1**)[a]

Entry	Rh (**2**) (mol%)	PTA (**1**) (mol%)	$T/°C$	t/min	Selectivity[b] (%)	**6a**[b] (%)
1	2	4	rt	5	100	100
2	1	2	rt	15	100	99
3	0.5	1	60	5	100	100
4	0.25	0.5	60	60	100	91
5	1	1	rt	30	100	21

[a] A solution of $[Rh(COD)(CH_3CN)_2]BF_4$ (**2**) and PTA (**1**) in degassed, deionised H_2O ([Rh] = 8 mM) was added to **5a** (0.4 mmol) and the mixture was stirred at the appropriate temperature for the time indicated under a nitrogen atmosphere. The tube was opened (if heated, the mixture was poured onto ice) and instantly extracted with diethyl ether. [b] Determined by ^{1}H-NMR spectroscopy.

acids[8] and bases[6b,d] have been used to promote transition-metal-catalysed isomerisations of allylic alcohols, and strong pH dependence was observed for some of the studied catalysts.[6f,g] In addition, PTA (**1**) has a pK_a of 5.7–6.0, and will be protonated to form $[PTA–H]^+$ in acidic water solutions.[10] Even though the pH of the deionized water in our lab varied noticeably from day to day (~4 to ~6), we could not observe any differences in reactivity between different days. Nevertheless, additional measurements were carried out in order to investigate any pH dependence of the catalytic system. The isomerisation of **5a** in buffered water solutions with pH ranging from 2 to 11 is shown in Fig. 2. In order to compare the reactivity, the reactions were analysed before they reached full conversion (after 5 min using 1 mol% Rh). The highest conversions (54–39%) were found from neutral to basic pH. At lower pH, the conversion drops. However, when unbuffered water solutions were used, the sensitivity towards low pH was not as pronounced, and when using 2 mol% of Rh (**2**) the reaction reached full conversion within 5 min from pH 3.4 to 9. A plausible explanation is that the salt concentration affects the outcome of the reaction, as it has been observed before for Rh-catalysed hydroformylation reactions in water.[20] In all cases, the reaction showed complete selectivity (the only product observed was **6a**). Nevertheless, no major differences were observed when switching between a neutral phosphate buffer (pH 7) and deionised water. Thus, any further reactions were run in regular deionised water.

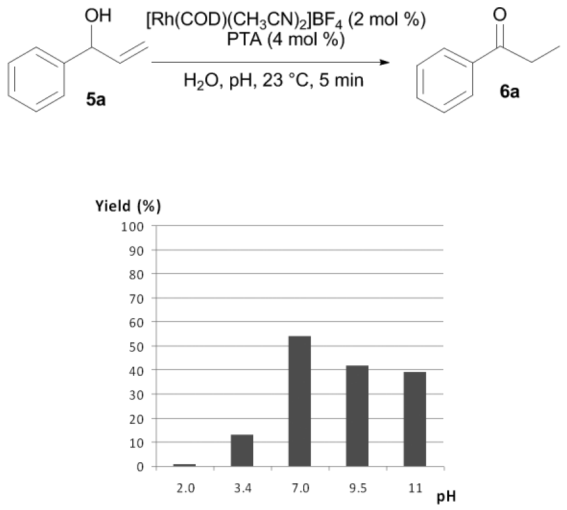
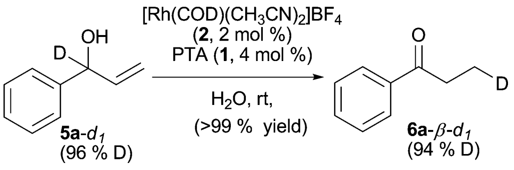


Fig. 2 Yield of **6a** after 5 min in phosphate buffered water solutions (50 mM) with varying pH. **5a**:[Rh]:PTA = 100 : 1 : 2. All reactions were run at ambient temperature.

