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Research paper

Ruthenium (II) complexes with C_2- and C_1-symmetric bis-(+)-camphopyrazole ligands and their evaluation in catalytic transfer hydrogenation of aldehydes

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This contribution is dedicated to Dr. Maurizio Peruzzini on the occasion of his 65th birthday.

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ABSTRACT

Ruthenium (II) piano-stool complexes with bis-(+)-camphopyrazole ligands of C_2 and C_1 symmetry were prepared in good yields (66–98%). New C_2-C_1 ligands and complexes were characterized by multinuclear NMR spectroscopy, FT-IR and elemental analysis. The catalytic performance of the Ru(II)-bis-(+)-camphopyrazole complexes in the transfer hydrogenation of benzaldehyde and valeraldehyde using isopropanol/potassium carbonate and formic acid/triethylamine mixtures as hydrogen donors, was evaluated, resulting in moderate yields (>54%) for the reduction to the desired primary alcohols. The system with isopropanol as hydrogen source proved to be more selective than the analogous system using the azeotropic formic acid/triethylamine mixture, allowing benzyl alcohol to be obtained in quantitative yield (>99%) for a particular catalyst precursor. Furthermore, complexes with C_2 symmetry ligands showed higher yields than those with C_1 symmetry ligands in all of the evaluated systems.

1. Introduction

Transfer hydrogenation (TH) of unsaturated compounds is one of the most important synthetic reactions, not only from the academic point of view, but also for its industrial importance. Given its operational simplicity, sustainability, and low impact on the environment, as well as its atom-economy, TH has emerged as a suitable candidate to obtain saturated compounds beyond the bench-scale [1,2]. This reaction involves the transfer of hydrogen from an organic donor molecule (e.g. formic acid or isopropanol) to an unsaturated bond using a metal catalyst, in most cases in the presence of a base. It is considered a reaction superior to conventional hydrogenation since it avoids the risks and restrictions associated with the use of molecular hydrogen [3]. It has also proven to be more selective and often requires milder working conditions in terms of temperature and pressure. Successful TH examples include functional groups such as: imines [4], nitroarenes [5], alkenes [6] and the partial reduction of alkynes to obtain alkenes [7]. Nevertheless, the carbonyl group and, in particular, ketones constitute, by far, a main focus of study of TH reactions. The hydrogenation of C═O moieties is challenging, being thermodynamically disadvantaged if compared, for example, to the hydrogenation of alkenes [8]. However, significantly fewer examples involve the TH of the formyl group [9–18], despite the fact that the reduction of aldehydes to obtain primary alcohol building-blocks is vital for the fragrances and flavors industries [19], and that other industries, such as alkene-based polymer manufacturing, could likewise benefit from these systems [20]. Due to the higher redox potentials of aldehydes compared to ketones, their TH is thermodynamically favored [21]. In addition to this, the lower steric hindrance of the formyl group compared to the ketone motif should facilitate the access of the substrate to the active species of the catalyst [22]. The difficulty to perform catalytic reduction of aldehydes lies in the side reactions that can occur during the reduction, which are generally favored by the basic media [12]. These transformations include Cannizzaro dismutation [23], Tischenko dimerization [24] and

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aldol condensations [25]. Also, the decarbonylation of the aldehyde substrate can deactivate the catalytically active species [26]. Many of the catalysts used in TH are sophisticated ruthenium-based complexes [27] or other precious-metal based systems [28,29]. Non-precious metals such as iron [30], cobalt [31] or manganese [32] have recently been used, and their complexes reach speeds that exceed, by far, those obtained by heterogeneous catalysts at lower temperatures. Although these are cheaper and more Earth-abundant metals than ruthenium, their complexes bear ligands which can be even more expensive than the metal used. Ruthenium (II)-arene piano stool complexes with a wide variety of ancillary ligands have been extensively studied in TH. The arene ligands are relatively inert towards substitution and act as spectator ligands, stabilizing and protecting the metal center and thereby preventing the rapid oxidation of the Ru (II) to Ru (III) [33]. On the other hand, ancillary ligands can modulate the activity of the complexes depending on their electronic and steric nature in any catalytic process [17,19,34]. To the best of our knowledge, no examples of metal complexes with ancillary chiral bis-(+)-camphopyrazole ligands have been reported in transfer hydrogenation reactions. Such fact is rather surprising, considering that bis-(+)-camphopyrazole ligands have been previously reported and exhibit a number of intrinsically useful characteristics for catalytic purposes, as previously shown [35–38]. Among these, their ability to modulate electronic and steric effects and their simple, high-yielding preparation. Furthermore, the size of the ligand would inhibit the discoordination of one of the nitrogen atoms of the chelate and the rotation out of the plane, avoiding possible dimerization processes of the catalyst or of the catalytically active species. Likewise, the substituents on the backbones and side structures would increase solubility in most of the conventional solvents. Lastly, they exhibit good thermal stability compared to ordinary *N*-monodentate ligands [39]. Similarly, the use of ligands that contain pyrazole ring is interesting given its π-donor ability [40]. This could increase the effectiveness of ruthenium complexes by allowing TH of aldehydes with high efficiency. The use of complexes with ligands containing pyrazole rings has been proven in different catalytic processes in the last decade, such as: carbon–carbon coupling [41], epoxidation [42,43], oxidation [44], hydrogenation/dehydrogenation [45–47] and other transformations [48]. However, only few examples of their use as ancillary ligands in the transfer hydrogenation of ketones can be found [49–54]. Considering the above, this work presents the synthesis and characterization of ruthenium (II) piano-stool complexes with chiral bis-(+)-camphopyrazole ligands of C_2 and C_1 symmetry, and their application in the reduction of benzaldehyde and valeraldehyde using isopropanol/potassium carbonate and formic acid/triethylamine as hydrogen sources.

2. Experimental

2.1. Materials and physical measurements

The reactions with air-sensitive compounds were carried out under anaerobic and anhydrous conditions, using standard Schlenk techniques. Tetrahydrofuran was distilled under nitrogen from purple sodium/benzophenone solution; triethylamine was dried with sodium followed by distilled under nitrogen. Chloroform was dried with Linde type 4 Å molecular sieves followed by distillation under atmospheric pressure [55]. Methanol, ethanol, isopropanol, and hexane were used without prior purification. NMR spectra were recorded on a Bruker 300 MHz spectrometer at Laboratorio Nacional de Resonancia Magnética Nuclear, Instituto Venezolano de Investigaciones Científicas (IVIC) or on a Bruker Avance 300 spectrometer at Laboratorium für Anorganische Chemie, ETH Zürich. Peak positions are relative to tetramethylsilane, for ^{1}H and $^{13}C\{^{1}H\}$. The chemical shifts (δ) are measured according to IUPAC [56], expressed in parts per million (ppm) and were calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet (^{13}C). Coupling constants *J* are given in Hertz (Hz) as absolute values. The multiplicity of the signals is indicated as s, d, t, q, or m for singlets, doublets, triplets, quartets, or multiplets, respectively. The abbreviation br. is given for broadened signals. All the NMR spectra were recorded at room temperature (25 °C) unless otherwise stated. Melting points were determined on an Electrothermal Mel-Tem apparatus in open capillary tubes and are not corrected. Elemental analyses were performed at Department Chemie und Pharmazie, Anorganische und Allgemeine Chemie, Friedrich–Alexander–Universität, on a Euro EA 3000 analyzer and samples were handled in air (hygroscopic compounds are corrected for water content). IR spectra were performed at Universidad Simón Bolívar and recorded in KBr medium on a Thermo Scientific Nicolet iS10 spectrophotometer.

2.2. General procedure for the preparation of C_2 and C_1 ligands

(+)-(1R,1′R)-3,3′-(1,2-Dihydroxyethane-1,2-diylidene)bis[(1,7,7-trimethyl-bicyclo[1,2,2]-heptan-2-one] (Tetraketone **I**), (+)-3,3′-[(1,2-Dihydroxyethane-1,2-diylidene)(1,7,7-trimethyl-bicyclo[1,2,2]-heptan-2-one)]-(1-phenyl-camphopyrazo-5-ol) or (+)-3,3′-[(1,2-dihydroxyethane-1,2-diylidene)(1,7,7-trimethyl-bicyclo[1,2,2]-heptan-2-one)]-((4′S,7′R)-7′,8′,8′-trimethyl-4′,6′,7′-trihydro-5′-ol-4′,7′-methano-1′-phenyl-indazol) (diketone intermediate **II**), C_2: $\mathbf{L_1}$, $\mathbf{L_2}$ and C_1: $\mathbf{L_4}$ symmetry ligands used in this work have been previously reported [35,36].

Tetraketone **I**: A mixture of (+)-camphor and diethyl oxalate in THF was added to a slurry of NaH in THF. The mixture was refluxed for 48 h, after which the solvent was removed by rotary evaporation. The reaction crude was added to an ice/HCl mixture and extracted with chloroform. The organic layer was dried over $MgSO_4$, filtered, and stripped to yellow oil. Slurrying and washing with methanol resulted in a yellow powder.

