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PAPER

Ruthenium(IV) catalysts for the selective estragole to *trans*-anethole isomerization in environmentally friendly media†

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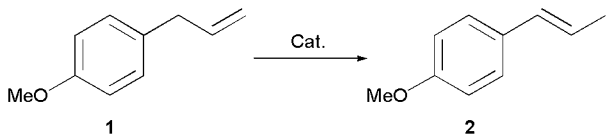
Several ruthenium(IV) complexes have been tested as potential catalysts for the isomerization of estragole into anethole using water and glycerol as alternative green reaction media. Best results in terms of activity and *E*-selectivity were obtained with the dimeric species [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl) and the mononuclear derivative [$RuCl_2$(η^3:η^3-$C_{10}H_{16}$){$P(OMe)_3$}]. In particular, using a ruthenium loading of 1 mol%, almost quantitative and stereoselective formation of *trans*-anethole (*trans*/*cis* ratios = 99 : 1) could be reached at 80 °C in short times (5–30 min) employing water–MeOH (EtOH) or glycerol–MeOH (EtOH) mixtures (1 : 1 v/v) as solvent. Recyclability issues have also been addressed.

Introduction

The catalytic isomerization of olefins is a well established process in organic chemistry with widespread academic and industrial applications.[1] Transformation of allyl-benzenes into the corresponding 1-propenyl derivatives is a clear example of the synthetic utility of this textbook reaction since the latter are common starting materials in the flavour and fragrance industries.[2] In this sense, the selective isomerization of estragole **1** (1-allyl-4-methoxybenzene), readily accessible by distillation of crude sulfate turpentine,[3] into *trans*-anethole **2** (1-methoxy-4-((*E*)-1-propenyl)benzene) represents nowadays the main route used for the large-scale production of this chemical (Scheme 1),[4,5] a naturally-occurring compound which has been traditionally extracted from anise or fennel oils.[6,7] The increasing demand of **2**, widely employed by industry to enhance the flavour of foods and alcoholic beverages,[2,6a] in the formulation of oral hygiene products[8] or as an advanced intermediate for the preparation of pharmaceutical compounds[9] and perfumery chemicals,[2,6a] has made extraction from natural sources not sufficient to supply the market, hence the need to produce it synthetically.[10]



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Scheme 1 The estragole **1** to *trans*-anethole **2** isomerization.

Currently, the industrial isomerization of estragole to anethole is performed with excess of KOH,[10,11] a procedure that presents several major drawbacks: (*i*) a high temperature is required (200 °C), (*ii*) yields are only moderate (*ca.* 60%), (*iii*) a large quantity of basic wastes are generated, which leads to inconvenient pollution effects, and (*iv*) the process is not stereoselective, *i.e.* a mixture of *trans* and *cis* isomers is formed in 82 : 18 ratio, making necessary an energy-consuming fractional distillation step to obtain *trans*-anethole **2** in pure form.[12] This stereoselectivity issue deserves to be highlighted: only the *trans* isomer is marketed since the *cis* one is characterized by its toxic nature and unpleasant organoleptic properties.[13] Accordingly, the food regulatory instructions given by the Joint FAO/WHO Expert Committee of Food Additives (JECFA) limit the *cis*-anethole content to a maximum of 1% for human use.[14] To overcome all these limitations, several protocols using heterogeneous[15] and homogeneous[16] metal-based catalysts have been devised. However, only a few generate anethole enriched above 97% in its *trans* isomer.[16a,e,h] Consequently, the search for efficient and selective catalytic systems able to promote the estragole **1** to *trans*-anethole **2** isomerization still remains a challenge for synthetic chemists.

On the other hand, chemical transformations are currently experiencing a deep change to meet sustainability criteria imposed by the Green Chemistry principles.[17] One of them is to circumvent the use of hazardous solvents, as they are responsible for a large part of the waste generated by the chemical processes. The wanted characteristics for a green

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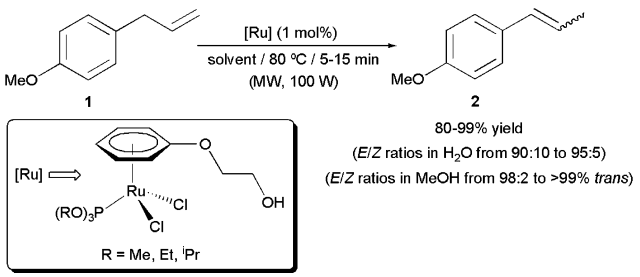
† Electronic supplementary information (ESI) available: Copies of the ^{1}H and ^{13}C{^{1}H} NMR and GC spectra of *trans*-anethole generated at 35 °C using **5f** as catalyst in water (Scheme 4). Copy of the GC spectrum of the *cis*/*trans*-anethole mixture generated at 80 °C using **5f** as catalyst in water (entry 11 in Table 2). See DOI: 10.1039/c0gc00417k

solvent include: no toxicity, no flammability, high availability, obtaining from renewable sources and biodegradability.[18] Water has been for long time the first solvent of choice regarding the aforementioned considerations.[18] Indeed, it is now well-accepted that water is a reliable alternative to the organic, petroleum-based, solvents commonly used by the chemical community.[19] In recent years, with the increase in biodiesel production worldwide, the availability of glycerol has tremendously increased and finding new applications for this low-cost raw material has become an urgent necessity.[20] As water, glycerol meets the requirements needed to be considered as a green solvent. In fact, its use as an alternative medium for organic reactions has emerged as a promising new field of research that is waiting to be explored in depth.[21,22]

Despite this growing interest to develop environmentally benign and safe processes, estragole to *trans*-anethole isomerizations using green reaction media have been neglected. Only in the context of a broader study by our own group, some experiments in water have been described employing elaborated (η^6-arene)-ruthenium(II) complexes as catalysts.[23] However, as shown in Scheme 2, the results obtained in this medium were not completely satisfactory in terms of *trans*/*cis* stereoselectivity. Only the use of methanol as solvent allowed to generate anethole with a *trans*-selectivity ≥99% with these Ru(II) catalysts.



Scheme 2 Estragole to anethole isomerization in methanol and water using hydrophilic (η^6-arene)-ruthenium(II) complexes.

With the aim of finding more readily accessible catalysts for this key transformation, we turned our attention to the commercially available bis(allyl)-ruthenium(IV) derivatives [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (**3**; $C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl) and [$RuCl_2$(η^3:η^2:η^3-$C_{12}H_{18}$)] (**4**; $C_{12}H_{18}$ = dodeca-2,6,10-triene-1,12-diyl) (see Fig. 1),[24] whose outstanding ability to promote C=C migrations in water has been largely demonstrated.[25] Thus, in this work an evaluation of their suitability for the selective estragole to *trans*-anethole isomerization in environmentally friendly media (water and glycerol) is presented.

