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Eugenol isomerization promoted by arene–ruthenium(II) complexes in aqueous media: influence of the pH on the catalytic activity†

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The catalytic activity of the arene–ruthenium(II) complexes $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)(L)]$ (L = $P(OMe)_3$ (**1a**), $P(OEt)_3$ (**1b**), $P(O^iPr)_3$ (**1c**), $P(OPh)_3$ (**1d**), PPh_3 (**1e**)) in the isomerization of eugenol into isoeugenol has been evaluated. Best results in terms of activity and selectivity were observed with those catalysts containing an aliphatic P-donor ligand (**1a–c**). Under optimized conditions, full conversions in extremely short reaction times (5 min), and with high levels of *trans*-selectivity (up to 98%), could be achieved. Addition of both NaOH or H_2SO_4 to the aqueous media resulted in rate enhancements, suggesting two different activation pathways of the pre-catalysts. We have evidenced that sodium hydroxide promotes the release of the η^6-coordinated arene ligand, while sulfuric acid favours the Ru–Cl bond dissociation and the formation of aquo-derivatives $[RuCl(H_2O)(\eta^6\text{-}C_6H_5OCH_2CH_2OH)(L)][Cl]$.

Introduction

Metal-promoted C=C bond migrations are fundamental processes in organic chemistry with widespread academic and industrial applications.[1] In particular, the isomerization of allylbenzenes offers an attractive synthetic approach to the corresponding β-methylstyrenes, which are common starting materials in the flavour and fragrance industries,[2] and valuable intermediates for the preparation of pharmaceutical compounds.[3] Such a transformation has been traditionally promoted by superstoichiometric quantities of strong bases,[4] but in recent years, the use of transition-metal catalysts allowed an enhancement in the selectivity and in the rate of this type of reactions, with a concomitant reduction of their environmental impact.[5]

During the last few years, in the context of studies on C=C bond migration processes involving different functionalized allylic substrates, our research group has brought to light highly efficient catalytic systems based on Ru(II) and Ru(IV) complexes.[6–9] Among them, the dimeric bis(allyl)–ruthenium(IV) derivative $[\{RuCl(\mu\text{-}Cl)(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})\}_2]$ ($C_{10}H_{16}$ = 2,7-dimethylocta-2,6-diene-1,8-diyl) featured the best catalytic performances in the isomerization of estragole, a natural occurring functionalized allylbenzene, into *trans*-anethole, combining a high activity with a complete chemo- and stereo-selectivity.[8] However, this ruthenium(IV) precursor suffers from some limitations since competing side reaction, *i.e.* dimerization, takes place when the allylbenzene contains an hydroxyl substituent on the arene ring.[9,10] Therefore alternative catalytic systems must be developed to selectively isomerize such compounds. In particular, the efficient, rapid and selective transformation of eugenol into *trans*-isoeugenol still remains a challenge (Scheme 1). Previous studies have demonstrated the ability of heterogeneous basic catalysts to promote this process, however long reaction times and high temperatures (*ca.* 200 °C) are generally required to obtain only low to moderate yields of isoeugenol, with quite moderate selectivities toward the *trans* isomer.[11] The low conversions attained in these cases are attributed to the competing deprotonation of the OH group and the methylenic hydrogens of the allyl function.[11d,i] More effective transformations were achieved with homogeneous catalysts,[5c,d,f,12] nonetheless long reaction times are, in general, still required. Only a ruthenium-based catalyst reported recently by Grotjahn and co-workers was able to selectively isomerize eugenol into *trans*-isoeugenol in a short reaction time.[13]

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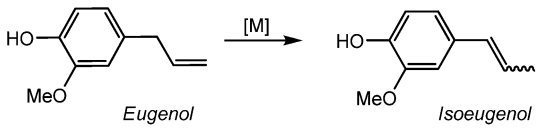
† Electronic supplementary information (ESI) available: Experimental details, products characterization and NMR spectra of **1b** in presence of H_2SO_4 and NaOH. See DOI: 10.1039/c3ra43030h



Scheme 1 Catalytic isomerization of eugenol into isoeugenol.