The catalytic activities of Rh (**2**)/PTA (**1**) towards a range of allylic alcohols were compared to investigate the scope and limitations of the catalytic system. The results are shown in Table 3. The highest activities were found towards aromatic allylic alcohols with only one substituent on the double bond (entries 1–5). Thus, alcohols **5a–5e** afforded the corresponding ketones in quantitative yield in short reaction times at ambient temperature. A gram-scale experiment, in which 10 mmol (1.35 g) of allylic alcohol **5a** were used, afforded the isomerisation product **6a** in excellent yield (>99% yield by NMR analysis, 83% isolated). Also aliphatic allylic alcohols **5f** and **5g** were efficiently isomerised (entries 6–7, respectively). The catalytic system is sensitive towards steric hindrance. Thus, **5h**, bearing two allylic alcohols with a different degree of substitution, yielded **6h** as the only product (entry 8). In general, when the double bond presents a higher degree of substitution, higher temperatures are needed and full conversion cannot always be achieved (entries 9–11). The cyclic allylic alcohol **5l** could be however isomerised in quantitative yield (entry 12). Primary allylic alcohols **5m** and **5n** were isomerised in moderate to good yields (entries 13–14). Unless otherwise stated, >99% selectivity was obtained.

Mechanistic investigations

Deuterated allylic alcohol **5a**-d_1 afforded ketone **6a**-β-d_1 in quantitative yield without deuterium loss, indicating that a 1,3-hydrogen (deuterium) shift takes place (Scheme 3).



Scheme 3

When allylic alcohol **5o** was subjected to the isomerisation conditions in the presence of an equimolar amount of deuterated allylic alcohol **5a**-d_1, deuterium scrambling was not observed.[21] Thus, the hydrogen (deuterium) shift takes place intramolecularly (Scheme 4).

Isomerisation of allylic alcohol **5a** in D_2O afforded α-deuterated ketone **6a** (**6a**-α-d_1, 97% D) (Scheme 5). A control experiment where non-deuterated ketone **6a** was subjected to the same reaction conditions during the same reaction time did not afford any detectable amounts of deuterated ketone

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Table 3 Rh-catalysed redox-isomerisation of allylic alcohols.[a]

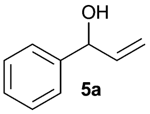
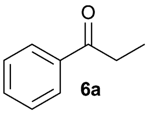
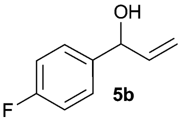
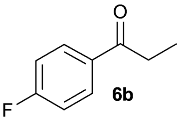
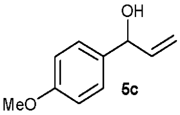
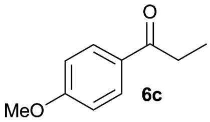
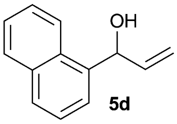
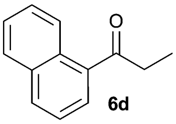
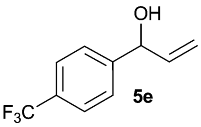
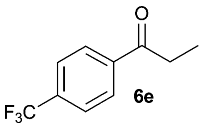
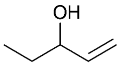
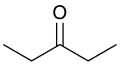
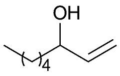
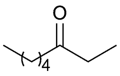
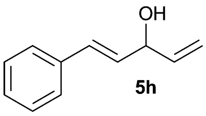
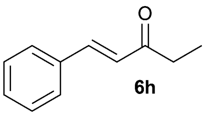
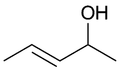
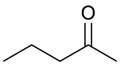
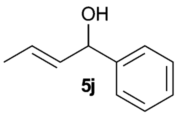
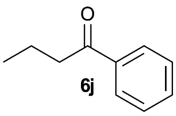
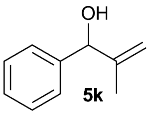
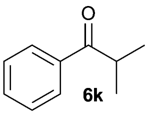
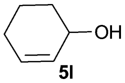
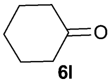
Entry	Substrate	Product	T/min	$T/°C$	Yield (%)[b]
1[c]	 **5a**	 **6a**	5	23	> 99
2	 **5b**	 **6b**	15	23	98
3	 **5c**	 **6c**	15	23	>99
4	 **5d**	 **6d**	60	23	> 99
5	 **5e**	 **6e**	60	23	>99
6	 **5f**	 **6f**	80	23	>99
7	 **5g**	 **6g**	120	23	>99
8	 **5h**	 **6h**	180	23	92[e]
9[d]	 **5i**	 **6i**	160	50	>99
10	 **5j**	 **6j**	720	50	51[f]
11	 **5k**	 **6k**	22	80	30[g]
12	 **5l**	 **6l**	720	23	>99