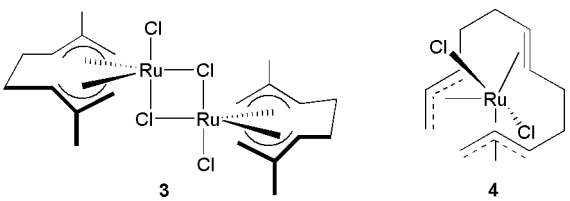
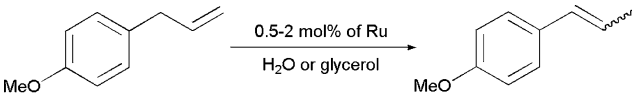


Fig. 1 Structure of the bis(allyl)-ruthenium(IV) complexes **3** and **4**.

Table 1 Estragole to anethole isomerization in environmentally friendly media using the bis(allyl)-ruthenium(IV) complexes **3** and **4**[a]



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Entry	Cat.	% Ru	Solvent	Temp.	Time	Yield[b]	*E*/*Z*[b]
1	**3**	1 mol (%)	H_2O	80 °C	30 min	>99%	97 : 3
2	**3**	1 mol (%)	Glycerol	80 °C	45 min	>99%	97 : 3
3	**4**	1 mol (%)	H_2O	80 °C	3 h	>99%	94 : 6
4	**4**	1 mol (%)	Glycerol	80 °C	6 h	>99%	95 : 5
5[c]	**3**	1 mol (%)	H_2O	80 °C	10 min	>99%	97 : 3
6[d]	**3**	1 mol (%)	H_2O	80 °C	15 min	>99%	97 : 3
7	**3**	0.5 mol (%)	H_2O	80 °C	2 h	>99%	96 : 4
8	**3**	2 mol (%)	H_2O	80 °C	30 min	>99%	97 : 3
9	**3**	1 mol (%)	H_2O	100 °C	15 min	>99%	97 : 3
10	**3**	1 mol (%)	H_2O	120 °C	5 min	>99%	95 : 5
11	**3**	1 mol (%)	H_2O	35 °C	21 h	>99%	99 : 1
12	**3**	1 mol (%)	Glycerol	35 °C	24 h	94%	98 : 2
13[e]	**3**	1 mol (%)	H_2O	80 °C	15 min	>99%	96 : 4

[a] Reactions performed under N_2 atmosphere using 2 mmol of substrate and 0.5 cm^3 of water or glycerol. [b] Determined by GC. [c] Reaction performed in the presence of 1 mol% of NaOH. [d] Reaction performed in the presence of 1 mol% of H_2SO_4. [e] Reaction performed under MW heating at the indicated temperature (initial MW power 100 W).

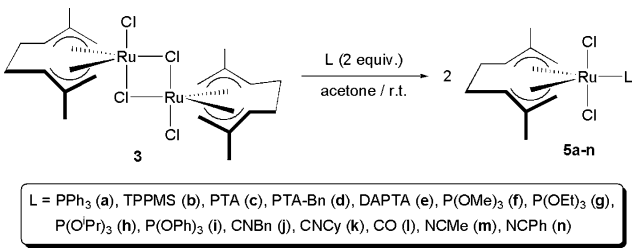
Results and discussion

Initial exploratory experiments were performed at 80 °C with 2 mmol of estragole, a ruthenium loading of 1 mol% and 0.5 cm^3 of the appropriate solvent (water or glycerol), monitoring the course of the reactions by GC analyses of aliquots. Under these conditions, we found that, regardless of the solvent employed, both Ru(IV) complexes are able to generate anethole in almost quantitative yield (≥99% by GC) after 0.5–6 h of heating (entries 1–4 in Table 1). However, the reactions proceeded significantly faster in water than in glycerol (entry 1 *vs.* 2 and 3 *vs.* 4). From these initial studies the dimeric species [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (**3**) emerged as the catalyst of choice due to its high efficiency (quantitative conversions in less than 1 h) and remarkable selectivity towards the desired *trans*-anethole isomer (*E*/*Z* ratios = 97 : 3) (entries 1–2).

Several attempts to improve the selectivity of the process were then performed using **3** under aqueous conditions. In this sense, we firstly explored the influence of the pH medium. To this end, reactions were performed in the presence of one equivalent of NaOH or H_2SO_4 per ruthenium (entries 5 and 6). Faster transformations were in both cases observed but, in terms of selectivity, the results obtained were identical to those reached in neutral water. No influence of the catalyst loading on the selectivity was observed (entries 7–8). Finally, the effect of the temperature was explored (entries 9–11) and, to our delight, we found that an almost complete selectivity towards *trans*-anethole can be reached (*E*/*Z* ratios = 99 : 1) performing the catalytic reaction at 35 °C (entry 11). However, an extremely long reaction time (21 h) was needed to totally consume the starting estragole. Similarly, improvement of the selectivity was also noticed at 35 °C when glycerol was used as solvent (entry 12), albeit an incomplete reaction was in this case observed after 24 h. By contrast, at higher temperatures (100–120 °C),

the reactions were significantly faster but less selective (entries 9–10). This temperature effect on the stereoselectivity is quite surprising since, as previously observed by others,[15b,d] an increase in temperature would lead to a greater selectivity towards the thermodynamically more stable *trans*-isomer.[26] Degradation of the catalytically active species with temperature could be responsible of these unexpected results. In accordance with the negative effect of temperature on the stereoselectivity, it is not surprising that a poor result was also obtained under MW heating, the only positive effect of microwave irradiations being the improvement of the reaction rate (entry 13).[27]

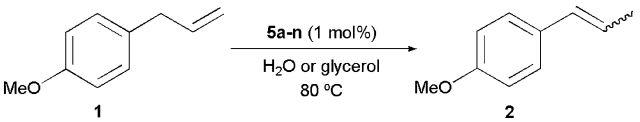
Seeking to find a more competitive catalyst, a series of mononuclear derivatives $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(L)]$ (**5a–n**) were synthesized by cleavage of the chloride bridges of $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (**3**) with phosphines (**5a–e**), phosphites (**5f–i**), isocyanides (**5j–k**), carbon monoxide (**5l**) or nitriles (**5m–n**) (see Scheme 3; details are given in the Experimental).[28] We reasoned that the introduction of these ligands, presenting quite different electronic and steric properties, on the coordination sphere of ruthenium should exert some influence on the outcome of the isomerization process in terms of activity as well as *trans*/*cis* selectivity. The ability of these mononuclear species to promote the estragole to anethole isomerization was evaluated in both water and glycerol. Table 2 provides a summary of the results obtained performing the catalytic reactions at 80 °C with a metal loading of 1 mol%.