For C_2 ligand $\mathbf{L_3}$: Tetraketone **I** (5.00 g, 13.9 mmol) was added over ethanol forming slurry and concentrated hydrochloric acid (12.0 M, 0.50 mL) was dropped slowly. The mixture was stirred for 15 min and then was added a solution of 4-bromophenyl hydrazine hydrochloride (6.21 g, 27.8 mmol) in ethanol. The resulting mixture was heated under reflux for 48 h. The solvent was then removed by filtration and the solid dried in vacuo. White solid product (6.74 g, 73%). M.P.: >320 °C (d). IR (KBr) (ν, cm^{-1}): 3062 (*w*), 2955 (*s*), 2871 (*m*), 1587 (*m*), 1507 (*s*), 1465 (*m*), 1277 (*m*), 1044 (*m*), 999 (*m*), 777 (*s*), 723 (*m*), 652 (*m*). ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm): 0.83 (s, 6H, $2CH_3$); 0.93 (s, 6H, $2CH_3$); 1.16 (s, 6H, $2CH_3$); 1.21–1.44 (m, 4H, $2CH_2$); 1.76–1.95 (m, 2H, CH_2); 2.02–2.24 (m, 2H, CH_2); 3.02–3.03 (d, $J = 3.6$ Hz, 2H, 2CH); 7.30–7.46 (d, $J = 4.0$ Hz, 4H, 4CH); 7.46–7.58 (d, $J = 4.0$ Hz, 4H, 4CH). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) (δ, ppm): 12.54 ($2CH_3$); 19.79 ($2CH_3$); 20.43 ($2CH_3$); 27.42 ($2CH_2$); 33.80 ($2CH_2$); 48.00 (2CH); 53.64 (2C); 63.37 (2C); 120.49 (2CH); 125.82 (4CH); 129.55 (2C); 131.71 (4CH); 139.34 (2C); 140.08 (2C); 154.17 (2C). Elemental analysis for $C_{34}H_{36}N_4Br_2$: Calculated: C, 61.83%; H, 5.49%; N, 8.48%. Found: C, 61.83%; H, 5.50%; N, 8.35%.

Diketone intermediate **II**: Acetic acid was added dropwise to a solution of tetraketone **I** in ethanol and allowed to react for 15 min. A solution of phenyl hydrazine in ethanol was then added dropwise to the above mixture and refluxed overnight. The solid crude product was isolated by filtration, and recrystallization from methanol at low temperature followed by high vacuum drying yielded a yellow powder.

For C_1 ligand $\mathbf{L_5}$: Following the same procedure before described for C_2 ligands. Diketone intermediate **II** (2.64 g, 5.89 mmol) and 4-bromophenyl hydrazine hydrochloride (1.97 g, 8.82 mmol). White solid product (2.47 g, 72%). M.P.: >320 °C (d). IR (KBr) (ν, cm^{-1}): 3062 (*w*), 2948 (*s*), 2872 (*w*), 1594 (*m*), 1503 (*s*), 1417 (*m*), 1328 (*w*), 1280 (*m*), 1266 (*m*), 1067 (*m*), 998 (*s*), 909 (*m*), 834 (*m*), 765 (*m*), 699 (*m*). ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm): 0.84 (s, 6H, $2CH_3$); 0.85 (s, 6H, $2CH_3$); 0.93 (s, 6H, $2CH_3$); 1.14–1.15 (m, 2H, 2CH); 1.20–1.46 (m, 2H, 2CH); 1.77–1.90 (m, 2H, 2CH); 2.09–2.20 (m, 2H, 2CH); 3.05–3.06 (d, $J = 3.5$ Hz, 1H, CH); 3.08–3.09 (d, $J = 3.5$ Hz, 1H, CH); 7.26–7.36 (t, $J = 7.2$ Hz, 1H, CH); 7.37–7.44 (d, $J = 4.0$ Hz, 4H, 4CH); 7.47–7.59 (d, $J = 4.0$ Hz, 4H, 4CH). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) (δ, ppm): 12.25 (CH_3); 12.49

(CH_3); 19.75 ($2CH_3$); 20.45 (CH_3); 20.46 (CH_3); 27.43 ($2CH_2$); 33.79 ($2CH_2$); 47.99 (CH); 48.02 (CH); 53.60 (C); 53.69 (C); 63.31 (C); 63.41 (C); 124.71 (2CH); 125.92 (2CH); 127.47 (C); 128.64 (CH); 129.01 (CH); 129.60 (CH); 131.75 (4CH); 139.11 (2C); 139.68 (2C); 154.74 (2C). Elemental analysis for $C_{34}H_{37}N_4Br$: Calculated: C, 70.22%; H, 6.41%; N, 9.63%. Found: C, 70.10%; H 6.40%; N, 9.32%.

2.3. General procedure to the synthesis of ruthenium complexes

The ligand was dissolved in dichloromethane or chloroform, and slowly added to a solution of the precursor [(*p*-cymene)$RuCl_2$] dissolved in the same solvent. The solution was stirred for 24 h at room temperature. The formed suspension was filtered to separate a solid identified as impurities. The resulting solution was rotavaporated, obtaining a solid that was dried under vacuum. This solid was dissolved in ethanol and ammonium hexafluorophosphate was added and stirred at room temperature. After 24 h of stirring, the solution was rotavaporated obtaining a solid which was dried under vacuum. This solid was dissolved in chloroform and filtered using a Pasteur pipette with silica gel. The resulting solution was rotavaporated to obtain a solid as the final product. The recrystallization of the complexes was carried out in an ethanol-hexane mixture. The mixture was cooled to −5 °C during an appropriate period, obtaining crystalline solids which were dried under vacuum.

Complex **1**: [(*p*-cymene)$RuCl_2$] (100 mg, 163 μmol) in chloroform (5.0 mL), ligand $\mathbf{L_1}$ (114 mg, 326 μmol) in chloroform (5.0 mL). Ammonium hexafluorophosphate (181 mg, 1.11 mmol). Orange solid product (146 mg, 70%). M.P.: 190–194 °C (d). IR (KBr) (ν, cm^{-1}): 3264 (*s*), 2964 (*s*), 2877 (*w*), 1554 (*w*), 1538 (*w*), 1472 (*m*), 1438 (*m*), 1392 (*m*), 1285 (*m*), 1135 (*w*), 848 (*s*), 558 (*s*). ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm): 0.62 (s, 3H, CH_3); 0.71 (s, 3H, CH_3); 0.85–0.86 (d, $J = 7.0$ Hz, 3H, *i*Pr-CH_3); 0.87–0.89 (d, $J = 6.8$ Hz, 3H, *i*Pr-CH_3); 0.91 (s, 3H, CH_3); 0.93 (s, 3H, CH_3), 1.05–1.12 (m, 2H, CH_2); 1.18–1.34 (m, 2H, CH_2); 1.37 (s, 3H, CH_3); 1.39 (s, 3H, CH_3); 1.81–1.93 (m, 2H, CH_2); 2.04–2.16 (m, 2H, CH_2); 2.20 (s, 3H, cymene-CH_3); 2.35–2.41 (m, 1H, *i*Pr-CH); 2.86–2.87 (d, $J = 3.7$ Hz, 1H, CH); 2.88–2.89 (d, $J = 3.7$ Hz, 1H, CH); 5.74–5.82 (dd, $J = 5.9$ Hz, 2H, cymene 2CH); 6.04–6.13 (dd, $J = 5.9$ Hz, 2H, cymene 2CH); 12.01 (s, 1H, NH); 12.18 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) (δ, ppm): 10.23 (CH_3); 10.48 (CH_3); 19.19 (CH_3); 19.26 (CH_3); 19.39 (CH_3); 20.07 (CH_3); 20.37 (CH_3); 21.81 (CH_3); 21.83 (CH_3); 26.83 (CH_2); 27.38 (CH_2); 31.06 (CH); 33.19 (CH_2); 33.25 (CH_2); 47.89 (2CH); 53.42 (C); 53.45 (C); 63.39 (C); 63.66 (C); 79.35 (CH); 79.59 (CH); 83.80 (CH); 83.99 (CH); 101.06 (C); 105.10 (C); 124.45 (C); 124.91 (C); 137.76 (C); 137.81 (C); 161.37 (C); 161.44 (C). Elemental analysis for $C_{32}H_{44}ClN_4PF_6Ru{\cdot}1.2H_2O$: Calculated: C, 48.79%; H, 5.94%; N, 7.11%; F, 14.47%. Found: C, 48.41%; H, 5.66%; N, 7.01%: F, 14.88%.

Complex **2**: [(*p*-cymene)$RuCl_2$] (274 mg, 448 μmol) in dichloromethane (5.0 mL), ligand $\mathbf{L_2}$ (450 mg, 895 μmol) in dichloromethane (5.0 mL). Ammonium hexafluorophosphate (722 mg, 4.42 mmol). Orange solid product (802 mg, 98%). M.P.: 242–244 °C (d). IR (KBr) (ν, cm^{-1}): 3056 (*w*), 2965 (*m*), 2875 (*w*), 1593 (*m*), 1492 (*m*), 1456 (*m*), 1432 (*m*), 1392 (*m*), 1275 (*m*), 1125 (*m*), 841 (*s*), 774 (*m*), 687 (*m*), 558 (*s*). ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm): 0.63 (s, 3H, CH_3); 0.70 (s, 6H, *i*Pr-$2CH_3$); 0.87 (s, 3H, CH_3); 0.93 (s, 3H, CH_3); 0.97 (s, 3H, CH_3); 1.02 (s, 3H, CH_3); 1.09 (s, 3H, CH_3); 1.39–1.75 (m, 2H, CH_2); 1.73–1.81 (m, 2H, CH_2); 2.01–2.14 (m, 4H, $2CH_2$); 2.27–2.31 (m, 1H, *i*Pr-CH); 2.62 (s, 3H, cymene CH_3); 2.95–2.96 (d, $J = 3.7$ Hz, 1H, CH); 3.05–3.06 (d, $J = 3.7$ Hz, 1H, CH); 3.73 (s, 2H, cymene 2CH); 4.74–4.79 (d, 2H, cymene 2CH); 7.62–7.96 (m, 10*H*, 10CH). $^{13}C\{^1H\}$NMR (75 MHz, $CDCl_3$) (δ, ppm): 10.19 (CH_3); 11.89 (CH_3); 19.03 (CH_3); 19.29 (CH_3); 20.18 (CH_3); 20.29 (CH_3) 21.52 (CH_3); 21.77 ($2CH_3$); 26.62 (CH_2); 27.37 (CH_2); 31.07 (CH); 33.40 (CH_2); 33.51 (CH_2); 47.80 (CH); 48.03 (CH); 54.35 (C); 55.03 (C); 62.37 (C); 64.94 (C); 78.18 (CH); 78.32 (CH); 84.41 (CH); 84.61 (CH); 100.70 (C); 105.31 (C); 126.28 (C); 126.55 (C); 129.63 (4CH); 130.76 (2CH); 130.92 (4CH); 137.31 (2C); 137.94 (C); 138.73 (C); 160.52 (C); 161.13 (C). Elemental analysis for $C_{44}H_{52}ClN_4PF_6Ru$: Calculated: C, 57.54%; H, 5.71%; N, 6.10%; F, 12.41%. Found: C, 57.16%; H, 5.58%; N 6.14%; F, 12.41%.