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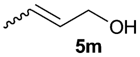
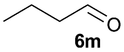
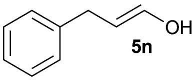
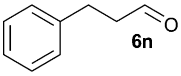
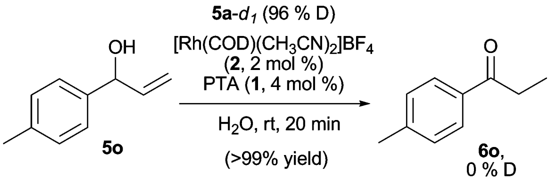
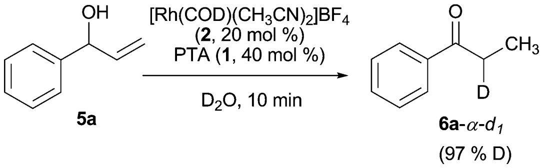
Table 3 *(Contd.)*

Entry	Substrate	Product	T/min	T/°C	Yield (%)[b]
13	 **5m**	 **6m**	90	23	92[h]
14	 **5n**	 **6n**	45	50	59[h,i]

[a] The reactions were carried out under a N_2 atmosphere using the corresponding allylic alcohols (0.4 mmol or 0.8 mmol), $[Rh(COD)(CH_3CN)_2]BF_4$ (**2**, 2 mol%) and PTA (**1**, 4 mol%) in degassed, deionised H_2O (1 mL or 2 mL) at the temperature indicated. [b] Yields were determined by ^1H NMR spectroscopy with respect to unconverted starting material or an internal standard. [c] When 10 mmol of **5a** were used, >99% yield of **6a** was obtained. [d] *cis*:*trans* ratio of **5i** ~1 : 9. [e] 8% unconverted **5h**. [f] Formed together with 4-phenyl-2-butanone (24%), 4-phenyl-3-buten-2-one (12%), 4-phenyl-3-buten-2-ol (4%) and 1-phenyl-butanol (9%). [g] 70% unconverted **5k**. [h] Yield measured with respect to 1,4-dimethoxybenzene as internal standard. [i] 100% conversion.



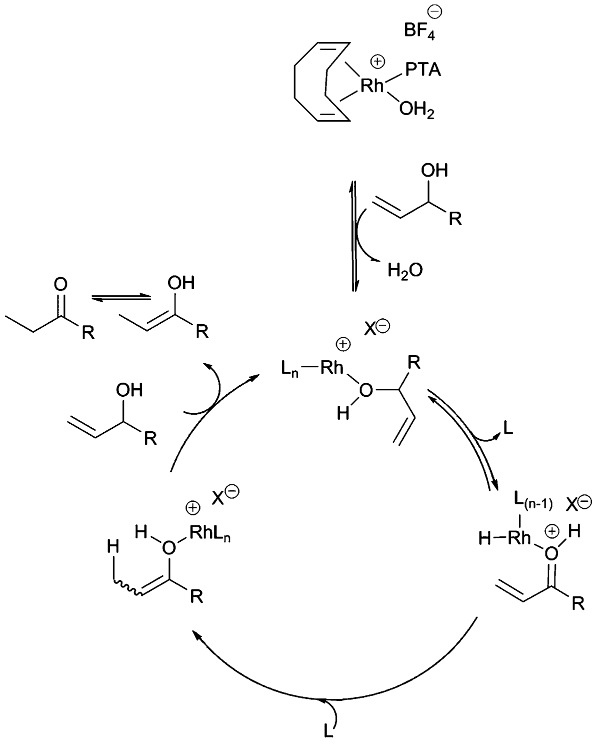
Scheme 4



Scheme 5

6a-α-d_1. These results indicate that enolates or enols are involved in the isomerisation mechanism. Importantly, if Rh–hydrides originating from the solvent were acting as catalytic species, deuterium incorporation at the β position of the ketone would have been observed.[22] To test this possibility, we used a higher catalyst loading (20 mol%) for this experiment (Scheme 5), and found that no deuterium was incorporated at the β position in ketone **6a**.[6h] This result, together with the crossover experiment in Scheme 4, leads us to exclude a mechanism in which the first step is the reaction of a Rh–hydride with the allylic alcohol.

