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Half-sandwich ruthenium(II) complexes with water-soluble Schiff base ligands: Synthesis and catalytic activity in transfer hydrogenation of carbonyl compounds

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Abstract

New ionic Schiff-base ligands have been synthesized by condensation of (3-formyl-4-hydroxybenzyl)triphenylphosphonium and 3-(3-formyl-4-hydroxybenzyl)-1-methyl-1*H*-imidazol-3-ium chloride and hexafluorophosphate salts with *N,N*-dimethylethylenediamine. Treatment of the dimeric derivative [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] with two equivalents of these ligands allowed the preparation of novel mononuclear water-soluble Ru(II) complexes, which proved to be catalytically active in the transfer hydrogenation of ketones and aldehydes under aqueous conditions.

Keywords: Schiff-base ligands; Ionic ligands; Ruthenium; Transfer hydrogenation; Ketones; Aqueous catalysis

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1. Introduction

In the past decades, Schiff-base ligands have attracted considerable interest due to their rich coordination chemistry [1-3]. The main advantages of these ligands stem from the easy access under smooth conditions, and the facility to modulate their structures and chemo-physical properties through the incorporation of additional functional groups. The resulting complexes have found numerous applications as catalysts [1], pharmaceuticals [2], and magnetic or luminescent materials [3]. Interestingly, the presence of an ionic or a highly polar substituent in the backbone of the Schiff-base usually induces an enhanced solubility of their derivatives in aqueous medium, a striking feature both for biological or catalytic uses. In this context, a wide range of ligands with sulfonate, carboxylate, amino, ammonium, imidazolium or phosphonium functionalities, and their corresponding complexes, have been described [4].

On the other hand, the η^6-arene-ruthenium(II) complexes represent an important class of compounds [5], well-known for promoting a great variety of catalytic reactions, such as C-H activation [6], nitrile hydration [7] or transfer hydrogenation processes [8] to name a few. In addition, their outstanding activities, combined with a good stability against water, make them ideal candidates to perform catalytic organic transformations in aqueous medium [9]. For this purpose, numerous water-soluble arene-ruthenium(II) complexes have been designed, the most common strategy to obtain such derivatives consisting in the coordination of an ionic ligand onto the metal center. In this context, a plethora of half-sandwich ruthenium(II) compounds with functionalized phosphines, *N*-heterocyclic carbenes or diamines, has been prepared [9d,10]. In marked contrast, arene-Ru(II) derivatives containing an ionic Schiff-base still remain very scarce [11].

With these precedents in mind, we decided to prepare new Schiff-base ligands tagged with a phosphonium or an imidazolium substituent and explore their coordination onto an arene-ruthenium(II) fragment. Furthermore, the catalytic activity of the resulting complexes has

been evaluated in the transfer hydrogenation of ketones and aldehydes under aqueous conditions.

2. Experimental

2.1. General information

All the reagents were obtained from commercial suppliers and used as received, with the exception of the aldehydes **1a-b** and **3a-b** [12], the imine **7** [13] and the dimeric precursor [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] [14], which were prepared following previously reported methodologies. All the manipulations with ruthenium complexes were performed under argon atmosphere using vacuum-line and standard Schlenk techniques. Organic solvents were dried by standard methods and distilled under argon before use [15]. IR spectra were recorded with a Perkin-Elmer 1720-XFT spectrometer. GC measurements were performed by using a Hewlett-Packard HP6890 apparatus (Supelco Beta-Dex™ 120 column, 30 m length, 250 μm diameter). Elemental analyses were performed by the Analytical Service of the Instituto de Investigaciones Químicas (IIQ-CSIC) of Sevilla. The NMR spectra were recorded with a Bruker DPX300 or AV400 spectrometer. The chemical shift values (δ) are given in parts per million and are referenced to the residual peak of the deuterated solvent employed (^{1}H and ^{13}C) or an external 85% aqueous H_3PO_4 solution (^{31}P).

*2.2. Synthesis of ligand **2a**.*

A mixture of aldehyde **1a** (0.50 g, 1.15 mmol) and *N,N*-dimethylethylenediamine (0.10 g, 1.15 mmol) in 30 mL of methanol was heated at reflux temperature for 4 hours. After cooling, the resulting solution was evaporated to dryness. Then, the yellow solid was washed 3 times with 20 mL of diethylether and vacuum-dried. Yield: 91 % (0.53 g); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 22.6 (s) ppm; ^{1}H NMR ($CDCl_3$): δ= 2.40 (s, 6 H, NMe_2), 2.75 and 3.72 (both t, 2 H each, $^3J_{HH}$ = 6.5 Hz, CH_2CH_2), 5.49 (d, 2 H, $^2J_{PH}$ = 13.8 Hz, CH_2P), 6.65 (d, 1 H, $^3J_{HH}$ = 8.6 Hz,

$CH_{aromatic}$), 6.81 (broad d, 1 H, $^{3}J_{HH}$ = 8.6 Hz, $CH_{aromatic}$), 7.41 (broad s, 1 H, $CH_{aromatic}$), 7.61-7.81 (m, 15 H, PPh_3), 8.20 (s, 1 H, CH=N), 13.5 (very broad s, 1 H, OH) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 29.6 (d, $^{1}J_{PC}$ = 46.4 Hz, CH_2P), 45.4 (s, NMe_2), 56.4 and 59.4 (s, CH_2), 116.3 (d, J_{PC} = 8.5 Hz, $C_{aromatic}$), 117.5 (s, $CH_{aromatic}$), 118.0 (d, $^{1}J_{PC}$ = 79.4 Hz, C_{ipso} of PPh_3), 118.8 (s, $C_{aromatic}$), 130. 1 (d, J_{PC} = 12.4 Hz, $C_{ortho\ or\ meta}$ of PPh_3), 134.4 (d, J_{PC} = 9.7 Hz, $C_{ortho\ or\ meta}$ of PPh_3), 134.8 (s, $CH_{aromatic}$), 134.9 (s, CH_{para} of PPh_3), 135.1 (d, J_{PC} = 5.8 Hz, $CH_{aromatic}$), 162.0 (s, C-OH), 165.7 (s, CH=N) ppm; IR (KBr, pellet): ν_{OH} = 3434 cm^{-1}, $\nu_{C=N}$ = 1641 cm^{-1}. Anal. calcd. for $C_{30}H_{32}ClN_2OP$ (503.0 g/mol): C, 71.63; H, 6.41; N, 5.57; found: C, 71.56; H, 6.51; N, 5.49 %.