Complex **3**: [(*p*-cymene)$RuCl_2$] (100 mg, 163 μmol) in dichloromethane (5.0 mL) and ligand $\mathbf{L_3}$ (217 mg, 326 μmol) in dichloromethane (5.0 mL). Ammonium hexafluorophosphate (164 mg, 4.12 mmol). Orange solid product (140 mg, 80%). M.P.: 192–195 °C (d). IR (KBr) (ν, cm^{-1}): 3050 (*w*), 2958 (*m*), 2875 (*w*), 1625 (*w*), 1597 (*w*), 1534 (*w*), 1507 (*w*), 1454 (*m*), 1438 (*m*), 1398 (*m*), 1134 (*m*), 854 (*s*), 741 (*m*), 705 (*m*), 557 (*s*). ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm): 0.60 (s, 3H, CH_3); 0.74 (s, 6H, *i*Pr-$2CH_3$); 0.88 (s, 3H, CH_3); 0.93 (s, 3H, CH_3); 0.97 (s, 3H, CH_3); 1.01 (s, 3H, CH_3); 1.13 (s, 3H, CH_3); 1.61 (s, 3H, cymene-CH_3); 1.69–1.86 (m, 4H, $2CH_2$); 1.91–2.17 (m, 4H, $2CH_2$); 2.20–2.37 (m, 1H, *i*Pr-CH); 2.93–2.94 (d, $J = 3.7$ Hz, 1H, CH); 3.04–3.05 (d, $J = 3.7$ Hz, 1H, CH); 3.78–4.05 (s, 2H, cymene-2CH); 4.80–5.02 (d, 2H, cymene-2CH); 7.79 (m, 8H, 8CH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) (δ, ppm): 12.05 (CH_3); 12.56 (CH_3); 19.07 (CH_3); 19.34 (CH_3); 19.81 (CH_3); 20.18 (CH_3); 20.30 (CH_3); 21.62 (CH_3); 21.80 (CH_3); 26.64 (CH_2); 27.31 (CH_2); 31.16 (CH); 33.23 (CH_2); 33.53 (CH_2); 47.83 (CH); 48.07 (CH); 54.55 (C); 55.25 (C); 62.47 (C); 65.19 (C); 78.42 (2CH); 84.47 (2CH); 101.50 (C); 104.97 (C); 124.94 (C); 125.84 (C); 125.10 (4CH); 126.81 (CH); 127.01 (CH); 132.83 (4CH); 136.23 (2C); 138.13 (C); 139.08 (C); 160.96 (C); 161.54 (C). Elemental analysis for $C_{44}H_{50}Br_2ClN_4RuPF_6$: Calculated: C, 49.11%; H, 4.68%; N, 5.21%. Found: C, 49.34%; H, 4.79%; N, 5.17%.

Complex **4**: [(*p*-cymene)$RuCl_2$] (100 mg, 163 μmol) in dichloromethane (5.0 mL) and ligand $\mathbf{L_4}$ (141 mg, 331 μmol) in dichloromethane (5.0 mL). Ammonium hexafluorophosphate (227 mg, 1.39 mmol). Orange solid product (152 mg, 66%). Reddish orange crystals were obtained (84 mg, 36%). M.P.: 256–260 °C (d). IR (KBr) (ν, cm^{-1}): 3356 (*m*), 3056 (*w*), 2962 (*m*), 2926 (*m*), 2874 (*w*), 1624 (*w*), 1534 (*w*), 1506 (*m*), 1455 (*m*), 1435 (*m*), 1391 (*m*), 1275 (*m*), 1133 (*m*), 841 (*s*), 737 (*w*), 701 (*m*), 557 (*s*). ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm): 0.64–2.31 (m, 72H, $18CH_3$, 18CH); 2.86–3.02 (m, 4H, 4CH); 4.14 (s, 2H, cymene 2CH); 4.81 (s, 2H, cymene 2CH); 5.45 (s, 2H, cymene 2CH); 5.87 (s, 2H, cymene 2CH); 7.65–7.73 (m, 10*H*, 10CH); 11.47 (s, 1H, NH); 11.54 (s, 1H, NH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) (δ, ppm): Isomer **A**: 9.85 (CH_3); 10.29 (CH_3); 19.09 (CH_3); 19.24 (CH_3); 20.16 (CH_3); 20.26 (CH_3); 21.53 (CH_3); 22.00 ($2CH_3$); 26.63 (CH_2); 27.40 (CH_2); 31.05 (CH); 32.96 (CH_2); 33.55 (CH_2); 47.71 (CH); 48.07 (CH); 53.76 (C); 53.80 (C); 62.51 (C); 63.74 (C); 78.15 (CH); 78.86 (CH); 82.87 (CH); 84.84 (CH); 97.19 (C); 104.50 (C); 125.72 (C); 125.93 (C); 129.61 (2CH); 130.90 (2CH); 131.08 (CH); 137.68 (C); 137.72 (C); 139.03 (C); 160.23 (C); 161.74 (C). Isomer **B**: 10.28 (CH_3); 11.87 (CH_3); 19.20 (CH_3); 19.27 (CH_3); 20.31 (CH_3); 20.40 (CH_3); 21.75 (CH_3); 22.07 ($2CH_3$); 26.87 (CH_2); 27.44 (CH_2); 31.10 (CH); 33.21 (CH_2); 33.73 (CH_2); 47.97 (CH); 48.07 (CH); 54.27 (C); 54.92 (C); 63.63 (C); 64.79 (C); 79.43 (CH); 79.76 (CH); 82.98 (CH); 84.98 (CH); 101.78 (C); 105.10 (C); 125.08 (C); 125.75 (C); 129.61 (2CH); 130.90 (2CH); 131.08 (CH); 137.68 (C); 137.47 (C); 138.58 (C), 160.98 (C); 161.93 (C). Elemental analysis for $C_{38}H_{48}ClN_4PF_6Ru{\cdot}0.4H_2O$: Calculated: C, 53.73%; H, 5.79%; N, 6.60%; F, 13.42%. Found: C, 53.72%; H, 5.67%; N, 6.47%; F, 13.53%.

Complex **5**: [(*p*-cymene)$RuCl_2$] (100 mg, 163 μmol) in dichloromethane (5.0 mL) and ligand $\mathbf{L_5}$ (190 mg, 326 μmol) in dichloromethane (5.0 mL). Ammonium hexafluorophosphate (263 mg, 1.17 mmol). Orange solid product (203 mg, 70%). M.P.: 298–300 °C (d). IR (KBr) (ν, cm^{-1}): 3060 (*w*), 2963 (*m*), 2930 (*w*), 2872 (*w*), 1621 (*w*), 1594 (*w*), 1489 (*m*), 1455 (*w*), 1456 (*w*), 1391 (*w*), 1129 (*m*), 841 (*s*), 776 (*m*), 701 (*m*), 557 (*s*). ^{1}H NMR (300 MHz, $CDCl_3$) (δ, ppm): 0.58–2.46 (m, 72H, $18CH_3$, $8CH_2$, 2CH); 2.91 (s, 2H, 2CH); 3.01 (s, 2H, 2CH); 3.50–3.98 (d, 4H, cymene 4CH); 4.50–5.16 (d, 4H, cymene 4CH); 7.42–8.20 (m, 18H, 18CH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) (δ, ppm): Isomer **A**: 10.28 (CH_3); 12.01 (CH_3); 19.09 (CH_3); 19.36 (CH_3); 20.21 (CH_3); 20.34 (CH_3); 21.57 (CH_3); 21.84 ($2CH_3$); 26.69 (CH_2); 27.35 (CH_2); 31.15 (CH); 33.23 (CH_2); 33.54 (CH_2); 47.87 (CH); 48.12 (CH); 54.47 (C); 55.16 (C); 62.42 (C); 65.08 (C); 78.43 (2CH); 84.55 (2CH); 101.19 (C); 105.23 (C);

124.90 (C); 126.52 (C); 126.80 (C); 129.70 (4CH); 130.87 (CH); 131.02 (2CH); 132.87 (2CH); 136.33 (2C); 137.88 (C); 138.71 (C); 160.65 (C); 161.26 (C). Isomer **B**: 10.37 (CH_3); 12.01 (CH_3); 19.11 (CH_3); 19.36 (CH_3); 20.26 (CH_3); 20.35 (CH_3); 21.65 (CH_3); 21.82 ($2CH_3$); 26.69 (CH_2); 27.43 (CH_2); 31.18 (CH); 33.51 (CH_2); 33.60 (CH_2); 47.87 (CH); 48.12 (CH); 54.56 (C); 55.24 (C); 62.56 (C); 65.15 (C); 78.43 (2CH); 84.55 (2CH); 101.19 (C); 105.23 (C); 125.07 (C); 126.69 (C); 126.88 (C); 129.70 (4CH); 130.87 (CH); 131.02 (2CH); 132.87 (2CH); 137.32 (2C); 138.33 (C); 139.20 (C); 161.01 (C); 161.56 (C). Elemental analysis for $C_{44}H_{51}BrClN_4RuPF_6 \cdot 0.29C_6H_{14}$: Calculated: C, 53.77%; H, 5.44%; N, 5.48%. Found: C, 53.61%; H, 5.45%; N, 5.33%.