Scheme 3 Synthesis of the mononuclear bis(allyl)-ruthenium(IV) complexes **5a–n**.

As shown in the table, despite all the complexes synthesized were found to be active catalysts in the isomerization of estragole, none of them proved to be more active or selective than dimer **3**. In fact, only $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\{P(OMe)_3\}]$ (**5f**) showed an effectiveness comparable to that of **3**, being able to convert quantitatively **1** into **2** after only 30 min (water) or 1 h (glycerol) of heating, albeit with a slightly lower *trans*/*cis* selectivity (95 : 5; entries 11–12). In the rest of the cases, longer reaction times were needed to attain similar conversions and, in general, higher amounts of the undesirable *cis* isomer were formed. At this point it should be mentioned that, as previously observed with complexes **3** and **4**, a two-phase system (water or glycerol/organic products) is in all cases formed, with the ruthenium catalyst remaining mainly in the aqueous or glycerolic phase (in some cases a suspension distributed between the two phases was observed).[29] Regarding complex $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\{P(OMe)_3\}]$ (**5f**) both phases were completely homogenous because of the unexpectedly high solubility of this complex in water and glycerol (8.3 and 2.5 mg mL^{-1}, respectively, at 20 °C). However, solubility grounds are not the only factor responsible for the high catalytic activity shown by **5f** since

Table 2 Estragole to anethole isomerization in environmentally friendly media using the mononuclear bis(allyl)-ruthenium(IV) complexes **5a–n**[a]

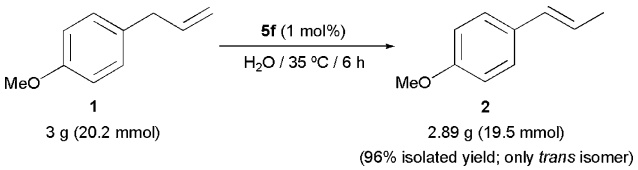


Entry	Catalyst	Solvent	Time	Yield[b]	*E*/*Z*[b]
1	**5a**	H_2O	6 h	>99%	87 : 13
2	**5a**	Glycerol	10 h	>99%	91 : 9
3	**5b**	H_2O	3 h	>99%	94 : 6
4	**5b**	Glycerol	6 h	>99%	95 : 5
5	**5c**	H_2O	21 h	>99%	94 : 6
6	**5c**	Glycerol	24 h	91%	93 : 7
7	**5d**	H_2O	21 h	97%	95 : 5
8	**5d**	Glycerol	24 h	96%	94 : 6
9	**5e**	H_2O	24 h	95%	93 : 7
10	**5e**	Glycerol	24 h	92%	93 : 7
11	**5f**	H_2O	30 min	>99%	95 : 5
12	**5f**	Glycerol	1 h	>99%	95 : 5
13	**5g**	H_2O	1 h	>99%	95 : 5
14	**5g**	Glycerol	2 h	>99%	95 : 5
15	**5h**	H_2O	1 h	>99%	92 : 8
16	**5h**	Glycerol	2 h	>99%	92 : 8
17	**5i**	H_2O	9 h	>99%	95 : 5
18	**5i**	Glycerol	9 h	>99%	93 : 7
19	**5j**	H_2O	1 h	>99%	93 : 7
20	**5j**	Glycerol	6 h	>99%	94 : 6
21	**5k**	H_2O	3 h	>99%	93 : 7
22	**5k**	Glycerol	6 h	>99%	94 : 6
23	**5l**	H_2O	1 h	>99%	88 : 12
24	**5l**	Glycerol	3 h	>99%	92 : 8
25	**5m**	H_2O	3 h	>99%	94 : 6
26	**5m**	Glycerol	9 h	>99%	95 : 5
27	**5n**	H_2O	3 h	>99%	93 : 7
28	**5n**	Glycerol	3 h	>99%	93 : 7
29[c]	**5f**	H_2O	6 h	>99%	>99% *trans*[d]
30[e]	**5f**	Glycerol	24 h	99%	98 : 2
31[c,e]	**5f**	H_2O	9 h	>99%	99 : 1

[a] Reactions performed at 80 °C under N_2 atmosphere using 2 mmol of substrate and 0.5 cm^3 of water or glycerol. [b] Determined by GC. [c] Reaction performed at 35 °C. [d] *Cis* isomer not detected. [e] Catalyst generated *in situ* from $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (**3**) and $P(OMe)_3$.

complexes **5b–e**, that also dissolve completely in water and glycerol due to the presence of the hydrophilic phosphine ligands TPPMS, PTA, PTA-Bn and DAPTA,[28] were comparatively much less effective (entries 3–10). The electronic nature of the ligands seems to play a key role on the catalytic activity of these mononuclear species, the best results being in general observed when π-accepting ligands, such as phosphites, isocyanides and carbon monoxide, are coordinated to ruthenium.

In complete accordance with the results obtained with dimer **3**, the selectivity of **5f** towards *trans*-anethole could be improved by performing the catalytic reactions at low temperature (35 °C; entries 29–30 *vs.* 11–12). In particular, using water as solvent (entry 29) a quantitative conversion of estragole into anethole could be reached after 6 h in a total stereoselective manner (*cis* isomer not detected by GC). Remarkably, using these optimal reaction conditions, the isomerization process could be easily scaled-up without detrimental effect on the stereoselectivity. Thus, as shown in Scheme 4, starting from 20.2 mmol of estragole, 2.89 grams of analytically pure *trans*-anethole were isolated (96% yield) after extraction with diethyl ether



1
3 g (20.2 mmol)

2
2.89 g (19.5 mmol)
(96% isolated yield; only *trans* isomer)

Scheme 4 Stereoselective isomerization of estragole in preparative scale.

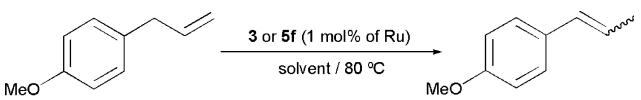
(3×10 cm^3) and subsequent filtration of the combined ethereal solutions over silica-gel (copies of the ^{1}H and ^{13}C{^{1}H} NMR and GC spectra obtained are included in the ESI†). It is also important to note that, the *in situ* generated catalyst (just by mixing the dimeric precursor [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (**3**) and two equivalents of trimethyl phosphite) presents a catalytic performance similar to that of the isolated complex **5f** (entry 31 in Table 2). This convenient *one-pot* procedure, based on the use of two commercially available air-stable reagents without the need of any purification, is an additional proof of the potential utility of **5f** for a practical application.