In the present work, we have studied the catalytic behaviour of the water-soluble arene–ruthenium(II) complexes $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)(L)]$[7g] in the isomerization of eugenol into isoeugenol. The optimization of the reaction conditions allowed a clean, rapid and highly stereo-selective process using an environmentally benign solvent (*i.e.* water).

Results and discussion

In our previous studies on the isomerization of other allylbenzene derivatives, we evidenced that the use of an alcoholic reaction medium is crucial for reaching high activities and selectivities.[7i,8,9] Hence, the catalytic behaviour of arene–ruthenium(II) complexes $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)(L)]$ (L = $P(OMe)_3$ (**1a**), $P(OEt)_3$ (**1b**), $P(O^iPr)_3$ (**1c**), $P(OPh)_3$ (**1d**), PPh_3 (**1e**), in Fig. 1) in the isomerization of eugenol was first evaluated using ethanol as solvent. Experiments were performed at 80 °C with 4 mmol of substrate, 1 mol% of Ru and 1 mL of EtOH (Table 1), the yield and selectivity of the process being monitored by GC analyses of aliquots each 5 min during the first hour and then the interval was increased progressively.

With all these catalysts, isoeugenol, resulting from the C=C bond migration (Scheme 1), was the only product generated with no traces of the corresponding dimer being detected. As a general trend, derivatives containing an aliphatic P-donor ligand, *i.e.* complexes **1a–c**, have presented higher activities and *trans*-selectivities as compared to those containing aromatic ligands.[14] In particular, compounds $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OMe)_3\}]$ (**1a**) and $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}]$ (**1b**) allowed complete conversions into isoeugenol within 40 min with a selectivity towards the *trans*-isomer of at least 97% (entries 1 and 2, Table 1).

For comparative purposes, the catalytic activity of the *p*-cymene analogues $[RuCl_2(\eta^6\text{-}p\text{-cymene})(L)]$ (**2a–e**, in Fig. 1) were also evaluated under the same experimental conditions (Table 2). These complexes proved to be much less efficient (final TOF values from 0.04 h^{-1} to 25 h^{-1} for **2a–e** *vs.* 0.8 h^{-1} to 200 h^{-1} for **1a–e**),[15] thus evidencing an influence of the arene ligand on the reaction outcome.[16]

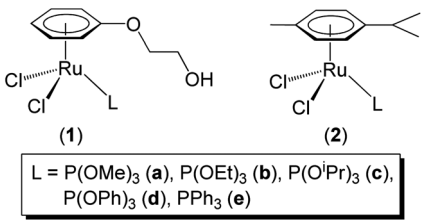


Fig. 1 Structure of arene–ruthenium(II) complexes **1a–e** and **2a–e**.

Table 1 Isomerization of eugenol catalyzed by complexes $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)(L)]$ (**1a–e**) in ethanol[a]

Entry	Catalyst [L]	Time	Yield[b] (%)	*Trans* : *cis*[b]
1	**1a** $[P(OMe)_3]$	30 min	>99	97 : 3
2	**1b** $[P(OEt)_3]$	40 min	>99	98 : 2
3	**1c** $[P(O^iPr)_3]$	4 h	>99	95 : 5
4	**1d** $[P(OPh)_3]$	23 h	18	87 : 13
5	**1e** $[PPh_3]$	6 h	>99	91 : 9

[a] Reactions carried out at 80 °C, using 4 mmol of eugenol, 1 mol% of Ru and 1 mL of ethanol. [b] GC determined.

Table 2 Isomerization of eugenol catalyzed by complexes $[RuCl_2(\eta^6\text{-}p\text{-cymene})(L)]$ (**2a–e**) in ethanol[a]

Entry	Catalyst [L]	Time	Yield[b] (%)	*Trans* : *cis*[b]
1	**2a** $[P(OMe)_3]$	4 h	>99	98 : 2
2	**2b** $[P(OEt)_3]$	6 h	>99	98 : 2
3	**2c** $[P(O^iPr)_3]$	8 h	>99	96 : 4
4	**2d** $[P(OPh)_3]$	23 h	1	—[c]
5	**2e** $[PPh_3]$	15 h	>99	94 : 6

[a] Reactions carried out at 80 °C, using 4 mmol of eugenol, 1 mol% of Ru and 1 mL of ethanol. [b] GC determined. [c] Not determined.