*2.3. Synthesis of ligand **2b**.*

Following a similar procedure, ligand **2b** was prepared as a yellow solid starting from aldehyde **1b** (0.50 g, 0.92 mmol) and *N,N*-dimethylethylenediamine (0.08 g, 0.92 mmol). Yield: 93 % (0.52 g); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ = 21.8 (s, PPh_3), -144.3 (sept, $^{1}J_{FP}$ = 714 Hz, PF_6) ppm; ^{1}H NMR ($CDCl_3$): δ = 2.30 (s, 6 H, NMe_2), 2.62 and 3.64 (both t, 2 H each, $^{3}J_{HH}$ = 6.4 Hz, CH_2), 4.45 (d, 2 H, $^{2}J_{PH}$ = 13.2 Hz, CH_2P), 6.61 (d, 1 H, $^{3}J_{HH}$ = 8.4 Hz, $CH_{aromatic}$), 6.69 (broad d, 1 H, $^{3}J_{HH}$ = 8.4 Hz, $CH_{aromatic}$), 6.96 (broad s, 1 H, $CH_{aromatic}$), 7.50 (m, 6 H, PPh_3), 7.63 (m, 6 H, PPh_3), 7.78 (t, 3 H, $^{3}J_{HH}$ = 7.2 Hz, PPh_3), 8.08 (s, 1 H, CH=N) ppm, OH signal not observed; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ = 29.6 (d, $^{1}J_{PC}$ = 48.6 Hz, CH_2P), 45.5 (s, NMe_2), 56.1 and 59.4 (s, CH_2), 114.9 (d, J_{PC} = 8.5 Hz, $C_{aromatic}$), 117.1 (d, $^{1}J_{PC}$ = 85.5 Hz, C_{ipso} of PPh_3), 118.1 (s, $CH_{aromatic}$), 118.8 (s, $C_{aromatic}$), 130.3 (d, J_{PC} = 12.5 Hz, $C_{ortho\ or\ meta}$ of PPh_3), 134.0 (d, J_{PC} = 9.6 Hz, $C_{ortho\ or\ meta}$ of PPh_3), 134.5 (d, J_{PC} = 3.8 Hz, $CH_{aromatic}$), 134.6 (d, J_{PC} = 5.6 Hz, $CH_{aromatic}$), 135.3 (s, CH_{para} of PPh_3), 162.9 (s, C-OH), 165.4 (s, CH=N) ppm; IR (KBr, pellet): ν_{OH} = 3434 cm^{-1}, $\nu_{C=N}$ = 1636 cm^{-1}, ν_{P-F} = 840 cm^{-1}; Elemental analysis calcd. for $C_{30}H_{32}F_6N_2OP_2$ (612.5 g/mol): C, 58.83; H, 5.27; N, 4.57; found: C, 58.92; H, 5.20; N, 4.46 %.

*2.4. Synthesis of ligand **4a**.*

Following a similar procedure, ligand **4a** was prepared as a yellow solid starting from aldehyde **3a** (0.50 g, 1.98 mmol) and *N,N*-dimethylethylenediamine (0.17 g, 1.98 mmol). Yield: 92 % (0.59 g); ^{1}H NMR (DMSO-d_6): δ= 2.20 (s, 6 H, NMe_2), 2.56 and 3.69 (both m, 2 H each, CH_2CH_2), 3.85 (s, 3 H, NMe), 5.36 (s, 2 H, CH_2), 6.89 (d, 1 H, $^{3}J_{HH}$ = 8.4 Hz, $CH_{aromatic}$), 7.43 (d, 1 H, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HH}$ = 1.5 Hz, $CH_{aromatic}$), 7.57, 7.72 and 7.80 (s, 1 H each, $CH_{aromatic}$ and $CH_{imidazolium}$), 8.54 (s, 1 H, CH=N), 9.30 (s, $CH_{imidazolium}$), 13.70 (very broad s, 1 H, OH) ppm; ^{13}C{^{1}H} NMR (DMSO-d_6): δ= 36.3 (s, Me), 45.6 (s, NMe_2), 51.8 (s, CH_2), 55.7 and 59.5 (both s, CH_2CH_2), 118.1 (s, $CH_{aromatic}$), 118.7 (s, $C_{aromatic}$), 122.5 and 124.3 (both s, $CH_{aromatic}$ or $CH_{imidazolium}$), 124.6 (s, $C_{aromatic}$), 132.6, 133.4 and 136.9 (all s, $CH_{aromatic}$ or $CH_{imidazolium}$), 162.7 (s, C-OH), 166.1 (s, CH=N) ppm; IR (KBr, pellet): ν_{OH} = 3391 cm^{-1}, $\nu_{C=N}$ = 1634 cm^{-1}; Elemental analysis calcd. for $C_{16}H_{23}ClN_4O$ (322.8 g/mol): C, 59.53; H, 7.18; N, 17.35; found: C, 59.42; H, 7.23; N, 17.25 %.

*2.5. Synthesis of ligand **4b**.*

Following a similar procedure, ligand **4b** was prepared as a yellow solid starting from aldehyde **3b** (0.50 g, 1.38 mmol) and *N,N*-dimethylethylenediamine (0.12 g, 1.38 mmol). Yield: 90 % (0.54 g); ^{31}P{^{1}H} NMR (CD_3OD): δ= -144.4 (sept, $^{1}J_{FP}$ = 710 Hz, PF_6) ppm; ^{1}H NMR (CD_3OD): δ= 2.62 (s, 6 H, NMe_2), 3.08 and 3.89 (both t, 2 H each, $^{3}J_{HH}$ = 6.2 Hz, CH_2CH_2), 3.92 (s, 3 H, NMe), 5.33 (s, 2 H, CH_2), 6.93 (d, 1 H, $^{3}J_{HH}$ = 8.4 Hz, $CH_{aromatic}$), 7.43 (dd, 1 H, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HH}$ = 2.1 Hz, $CH_{aromatic}$), 7.51 (d, 1 H, $^{4}J_{HH}$ = 2.1 Hz, $CH_{aromatic}$), 7.55 and 7.57 (both d, 1 H each, $^{3}J_{HH}$ = 1.8 Hz, $CH_{imidazolium}$), 8.56 (s, 1 H, CH=N) ppm, 9.08* (s, 1 H, $CH_{imidazolium}$), OH signal not observed; *Only observed in freshly prepared MeOD-d_4 solutions due to H/D exchange. IR (KBr, pellet): ν_{OH} = 3434 cm^{-1}, $\nu_{C=N}$ = 1638 cm^{-1}, ν_{P-F} = 840 cm^{-1}; Elemental analysis calcd. for $C_{16}H_{23}F_6N_4OP$ (432.4 g/mol): C, 44.45; H, 5.36; N, 12.96; found: C, 44.38; H, 5.42; N, 13.00 %.

*2.6. Synthesis of the ruthenium(II) complex **5a**.*

The ruthenium(II) dimer [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (0.12 g, 0.20 mmol) was added to a solution of ligand **2a** (0.20 g, 0.40 mmol) in 30 mL of methanol, and the mixture stirred for 2 hours at room temperature. Solvent was then removed under reduced pressure and the resulting residue was washed first with diethylether, then with a 1:4 mixture of dichloromethane and diethylether, and finally with a 1:1 mixture of acetone and diethylether to give an orange solid. Yield: 75 % (0.24 g); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 20.7 (s) ppm; ^{1}H NMR ($CDCl_3$): δ = 1.08 and 1.20 (both d, 3 H each, $^3J_{HH}$ = 6.2 Hz, CH*Me*$_2$), 2.28 (s, 3 H, Me), 2.70 (m, 1 H, C*H*Me$_2$), 2.89 and 3.00 (both s, 3 H each, NMe$_2$), 3.39, 4.14, 4.44 and 4.69 (all m, 1 H each, CH_2), 4.94 (m, 2 H, CH_2), 5.48, 5.57, 5.66 and 6.02 (all broad s, 1 H each, CH of *p*-cymene), 6.48 and 6.59 (both d, 1 H each, $^3J_{HH}$ = 7.5 Hz, $CH_{aromatic}$), 7.13 (s, 1 H, $CH_{aromatic}$), 7.52-7.92 (m, 15 H, PPh_3), 8.35 (s, 1 H, CH=N), 12.1 (very broad s, 1 H, OH) ppm; IR (KBr, pellet): ν_{OH} = 3428 cm^{-1}, $\nu_{C=N}$ = 1617 cm^{-1}; Elemental analysis calcd. for $C_{40}H_{46}Cl_3N_2OPRu$ (809.2 g/mol): C, 59.37; H, 5.73; N, 3.46; found: C, 59.23; H, 5.86; N, 3.39 %.