In our previous work using (η^6-arene)-ruthenium(II) complexes (Scheme 2),[23] the best results were obtained using methanol and ethanol as solvents (quantitative conversions after 15–30 min of heating at 80 °C with *trans*-selectivities ≥99%). This fact prompted us to study the behaviour of [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (**3**) and [$RuCl_2$(η^3:η^3-$C_{10}H_{16}$){$P(OMe)_3$}] (**5f**) in these media. We note that, although methanol and ethanol are not commonly considered as "green" solvents, they represent a good alternative to the widely used petroleum-based ones since they can be produced from biomass. In fact, their use is highly recommended, especially in the pharmaceutical industry.[18c,30]

As shown in Table 3, performing the catalytic reactions at 80 °C with a ruthenium loading of 1 mol%, the selectivity of the isomerization process in MeOH and EtOH was in all cases higher than that observed under the same conditions in water or glycerol (entries 3–4 *vs.* 1–2 and 11–12 *vs.* 9–10), reducing the content of the undesirable *cis* isomer in the final anethole to a maximum of 1%. Improvement of the activity was also in most cases observed. Interestingly, this high stereoselectivity was maintained when H_2O–MeOH (EtOH) or glycerol–MeOH (EtOH) mixtures (1 : 1 v/v) were used as solvent, the reactions proceeding even faster when compared to those performed using a single solvent alone (quantitative conversions after 5–30 min; entries 5–8 and 13–16). In particular, quantitative conversion of estragole into anethole (*trans*/*cis* ratio = 99 : 1) could be reached after only 5 min of heating performing the catalytic reactions with [$RuCl_2$(η^3:η^3-$C_{10}H_{16}$){$P(OMe)_3$}] (**5f**) in H_2O–MeOH or H_2O–EtOH mixtures (entries 13–14; 10 min if glycerol-based mixtures are employed: see entries 15–16). The beneficial effect of methanol and ethanol can be attributed to their ability to generate the catalytically active ruthenium-hydride species, *via* a β-hydride elimination process on the corresponding Ru-alcoholate intermediates.

Remarkably, the use of all these mixtures of solvents led again to biphasic reaction media (solvents/products). As in the precedent cases, the ruthenium catalysts remained dissolved mainly in the solvents phase, leading to almost completely homogenous solutions even in the case of the poorly soluble dimer [{RuCl(μ-Cl)(η^3:η^3-$C_{10}H_{16}$)}$_2$] (**3**) (an illustrative example is given in Fig. 2).

Table 3 Estragole to anethole isomerization using complexes **3** and **5f** in different solvents[a]



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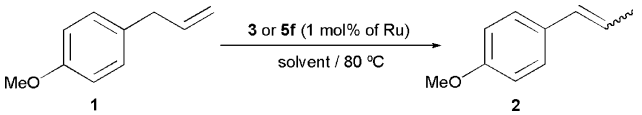
Entry	Cat.	Solvent	Time	Yield[b]	*E*/*Z*[b]
1	**3**	H_2O	30 min	>99%	97 : 3
2	**3**	Glycerol	45 min	>99%	97 : 3
3	**3**	MeOH	30 min	>99%	99 : 1
4	**3**	EtOH	30 min	>99%	99 : 1
5	**3**	H_2O–MeOH[c]	10 min	>99%	99 : 1
6	**3**	H_2O–EtOH[c]	10 min	>99%	99 : 1
7	**3**	Glycerol–MeOH[c]	30 min	>99%	99 : 1
8	**3**	Glycerol–EtOH[c]	30 min	>99%	99 : 1
9	**5f**	H_2O	30 min	>99%	95 : 5
10	**5f**	Glycerol	1 h	>99%	95 : 5
11	**5f**	MeOH	10 min	>99%	>99% *trans*[d]
12	**5f**	EtOH	10 min	>99%	99 : 1
13	**5f**	H_2O–MeOH[c]	5 min	>99%	99 : 1
14	**5f**	H_2O–EtOH[c]	5 min	>99%	99 : 1
15	**5f**	Glycerol–MeOH[c]	10 min	>99%	99 : 1
16	**5f**	Glycerol–EtOH[c]	10 min	>99%	99 : 1

[a] Reactions performed at 80 °C under N_2 atmosphere using 2 mmol of substrate and 0.5 cm^3 of the indicated solvent. [b] Determined by GC. [c] 1 : 1 v/v ratio. [d] *Cis* isomer not detected.

Fig. 2 The biphasic system resulting from the reaction described in entry 7 of Table 3.

The appearance of a biphase, along with the remarkable activity and *trans*-selectivity shown by complexes **3** and **5f** in these mixtures of solvents, prompted us to study their recyclability. To this end, mixtures H_2O–MeOH and glycerol–MeOH were used, separating the final anethole with the aid of a Pasteur pipette and washing the aqueous or glycerolic phase with *n*-heptane (3×2 cm^3) prior to a new addition of estragole. Gratifyingly, as shown in Table 4, the aqueous or glycerolic phase containing the catalysts could be re-used up to five consecutive runs. However, an important decrease of the activity, accompanied by a slight loss of the *trans*-selectivity, was observed after each cycle. Best results were obtained using the mononuclear complex **5f** in glycerol–MeOH, which after five consecutive runs was still able to generate anethole in 96% yield and high stereoselectivity (*trans*/*cis* ratio = 95 : 5) after 24 h of heating (entry 4). Partial decomposition of the catalysts

Table 4 Estragole to anethole isomerization using complexes **3** and **5f**: Catalyst recycling[a]



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Entry	Cat.	Solvent	Cycle	Time	Yield[b]	*E*/*Z*[b]
1	**3**	H_2O–MeOH[c]	1	10 min	>99%	99 : 1
			2	6 h	>99%	96 : 4
			3	17 h	>99%	93 : 7
			4	24 h	>99%	92 : 8
2	**3**	Glycerol–MeOH[c]	1	30 min	>99%	99 : 1
			2	6 h	>99%	97 : 3
			3	17 h	>99%	97 : 3
			4	24 h	99%	97 : 3
3	**5f**	H_2O–MeOH[c]	1	5 min	>99%	99 : 1
			2	15 min	>99%	98 : 2
			3	9 h	>99%	94 : 6
			4	24 h	96%	93 : 7
4	**5f**	Glycerol–MeOH[c]	1	10 min	>99%	99 : 1
			2	30 min	>99%	99 : 1
			3	1 h	>99%	98 : 2
			4	6 h	>99%	97 : 3
			5	24 h	96%	95 : 5

[a] Reactions performed at 80 °C under N_2 atmosphere using 2 mmol of substrate and 0.5 cm^3 of the indicated solvent. [b] Determined by GC. [c] 1 : 1 v/v ratio.

seems to be responsible for their lower activity and selectivity after each catalytic cycle. In this sense, analysis by $^{31}P\{^1H\}$ NMR spectroscopy of the crude anethole generated using **5f** showed the presence of trace amounts of trimethylphosphate (δ_P 0.3 ppm),[31] resulting from the oxidation of free $P(OMe)_3$ ligand. The ruthenium content in crude anethole was also investigated by means of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis. The weight percentage of ruthenium in samples generated from complexes **3** and **5f** in glycerol/methanol mixtures was 280 and 320 ppm, respectively, confirming that Ru-leaching also takes place during recycling.