2.4. General procedure for the transfer hydrogenation of aldehydes

With either one of the procedures for the catalytic studies described below, the products obtained were identified by a Buck Scientific 910 gas chromatograph (FID detector) fitted with a capillary column MTX-1 (30 m × 0.52 mm × 1.0 mm). The retention times of benzaldehyde, benzyl alcohol and biphenyl under an isothermal run at 180 °C were: 0.816; 0.950 and 3.050 min, respectively. Yield and conversion values were determined by FID coupled gas chromatography using the internal standard method. Yield was determined based on the amount of a benzyl alcohol obtained, while conversion was determined based on the amount of benzaldehyde consumed.

Using potassium carbonate and isopropanol:

Complex **2** (10.0 mg, 10.9 μmol), potassium carbonate (576 mg, 4.36 mmol) and biphenyl (111 mg, 727 μmol), used as internal standard, were placed in a Schlenk. Isopropanol (5.0 mL) was added under an inert atmosphere. Benzaldehyde (220 μL, 2.18 mmol) was added and the system was immersed in a silicone bath with stirring. It was heated at the reflux temperature of the solvent for 2 h. On completion of the reaction, hexane (5.0 mL) was added, and the mixture was filtered using a column of silica gel to later be analyzed.

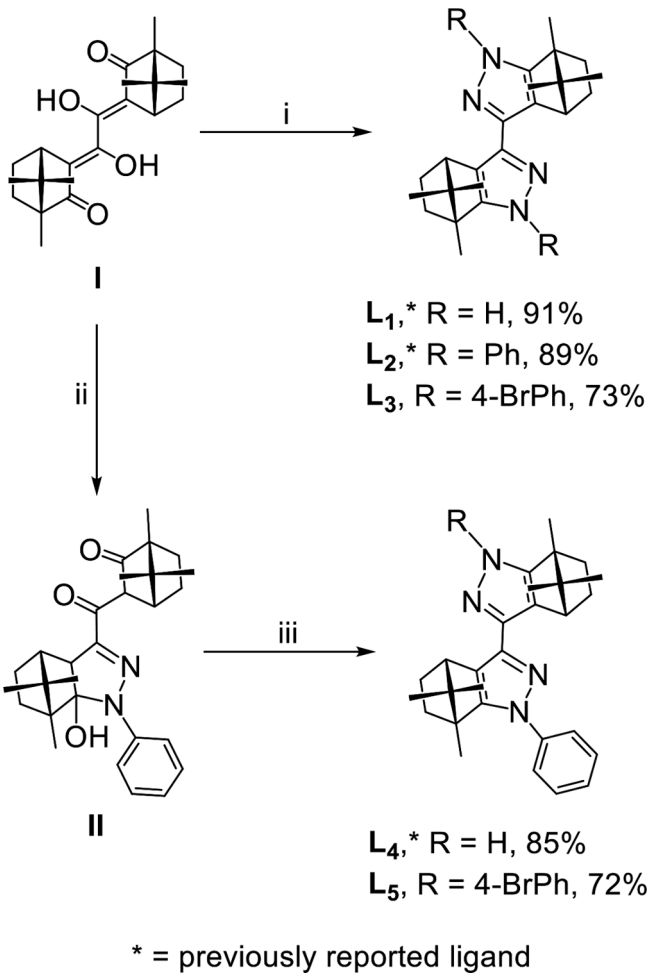
Using formic acid/triethylamine azeotrope as hydrogen source:

Complex **2** (5.0 mg, 5.4 μmol) and biphenyl (55.3 mg, 364 μmol) were placed in a Schlenk. Chloroform (2.5 mL) was added as a co-solvent. Dry and deoxygenated HCOOH/NEt_3 azeotrope 5:2 (2.5 mL) was added under an inert atmosphere. Benzaldehyde (110 μL, 1.09 mmol) was added and the system was immersed with stirring in a silicone bath. It was heated at reflux temperature for 2 h. Upon completion, the temperature was allowed to reach room temperature and the crude was filtered using a column of silica gel to later be analyzed.

3. Results and discussion

3.1. Synthesis and characterization of ligands and complexes

The new C_2 *and* C_1-symmetric (+)-camphopyrazole ligands, $\mathbf{L_3}$ and $\mathbf{L_5}$, respectively, were prepared following a modification of the published procedure for $\mathbf{L_1}$, $\mathbf{L_2}$ and $\mathbf{L_4}$ [35,36]. For the C_2-symmetric ligand: $\mathbf{L_3}$, the synthesis involves a single step procedure in which the reported tetraketone **I** is treated with two equivalents of 4-bromophenyl hydrazine hydrochloride, Scheme 1 (i). The new C_1-symmetric ligand $\mathbf{L_5}$, was prepared following a two-step procedure, in which the reported diketone intermediate **II** was initially obtained from tetraketone **I**, and then condensed with 4-bromophenyl hydrazine hydrochloride. This procedure afforded the respective ligand, as shown in Scheme 1 (ii) and (iii). The set of ligands was prepared in good yields (72–73%). Characteristic ^{1}H NMR signals of C_2 and C_1 ligands corresponding to bridge-head protons in each camphor unit depend on its symmetry. In the case of the C_2-symmetric ligands, $\mathbf{L_2}$-$\mathbf{L_3}$, their symmetric environment is reflected in the fact that the number of signals and the integrals in their ^{1}H

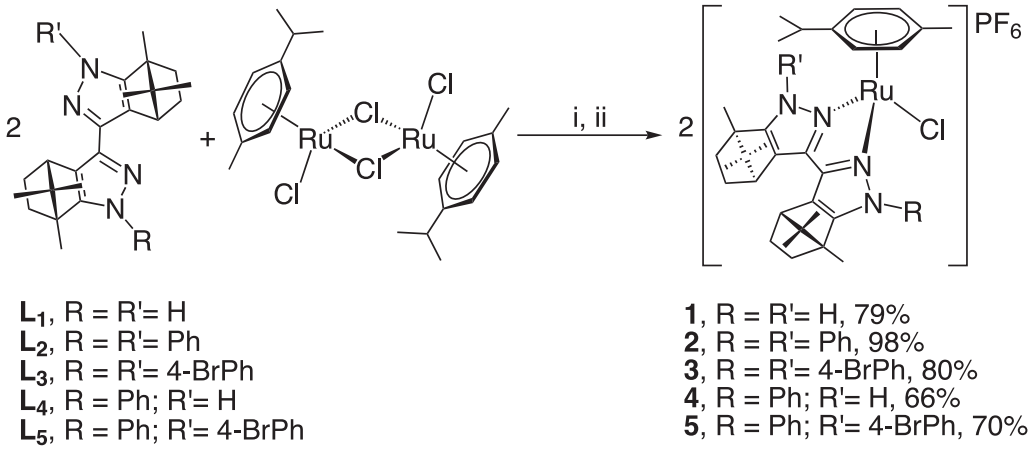


Scheme 1. Synthesis of C_2 and C_1 (+)-camphopyrazole ligands. (i) Ethanol, reflux, 48 h; For $\mathbf{L_1}$: Hydrazine hydrate, concentrated hydrochloric acid; For $\mathbf{L_2}$: Phenyl hydrazine, concentrated hydrochloric acid; For $\mathbf{L_3}$: 4-Bromophenyl hydrazine hydrochloride. (ii) Acetic acid, ethanol, phenyl hydrazine, reflux, overnight. (iii) Ethanol, reflux, 48 h; For $\mathbf{L_4}$: Hydrazine hydrate, concentrated hydrochloric acid; For $\mathbf{L_5}$: 4-Bromophenyl hydrazine hydrochloride.

spectra correspond to half of the total number of expected signals. On the other hand, for C_1 ligands: $\mathbf{L_4}$-$\mathbf{L_5}$ two doublet signals appear corresponding to bridge-head protons in each camphor moieties present in the ligands, Table S1 (Supplementary information). Most of the signals in the ^{1}H NMR spectra for C_1 ligands are not equivalent for each fragment camphor-pyrazole, since these lack of symmetry elements. Similar features are observed on the corresponding ^{13}C spectra of the C_2 and C_1-symmetric ligands.

The coordination chemistry of the prepared (+)-camphopyrazole ligands toward Ru(II) was studied. The route shown in Scheme 2 describes the general procedure used for the synthesis of the ruthenium (II) complexes [(*p*-cymene)RuClL_n]PF_6 (L_n = $\mathbf{L_1}$-$\mathbf{L_5}$, **1**–**5**). The reaction of two equivalents of the respective (+)-camphopyrazole ligand with one equivalent of the ruthenium precursor in chloroform or dichloromethane, followed by anion metathesis in ethanol at room temperature afforded complexes **1**–**5** in good to excellent yields (66–98%). These complexes are air-stable for some weeks and highly soluble in most of the common polar hydrocarbon solvents. The characterization of the complexes was carried out *via* multinuclear NMR and IR spectroscopy. A good correlation between experimental and calculated elemental analysis values for the ruthenium complexes **1**–**5** and for the new ligands prepared was found, thus confirming their analytical purity.