*2.7. Synthesis of the ruthenium(II) complex **5b**.*

Following a similar procedure, complex **5b** was prepared as an orange solid starting from [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (0.10 g, 0.16 mmol) and ligand **2b** (0.20 g, 0.32 mmol). Yield: 76 % (0.22 g); ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 20.0 (s, PPh_3), -144.6 (sept, $^1J_{FP}$ = 714 Hz, PF_6) ppm; ^{1}H NMR ($CDCl_3$): δ = 1.11 and 1.22 (both d, 3 H each, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$), 2.31 (s, 3 H, Me), 2.70 (m, 1 H, C*H*Me$_2$), 2.82 and 2.90 (both s, 3 H each, NMe$_2$), 3.09, 4.00, 4.13 and 4.92 (all m, 1 H each, CH_2), 4.43 (m, 2 H, CH_2), 5.47 and 5.58 (both d, 1 H each, $^3J_{HH}$ = 6.2 Hz, CH of *p*-cymene), 5.63 and 5.94 (both d, 1 H each, $^3J_{HH}$ = 5.4 Hz, CH of *p*-cymene), 6.47 and 6.61 (both d, 1 H each, $^3J_{HH}$ = 8.7 Hz, $CH_{aromatic}$), 6.91 (s, 1 H, $CH_{aromatic}$), 7.41-7.84 (m, 16 H, PPh_3 and CH=N), 12.0 (very broad s, 1 H, OH) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 18.8 (s, Me),

21.9 and 22.7 (both s, CH*Me*$_2$), 30.2 (d, $^1J_{PC}$ = 47.5 Hz, CH_2P), 30.7 (s, *C*HMe$_2$), 42.3 and 44.5 (both s, NMe_2), 56.7 and 64.1 (both s, CH_2CH_2), 80.8, 81.6, 82.8 and 88.4 (all s, CH of *p*-cymene), 99.9 and 100.3 (both s, C of *p*-cymene), 109.5 (d, J_{PC} = 8.4 Hz, $C_{aromatic}$), 117.1 (d, $^1J_{PC}$ = 85.1 Hz, C_{ipso} of PPh_3), 119.2 (s, $C_{aromatic}$), 122.8 (s, $CH_{aromatic}$), 130.4 (d, J_{PC} = 12.3 Hz, $CH_{ortho\ or\ meta}$ of PPh_3), 133.9 (d, J_{PC} = 9.4 Hz, $CH_{ortho\ or\ meta}$ of PPh_3), 135.4 (s, CH_{para} of PPh_3), 136.4 (s, $CH_{aromatic}$), 138.7 (d, J_{PC} = 6.2 Hz, $CH_{aromatic}$), 165.0 (s, C-OH), 167.0 (s, CH=N) ppm; IR (KBr, pellet): ν_{OH} = 3429 cm^{-1}, $\nu_{C=N}$ = 1620 cm^{-1}, ν_{P-F} = 841 cm^{-1}; Elemental analysis calcd. for $C_{40}H_{46}F_6Cl_2N_2P_2ORu$ (918.7 g/mol): C, 52.29; H, 5.05; N, 3.05; found: C, 52.14; H, 4.98; N, 2.96 %.

*2.8. Synthesis of the ruthenium(II) complex **6a**.*

Following a similar procedure, complex **6a** was prepared as an orange solid starting from [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (0.19 g, 0.31 mmol) and ligand **4a** (0.20 g, 0.62 mmol). Yield: 69 % (0.27 g); ^{1}H NMR (CD_3OD): δ= 1.17 (m, 6 H, CH*Me*$_2$), 2.21 (s, 3 H, Me), 2.69 (m, 1 H, C*H*Me$_2$), 2.96 (broad s, 7 H, NMe_2 and CH_2), 3.55, 4.11 and 4.63 (all m, 1 H each, CH_2), 3.93 (s, 3 H, NMe), 5.25 (s, 2 H, CH_2) 5.51, 5.63, 5.70 and 5.83 (all broad s, 1 H each, CH of *p*-cymene), 6.92 and 7.34 (both d, 1H each, $^3J_{HH}$ = 8.9 Hz, $CH_{aromatic}$), 7.38 (s, 1 H, $CH_{aromatic}$ or $CH_{imidazolium}$), 7.59 (s, 2 H, $CH_{aromatic}$ or $CH_{imidazolium}$), 8.35 (s, 1 H, CH=N), 9.00 (s, 1 H, $CH_{imidazolium}$) ppm, OH not observed; $^{13}C\{^1H\}$ NMR (CD_3OD): δ= 17.6 (s, Me), 20.7 and 21.7 (both s, CH*Me*$_2$), 30.6 (s, *C*HMe$_2$), 35.2 (s, NMe), 41.2 and 43.8 (both s, NMe_2), 52.0, 58.1 and 64.1 (all s, CH_2), 80.0, 81.3, 82.8 and 87.9 (all s, CH of *p*-cymene), 99.7 and 100.9 (both s, C of *p*-cymene), 118.9 and 119.8 (both s, $C_{aromatic}$), 121.9, 122.4, 123.8, 135.4, 136.3 and 136.4 (all s, $CH_{aromatic}$ or $CH_{imidazolium}$), 164.9 (s, C-OH), 167.4 (s, CH=N) ppm; IR (KBr, pellet): ν_{OH} = 3419 cm^{-1}, $\nu_{C=N}$ = 1620 cm^{-1}; Elemental analysis calcd. for $C_{26}H_{37}N_4Cl_3ORu$ (629.0 g/mol): C, 49.65; H, 5.93; N, 8.91; found: C, 49.73; H, 5.89; N, 8.84 %.

*2.9. Synthesis of the ruthenium(II) complex **6b**.*

Following a similar procedure, complex **6b** was prepared as an orange solid starting from [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (0.14 g, 0.23 mmol) and ligand **4b** (0.20 g, 0.46 mmol). Yield: 71 % (0.24 g); $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ = -144.1 (sept, $^1J_{FP}$ = 711 Hz, PF_6) ppm; ^{1}H NMR (DMSO-d_6): δ = 1.09 (m, 6 H, CH*Me*$_2$), 2.16 (s, 3 H, Me), 2.81 (broad s, 6 H, NMe_2), 3.65, 4.52, 4.73 and 5.37 (all m, 1 H each, CH_2), 3.83 (s, 3 H, NMe), 5.19 (s, 2 H, CH_2), 5.61 (broad s, 2 H, CH of *p*-cymene), 5.69 and 5.85 (both broad s, 1 H each, CH of *p*-cymene), 6.71, 7.11 and 7.25 (all s, 1 H each, $CH_{aromatic}$ or $CH_{imidazolium}$), 7.73 (m, 2 H, $CH_{aromatic}$ or $CH_{imidazolium}$), 8.04 (s, 1 H, CH=N), 9.22 (s, 1 H, $CH_{imidazolium}$), 10.5 (very broad s, 1 H, OH) ppm, C*H*Me_2 not observed (overlapped by the deuterated solvent); IR (KBr, pellet): ν_{OH} = 3428 cm^{-1}, $\nu_{C=N}$ = 1622 cm^{-1}, ν_{P-F} = 839 cm^{-1}; Elemental analysis calcd. for $C_{26}H_{37}F_6N_4Cl_2OPRu$ (738.6 g/mol): C, 42.28; H, 5.05; N, 7.59; found: C, 42.19; H, 5.16; N, 7.39 %.