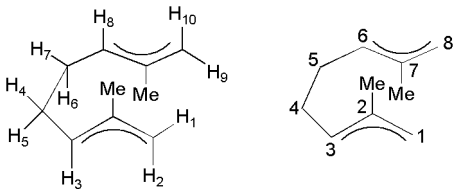
Conclusions

In summary, we have developed new ruthenium-based catalytic systems able to promote the isomerization of estragole into anethole. To the best of our knowledge, these systems constituted by the bis(allyl)-ruthenium(IV) complexes $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ and $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\{P(OMe)_3\}]$, along with the ruthenium(II) examples $[RuCl_2(\eta^6\text{-arene})(L)]$ previously reported by us,[23] are the most efficient catalysts reported to date for this transformation. The best results in terms of stereoselectivity have been observed when using methanol as solvent. In this medium, anethole is generated with a *trans*-selectivity ≥99%, thus fulfilling the strict criteria imposed by the FAO/WHO committee. More importantly, such a remarkable *trans*-selectivity is maintained when the catalytic reactions are performed in water–methanol and glycerol–methanol mixtures. In addition, the use of these environmentally friendly media resulted also in an improvement of the reaction rates compared to those observed using one of the three solvents alone. Overall, the results presented herein represent the first green synthetic approach to the industrially relevant additive *trans*-anethole.

Experimental

General methods

The manipulations were performed under inert N_2 atmosphere using vacuum-line and standard Schlenk or sealed-tube techniques. All reagents were obtained from commercial suppliers with the exception of compounds $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (**3**),[32] $[RuCl_2(\eta^3{:}\eta^2{:}\eta^3\text{-}C_{12}H_{18})]$ (**4**),[33] $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PPh_3)]$ (**5a**),[34] $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(TPPMS)]$ (**5b**),[35] $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PTA)]$ (**5c**),[35] $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(PTA\text{-}Bn)]$ (**5d**),[35] $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(DAPTA)]$ (**5e**),[35] $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\{P(OMe)_3\}]$ (**5f**),[36] $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\{P(OEt)_3\}]$ (**5g**),[37] $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\{P(OPh)_3\}]$ (**5i**),[38] $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(CO)]$ (**5l**),[34] $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(NCMe)]$ (**5m**)[39] and $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(NCPh)]$ (**5n**),[37] which were prepared following the methods reported in the literature. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. Elemental analyses were performed with a Perkin–Elmer 2400 microanalyzer. GC measurements were made on a Hewlett–Packard HP6890 equipment using a Supelco Beta-Dex™ 120 column (30 m length; 250 μm diameter). NMR spectra were recorded on a Bruker DPX-300 instrument at 300 MHz (^1H), 75.4 MHz (^{13}C) or 121.5 (^{31}P) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the compounds reported. The numbering for protons and carbons of the 2,7-dimethylocta-2,6-diene-1,8-diyl skeleton is as follows:



Preparation of complexes $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})(L)]$ (L = $P(O^iPr)_3$ (5h), CNBn (5j), CNCy (5k))

A purple solution of dimer $[\{RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ (**3**) (0.308 g, 0.5 mmol) in acetone (20 cm^3) was treated, at room temperature, with the corresponding two-electron donor ligand L (1 mmol) for 1 h. The resulting yellow solution was then evaporated to dryness, and the resulting solid residue washed with diethyl ether (3 × 5 cm^3) and dried *in vacuo*.

$[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})\{P(O^iPr)_3\}]$ (5h). Yellow solid; Yield: 92% (0.475 g); IR (KBr): *ν* 491 (w), 858 (m), 701 (w), 743 (m), 755 (m), 859 (w), 882 (m), 976 (s), 1006 (s), 1105 (s), 1138 (w), 1176 (w), 1370 (m), 1382 (m), 1452 (w), 2860 (w), 2926 (w), 2974 (w) cm^{-1}; $^{31}P\{^1H\}$ NMR ($CDCl_3$): *δ* 117.4 (s) ppm; ^1H NMR ($CDCl_3$): *δ* 1.35 and 1.39 (d, $^3J_{HH}$ = 6.0 Hz, 9H each, $CHMe_2$), 2.18 (s, 6H, Me), 2.65 (br, 2H, H_4 and H_6), 3.39 (br, 2H, H_2 and H_{10}), 3.51 (br, 2H, H_5 and H_7), 4.54 (d, $^3J_{HP}$ = 8.5 Hz, 2H, H_1 and H_9), 4.80 (m, 3H, $CHMe_2$), 5.13 (br, 2H, H_3 and H_8) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$): *δ* 20.6 (s, Me), 23.8 (s, $CHMe_2$), 36.7 (s, C_4 and C_5), 62.7 (d, $^2J_{CP}$ = 7.9 Hz, C_1 and C_8), 71.1 (d, $^2J_{CP}$ = 10.7 Hz, $CHMe_2$), 109.0 (d, $^2J_{CP}$ = 15.2 Hz, C_3 and C_6), 124.0 (s, C_2 and C_7) ppm; Elemental analysis calcd (%) for $C_{19}H_{37}O_3Cl_2PRu$: C 44.19, H 7.22; found: C 44.04, H 7.31.

[$RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})(CNBn)$] (5j). Yellow solid; Yield: 73% (0.310 g); IR (KBr): *ν* 493 (w), 601 (w), 693 (m), 735 (s), 784 (w), 854 (m), 962 (m), 1025 (m), 1308 (w), 1354 (m), 1456 (s), 2215 (vs), 2855 (w), 2912 (w), 3006 (w) cm^{-1}; ^1H NMR (C_6D_6): *δ* 2.28 (br, 2H, H_4 and H_6), 2.31 (s, 6H, Me), 3.23 (br, 2H, H_2 and H_{10}), 4.03 (br, 2H, H_5 and H_7), 4.10 (s, 2H, NCH_2), 4.73 (br, 2H, H_1 and H_9), 5.39 (br, 2H, H_3 and H_8), 7.07–7.21 (m, 5H, Ph) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6): *δ* 21.2 (s, Me), 37.9 (s, C_4 and C_5), 48.1 (s, NCH_2), 63.7 (s, C_1 and C_8), 109.1 (s, C_3 and C_6), 125.4 (s, C_2 and C_7), 126.3, 128.3 and 128.9 (s, CH of Ph), 130.0 (s, C of Ph), 132.8 (s, Ru-CN) ppm; Elemental analysis calcd (%) for $C_{18}H_{23}Cl_2NRu$: C 50.83, H 5.45, N 3.29; found: C 50.90, H 5.36, N 3.20.