Based on the results shown in Schemes 3–5, we believe that the mechanism of the isomerisation under our reation conditions is similar to that proposed by Trost and Kulawiec,[23] and recently studied theoretically by Cadierno, Sordo, and Gimeno.[6a] Thus, after formation of an alcohol complex, the first step is the oxidation of the allylic alcohol to the corresponding α,β-unsaturated ketone producing a [Rh–H] species (Scheme 6). The hydride is immediately transferred to the double bond of the same molecule, producing a metal enol or enolate intermediate,[24] depending on the pH of the reaction mixture. The reaction works in a very wide range of pH, as shown in Fig. 2. We believe that the mechanism may change with the pH, and that at neutral or slightly acidic pH, metal alcohol complexes rather that metal alkoxide complexes may be involved.



Scheme 6 Proposed mechanism.

Conclusions

The cationic complex $[Rh(COD)(CH_3CN)_2]BF_4$ (**2**) in combination with phosphatriazaadamantane (PTA, **1**) catalyses the isomerisation of allylic alcohols at ambient temperature in aqueous media. The isomerisations take place very quickly, and in some instances the reaction is completed in less that 5 min. The catalyst is prepared *in situ* from commercially available sources, and catalyst loadings as low as 0.5 mol% can be used. Mechanistic investigations using deuterium labelled allylic alcohols or deuterated water indicate that a 1,3-hydrogen shift takes place intramolecularly, and that a consecutive formation of Rh–alcohol, –enone, and –enol intermediates may take place. To the best of our knowledge, this is the most efficient isomerisation of allylic alcohols using water as the only solvent under very mild (ambient temperature, neutral pH) reaction conditions.

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Experimental

General

All reactions were carried out under a nitrogen atmosphere. Deionised water was degassed by bubbling through a stream of nitrogen for 30 min prior to use. Reagents were of analytical grade, and used as obtained from commercial suppliers without further purification. Compounds **4**,[25] **5a–e**, **5h**, **5j**,[26] and **5a**-d_1[12a] were prepared by methods previously described in the literature. Compounds **5f–g**, **5i**, **5l–n** were used as obtained from supplier. Flash chromatography was carried out on 60 Å (35–70 μm) silica gel. ^{1}H and ^{13}C NMR spectra were recorded at 400 or 500 MHz and at 100 or 125 MHz, respectively, on a Bruker Advance spectrometer. Chemical shifts (δ) are reported in ppm, using the residual solvent peaks in $CDCl_3$ (δ_H 7.26 and δ_C 77.00) as internal standard. Coupling constants (J) are given in Hz. High resolution mass spectra (HRMS) were recorded on a Bruker microTOF ESI-TOF mass spectrometer.

General procedure for the isomerisation of allylic alcohols in water

To the allylic alcohol (**5**, 0.4 mmol or 0.8 mmol) was added an 8 mM solution of $[Rh(COD)(MeCN)_2]BF_4$ (**2**, 1 or 2 mL, 0.008 mmol or 0.016 mmol, 2 mol%) and PTA (**1**, 0.016 mmol or 0.032 mmol, 4 mol%) in water. The reaction was vigorously stirred (1500 rpm) in a closed tube at room temperature (or the temperature indicated) for the appropriate time (see Table 3). The tube was opened, and the reaction mixture immediately extracted with Et_2O (3×0.5 mL). If heated, the mixture was poured onto ice prior to extraction. The reactions were analysed by TLC and ^{1}H-NMR spectroscopy.

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