Table 3 Isomerization of eugenol catalyzed by complexes $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)(L)]$ (**1a–e**) in water[a]

Entry	Catalyst [L]	Time	Yield[b] (%)	*Trans* : *cis*[b]
1	**1a** $[P(OMe)_3]$	10 min	>99	97 : 3
2	**1b** $[P(OEt)_3]$	15 min	>99	98 : 2
3	**1c** $[P(O^iPr)_3]$	15 min	>99	97 : 3
4	**1d** $[P(OPh)_3]$	23 h	91	86 : 14
5	**1e** $[PPh_3]$	75 min	>99	95 : 5

[a] Reactions carried out at 80 °C, using 4 mmol of eugenol, 1 mol% of Ru and 1 mL of water. [b] GC determined.

Interestingly, when the catalytic reactions were performed with the complexes **1a–e** in water rather than ethanol, the reaction rates increased substantially, and the stereo-selectivities remained very high (Table 3; final TOF values from 4 h^{-1} to 600 h^{-1} in water *vs.* 0.8 h^{-1} to 200 h^{-1} in ethanol). This phenomenon was also observed with the *p*-cymene complexes (see data in the ESI†). As an example, full conversion of eugenol was attained after 2 hours using $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{P(OMe)_3\}]$ (**2a**) in water (*vs.* 4 hours in EtOH; *trans* : *cis* ratio = 98 : 2 in each case).

This activity enhancement in aqueous media contrasts with the results obtained in the isomerization of estragole to anethole, for which alcohols, and especially methanol, were the solvents of choice to attain good catalytic efficiencies.[7i,9] The different water-solubility of the substrates may be responsible of this behaviour, eugenol being more soluble in aqueous medium than estragole due to the presence of a phenol unit in its structure.[17]

On the other hand, we also observed that the pH of the medium significantly alters the reaction rates (Table 4). For example, the isomerization process promoted by **1b** in water was accelerated both under basic (pH = 12.9, entry 6) and acidic conditions (pH = 4.8, entry 1), slower transformations taking place at almost neutral pH (pH between 7 and 8.5, entries 3 and 4). Similar trends were also observed for catalysts **1a** and **1c–e** (see details in the ESI†). The most impressive changes in

Table 4 Influence of pH on the catalytic activity[a]

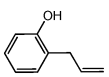
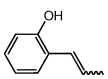
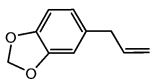
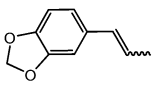
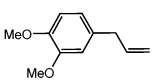
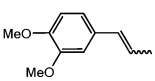
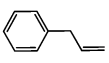
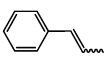
Entry	pH	Time	Yield[b] (%)	*Trans* : *cis*[b]
1	4.8	10 min	>99	98 : 2
2	5.2	10 min	>99	98 : 2
3	7.2	15 min	>99	98 : 2
4	8.5	30 min	>99	97 : 3
5	10.2	10 min	>99	97 : 3
6	12.9	5 min	>99	98 : 2
7[c]	4.8	7 h	>99	89 : 11
8[c]	12.9	7 h	>99	90 : 10
9[d]	7.2	3.5 h	>99	97 : 3
10[d]	4.8	1.75 h	>99	98 : 2
11[d]	12.9	1.5 h	>99	97 : 3

[a] Reactions carried out at 80 °C, using 4 mmol of eugenol, 1 mol% of **1b**, 1 mL of water and appropriate quantity of NaOH or H_2SO_4 to reach the pH indicated. [b] GC determined. [c] Using 1 mol% of **1d** as catalyst. [d] Using 1 mol% of **2b** as catalyst.

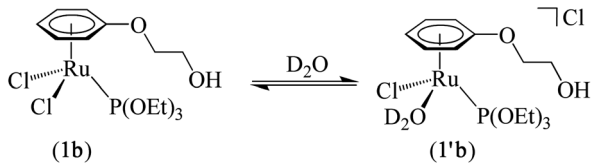
activity were achieved with $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OPh)_3\}]$ (**1d**), which required only 7 hours at pH = 4.8 or pH = 12.9 to reach full conversions (Table 4, entries 7 and 8, final TOF = 14 h^{-1}), while incomplete reaction was observed after 23 hours under neutral conditions (Table 3, entry 4, TOF = 0.8 h^{-1}). In blank experiments, we have checked that NaOH (at pH = 12.9) or H_2SO_4 (at pH = 4.8) are not able to promote the isomerization in absence of the metallic precursor, even after several hours of heating (48 h).