^{1}H NMR characterization of complexes **1**–**5** featured the signals



Scheme 2. Synthesis of ruthenium (II) complexes **1**–**5** with C_2 and C_1 (+)-camphopyrazole ligands. i) $CHCl_3$ or CH_2Cl_2, room temperature, 24 h. ii) Ethanol, NH_4PF_6, room temperature, 24 h.

corresponding to the C_2 or C_1 symmetric ligands and the coordinated *p*-cymene ligand. The spectra of complexes **1**–**3**, bearing C_2-symmetric ligands, display similar features in general. Thus, considering the similarities observed, only the diagnostic signals of complex **1** will be herein discussed. In the ^{1}H NMR spectrum of **1** the methyl groups of the (+)-camphor motif are observed as individual singlets (6 singlets, between 0.62 and 1.39 ppm), while those of the isopropyl group on the *p*-cymene ligand appear as doublets (0.85 and 0.89 ppm). Two doublet signals between 2.86 and 2.89 ppm correspond to the bridge-head protons in each camphor unit on the methinic carbon atoms of bicyclo. Further, singlet signals appear at 12.01 and 12.18 ppm, assigned to the protons of the N—H groups of the pyrazole ring in the coordinated ligand. The rest of the protons on the complex were also assigned *via* ^{1}H NMR. For complexes **2** and **3**, the main difference observed in the NMR characterization corresponds to the signals of the aromatic protons on the unsubstituted and *para*-Br substituted phenyl groups on the pyrazole rings, respectively.

Similarly, analysis of the $^{13}C\{^1H\}$ NMR spectrum of complex **1**, allowed for the assignment of nine signals (between 10.23 and 21.83 ppm) as those corresponding to the carbon atoms of the methyl groups of the (+)-camphor bicyclo and *p*-cymene ligand. The rest of the methylene, methine and quaternary carbon atoms of the camphopyrazole and *p*-cymene ligands have been unequivocally assigned. For complexes **2** and **3**, the spectra featured similar characteristics regarding the general framework of the ligands, with additional signals corresponding to the carbon atoms on the phenyl substituents. With respect to the free C_2 symmetric ligands, the main feature to highlight is the fact that, for complexes **1**–**3** most of the $^{13}C\{^1H\}$ NMR signals appear duplicated, except for the aromatic rings.

The ^{1}H NMR spectra of complexes **4** and **5**, with C_1 symmetric ligands, features broad, low-resolution signals, which overlap each other in the region of the aliphatic protons. Analogously, since both complexes present similar NMR features, only the spectrum of complex **4** will be discussed. In such a case, as mentioned above, a broad multiplet (between 0.20 and 2.45 ppm) was assigned to the protons of the (+)-camphor and the aliphatic protons of the *p*-cymene ligand. Two broad doublets (between 2.64 and 3.18 ppm) correspond to the bridge-head protons in the bicyclo. The rest of the signals of the *p*-cymene ligand and phenyl substituents on the pyrazole ligand, were also assigned. Broad singlet signals at 11.47 and 11.54 ppm, assigned to the protons on the nitrogen atom of the pyrazole ring in the coordinated ligand, could be indicative of the existence of an isomeric mixture in solution for this complex. These N—H proton signals appear at lower fields than in the respective free ligand **L4** (11.32 ppm), evidencing that, upon coordination to the metallic center, the electronic deficiency of the pyrazole ring in the ligand increases. The possible existence of isomers in solution becomes more evident upon analysis of the ^{13}C NMR spectra of complexes **4** and **5**. For these, all of the signals have been unequivocally assigned. However, while a single signal was expected for each carbon atom, given the fact that their structures lack of symmetry elements, two signals are observed for each carbon atom instead (for example, twelve signals between 9.85 and 20.40 ppm, corresponding to the carbon atoms of the methyl groups of the (+)-camphor bicyclo).

To discuss the general trends of the NMR results, the chemical shifts of the characteristic bridge-head protons of the (+)-camphopyrazole ligands in the synthesized complexes have been summarized in Table S2 (Supplementary information). For complexes **1**–**3** with C_2 symmetric ligands, the characteristic signals of the bridge-head protons of the coordinated ligand appears as two doublet signals with coupling constants of 3.7 Hz. In the free C_2 ligands, these protons appear as unique doublets (Table S1). The presence of double the signals with respect to the free ligands in the ^{1}H NMR spectra is also observed in the aliphatic region for the rest of the prepared complexes, which indicates that the protons of each (+)-camphopyrazole fragment are in different chemical environments. The coupling constant in the free ligands varies slightly with respect to coordinated ligands. This suggests that the angles of these protons with their neighboring protons change when the ligand is *cis*-oriented, reducing the orbital interaction of the spins, as indicated by the Karplus diagrams [57]. In Fig. 1, the C_2-symmetry axis in the free ligands, and the C_1 axis in the Ru(II) complexes, can be observed. The loss of the C_2 symmetry in the ligands when *cis*-coordinated creates a non-equivalent environment for the bridge-head protons. This fact has been reported in the literature for other piano-stool complexes with different C_2 symmetric ligands [58–61]. This loss of C_2-symmetry was also evidenced from the duplicity of most of the $^{13}C\{^1H\}$ NMR signals, as previously discussed.

On the other hand, for complexes **4**–**5**, the bridge-head protons on the ligands appear as broad multiplets, unlike the free C_1 ligands where

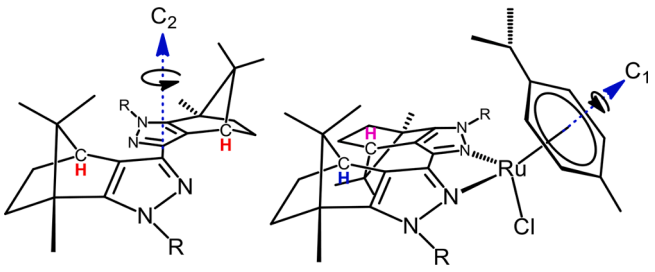


Fig. 1. Structure and axes of rotation in the C_2 symmetry bis-(+)-camphopyrazole ligands and their ruthenium (II) complexes. Bridge-head protons are marked in color.

these appear as two well-defined doublets (Table S1). This observation was attributed to the possible presence of isomers in solution, as mentioned above. The isomerism of this type of complexes can have different origins. In Fig. 2, two possible isomers for complexes with C_1 symmetric ligands can be seen, which are based on the different orientation of the substituents R and R' in the bis-(+)-camphopyrazole ligand, and correspond to the existence of diastereoisomers. It has been reported that piano-stool ruthenium (II) complexes with C_1 symmetry ligands can generate diastereoisomers in solution [59,60]. In complexes with C_2 symmetry ligands, this isomerism is not possible since the substituents on both sides of the ligand are identical.

Hence, the ^{13}C NMR spectra of complexes **1**–**3** confirm the presence of a single species in solution and indicates that the origin of isomerism in complexes **4** and **5** is mainly due to the spatial arrangement of the substituents on the ligand. This also excludes the possible observation of other types of isomerism, which could originate due to rotation of the bond between the metal center and the *p*-cymene ligand.

Finally, a comparison between the chemical shift ranges of the signals assigned to the *p*-cymene ligand in the ^1H NMR spectrum of complexes **1**–**5** with those of the dimeric precursor [(*p*-cymene)$RuCl_2$]$_2$ could give information about the electronic effect of ligands on the metal center. These are shown in Table 1.

The signals corresponding of the olefinic protons of the *p*-cymene ligand in complex **1** appear at lower fields, relative to the dimeric precursor. This could indicate that bis-(+)-camphopyrazole ligand in the complex **1** attracts electron density of the metal center, disfavoring the metal-arene backdonation more than in the precursor. This low-field shift has been reported for piano-stool complexes with π-acceptor ligands, such as bipyridines and phosphines [62–65]. In the dimeric precursor, without bidentate ligands, the arene ligand orbitals have double bond characteristics and appear more shielded. On the other hand, for the complexes **2**–**5** chemical shifts of protons on the methine carbon atoms of the *p*-cymene ligands appear at higher fields than in the dimer precursor. This phenomenon has been reported in the literature for piano-stool complexes with bidentate ligands with S, N and O donor atoms [66–68]. Such observation suggests that the backdonation from the metal to the *p*-cymene ligand is more favored in these complexes, probably since the substituted phenyl ligands donate electron density to the metallic center. Thus, ruthenium (II) can populate the π-antibonding orbitals of arene ligand with this electron density, making its orbitals have single bond characteristics [69].

Additional characterization was carried out *via* IR spectroscopy for complexes **1**–**5**. Characteristic bands of the corresponding ligands in the prepared complexes. The bands of greatest interest correspond to the stretching frequencies of the C═N and C═C bonds in the pyrazole rings, since these can interact with the metal center through the π system. Values of the stretch frequencies for the complexes with C_2 and C_1 symmetry ligands are shown in Table 2. Furthermore, characteristic

Table 1
Chemical shift ranges (δ) of the olefinic protons in the *p*-cymene ligand on the dimeric precursor and ruthenium complexes **1**–**5** with bis-(+)-camphopyrazole ligands.

Complex	δ (ppm)
[(*p*-cymene)$RuCl_2$]$_2$	5.29–5.45
1	5.74–6.13
2	3.73–4.79
3	4.08–5.91
4	3.78–5.02
5	3.50–5.16

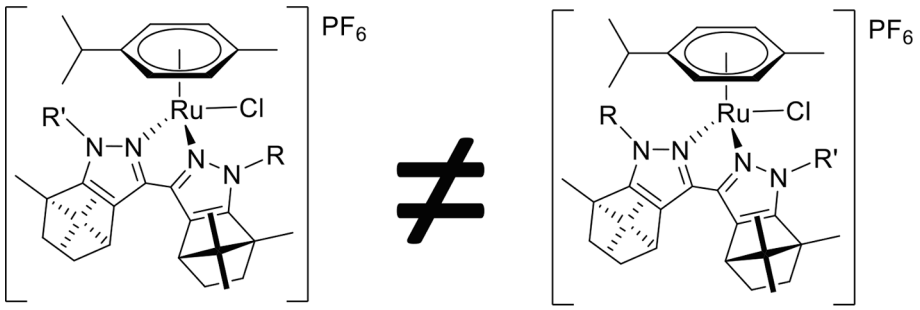
Table 2
Values of stretching frequencies of the C═N and C═C bonds of the pyrazole ring for complexes **1**–**5** with C_2 and C_1 symmetry bis-(+)-camphopyrazole ligands.