[$RuCl_2(\eta^3:\eta^3\text{-}C_{10}H_{16})(CNCy)$] (5k). Yellow solid; Yield: 64% (0.267 g); IR (KBr): *ν* 531 (w), 656 (w), 670 (s), 787 (w), 856 (m), 960 (w9, 1025 (m), 1127 (w), 1269 (w), 1321 (w), 1456 (m), 2196 (vs), 2851 (w), 2934 (m), 2994 (w) cm^{-1}; ^1H NMR (C_6D_6): *δ* 0.90–1.65 (m, 10H, CH_2), 2.29 (br, 2H, H_4 and H_6), 2.35 (s, 6H, Me), 3.25 (m, 3H, NCH, H_2 and H_{10}), 4.05 (br, 2H, H_5 and H_7), 4.76 (br, 2H, H_1 and H_9), 5.40 (br, 2H, H_3 and H_8) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6): *δ* 21.3 (s, Me), 22.4, 25.1 and 32.3 (s, CH_2 of Cy), 38.01 (s, C_4 and C_5), 55.1 (s, CH of Cy), 63.7 (s, C_1 and C_8), 108.7 (s, C_3 and C_6), 125.1 (s, C_2 and C_7), 131.9 (s, Ru-CN) ppm; Elemental analysis calcd (%) for $C_{17}H_{27}Cl_2NRu$: C 48.92, H 6.52, N 3.36; found: C 49.04, H 6.60, N 3.44.

General procedure for the catalytic reactions

Under nitrogen atmosphere, the ruthenium catalyst precursor (0.01 mmol of **3** or 0.02 mmol of **4** and **5a–n**; 1 mol% of Ru), 0.5 cm^3 of the indicated solvent and estragole (0.307 cm^3, 2 mmol) were introduced into a teflon-capped sealed tube. Then, the mixture was heated at 80 °C or 35 °C in an oil-bath for the indicated time. The course of the reaction was monitored by taking regularly samples of *ca.* 20 μL which after extraction with CH_2Cl_2 (3 cm^3) were analyzed by GC [Supelco Beta-Dex™ 120 (30 m length; 250 μm diameter) column; helium 4 mL min^{-1}, 160 °C, 10 °C min^{-1} to 210 °C: 1.68 min (estragole), 1.91 min (*cis*-anethole) and 2.10 min (*trans*-anethole)].

Catalyst recycling

After completion of the reaction, the mixture was allowed to reach the room temperature and two phases appeared. Most of anethole was separated with the aid of a Pasteur pipette and the remaining extracted from the aqueous or glycerolic phase with *n*-heptane (3 × 2 cm^3). To the aqueous or glycerolic phase a new load of estragole (0.307 cm^3, 2 mmol) was then added and the mixture heated at 80 °C in an oil-bath for the indicated time.

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Notes and references

1 See, for example: (*a*) *Metal-Catalysis in Industrial Organic Processes*, ed. G. P. Chiusoli and P. M. Maitlis, RSC Publishing, Cambridge, 2008; (*b*) P. W. N. M. van Leeuwen, in *Homogeneous Catalysis: Understanding the Art*, Kluwer Academic Publishers, Dordrecht, 2004; (*c*) G. W. Parshall and S. D. Ittel, in *Homogeneous Catalysis*, John Wiley & Sons, New York, 2nd edn, 1992.

2 See, for example: (*a*) G. Reineccius, in *Flavor Chemistry and Technology*, CRC Press, Boca Raton, 2nd edn, 2006; (*b*) K. Bauer, D. Garbe and H. Surburg, in *Common Fragrance and Flavour Materials*, Wiley-VCH, Weinheim, 4th edn, 2001; (*c*) P. R. Ashurst, in *Food Flavorings*, Aspen Publishers, Maryland, 3rd edn, 1999; (*d*) A. J. Chalk, in *Flavors and Fragrances: A World Perspective*, ed. B. M. Lawrence, B. D. Mookherjee and B. J. Willis, Elsevier Science Publishers, Amsterdam, 1988.

3 (*a*) T. Derfer, in *The Chemistry of Turpentine in "Naval Stores"*, ed. D. Zinkel and J. Russell, Pulp Chemicals Association, New York, 1992; (*b*) See also the following report: "*Test Plan for Estragole*" submitted by the Flavor and Fragrance High Production Volume Consortia (FFHPVC) to the United States Environmental Protection Agency (EPA) in 2002. Available on-line at http://www.epa.gov/hpv/pubs/summaries/estragole/c14022tc.htm (accessed July 26, 2010).

4 Other routes for the large-scale synthesis of anethole, involving the treatment of anisole with propionic acid derivatives or propionaldehyde, are known: (*a*) G. E. Svadkowskaya, L. A. Kheifits, A. I. Platova and K. Denisenlova, *USSR Patent*, SU 261380, 1970; (*b*) K. Bauer and R. Molleken, *Ger. Offen.*, DE 2418974, 1978.

5 Anethole formation can also be achieved through different C–C coupling and reduction reactions. However, these methods are not economically viable alternatives for its large-scale production. See, for example: (*a*) J. C. Roberts and J. A. Pincock, *J. Org. Chem.*, 2006, **71**, 1480; (*b*) J. A. Miller and J. W. Dankwardt, *Tetrahedron Lett.*, 2003, **44**, 1907; (*c*) G. Cahiez and H. Avedissian, *Tetrahedron Lett.*, 1998, **39**, 6159; (*d*) A. D. Buss, R. Mason and S. Warren, *Tetrahedron Lett.*, 1983, **24**, 5293; (*e*) S. Cabiddu, A. Maccioni and M. Secci, *Ann. Chim.*, 1962, **52**, 1261.

6 See, for example: (*a*) I. A. Khan and E. A. Abourashed, in *Leung's Encyclopedia of Common Natural Ingredients Used in Food, Drugs and Cosmetics*, John Wiley & Sons, Hoboken, 3rd edn, 2010; (*b*) B. Simándi, A. Deák, E. Rónyai, G. Yanxiang, T. Verres, E. Lemberkovics, M. Then, A. Sass-Kiss and Z. Vámos-Falusi, *J. Agric. Food Chem.*, 1999, **47**, 1635; (*c*) D. Q. Tuan and S. G. Ilangantileke, *J. Food Eng.*, 1997, **31**, 47.

7 Anethole is also a principal constituent of other essential oils derived from medicinal plants with anti-oxidant, anti-inflammatory, gastroprotective, psycholeptic and anaesthetic properties: P. M. G. Soares, R. F. Lima, A. de Freitas Pires, E. P. Souza, A. M. S. Assreuy and D. N. Criddle, *Life Sci.*, 2007, **81**, 1085 and references cited therein.