*2.10. Synthesis of the ruthenium(II) complex **8**.*

Following a similar procedure, complex **8** was prepared as an orange solid starting from [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] (0.32 g, 0.52 mmol) and ligand **7** (0.20 g, 1.04 mmol). Yield: 85 % (0.44 g); ^{1}H NMR ($CDCl_3$): δ = 1.06 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CH*Me*$_2$), 1.19 (d, 3 H, $^3J_{HH}$ = 6.9 Hz, CH*Me*$_2$), 2.26 (s, 3 H, Me), 2.30 (s, 3 H, NMe), 2.64 (broad s, 4 H, NMe and C*H*Me_2 overlapped), 3.19, 3.90, 4.25 and 5.04 (all m, 1 H each, CH_2CH_2), 5.50 and 5.62 (both d, 1 H each, $^3J_{HH}$ = 6.1 Hz, CH of *p*-cymene), 5.58 and 5.93 (both d, 1 H each, $^3J_{HH}$ = 5.4 Hz, CH of *p*-cymene), 6.44 and 7.20 (both t, 1 H each, $^3J_{HH}$ = 7.5 Hz, $CH_{aromatic}$), 6.91 and 7.02 (both d, 1 H each, $^3J_{HH}$ = 7.5 Hz, $CH_{aromatic}$), 7.96 (s, 1 H, CH=N), 11.93 (broad s, 1 H, OH) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 18.8 (s, Me), 21.6 and 22.9 (both s, CH*Me*$_2$), 30.6 (s, *C*HMe_2), 56.9 and 65.1 (both s, CH_2CH_2), 80.9, 81.1, 82.8 and 88.6 (all s, CH of *p*-cymene), 99.1 and 100.3 (both s, C of *p*-cymene), 114.3, 122.5, 135.1 and 135.7 (all s, $CH_{aromatic}$), 118.0 (s, $C_{aromatic}$), 165.1 (s, C-OH), 166.3 (s, CH=N) ppm; IR (KBr, pellet): ν_{OH} = 3501 cm^{-1}, $\nu_{C=N}$ = 1613 cm^{-1}; Elemental

analysis calcd. for $C_{21}H_{30}Cl_2N_2ORu$ (498.4 g/mol): C, 50.60; H, 6.07; N, 5.62; found: C, 50.68; H, 6.00; N, 5.47 %.

2.11. General procedure for the catalytic transfer hydrogenation of carbonyl compounds.

A solution of HCO_2Na (1.02 g, 15 mmol) in 3 mL of water was introduced, under argon atmosphere, in a Schlenk tube equipped with a condenser. The ketone or aldehyde (1 mmol) and the appropriate ruthenium catalyst (0.02 mmol) were added, and the mixture heated at 80 ºC in an oil bath. The course of the catalytic reactions was monitored taking aliquots (*ca* 20 μL), which after extraction with dichloromethane (3 mL) were analyzed by GC. The identity of the alcohols formed was assessed by comparison of their retention times with those of commercially available samples.

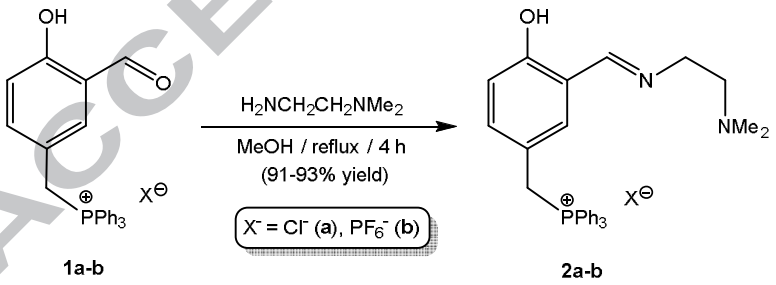
*2.12. Recycling tests in the transfer hydrogenation of 2,2,2-trifluoroacetophenone promoted by complex **5b**.*

After the first run, the 1-phenyl-2,2,2-trifluoroethanol formed was extracted with diethylether (3 x 3 mL) and traces of organic solvent were eliminated from the aqueous phase at reduced pressure. Then, 136 μL (1 mmol) of 2,2,2-trifluoroacetophenone and hydrogen source were added to the aqueous solution, and the mixture was heated at 80ºC. Both sodium formate (1.02 g, 15 mmol, Table 1, entry 6) and formic acid (0.57 mL, 15 mmol, Table 1, entry 7) have been tested as hydrogen source for the recycling.

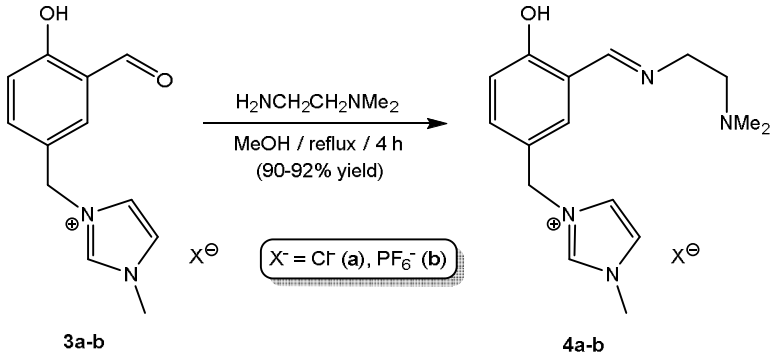
3. Results and discussion

The synthesis of the new Schiff-base ligands was carried out by condensation of the corresponding aldehyde precursors with the appropriate primary amine (see Schemes 1 and 2). Thus, the reaction of the (3-formyl-4-hydroxybenzyl)triphenylphosphonium chloride (**1a**) and hexafluorophosphate (**1b**) salts with one equivalent of *N,N*-dimethylethylenediamine in

refluxing methanol led to the selective formation of the corresponding imines **2a-b** (Scheme 1). Similarly, the treatment of the 3-(3-formyl-4-hydroxybenzyl)-1-methyl-1*H*-imidazol-3-ium salts **3a-b** with $Me_2NCH_2CH_2NH_2$ allowed the preparation of the imino-ligands **4a-b** (Scheme 2). In all the cases, the transformation of the aldehyde function into a -CH=N- moiety was evidenced by ^{1}H NMR spectroscopy with the disappearance of the -CH=O signal at *ca* 10-11 ppm and the observation of a new resonance at 8.20-8.56 ppm [16]. The formation of the iminic group was also supported by the presence of a singlet resonance at *ca* 165 ppm in the $^{13}C\{^1H\}$ NMR spectra. Worthy of note, the comparison of the spectroscopic data for the chloride and hexafluorophosphate salts (*i.e.* **2a** *vs* **2b** and **4a** *vs* **4b**) shows similar NMR patterns for the cation albeit with different chemical shifts, evidencing therefore the existence of ion pairing in solution. As an example, the CH_2P unit of ligands **1a** and **1b** gives rise to a doublet resonance at 5.49 and 4.45 ppm (^{1}H NMR in $CDCl_3$), respectively [17]. On the other hand, the ligand **4a** exhibits a resonance at 10.78 ppm for the imidazolium N-CH=N proton, whereas a signal at 8.77 ppm (^{1}H NMR, $CDCl_3$) is observed for the same group in its hexafluorophosphate counterpart **4b** [18,19]. As previously observed by other authors, the interaction between cations and anions is expected to be stronger with the Cl^- than with PF_6^-, inducing therefore a major shift toward low field [19].