Complex	Stretching frequencies (cm^{-1})	
	C═N (pz)	C═C (pz)
1	1554	1472
2	1593	1492
3	1597	1534
4	1596	1455
5	1594	1456

intense bands around 850 cm^{-1} (P-F stretching frequencies), confirm the presence of the hexafluorophosphate counterion for all the complexes, **1**–**5** [70].

The trend found in the values of the frequencies of the C═N and C═C bonds in the complexes with C_2 symmetric ligands is: **3** > **2** > **1**. This can be attributed to a modification of the electron density of the pyrazole rings, due to the different substitution of the nitrogen atoms in the pyrazole rings of the ligands. The values of the stretch frequencies of the C═N and C═C bonds in the complexes **4**–**5** with C_1 symmetric ligands, do not vary significantly from each other. This suggests that electronic effects of the substituents are not significant in this case.

Comparing the values of the stretch frequencies in the C═C bonds in the pyrazole rings of complexes **1**–**3** with the free ligands of C_2 symmetry: $\mathbf{L_1}$ (1471 cm^{-1}), $\mathbf{L_2}$ (1452 cm^{-1}) and $\mathbf{L_3}$ (1465 cm^{-1}), it is found that the former are higher. This suggests that C_2 ligands are electron density donors through their π system in the complexes, that is, pyrazole rings donate electron density to the metal center, increasing the frequency values. Likewise, the values of the stretching frequencies of the C═N bond in complex **3** also increase with respect to free ligand $\mathbf{L_3}$ (1587 cm^{-1}). However, it is observed that the values of the stretching frequencies of the C═N bonds decrease for complexes **1** and **2** with respect to free ligands $\mathbf{L_1}$ (1571 cm^{-1}) and $\mathbf{L_2}$ (1596 cm^{-1}), respectively. This could indicate that the C═N bonds in complex **1** receive electron density *via* backdonation from the metal center.



4: R=H, R'=Ph
5: R=4-BrPh, R'=Ph

4': R=Ph, R'=H
5': R=Ph, R'=4-BrPh

Fig. 2. Proposed structure for possible diastereoisomers: **4**′ and **5**′ in ruthenium (II) complexes with bis-(+)-camphopyrazole ligands of C_1 symmetry: **4** and **5**.

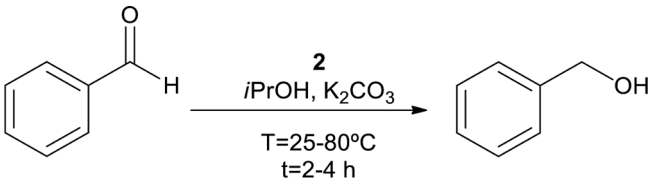


Fig. 3. TH of benzaldehyde with *i*PrOH/K_2CO_3 using complex **2**.

A comparison of the values of the stretch frequencies for the C═N and C═C bonds in complexes **4** and **5** with C_1 symmetry free ligands: $\mathbf{L_4}$ (1596 and 1454 cm^{-1}) and $\mathbf{L_5}$ (1596 and 1454 cm^{-1}), reveals no significant differences. This could be attributed to the fact that the metal–ligand orbital interaction in these complexes with C_1 symmetry ligands is less than in the complexes with C_2 symmetry ligands. However, to determine the reason behind the lack of variation between frequencies, additional in-depth studies should be carried out with the aid of computational tools.

3.2. Catalytic studies

The initial evaluation of the transfer hydrogenation reaction was performed using complex **2** as catalyst precursor, benzaldehyde as model substrate and isopropanol as the hydrogen source, and varying reaction conditions such as: temperature, time, base/substrate and substrate/catalyst ratios, see Fig. 3. A comparison between catalytic runs carried out under an inert atmosphere and in air revealed no significant differences in the yield values obtained. Therefore, the reactions were conducted in the presence of air. Complex **2** was the precursor of choice among the prepared complexes since a larger quantity of this compound was more available, being the one obtained with a higher synthetic yield. Potassium carbonate was selected as base for these reactions, since it is an easy-to-handle, cheap, and air-stable compound.

Considering that the variation of reaction conditions resulted in low yield and conversion values (<15%), the influence of the amount of solvent in the TH reaction was studied. The results obtained are shown in the Table S3 (Supplementary information). As the amount of solvent is increased, yield and conversion values are observed to increase significantly to a maximum of 57% and 66%, respectively. To explain this result, it must be considered that the TH of benzaldehyde with isopropanol as hydrogen source is a thermodynamically neutral reaction [71]. This implies that the reaction is quite close to the equilibrium and that the formation of the product can be favored using *Le Chatelier* principle. By increasing the amount of isopropanol, which is at the same time one of the reagents, the increase in the equilibrium constant displaces the reaction towards the formation of products. Furthermore, an increase in the amount of dissolved potassium carbonate could be an additional benefit of using a larger amount of solvent. To avoid excessive solvent expenditure, successive reactions were carried out using an intermediate amount of isopropanol (15 mL).

The catalytic potential of the prepared ruthenium (II) complexes with C_2 and C_1-symmetric bis-(+)-camphopyrazole ligands, **1**–**5**, in the TH of benzaldehyde (as model substrate) using isopropanol as hydrogen source, was evaluated. The results obtained are shown in the Table 3. The best substrate/complex (catalyst)/base (S/C/B) ratio found was 100/1/400.

In the absence of catalyst, or by using the precursor [(*p*-cymene)$RuCl_2]_2$ as catalyst no conversion toward the expected product was observed (entry 1). In the presence of 1.0 mol% of complex **3**, with a C_2-symmetric ligand, the TH of benzaldehyde proceeded to completion, affording benzyl alcohol quantitatively. By contrast, attempts to use a smaller catalyst load, such as 0.5 mol% were unsuccessful, leading only to moderate yield of the product (entry 4). It was observed that the influence of the catalyst load in the yield and conversion values was not as significant when complexes **1** and **2** were used as catalysts, although a slight decrease were also noted (entries 3 and 2). With complex **3** (catalyst load = 1.0 mol%) the TH reaction is more selective, with conversion occurring only to the desired product without formation of by-products (entry 4). By contrast, complex **2** (1.0 mol%) seems to promote side reactions, since the differences between the yield and conversion values become more evident in such a case (entry 3). In general, the trend in the yield and conversion values for the complexes with C_2 symmetric ligands is **3** > **2** > **1**, regardless of the catalytic load. On the other hand, for the complexes bearing ligands with C_1 symmetry, it was observed that the yield and conversion values using complexes **4** and **5** do not vary significantly with an increase in catalyst loading (entries 5 and 6).

To expand the scope of the complexes studied we consider evaluating substituted benzaldehydes, however recent studies have shown that the electronic nature of the substituents affects very little their yields [17,18] and therefore we chose valeraldehyde, an aliphatic aldehyde. This was studied under the best conditions previously determined for benzaldehyde. In general, this type of substrate is usually more sensitive to the basic conditions of TH due to the presence of hydrogen atoms in α position to the carbonyl group. As a result, such substrate is susceptible to participating in aldol condensation reactions generating different by-products in addition to the one of interest. The results of the TH reactions of valeraldehyde are also shown in Table 3. The reaction in absence of complex shows a high conversion value (entry 1), which indicates that under the conditions used, the formation of by-products other than the product of interest, *n*-pentanol, is favored. The trend in the behavior of complexes with C_2 symmetry ligands in TH of valeraldehyde is similar as in TH of benzaldehyde: **3** > **2** > **1**. However, complex **1** does not generate the product in appreciable amounts (entry 2), probably due to their instability in solution and the π-acceptor nature of ligand in the complex, as previously explained. Conversion using complex **1** is complete, while with complexes **2** and **3** the conversion values are moderate (entries 2–4). This indicates that complex **1** favors the transformation of the substrate through side reactions. The catalytic behavior of complex **3** is better, with respect to the rest of the complexes, probably due to the electro-donating effect of the bromine atoms, as mentioned above. This effect can increase the electron density in the

Table 3
TH of benzaldehyde and valeraldehyde with *i*PrOH using the ruthenium (II) complexes **1**–**5**.

Entry	Complex	Benzaldehyde		Valeraldehyde	
		Yield (%)	Conversion (%)	Yield (%)	Conversion (%)
1	–	0[i,ii]	0[i,ii]	0[ii]	58[ii]
2	**1**	24(16)	28(20)	<1	>99
3	**2**	34(34)	44(36)	18	53
4	**3**	>99(62)	>99(69)	45	65
5	**4**	20(23)	23(28)	8	41
6	**5**	35(30)	40(32)	<1	55

Reaction conditions: Reflux; Time = 4 h; $V_{(iPrOH)}$ = 15 mL; Base = K_2CO_3; S/C/B = 100/1/400; Yields and conversions in parentheses are using S/C/B = 200/1/400.
[i] Reactions in presence of [(*p*-cymene)$RuCl_2]_2$;
[ii] Reactions in absence of metal complex.

coordinated pyrazole rings, which in turn increases the electron density of the metal center and therefore their ability to mediate TH reactions. This complex **3**, also shows the highest selectivity since the difference between the yield and conversion values is less than in the rest of the complexes, which implies the formation of smaller amounts of by-products. Complexes **2**–**3**, with C_2 symmetric ligands afford higher yield and conversion values than complexes **4**–**5**, with C_1 symmetric ligands (entries 3–4 vs 5–6). This is consistent with the behavior previously shown by the complexes with the C_2 symmetric ligand used in the TH of benzaldehyde. The complexes with the C_1 symmetric ligands lead to lower yields, however, their conversion values are moderate. This suggests that by-product formation is favored over the reduction reaction to the alcohol of interest. The trend according to the catalytic behavior of the complexes is **4** > **5**. Complex **4** affords a slightly higher yield within this group, probably since it is more selective towards TH than to the possible side-reactions, as established for the TH benzaldehyde. For complex **5**, the alcohol of interest is not observed, however, the conversion value is moderate, indicating that side reactions are favored.