8 See, for example: (*a*) G. H. Eirew, *U.S. Pat,. Appl.*, US 2009035229, 2009; (*b*) U. Glenert, *Eur. J. Pharmacol., Mol. Pharmacol. Sect.*, 1992, **226**, 43; (*c*) J. B. Epstein and M. M. Schubert, *Oral Surg., Oral Med., Oral Pathol.*, 1987, **64**, 179.

9 See, for example: (*a*) D. Mansuy, A. Sassi, P. M. Dansette and M. Plat, *Biochem. Biophys. Res. Commun.*, 1986, **135**, 1015; (*b*) K.-I. Fujita, T. Fujita and I. Kubo, *Phytother. Res.*, 2007, **21**, 47; (*c*) E. Enan, *PCT Int. Appl.*, 2008003007, 2008; (*d*) V. V. Kouznetsov and D. R. Merchan Arenas, *Tetrahedron Lett.*, 2009, **50**, 1546 and references cited therein.

10 Some data on anethole production and consumption can be found in the report: "*Test Plan for Anethole*" submitted by FFHPVC to EPA (http://www.epa.gov/hpv/pubs/summaries/anethole/c14069tc.htm; accessed July 26, 2010).

11 (*a*) A. P. Wagner, *Manuf. Chemist*, 1952, **23**, 56; (*b*) H. Pines and W. M. Salik, in *Base-Catalyzed Reactions of Hydrocarbons and Related Compounds*, Academic Press Inc, New York, 1977.

12 Crystallization at low temperature can also be used to purify *trans*-anethole: C. B. Davies, *U.S. Pat. Appl.*, US 4902850, 1990.

13 See, for example: (*a*) F. Caujolle and D. Meynier, *Acad. Sci.*, 1958, **246**, 1465; (*b*) J. M. Taylor, P. M. Jenner and W. I. Jones, *Toxicol. Appl. Pharmacol.*, 1964, **6**, 378; (*c*) J. R. Boissier, P. Simon and B. Le Bourhis, *Therapie*, 1967, **22**, 309; (*d*) R. Hänsel and J. Hölzl, in *Lehrbuch der Pharmazeutishen Biologie*, Springer-Verlag, Berlin, 1996, p 162.

14 Available on-line at http://www.fao.org/ag/agn/jecfa-flav (accessed July 26, 2010).

15 See, for example: (*a*) V. K. Srivastava, H. C. Bajaj and R. V. Jasra, *Catal. Commun.*, 2003, **4**, 543; (*b*) D. Kishore and S. Kannan, *J. Mol. Catal. A: Chem.*, 2006, **244**, 83; (*c*) C. M. Jinesh, C. A. Antonyraj and S. Kannan, *Catal. Today*, 2009, **141**, 176; (*d*) S. K. Sharma, P. A. Parikh and R. V. Jasra, *J. Mol. Catal. A: Chem.*, 2010, **317**, 27.

16 See, for example: (*a*) I. R. Baxendale, A.-L. Lee and S. V. Ley, *Synlett*, 2002, 516; (*b*) M. Arisawa, Y. Terada, M. Nakagawa and A. Nishida, *Angew. Chem., Int. Ed.*, 2002, **41**, 4732; (*c*) S. K. Sharma, V. K. Srivastava, P. H. Pandya and R. V. Jasra, *Catal. Commun.*, 2005, **6**, 205; (*d*) H. S. Lee and G. Y. Lee, *Bull. Korean Chem. Soc.*, 2005, **26**, 461; (*e*) S. K. Sharma, V. K. Srivastava and R. V. Jasra, *J. Mol. Catal. A: Chem.*, 2006, **245**, 200; (*f*) G. R. A. Adair, K. K. Kapoor, A. L. B. Scolan and J. M. J. Williams, *Tetrahedron Lett.*, 2006, **47**, 8943; (*g*) G. Erdogan and D. B. Grotjahn, *J. Am. Chem. Soc.*, 2009, **131**, 10354; (*h*) A. Scarso, M. Colladon, P. Sgarbossa, C. Santo, R. A. Michelin and G. Strukul, *Organometallics*, 2010, **29**, 1487; (*i*) D. Gauthier, A. T. Lindhardt, E. P. K. Olsen, J. Overgaard and T. Skrydstrup, *J. Am. Chem. Soc.*, 2010, **132**, 7998; (*j*) N. Nishiwaki, R. Kamimura, K. Shono, T. Kawakami, K. Nakayama, K. Nishino, T. Nakayama, K. Takahashi, A. Nakamura and T. Hosokawa, *Tetrahedron Lett.*, 2010, **51**, 3590.

17 (*a*) P. T. Anastas and J. C. Warner, *Green Chemistry Theory and Practice*, Oxford University Press, Oxford, 1998; (*b*) A. S. Matlack, *Introduction to Green Chemistry*, Marcel Dekker, New York, 2001; (*c*) *Handbook of Green Chemistry and Technology*, ed. J. H. Clark and D. J. Macquarrie, Blackwell Publishing, Abingdon, 2002; (*d*) M. Lancaster, *Green Chemistry: An Introductory Text*, RSC Editions, Cambridge, 2002; (*e*) M. Poliakoff, J. M. Fitzpatrick, T. R. Farren and P. T. Anastas, *Science*, 2002, **297**, 807.

18 See, for example: (*a*) W. M. Nelson, *Green Solvents for Chemistry: Perspectives and Practice*, Oxford University Press, New York, 2003; (*b*) J. H. Clark and S. J. Taverner, *Org. Process Res. Dev.*, 2007, **11**, 149; (*c*) F. M. Kerton, *Alternative Solvents for Green Chemistry*, RSC Publishing, Cambridge, 2009.

19 For leading references in this field, see: (*a*) C. J. Li and T. H. Chan, in *Comprehensive Organic Reactions in Aqueous Media*, John Wiley & Sons, New Jersey, 2007; (*b*) *Organic Reactions in Water: Principles, Strategies and Applications*, ed. U. M. Lindstrom, Blackwell Publishing Ltd., Oxford, 2007; (*c*) *Aqueous-Phase Organometallic Catalysis: Concepts and Applications*, ed. B. Cornils and W. A. Herrmann, Wiley-VCH, Weinheim, 1998; (*d*) F. Joó, in *Aqueous Organometallic Catalysis*, Kluver, Dodrecht, 2001.