The higher water-solubility of eugenol in basic medium, due to the generation of the corresponding phenolate, could have explained the increased activity in presence of NaOH. However, this could be discarded since the rate enhancement was also observed with other substrates, regardless of the presence or not of an OH function on the aromatic ring. Thus, basic conditions improved the isomerization of 2-allylphenol (entry 1, Table 5),[18] a phenolic compound, as well as those of the non-phenolic derivatives 1,2-dimethoxy-4-allylbenzene, safrole and allylbenzene (entries 2–4, Table 5). As an example, complete transformation of allylbenzene into β-methylstyrene was achieved in 45 min under neutral conditions, while only 20 min were required in the presence of NaOH (entry 4).

Table 5 Isomerization of different allylbenzenes catalyzed by **1b** in water with or without base[a]

Substrate	Product	Time[b]	*Trans* : *cis*[c]
1			15 min 10 min[d]	50 : 50 60 : 40
2			30 min 10 min[d]	98 : 2 98 : 2
3			10 min 5 min[d]	98 : 2 98 : 2
4			45 min 20 min[d]	96 : 4 97 : 3

[a] Reactions carried out at 80 °C, using 4 mmol of substrate, 1 mol% of **1b** and 1 mL of water. [b] Time required to achieving a full conversion of the substrate. [c] GC determined. [d] Reaction performed in the presence of NaOH (pH = 12.9).



Scheme 2 Aquation of complex **1b** to generate **1′b**.

To better understand these rate enhancements, the stoichiometric reactivity of complex **1b** towards H_2SO_4 and NaOH was explored. First of all, variable quantities of aqueous H_2SO_4 was added to deuterated water solutions of $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}]$ (**1b**), conducing, in all cases, to a mixture of the aquo-derivative $[RuCl(D_2O)(\eta^6\text{-}C_6H_5OCH_2CH_2OH)\{P(OEt)_3\}][Cl]$ (**1′b**) and the initial complex **1b** (Scheme 2; see NMR spectra in the ESI†).

The generation of **1′b**, through Ru–Cl bond cleavage and D_2O coordination, is favoured by the presence of H_2SO_4 since the relative proportion of **1′b** increased progressively with the medium acidity (*ca.* 20, 32, 37, 43, 45 and 47% of **1′b** observed after addition of 0, 0.5, 1, 5, 10 and 20 equivalents of H_2SO_4 per Ru, respectively).[19] The equilibrium shift towards the formation of the ionic aquo-compound **1′b** under these conditions is most probably due to the enhanced ionic strength of the medium.[20] Hence, these observations suggest that the role of H_2SO_4 during the catalytic events is to favour the chloride ligand dissociation. In this sense, we note that the cleavage of Ru–Cl bond is usually proposed as a key step in C=C bond migration processes promoted by chloride–ruthenium catalyst precursors.[21] In agreement with this, a similar rate enhancement was also achieved by addition of a chloride abstractor ($AgNO_3$) to the catalytic reaction.[22] Reversely, the efficiency of complex **1b** dramatically dropped in the presence of Cl^- sources, such as HCl or NaCl.[23]

On the other hand, treatment of aqueous solutions of **1b** with different amounts of NaOH (0.25, 0.5, 0.75, 1 or 2 equivalents per Ru) gave rise to complex mixtures of unidentified organometallic compounds. However, NMR analyses clearly evidenced that partial release of the arene ligand took place.[24] In accord with this, ^{1}H NMR spectra exhibit different sets of signals between 5.0 and 7.3 ppm. The resonances at 7.30, 6.98 and 6.95 ppm correspond, respectively, to the *ortho*, *para* and *meta* hydrogen nuclei of the free phenoxyethanol (see the NMR spectra in the ESI†), while signals between 5.0 and 6.1 ppm reflect the presence of different complexes with a η^6-coordinated $C_6H_5OCH_2CH_2OH$ ligand.[24] The relative proportion of free arene increases with the quantity of NaOH added to the medium. Interestingly, this behaviour is specific to the phenoxyethanol derivatives since the treatment of aqueous solution of $[RuCl_2(\eta^6\text{-}p\text{-cymene})\{P(OMe)_3\}]$ with one equivalent of NaOH does not provoke the arene displacement.[25]