The evaluated complexes afford moderate yield and conversion values, compared to some of the systems reported in the literature [12,14,15,17,18]. However, in most of these reports involving Ru (II) complexes, the effect of the base in the absence of the complex on the yield values obtained was not fully understood.

To determine the effect of the base strength on TH of benzaldehyde, catalytic reactions were carried out using potassium *tert*-butoxide and sodium hydride with complexes **1**, **2** and **4**. The results obtained are shown in the Table 4.

TH reactions carried out in absence of complex could assess on the stability of benzaldehyde in the reaction medium. When 200 mol% of potassium carbonate was used no product was obtained (entry 1), while that when the same amount of potassium *tert*-butoxide was used it was possible to demonstrate that strongly basic conditions lead to the formation of the product of interest with good yield and conversion values (entry 2). This is probably because alkali metals can catalyze hydrogen transfer reactions through of the Meerwein-Ponndorf-Verley (MPV) mechanism. It has been shown that potassium *tert*-butoxide can act as a reducing agent in the presence of isopropanol with good yields [72]. The yield and conversion values using the complexes **1** and **2** in the presence of this base do not vary significantly with respect to the reaction in the absence of the complex (entries 2–4), while using complex **4** the yield of the product was lower (entry 5).

Taking into account the lower stability and availability of potassium *tert*-butoxide, we turned our attention to sodium hydride as a base in the reactions of TH. In this way, the yield and conversion values in the reactions carried out in absence of complex with this base can also be attributed to the same base-mediated effect described before (entry 6). Therefore, the amount of sodium hydride used was reduced from 200 to 5 mol% to favor the ruthenium-mediated formation of the product of interest and to reduce the amount of side products by effect of the base (entries 7–8). Considering only the conversion values it can be noted that the stability of benzaldehyde using NaH was lower than using K_2CO_3.

On the other hand, it was found that the yield and conversion values increase when complex **1**, **2** and **4** were used with a strong base with less nucleophilic character and greater solubility such as sodium hydride, contrasting with the behavior of the same complexes using potassium carbonate (Table 4, entries 9–11 versus Table 3, entries 2, 3 and 5). This is attributed to the increase in the concentration of the isopropoxide ion, which participates in the formation of the intermediates in the catalytic process. Using NaH, complex **4**, with the ligand of C_1 symmetry, showed higher yield and conversion values than complexes **1**–**2** with C_2 symmetric ligands.

Finally, the TH reaction of benzaldehyde was evaluated using formic acid as hydrogen source and triethylamine as base. The general reaction is observed in Fig. 4. A brief evaluation of the reaction conditions: inert atmosphere or air, temperature, time, substrate/catalyst ratio, formic acid/triethylamine ratio and co-solvent was carried out using complex **2**. The results are shown in Table 5.

The stability of the system was determined without an inert atmosphere. For this, comparative catalytic reactions were carried out in air and under a nitrogen atmosphere using the best conditions found in TH with isopropanol. No significant differences were found in conversion and yield values when performing catalytic tests under inert atmosphere and in air (entries 1–2), as previously observed for the system using isopropanol as hydrogen source. Therefore, subsequent reactions were carried out in air. The effect of catalytic loading was also studied. As the catalytic loading decreases, a considerable decrease in the yield and conversion values occurs (entries 2 vs 3 and 4 vs 5). A catalytic loading of 1.0 mol% was then selected since it produces the highest yield value (entry 2). Likewise, the effect of the temperature on the TH of benzaldehyde was evaluated. The yield and conversion values are higher when the reaction is carried out at the reflux temperature of chloroform (entry 4 vs 6) and, therefore, it was established as the best condition. Unlike the isopropanol system, this reaction generates benzyl alcohol at room temperature, demonstrating the exergonic character of the reduction reaction using formic acid compared to isopropanol as hydrogen source [3]. Subsequently, the effect of the reaction time on the benzaldehyde TH was determined. By decreasing the reaction time, a decrease in the yield and conversion values was obtained (entry 3 vs 4). The difference between yield and conversion values decreases with decreasing reaction time, indicating either that long reaction times decrease selectivity or that longer reaction times favor the transformation of the substrate or product(s) into by-products. This is an expected phenomenon since other TH aldehyde systems require short reaction times to avoid decreases in selectivity [73]. Also, the effect of the formic acid/triethylamine ratio on the TH of benzaldehyde was evaluated. The 5:2 azeotropic mixture was compared with the best ratio reported in the literature for the carbonyl TH reaction, 1:5 azeotropic mixture [74]. By using the mixture of formic acid/triethylamine in 1:5 M ratio, a low yield value is obtained, but the conversion value increases (entry 7 vs 4). This can probably be attributed to the excess base present, which generates side reactions that convert aldehyde into by-products. When THF was used as co-solvent in a TH reaction, exceptionally low yield and conversion values were obtained (entry 8 vs 4). This is probably due to

Table 4
TH of benzaldehyde using ruthenium complexes **1**, **2** and **4** as catalyst precursors with NaH and KO*t*Bu in isopropanol.

Entry	Complex	Base	S/C/B	Yield (%)	Conversion (%)
1	*	K_2CO_3	200/0/400	0	0
2	*	KO*t*Bu	200/0/400	62	>99
3	**1**	KO*t*Bu	200/1/400	67	>99
4	**2**	KO*t*Bu	200/1/400	68	>99
5	**4**	KO*t*Bu	200/1/400	53	>99
6	*	NaH	200/0/400	70	72
7	*	NaH	200/0/50	14	22
8	*	NaH	200/0/10	0	14
9	**1**	NaH	200/1/10	45	51
10	**2**	NaH	200/1/10	53	58
11	**4**	NaH	200/1/10	69	77

Reaction conditions: Reflux; Time = 4 h; V_{iPrOH} = 15 mL; * Reactions in absence of metal complex.

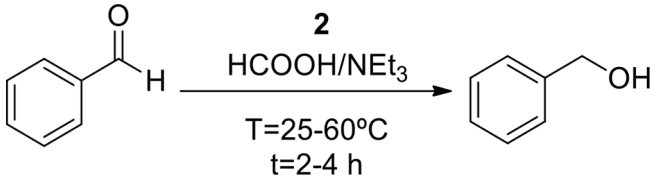


Fig. 4. TH of benzaldehyde with formic acid/triethylamine using complex **2**.

Table 5
TH of benzaldehyde with formic acid/triethylamine: Screening of reaction conditions using complex **2** and evaluation of the ruthenium (II) complexes **1**, **3**–**5**.

Entry	Complex	S/C	Time (h)	Yield (%)	Conversion (%)
1[i]	**2**	100/1	4	54	>99
2	**2**	100/1	4	55	>99
3	**2**	200/1	4	37	66
4	**2**	200/1	2	23	35
5	**2**	400/1	2	18	40
6[ii]	**2**	200/1	2	9	24
7[iii]	**2**	200/1	2	14	52
8[iv]	**2**	200/1	2	1	14
9[v]	–	100/1	4	0	10
10[vi]	–	100/1	4	0	9
11	**1**	100/1	4	45	>99
12	**3**	100/1	4	65	>99
13	**4**	100/1	4	16	26
14	**5**	100/1	4	30	46

Reaction condition: Air; Reflux; $V_{(HCOOH/NEt3\ 5:2)} = 2.5$ mL;$V_{(CHCl3)} = 2.5$ mL;
[i] N_2;
[ii] Room temperature;
[iii] $V_{(HCOOH/NEt3\ 1:5)} = 2.5$ mL;
[iv] $V_{(THF)} = 2.5$ mL;
[v] Reaction in absence of complex;
[vi] Reaction in presence of $[(p\text{-cymene})RuCl_2]_2$

the coordinating nature of this solvent, which could be deactivating the catalytically active species by occupying a vacant coordination site necessary for the substrates.

Once the best reaction conditions have been established using complex **2**: reflux temperature, 1.0 mol% catalytic loading, 4 h of reaction time, chloroform as co-solvent and a formic acid/triethylamine mixture with a molar ratio 5:2, the ruthenium (II) complexes **1** and **3**–**5** with bis-(+)-camphopyrazole ligands were evaluated in the TH of benzaldehyde using formic acid/triethylamine as hydrogen source. The results are also shown in Table 5. In absence of complex or using the precursor $[(p\text{-cymene})RuCl_2]_2$ as catalyst, the formation of benzyl alcohol is not observed (entries 9 and 10). This highlights the role of the ruthenium complexes **1**–**5** as catalysts in TH under these conditions, and the effect of the bis-(+)-camphopyrazole ligands to generate/stabilize the catalytically active species. However, the low conversion values obtained indicate the formation of by-products mostly because of the reaction conditions used.

The yield values in the TH of benzaldehyde with formic acid/triethylamine mixture as hydrogen source using the prepared complexes **1**–**3**, with C_2 symmetric ligands, are greater than those obtained with isopropanol/potassium carbonate. By contrast, the conversion values are higher than those found with isopropanol, indicating that the reaction with the formic acid/triethylamine mixture is less selective (Table 5 vs Table 3). This could be because the alcohol produced reacts to generate by-products. Complex **3** was the most active under these TH conditions (entry 12) probably due to the resonance electro-donating effect of bromine atoms in the *para* position, as previously described. Interestingly, complex **1** turned out to be more active with this hydrogen source than with isopropanol (Table 5, entry 11 versus Table 3, entry 2) suggesting a greater stability in the $HCOOH/NEt_3$ mixture. The trend in catalytic behavior found for these complexes is **3** > **2** > **1**. The lower performance of complex **1** could be attributed to the π-acceptor nature of ligand, as demonstrated by NMR analysis. In the TH using formic acid/triethylamine azeotrope, no color changes were observed during the course of the reaction when complex **1** was used as catalyst precursor. In such a case, the solution remained yellowish-orange during the whole period of time. By contrast, in the TH using isopropanol, the solution of complex **1** is yellow, when it reaches the reflux temperature it changes to red and after 5 min it turns brown. This seems to indicate that under TH conditions with isopropanol/potassium carbonate, complex **1** is unstable. The pyrazole ring has a $pKa = 2.48$, low enough to be deprotonated by potassium carbonate [75]. It is likely that in complex **1**, the ligand is de-protonated, generating a pyrazolate which can donate higher electron density to the ruthenium (II) metal center. This would favor oxidation processes to ruthenium (III) and therefore its instability. On the other hand, with formic acid the medium is essentially acidic, being the acid in excess. Thus, it was proposed that the nitrogen atoms of the pyrazole rings in the ligand in complex **1** remain protonated under these conditions, which would explain the greater stability in solution in the formic acid/triethylamine mixture, when compared to the system in isopropanol.