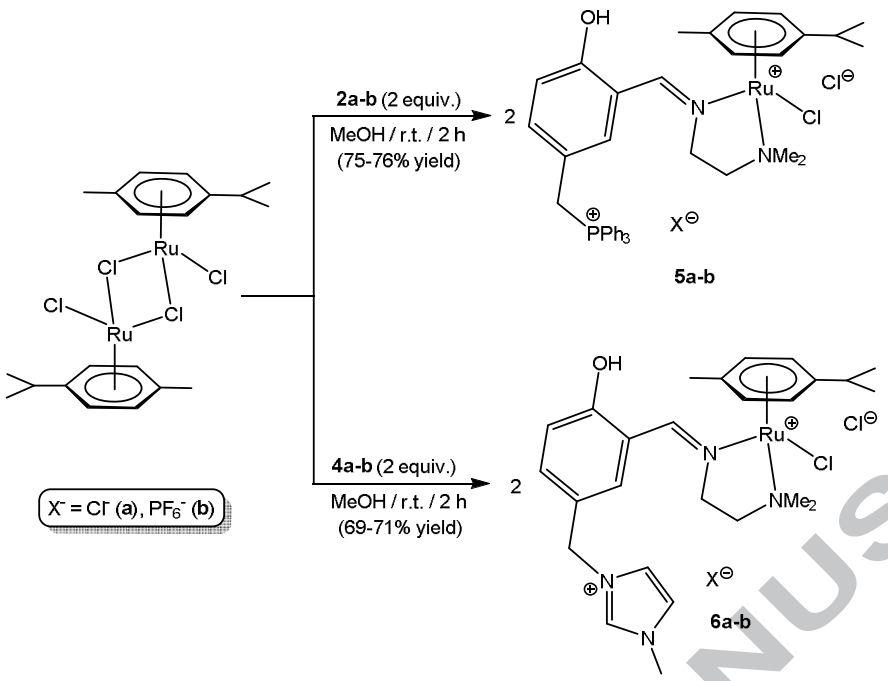


Scheme 1. Synthesis of ligands **2a-b** with a phosphonium group pendant.



Scheme 2. Synthesis of ligands **4a-b** with an imidazolium group pendant.

Treatment of the dimeric ruthenium(II) precursor [{RuCl(μ-Cl)(η^6-*p*-cymene)}$_2$] with two equivalents of the Schiff-bases **2a-b** and **4a-b**, in methanol at room temperature for 2 hours, led to the clean formation of the corresponding mononuclear complexes [RuCl(η^6-*p*-cymene)(κ^2-*N,N'*-$Me_2NCH_2CH_2N$=CH-C_6H_3-2-OH-5-R)][Cl] (R = CH_2PPh_3[Cl] (**5a**), CH_2PPh_3[PF_6] (**5b**), CH_2-1-methylimidazolium[Cl] (**6a**), 1-methylimidazolium[PF_6] (**6b**)), in which the functionalized ligand acts as a chelate through the *N,N'*-coordination of the diamine moiety (see Scheme 3). The proposed structures for the arene-ruthenium(II) compounds **5-6a-b**, isolated as air-stable orange solids in 69-76% yield, were supported by elemental analyses, IR and NMR spectroscopies. In particular, the coordination of the NMe_2 group to the ruthenium atom is inferred by the inequivalence of the two methyl groups in the ^{1}H and ^{13}C{^{1}H} NMR spectra (see details in the Experimental section). On the other hand, the lowering of the ν(C=N) absorption bands (1617-1622 cm^{-1} in **5-6a-b**; Δν between -14 and -24 cm^{-1}) respective to those observed in the free ligands (1634-1641 cm^{-1} in **2,4a-b**) is indicative of the complexation of the imine function to the metal center [20]. Additional confirmation of the *N,N'*-chelation of the ligands is given by the chemical and magnetic inequivalence of the *p*-cymene ring protons, which appear as four distinct signals in the ^{1}H NMR spectra as a consequence of the stereogenic nature of the ruthenium atom. The loss of the symmetry is also reflected by the diastereotopic nature of the different CH_2 units of the coordinated ligands.

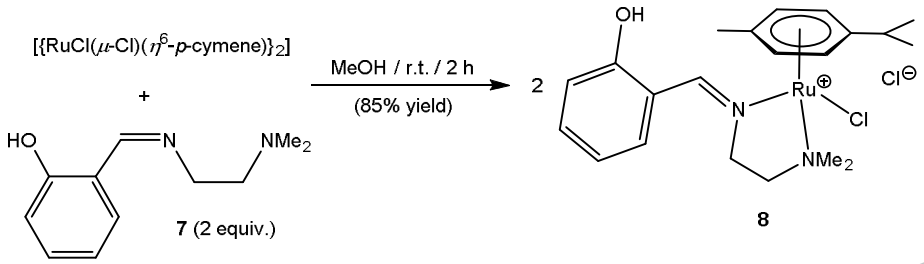


Scheme 3. Synthesis of arene-ruthenium(II) complexes **5-6a-b** containing an ionic Schiff-base ligand.

At this point, it should be noted that Schiff-bases generated from salicylaldehyde derivatives are prone to coordinate metallic ions in a κ^2-*N,O*-mode, after deprotonation of the phenol group [21]. In this context, a wide range of arene-ruthenium(II) complexes featuring these κ^2-*N,O*-coordinated ligands have been described in the literature [22]. Also of note is the fact that Schiff-bases containing an imidazolium fragment in their backbone are suitable precursors for *N*-heterocyclic carbene species [19c], and are known to be sensitive to nucleophilic attacks (e.g. by methanol), giving rise to the release of the corresponding imidazole [19c]. In our study none of these reactivity patterns was observed, the formation of complexes **5-6a-b** taking place selectively under the experimental conditions employed.

In order to evaluate the benefit of the ionic substituents in **5-6a-b** for further applications in catalytic processes in aqueous media, we also prepared and characterized the analogous ruthenium derivative [RuCl(η^6-*p*-cymene)($Me_2NCH_2CH_2N$=CH-C_6H_4-2-OH)][Cl] (**8**) using the known neutral Schiff-base **7** (Scheme 4). The full analytical and spectroscopic characterization

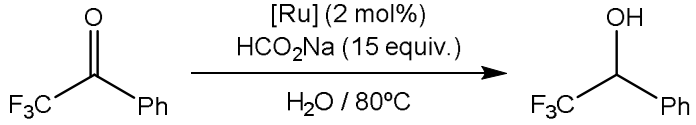
of this compound is included in the Experimental section, all the data obtained being in complete accord with the proposed formulation.



Scheme 4. Synthesis of the arene-ruthenium(II) complex **8** containing a neutral Schiff-base ligand.