Hence, two different types of activations are possible for the pre-catalysts $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)(PR_3)]$ (**1a–e**): (i) through chloride dissociation under neutral and, above all, under acid conditions, or (ii) by arene release at basic pH. This chemical behaviour is in accord with the activities reached for **1a–e** as function of the pH medium, highly basic and acidic conditions favouring the catalytic reactions. Moreover, the differences in activity observed between the phenoxyethanol (**1a–e**) and *p*-cymene (**2a–e**) complexes in the presence of a base are thus attributed to the capacity of the formers to lose the arene ligand (see Table 4 entry 11 *vs.* entry 6 and ESI†). However, the higher efficiencies of **1a–e** *vs.* **2a–e** under neutral (entry 9 *vs.* entry 3 and ESI†) or acid conditions (entry 10 *vs.* 1 and ESI†) remain unexplained. In effect, the *p*-cymene complexes $[RuCl_2(\eta^6\text{-}p\text{-cymene})(PR_3)]$ (**2a–e**) are more likely to form the corresponding aquo-species $[RuCl(H_2O)(\eta^6\text{-}p\text{-cymene})(PR_3)][Cl]$[26] than their phenoxyethanol counterparts (**1a–e**) and then, they are expected to be more active. The lower activities of *p*-cymene derivatives are perhaps related to a higher steric congestion due to the presence of a di-substituted arene.

Conclusions

In summary, we have developed new efficient and selective catalytic systems for the isomerization of eugenol into isoeugenol based on the arene-ruthenium(II) complexes $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)(L)]$ (**1a–e**). Under optimized conditions, full transformation was achieved within 5 min, with a selectivity towards the *trans*-isomer of 98%. Although these results do not surpass those recently reported by Grotjahn and co-workers,[13] they represent a clear improvement in respect to the other previous studies.[11,12] On the other hand, we have demonstrated that either NaOH or H_2SO_4 allow for a rate enhancement. Two different pre-catalysts activation pathways seem to take place depending on the reaction conditions. Thus, in the presence of NaOH, complexes **1a–e** evolve through the decoordination of the η^6-arene, while H_2SO_4 favours the dissociation of the Ru–Cl bond. In both cases, open coordination sites on the metal are generated, thus favouring the coordination of the substrate.

Experimental section

General methods

Organic solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers and used without further purification, with the exception of compounds $[RuCl_2(\eta^6\text{-}C_6H_5OCH_2CH_2OH)(L)]$ (**1a–e**)[7g] and $[RuCl_2(\eta^6\text{-}p\text{-cymene})(L)]$ (**2a–e**),[7g,27] which were prepared by following the methods reported in the literature. GC measurements were made on a Hewlett-Packard HP6890 equipment using a Supelco Beta-Dex™ 120 column (30 m length, 250 μm diameter). GC/MSD measurements were performed with an Agilent 6890N equipment coupled to a 5973 mass detector (70 eV electron impact ionization) using a HP-1MS column. Flash chromatography was performed using Merck silica gel 60 (230–400 mesh). $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker DPX-300 or Bruker AV-400 instruments.

General procedure for the isomerization of eugenol catalyzed by 1a–e and 2a–e

Under a nitrogen atmosphere, the ruthenium catalyst precursor (0.04 mmol, 1 mol%), 1 mL of the indicated solvent and eugenol (0.616 mL, 4 mmol) were introduced into a teflon-cap sealed tube and the mixture was heated at 80 °C. The complexes **1a–c** and **2a–c** resulted completely soluble under the experimental conditions used, whereas **1d,e** and **2d,e** were only partially soluble. The yield and selectivity of the catalytic process were monitored by GC analyses of aliquots each 5 min during the first hour and then the interval was increased progressively. Similar procedures have been employed to perform the isomerization of 1,2-dimethoxy-4-allylbenzene, safrole, 2-allylphenol and allylbenzene (Table 5). In all cases, only the product resulting from the C=C bond migration was generated. The identity of the isolated products was assessed by comparison of their NMR spectroscopic data with those reported in the literature and their fragmentation in GC/MSD. The C=C bond stereochemistry was confirmed by ^1H NMR.