Complexes **4**–**5** with C_1 symmetric ligands, afford low yield and conversion values comparable to those obtained with isopropanol. The trend in catalytic behavior found for these complexes is **5** > **4**. Complex **5** shows the highest yield in this series probably due to the effect of the bromine atom in *para* position, similar to complex **3**. After comparison of both types of complexes, it becomes evident that by using complexes **1**–**3** higher yield values are obtained than with compounds **4**–**5**. As described above, this could be attributed to the fact that the metal–ligand interaction for complexes with C_2 symmetric ligands is stronger, as indicated by IR analyses. Conversion values using complexes **1**–**3** with the C_2 symmetry ligands are almost quantitative, while in complexes **4**–**5** with C_1 symmetric ligands these values do not exceed a 46% conversion. This again indicates that complexes with C_2 symmetric ligands show a better catalytic behavior and that the number of by-products increases with the amount of alcohol of interest present in the mixture.

The preparation and characterization of these Ru (II) complexes with bis-(+)- camphopyrazole ligands of C_1 and C_2 symmetry opens a window of possibilities to study asymmetric transfer hydrogenation of prochiral substrates in future works to be carried out by our research group. Similarly, reported complexes in this work will be considered in more detail to be studied in transfer hydrogenation reactions with a wide variety of substituted benzaldehydes and other substrates, such as nitro compounds, in an extensive work in progress.

Considering the effect of the ligand in the complexes on the studied TH reactions, an internal sphere mechanism might be proposed. This pathway involves the formation of metal-hydride intermediate, which is generated through coordination of the donor and hydrogen acceptor to the metal center in separate steps. Fig. 5 shows the internal sphere mechanism proposed for the ruthenium (II) complexes that contain bis-(+)-camphopyrazole ligands using isopropanol/potassium carbonate and formic acid/triethylamine, based on reports from the literature [17,76].

On step **I** of the mechanism using isopropanol/potassium carbonate, the formation of an isopropoxide-metal species as catalytic intermediate, generated by exchange with the chloride after deprotonation of isopropanol by the base, is proposed. Then, a β- elimination reaction generates acetone and a hydride complex, step **II**. This intermediate is electronically saturated to continue with the catalytic cycle, and therefore an available coordination site is required. This can be achieved through the change in hapticity of the *p*-cymene ligand. The hapticity change has been proposed by some authors for internal sphere mechanisms based on the conformational rigidity [77], and the donor nature of the ligands [78]. Therefore, it is postulated that step **III** of this mechanism is the change in hapticity from η^6 to η^4 followed by simultaneous coordination of the substrate. Then, in the step **IV**, migratory insertion of the formyl group at the Ru-H bond allows for the formation of the primary alkoxide. Finally, an isopropanol-mediated proton transfer process occurs, in which the alkoxide of interest leaves the coordination sphere as benzyl alcohol to regenerate the catalytically active species with a coordinated isopropoxide ligand, step **V**.

The reaction in formic acid/triethylamine occurs probably through step **I′** to obtain a hydride complex. Similar steps: **III**, **IV** would allow the formation of the primary alkoxide, while **V′** would lead to the formation of the product, regenerating the catalytically active species. The experimental evidence obtained indicates that, upon addition of the complexes to the formic acid/triethylamine mixture in the absence of

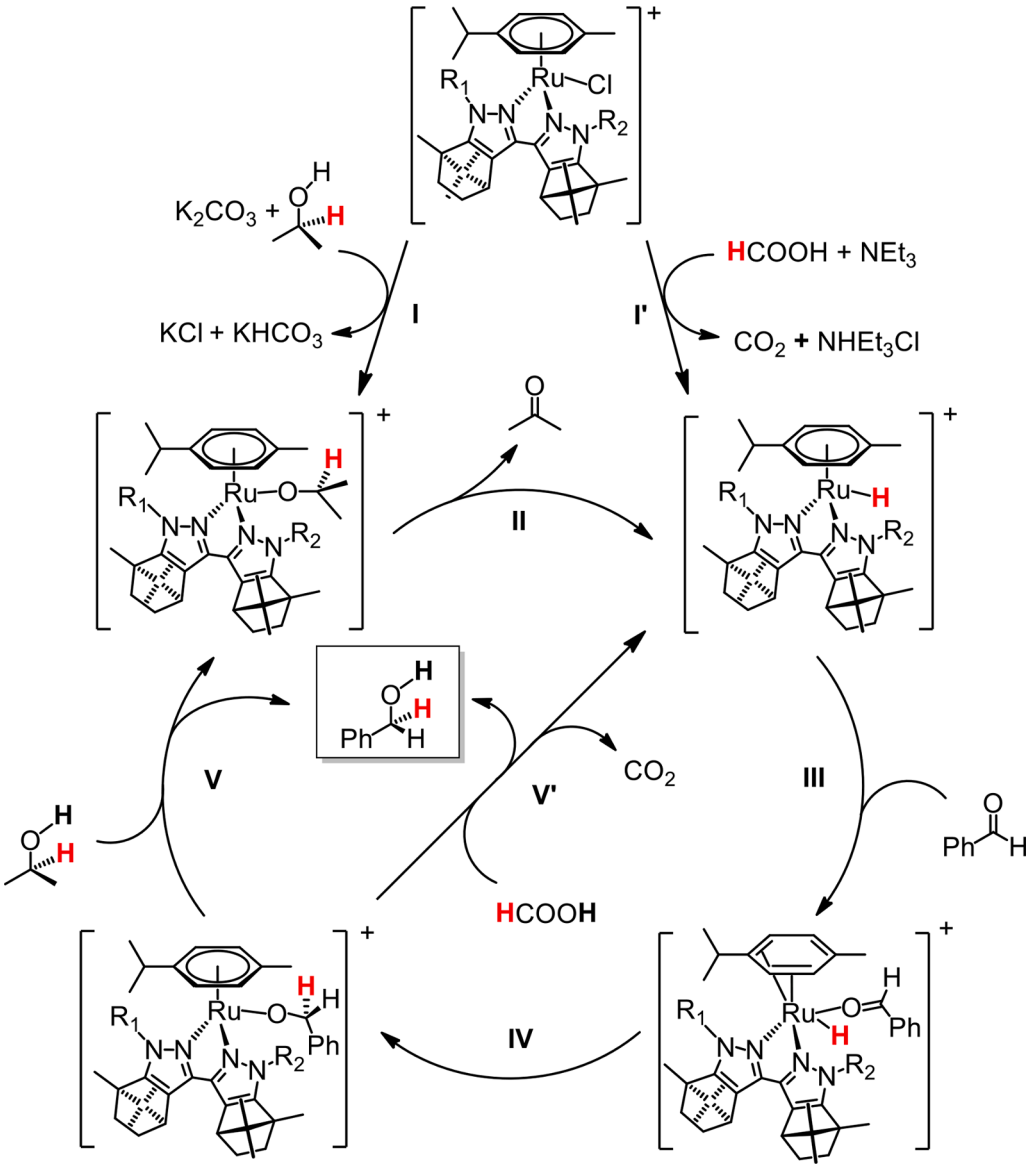


Fig. 5. Proposed internal sphere mechanism for transfer hydrogenation of benzaldehyde with *i*PrOH/K_2CO_3 and HCOOH/NEt_3 using Ru (II) complexes with bis-(+)-camphopyrazole ligand.

aldehyde, a gas release is observed. Such gas evolution was attributed to the release of carbon dioxide, product of the dehydrogenation of formic acid. This observation could confirm that the formation of the hydride intermediate in such hydrogen source is favored, and that the reaction rate is controlled by the steps following it.

4. Conclusions

Five piano-stool ruthenium (II) complexes with new bis-(+)-camphopyrazole bidentate ligands were prepared with good yields and characterized. The complexes were evaluated in the TH of benzaldehyde and valeraldehyde in air using potassium carbonate as a less expensive and easy-to-handle base, and isopropanol as hydrogen source, affording moderate yields (>54%). One of the catalytic precursors, bearing the C_2-symmetric ligand with a 4-bromophenyl substituent, afforded quantitative yields of benzyl alcohol (>99%). The use of a strong base with less nucleophilic character and better solubility increases the yield and conversion values of the synthesized complexes. Also, the TH of benzaldehyde was evaluated with a formic acid/triethylamine mixture, finding yields and conversion values higher for complexes with C_2-symmetric ligand to those obtained using isopropanol as solvent/hydrogen source.

CRediT authorship contribution statement

Christian O. Blanco: Investigation, Formal analysis, Writing - original draft, Visualization. **Ligia Llovera:** Investigation, Data curation, Resources. **Alberto Herrera:** Investigation, Data curation, Resources. **Romano Dorta:** Conceptualization, Investigation, Resources. **Giuseppe Agrifoglio:** Conceptualization, Resources. **Doménico Venuti:** Investigation, Data curation, Resources. **Vanessa R. Landaeta:** Data curation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Jesús Pastrán:** Conceptualization, Formal analysis, Methodology, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2021.120429.

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