20 (*a*) M. Pagliaro and M. Rossi, in *The Future of Glycerol: New Usages for a Versatile Raw Material*, RSC Publishing, Cambridge, 2008; (*b*) M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi and C. D. Pina, *Angew. Chem., Int. Ed.*, 2007, **46**, 4434; (*c*) A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411; (*d*) C.-H. Zhou, J. N. Beltramini, Y.-X. Fan and G. Q. Lu, *Chem. Soc. Rev.*, 2008, **37**, 527; (*e*) A. Behr, J. Eilting, K. Irawadi, J. Leschinski and F. Lindner, *Green Chem.*, 2008, **10**, 13; (*f*) F. Jérôme, Y. Pouilloux and J. Barrault, *ChemSusChem*, 2008, **1**, 586; (*g*) C. J. A. Mota, C. X. A. da Silva and V. L. C. Gonçalves, *Quim. Nova*, 2009, **32**, 639.

21 For a specific review on the use of glycerol as a green solvent, see: Y. Gu and F. Jérôme, *Green Chem.*, 2010, **12**, 1127.

22 For recent examples not included in reference 21, see: (*a*) N. Bakhrou, F. Lamaty, J. Martinez and E. Colacino, *Tetrahedron Lett.*, 2010, **51**, 3935; (*b*) G. Perin, L. G. Mello, C. S. Radatz, L. Savegnago, D. Alves, R. G. Jacob and E. J. Lenardão, *Tetrahedron Lett.*, 2010, **51**, 4354; (*c*) D. Tavor, O. Sheviev, C. Dlugy and A. Wolfson, *Can. J. Chem.*, 2010, **88**, 305; (*d*) J. Francos and V. Cadierno, *Green Chem.*, 2010, **12**, 1552; (*e*) S. Balieu, A. El Zein, R. De Sousa, F. Jérôme, A. Tatibouët, S. Gatard, Y. Pouilloux, J. Barrault, P. Rollin and S. Bouquillon, *Adv. Synth. Catal.*, 2010, **352**, 1826.

23 (*a*) B. Lastra-Barreira, J. Díez and P. Crochet, *Green Chem.*, 2009, **11**, 1681; (*b*) B. Lastra-Barreira and P. Crochet, *Green Chem.*, 2010, **12**, 1311.

24 (*a*) Available from Strem Chemicals, Inc (catalog number 44-0203 and 44-0172, respectively). For a review on the coordination chemistry and catalytic applications of these complexes, see: (*b*) V. Cadierno, P. Crochet, S. E. García-Garrido and J. Gimeno, *Curr. Org. Chem.*, 2006, **10**, 165.

25 (*a*) V. Cadierno, S. E. García-Garrido and J. Gimeno, *Chem. Commun.*, 2004, 232; (*b*) V. Cadierno, S. E. García-Garrido, J. Gimeno and N. Nebra, *Chem. Commun.*, 2005, 4086; (*c*) V. Cadierno, S. E. García-Garrido, J. Gimeno, A. Varela-Álvarez and J. A. Sordo, *J. Am. Chem. Soc.*, 2006, **128**, 1360; (*d*) V. Cadierno, J. Francos, J. Gimeno and N. Nebra, *Chem. Commun.*, 2007, 2536; (*e*) V. Cadierno, J. Gimeno and N. Nebra, *Chem.–Eur. J.*, 2007, **13**, 6590; (*f*) V. Cadierno, P. Crochet and J. Gimeno, *Synlett*, 2008, 1105; (*g*) V. Cadierno, P. Crochet, J. Francos, S. E. García-Garrido, J. Gimeno and N. Nebra, *Green Chem.*, 2009, **11**, 1992.

26 DFT calculations on the relative stability of the *E* and *Z* isomers of different 1-propenyl-benzenes have been recently performed by Strukul and co-workers (see ref. 16*h*). The calculations clearly indicate that the relative stability of the *E vs. Z* isomers increases with temperature.

27 The combined use of MW-irradiation, as a nonclassical low-energy-consuming heating source, and water, as an environmentally friendly solvent, to perform organic reactions has recently emerged as a promising new field of research. For reviews and a recent book on this topic, see: (*a*) D. Dallinger and C. O. Kappe, *Chem. Rev.*, 2007, **107**, 2563; (*b*) V. Polshettiwar and R. S. Varma, *Chem. Soc. Rev.*, 2008, **37**, 1546; (*c*) V. Polshettiwar and R. S. Varma, *Acc. Chem. Res.*, 2008, **41**, 629; (*d*) *Aqueous Microwave Assisted Chemistry*, ed. V. Polshettiwar and R. S. Varma, RSC Publishing, Cambridge, 2010.

28 Abbreviations used: TPPMS = 3-diphenylphosphino-benzenesulfonate sodium salt; PTA = 1,3,5-triaza-7-phosphatricyclo[3.3.1.1^{3,7}]decane; PTA-Bn = 1-benzyl-3,5-diaza-1-azonia-7-phosphatricyclo[3.3.1.1^{3,7}]decane chloride; DAPTA = 3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane.

29 This happens for example when the poorly soluble dimer **3** is used as catalyst.

30 (*a*) K. Alfonsi, J. Colberg, P. J. Dunn, T. Fevig, S. Jennings, T. A. Johnson, H. P. Kleine, C. Knight, M. A. Nagy, D. A. Perry and M. Stefaniak, *Green Chem.*, 2008, **10**, 31; (*b*) B. W. Cue and J. Zhang, *Green Chem. Lett. Rev.*, 2009, **2**, 193.

31 E. Pretsch, P. Bühlmann and M. Badertscher, *Structure Determination of Organic Compounds: Tables of Spectral Data, Springer*, Heidelberg, 4th edn, 2009, p. 265.

32 (*a*) L. Porri, M. C. Gallazzi, A. Colombo and G. Allegra, *Tetrahedron Lett.*, 1965, **47**, 4187; (*b*) A. Salzer, A. Bauer, S. Geyser and F. Podewils, *Inorg. Synth.*, 2004, **34**, 59.

33 J. K. Nicholson and B. L. Shaw, *J. Chem. Soc. A*, 1966, 807.

34 R. A. Head, J. F. Nixon, J. R. Swain and C. M. Woodard, *J. Organomet. Chem.*, 1974, **76**, 393.

35 V. Cadierno, J. Díez, J. Francos and J. Gimeno, *Chem.–Eur. J.*, 2010, **16**, 9808.

36 D. N. Cox and R. Roulet, *J. Chem. Soc., Chem. Commun.*, 1988, 951.

37 S. C. Glander, O. Nuyken, W. C. Schattenmann and W. A. Herrmann, *Macromol. Symp.*, 1998, **127**, 67.

38 S. Wache, W. A. Herrmann, G. Artus, O. Nuyken and D. Wolf, *J. Organomet. Chem.*, 1995, **491**, 181.

39 D. N. Cox and R. Roulet, *Inorg. Chem.*, 1990, **29**, 1360.