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14 The extremely low activity of **1d** is probably due to the easy deactivation of the catalytic species through orthometallation of one of the aromatic rings of $P(OPh)_3$ generating a stable 5-membered metallacycle. See: F. L. Joslin, J. T. Mague and D. M. Roundhill, *Organometallics*, 1991, **10**, 521.

15 Final TurnOver Frequencies values ((mol product/mol Ru)/time) have been calculated at the time indicated in the tables.

16 The electronic properties of compounds **1a–e** and **2a–e** have been previously evaluated. See ref. 7*g*.

17 Water-solubilities of estragole and eugenol are, respectively, of 178 mg L^{-1} (at 20 °C) and 2.46 g L^{-1} (at 25 °C). Available on-line in the "Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung" databank at http://gestis.itrust.de/nxt/gateway.dll/gestis_de, accessed October 31, 2012.

18 Starting from 2-allylphenol, unusually high proportions of the thermodynamically unfavourable *cis*-isomer were obtained under both neutral and basic conditions, at short reaction time. This selectivity is probably due to the ability of the final product to chelate the metallic center by coordination of the oxygen atom and the C=C bond. *Cis*-disposition of the olefin moiety conduces to less sterically congested complex. We note that a prolongated heating of the reaction mixture provokes the gradual isomerization of *cis*-2-propenylphenol to *trans*-2-propenylphenol, a *trans* : *cis* ratio of 90 : 10 (without base) and 91 : 9 (with base) being obtained after 22 h. For similar process, see: T. Sato, N. Komine, M. Hirano and S. Komiya, *Chem. Lett.*, 1999, 441.

19 Formation of **1′b** is the only process observed in the presence of H_2SO_4. The acidic solutions do not suffer any decomposition even after 24 h, at least at room temperature.

20 Similar effect has been already reported for a biologically active ruthenium(II)–arene complex: A. K. Renfrew, A. D. Phillips, E. Tapavicza, R. Scopelliti, U. Rothlisberger and P. J. Dyson, *Organometallics*, 2009, **28**, 5061.

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22 The catalytic isomerization reaction carried out with 1 mol% of **1b** and $AgNO_3$ (1 equiv. per Ru) led to a complete conversion of eugenol in 5 min, giving rise to isoeugenol as a 96 : 4 mixture of the *trans*- and *cis*-isomers.

23 Catalytic experiments performed in the presence of HCl and NaCl (1 equiv. per Ru, 1 mol% of **1b**, 80 °C) allowed, respectively, only 10% and 8% of isoeugenol after 1 hour of heating.

24 *Ortho*, *meta* and *para* hydrogen nuclei of the η^6-coordinated $C_6H_5OCH_2CH_2OH$ ligand, commonly appear at 5.1–6.7. See ref. 7*g* and: (*a*) J. Soleimannejad, A. Sisson and C. White, *Inorg. Chim. Acta*, 2003, **352**, 121; (*b*) H. S. Chae and D. J. Burkey, *Organometallics*, 2003, **22**, 1761; (*c*) J. Soleimannejad and C. White, *Organometallics*, 2005, **24**, 2538; (*d*) C. Aliende, M. Pérez-Manrique, F. A. Jalón, B. R. Manzano, A. M. Rodríguez and G. Espino, *Organometallics*, 2012, **31**, 6106; (*e*) B. Lastra-Barreira, J. Díez, P. Crochet and I. Fernández, *Dalton Trans.*, 2013, **42**, 5412; (*f*) L. C. Matsinha, S. F. Mapolie and G. S. Smith, *Polyhedron*, 2013, **53**, 56.

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26 As an example, the NMR analyses of 0.14 M solutions of **1b** and **2b** in D_2O show the presence of the corresponding aquo-complex in a 20% and 56%, respectively.

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