Compounds [RuCl(η^6-*p*-cymene)($Me_2NCH_2CH_2N$=CH-C_6H_3-2-OH-5-R)][Cl] (R = CH_2PPh_3[Cl] (**5a**), CH_2PPh_3[PF_6] (**5b**), CH_2-1-methylimidazolium[Cl] (**6a**), 1-methylimidazolium[PF_6] (**6b**), H (**8**)) are soluble and stable in water [23], hydrolytic decomposition of the coordinated Schiff base ligands being not observed [24,25]. Thus, taking advantage of their stability and solubility in water, we decide to explore the potential of these complexes for aqueous catalysis. In particular, we evaluated their behavior in the catalytic transfer hydrogenation of carbonyl compounds in aqueous media employing 2,2,2-trifluoroacetophenone as a representative substrate. Experiments were carried out with 1 mmol of the ketone, a ruthenium loading of 2 mol% and 15 equivalents of HCO_2Na as the hydrogen source, in water at 80ºC. Under these conditions, all the complexes synthesized proved to be catalytically active giving rise to the selective formation of the desired 1-phenyl-2,2,2-trifluoroethanol in moderate to high yield after 7 hours of heating (Table 1). In particular, the best result was achieved with complex [RuCl(η^6-p-cymene){$Me_2NCH_2CH_2N$=CH-C_6H_3-2-OH-5-CH_2PPh_3[PF_6]}][Cl] (**5b**) which contains a phosphonium pendant as the corresponding hexafluorophosphate salt (entry 2).

Table 1. Catalytic activity of complexes [RuCl(η^6-*p*-cymene)($Me_2NCH_2CH_2N$=CH-C_6H_3-2-OH-5-R)][Cl] (**5-6a-b**, **8**) in the transfer hydrogenation of 2,2,2-trifluoroacetophenone.[a]



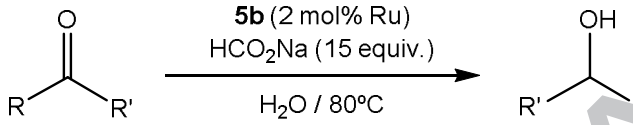
Entry	Catalyst	Time	Yield[b]	TOF[c]
1	R = CH_2PPh_3[Cl] (**5a**)	0.5 h	35 %	35 h^{-1}
		7 h	82 %	5.9 h^{-1}
2	R = CH_2PPh_3[PF_6] (**5b**)	0.5 h	43 %	43 h^{-1}
		7 h	98 %	7.0 h^{-1}
3	R = CH_2-1-methylimidazolium[Cl] (**6a**)	0.5 h	37 %	37 h^{-1}
		7 h	90 %	6.4 h^{-1}
4	R = CH_2-1-methylimidazolium[PF_6] (**6b**)	0.5 h	40 %	40 h^{-1}
		7 h	93 %	6.6 h^{-1}
5	R = H (**8**)	0.5 h	24 %	24 h^{-1}
		7 h	73 %	5.2 h^{-1}
6[d]	R = CH_2PPh_3[PF_6] (**5b**)	7 h	38 %	2.7 h^{-1}
7[e]	R = CH_2PPh_3[PF_6] (**5b**)	7 h	67%	4.7 h^{-1}

[a] Reactions carried out with 1 mmol of 2,2,2-trifluoroacetophenone, 2 mol% of catalyst, 15 mmol of HCO_2Na and 3 mL of water at 80ºC. [b] Yield of the corresponding alcohol. GC determined. [c] Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case. [d] Recycling test, carried out with HCO_2Na. [e] Recycling test, carried out with HCO_2H.

As a general trend, the activity of the PF_6^--containing derivatives was higher than that of their chloride counterparts (entries 2 and 4 *vs* 1 and 3), probably due to the greater capacity of the Cl^- to coordinate the metal center and therefore to compete with the complexation of the substrate or the formate anion [26]. Worthy of note, complex **8**, containing a non-ionic Schiff-base, generates an active species only partially soluble under the experimental conditions

selected and consequently conduces to lower conversion than catalysts **5-6a-b** (entry 5 *vs* entries 1-4). On the other hand, since pH is known to dramatically affect the course of the transfer hydrogenation reactions [27], different experiments were also performed in the pH range 4-12. However, no improvements could be achieved, the best results being obtained in the absence of basic or acidic additives [28]. As an example, the conversions of 2,2,2-trifluoroacetophenone at pH = 4 and pH = 12 with the complex **5b** were only 77% and 33%, respectively, after 7 hours.

Table 2. Catalytic activity of complex [RuCl(η^6-*p*-cymene){$Me_2NCH_2CH_2N$=CH-C_6H_3-2-OH-5-$CH_2PPh_3[PF_6]$}][Cl] (**5b**) in the transfer hydrogenation of different carbonyl compounds.[a]



Entry	Substrate	Time	Yield[b]	TOF[c]
1	R = CF_3, R' = Ph	7 h	98 %	7.0 h^{-1}
2	R = Me, R' = Ph	20 h	96 %	2.4 h^{-1}
3	R, R' = -$(CH_2)_5$-	12 h	98 %	4.1 h^{-1}
4	R, R' = -$(CH_2)_4$-	12 h	98 %	4.1 h^{-1}
5	R = Me, R' = Et	12 h	97 %	4.0 h^{-1}
6	R = Ph, R' = H	7 h	99 %	7.1 h^{-1}
7	R = 4-C_6H_4OMe, R' = H	12 h	96 %	4.0 h^{-1}
8	R = C_6F_5, R' = H	5 h	97 %	9.7 h^{-1}

[a] Reactions carried out with 1 mmol of ketone or aldehyde, 2 mol% of catalyst, 15 mmol of HCO_2Na and 3 mL of water at 80ºC. [b] Yield of the corresponding alcohol. GC determined. [c] Turnover frequencies ((mol product/mol Ru)/time) were calculated at the time indicated in each case.

The scope of the reaction was explored with the most efficient catalyst, *i.e.* complex [RuCl(η^6-p-cymene){$Me_2NCH_2CH_2N$=CH-C_6H_3-2-OH-5-$CH_2PPh_3[PF_6]$}][Cl] (**5b**). As observed in Table 2, acetophenone, cyclohexanone, cyclopentanone and 2-butanone could also be reduced in high yield under the selected conditions. As expected, these ketones, more electron-rich than the 2,2,2-trifluoroacetophenone turned to be less reactive, requiring longer reaction times to reach good conversions (Entries 2-5 *vs* entry 1). The catalytic system resulted also operative for the transfer hydrogenation of aldehydes (Entries 6-8, Table 2). Once again, the rate of the reaction clearly depends on the electronic properties of the substrate employed, an electron-deficient aldehyde being more reactive than an electron-rich one (entry 8 vs entry 7).

Finally, the possibility for recycling the catalytic system has been investigated. After the full conversion of 2,2,2-trifluoroacetophenone by complex **5b**, the alcohol was extracted with diethylether, and a second catalytic run was performed after adding a new batch of sodium formate and ketone to the aqueous phase (see details in the experimental section). By this way, 38% of the desired 1-phenyl-2,2,2-trifluoroethanol were generated after 7 hours of heating (Table 1, entry 6). The low activity observed in this case could be due to the accumulation of the HCO_2Na in the medium that induces a dramatic increase of the pH [29,30], an important factor taking in account the poor efficiency displayed by complex **5b** under basic conditions. In agreement with this, better results were achieved when the recycling was performed with HCO_2H instead of HCO_2Na (Table 1, entry 7).

4. Conclusions

In summary, the synthesis of new ionic Schiff-bases, containing a $NCH_2CH_2NMe_2$ moiety and a phosphonium or imidazolium pendant, has been presented. The selective coordination of these ligands onto a η^6-arene-ruthenium(II) fragment, through *N,N'*-chelation, furnished highly

water-soluble complexes of the type [RuCl(η^6-*p*-cymene)(*N,N'*-$Me_2NCH_2CH_2N$=CH-C_6H_3-2-OH-5-R)][Cl]. These derivatives proved to be able to promote the transfer hydrogenation of the fluorinated ketone 2,2,2-trifluoroacetophenone and resulted more convenient to perform this transformation in aqueous media than non-functionalized catalyst with similar structure. The most active catalyst, *i.e.* [RuCl(η^6-p-cymene){$Me_2NCH_2CH_2N$=CH-C_6H_3-2-OH-5-$CH_2PPh_3[PF_6]$}][Cl] (**5b**) proved to be also active in the reduction of other ketones and aldehydes.

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6. References

[1] See for example: (a) F. Ding, Y. Sun, S. Monsaert, R. Drozdzak, I. Dragutan, V. Dragutan, F. Verpoort, Curr. Org. Synth. 5 (2008) 291-304; (b) K.C. Gupta, A.K. Sutar, Coord. Chem. Rev. 252 (2008) 1420-1450; (c) A.W. Kleij, Eur. J. Inorg. Chem. (2009) 193-205; (d) G. Grivani, V. Tahmasebi, A.D. Khalaji, Polyhedron 68 (2014) 144-150; (e) P. Das, W. Linert, Coord. Chem. Rev. 311 (2016) 1-23.

[2] See for example: (a) I. Kostova, L. Saso, Curr. Med. Chem. 20 (2013) 4609-4632; (b) D. Utreja, Vibha, S. Singh, M. Kaur, Curr. Bioact. Compd. 11 (2015) 215-230; (c) C.R. Munteanu, K. Suntharalingam, Dalton Trans. 44 (2015) 13796-13808.

[3] (a) H. Miyasaka, A. Saitoh, S. Abe, Coord. Chem. Rev. 251 (2007) 2622-2664; (b) R. M. Clarke, T. Storr, Dalton Trans. 43 (2014) 9380-9391; (c) M. Andruh, Dalton Trans. 44 (2015) 16633-16653.

[4] See, for example: (a) R.I. Kureshy, K.J. Prathap, T. Roy, N. C. Maity, N.H. Khan, S.H.R. Abdi, H.C. Bajaj, Adv. Synth. Catal. 352 (2010) 3053-3060; (b) C. Bibal, J.-C. Daran, S. Deroover, R. Poli, Polyhedron 29 (2010) 639-647; (c) N.H. Campbell, N.H. Abd Karim, G.N. Parkinson, M. Gunaratnam, V. Petrucci, A.K. Todd, R. Vilar, S. Neidle, J. Med. Chem. 55 (2012) 209-222; (d) L. Liang, W. Wang, J. Wu, F. Xu, Y. Niu, B. Xu, P. Xu, Chem. Eur. J. 19 (2013) 13774-13782; (e) N.H. Abd Karim, O. Mendoza, A. Shivalingam, A.J. Thompson, S. Ghosh, M.K. Kuimova, R. Vilar, RSC Adv. 4 (2014) 3355-3363; (f) M. Asadi, Z. Asadi, L. Zarei, S. B. Sadi, Z. Amirghofran, Spectrochim. Acta A 133 (2014) 697-706; (g) L. Lecarme, E. Prado, A. De Rache, M.-L. Nicolau-Travers, R. Bonnet, A. van Der Heyden, C. Philouze, D. Gomez, J.-L. Mergny, H. Jamet, E. Defrancq, O. Jarjayes, F. Thomas, Inorg. Chem. 53 (2014) 12519-12531; (h) S. Siangwata, N. Baartzes, B.C.E. Makhubela, G. S. Smith, J. Organomet. Chem. 796 (2015) 26-32; (i) H.-D. Bian, J. Wang, Y. Wei, J. Tang, F.-P. Huang, D. Yao, Q. Yu, H. Liang, Polyhedron 90 (2015) 147-153; (j) K.J. Davis, C. Richardson, J.L. Beck, B.M. Knowles, A. Guédin, J.-L. Mergny, A.C. Willis, S.F. Ralph, Dalton Trans. 44 (2015) 3136-3150; (k) A. Terenzi, D. Lötsch, S. van Schoonhoven, A. Roller, C.R. Kowol, W. Berger, B.K. Keppler, G. Barone, Dalton Trans. 45 (2016) 7758-7767.

[5] (a) F.C. Pigge, J.J. Coniglio, Curr. Org. Chem. 5 (2001) 757-784; (b) J.H. Rigby, M. A. Kondratenko, Top. Organomet. Chem. 7 (2004) 181-204; (c) J. Gimeno, V. Cadierno, P. Crochet, in: R.H. Crabtree, D.M.P. Mingos (Eds.), Comprehensive Organometallic Chemistry III, vol. 6, Elsevier, Oxford, 2007, pp. 465-550; (d) B. Therrien, Coord. Chem. Rev. 253 (2009) 493-519; (e) L. Delaude, A. Demonceau, Dalton Trans. 41

(2012) 9257-9268; (f) P. Kumar, R.K. Gupta, D.S. Pandey, Chem. Soc. Rev. 43 (2014) 707-733; (g) B. Therrien, CrysEngComm 17 (2015) 484-491.

[6] (a) S. I. Kozhushkov, L. Ackermann, Chem. Sci. 4 (2013) 886-896; (b) S. De Sarkar, W. Liu, S. I. Kozhushkov, L. Ackermann, Adv. Synth. Catal. 356 (2014) 1461-1479.

[7] (a) R. García-Álvarez, J. Francos, E. Tomás-Mendivil, P. Crochet, V. Cadierno, J. Organomet. Chem. 771 (2014) 93-104; (b) P. Crochet, V. Cadierno, Top. Organomet. Chem. 48 (2014) 81-118.

[8] (a) A.L. Noffke, A. Habtemariam, A.M. Pizarro, P.J. Sadler, Chem. Commun. 48 (2012) 5219-5246; (b) F. Foubelo, C. Nájera, M. Yus, Tetrahedron: Asymmetry 26 (2015) 769-790; (c) D. Wang, D. Astruc, Chem. Rev. 115 (2015) 6621-6686.

[9] (a) M. Wang, C.-J. Li, Top. Organomet. Chem. 11 (2004) 321-336; (b) J. Vaclavik, P. Kacer, M. Kuzma, L. Cerveny, Molecules 16 (2011) 5460-5495; (c) A. Robertson, T. Matsumoto, S. Ogo, Dalton Trans. 40 (2011) 10304-10310; (d) P. Crochet, V. Cadierno, Dalton Trans. 43 (2014) 1244-12462; (e) G. Süss-Fink, J. Organomet. Chem. 751 (2014) 2-19.

[10] For recent examples, see: (a) S. E. García-Garrido, J. Francos, V. Cadierno, J.-M. Basset, V. Polshettiwar, ChemSusChem 4 (2011) 104-111; (b) R. García-Álvarez, M. Zablocka, P. Crochet, C. Duhayon, J.-P. Majoral, V. Cadierno, Green Chem. 15 (2013) 2447-2456; (c) D. Jantke, M. Cokoja, A. Pöthig, W.A. Hermann, F.E. Kühn, Organometallics 32 (2013) 741-744; (d) X. Liu, C. Chen, Y. Xiu, A. Chen, L. Guo, R. Zhang, J. Chen, Z. Hou, Catal. Commun. 67 (2015) 90-94.

[11] N. Baartzes, T. Stringer, P. Chellan, J.M. Combrinck, P.J. Smith, A.T. Hutton, G.S. Smith, Inorg. Chim. Acta 446 (2016) 111-115.

[12] (a) A.Z. El-Sonbati, A.A. El-Bindary, I.G.A. Rashed, Spectrochim. Acta A 58 (2002) 1411-1424; (b) P.U. Naik, G.J. McManus, M.J. Zaworotko, R.D. Singer, Dalton Trans. (2008) 4834-4836; (c) M. Neamţu, F. Macaev, V. Boldescu, V.-D. Hodoroaba, C.

Nădejde, R.J. Schneider, A. Paul, G. Abadei, U. Panne, Appl. Catal. B 183 (2016) 335-342; (d) Z. Mandegani, Z. Asadi, M. Asadi, H.R. Karbalaei-Heidarib, B. Rastegari, Dalton Trans. 45 (2016) 6592-6611.

[13] C.M. Anderson, M. Crespo, M.C. Jennings, A.J. Lough, G. Ferguson, R.J. Puddephatt, Organometallics 10 (1991) 2672-2679.

[14] M.A. Bennett, T.-N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74-78.

[15] W.L.F. Armarego, C.L.L. Chai, in: Purification of Laboratory Chemicals (5th Ed.), Butterworth-Heinemann, Oxford, 2003.

[16] R. García-Álvarez, J. Díez, P. Crochet, V. Cadierno, Organometallics 29 (2010) 3955-3965.

[17] An analogous behavior was observed for other ionic Schiff-bases with similar structures. See, for example: T. Chang, L. Jin, H. Jing, ChemCatChem 1 (2009) 379-383.

[18] Due to their low solubility in chlorinated solvents ($CDCl_3$, CD_2Cl_2), ligands **4a-b** are better characterized in highly polar solvents (DMSO-d_6, CD_3OD). In these solvents the difference in the chemical shifts of chloride and hexafluorophosphate salts is not so important (see the Experimental section) since the ion pairing is not favored.

[19] (a) B. Erguillor, M.A. Esteruelas, M. Oliván, M. Puerta, Organometallics 27 (2008) 445-450; (b) N. Ríos-Lombardía, E. Busto, V. Gotor-Fernández, V. Gotor, R. Porcar, E. García-Verdugo, S.V. Luis, I. Alfonso, S. García-Granda, A. Menéndez-Velázquez, Chem. Eur. J. 16 (2010) 836-847; (c) R. Zhong, Y.-N. Wang, X.-Q. Guo, Z.-X. Chen, X.-F. Hou, Chem. Eur. J. 17 (2011) 11041-11051.

[20] (a) P. Crochet, J. Gimeno, S. García-Granda, J. Borge, Organometallics 20 (2001) 4369-4377; (b) P. Crochet, J. Gimeno, J. Borge, S. García-Granda, New J. Chem. 27 (2003) 414-420; (c) A. E. Díaz-Álvarez, P. Crochet, M. Zablocka, V. Cadierno, L. Vendier, J.

Gimeno, J.-P. Majoral, Polyhedron 26 (2007) 933-940; (d) J. M. Gichumbi, H. B. Friedrich, B. Omondi, J. Organomet. Chem. 808 (2016) 87-96.

[21] See, for example: (a) W.-J. Lian, X.-T. Wang, C.-Z. Xie, H. Tian, X.-Q. Song, H.-T. Pan, X. Qiao, J.-Y. Xu, Dalton Trans. 45 (2016) 9073-9087; (b) M.D. Santana, L. López-Banet, G. Sánchez, J. Pérez, E. Pérez, L. García, J. L. Serrano, A. Espinosa, Dalton Trans. 45 (2016) 8601-8613; (c) N. Oncel, V.T. Kasumov, E. Sahin, M. Ulusoy, J. Organomet. Chem. 811 (2016) 81-90; (d) V.T. Kasumov, O. Sahin, H.G. Aktas, Polyhedron 115 (2016) 119-127; (e) M. Enamullah, G. Makhloufi, R. Ahmaed, B.A. Joy, M.A. Islam, D. Padula, H. Hunter, G. Pescitelli, C. Janiak, Inorg. Chem. 55 (2016) 6449-6464.

[22] See, for example: (a) S. Dayan, N.K. Ozpozan, N. Özdemir, O. Dayan, J. Organomet. Chem. 770 (2014) 21-28; (b) K. Ghebreyessus, A. Peralta, M. Katdare, K. Prabhakaran, S. Paranawithana, Inorg. Chim. Acta 434 (2015) 239-251; (c) E. Ekengard, L. Glans, I. Cassells, T. Fogeron, P. Govender, T. Stringer, P. Chellan, G.C. Lisensky, W.H. Hersh, I. Doverbratt, S. Lidin, C. de Kock, P.J. Smith, G.S. Smith, E. Nordlander, Dalton Trans. 44 (2015) 19314-19329; (d) W.-G. Jia, H. Zhang, T. Zhang, S. Ling, Inorg. Chem. Commun. 66 (2016) 15-18; (e) H. S. Çalık, E. Ispir, Ş. Karabuga, M. Aslantas, J. Organomet. Chem. 801 (2016) 122-129; (f) W.-G. Jia, H. Zhang, T. Zhang, D. Xie, S. Ling, E.-H. Sheng, Organometallics 35 (2016) 503-512; (g) M. Maroto-Díaz, B.T. Elie, P. Gómez-Sal, J. Pérez-Serrano, R. Gómez, M. Contel, J. de la Mata, Dalton Trans. 45 (2016) 7049-7066.

[23] NMR spectra of complexes **5-6a-b** and **8** in D_2O only showed the chloride- and aquo-derivatives, $[RuCl(\eta^6\text{-}p\text{-cymene})(Me_2NCH_2CH_2N{=}CH\text{-}C_6H_3\text{-}2\text{-}OH\text{-}5\text{-}R)]^+$ and $[Ru(H_2O)(\eta^6\text{-}p\text{-cymene})(Me_2NCH_2CH_2N{=}CH\text{-}C_6H_3\text{-}2\text{-}OH\text{-}5\text{-}R)]^{2+}$ respectively, even after 24 hours in solution. Both species are in equilibrium and the formation of the aquo-derivative could be suppressed by adding NaCl to the solution. This phenomena is

general for the arene-ruthenium(II) complexes of the type [$RuCl_2(\eta^6$-arene)(L)] and [$RuCl(\eta^6$-arene)$(L)_2]^+$ when dissolved in water. See, for example: (a) P. Csabai, F. Joó, Organometallics 23 (2004) 5640-5643; (b) B. Lastra-Barreira, J. Díez, P. Crochet, Green Chem. 11 (2009) 1681-1686; (c) I. Romero-Canelón, L. Salassa, P. J. Sadler, J. Med. Chem. 56 (2013) 1291-1300.

[24] However, the free Schiff-base ligands **1a-b**, **3a-b** and **7** were smoothly hydrolyzed in D_2O solutions, giving rise to the complete conversion into the corresponding aldehydes and *N,N*-dimethylethylenediamine after 24 hours at room temperature. The higher stability of the coordinated Schiff-bases respective to free ligands is usual albeit strongly dependent of the metallic fragment involved. See, for example: E. Delahaye, M. Diop, R. Welter, M. Boero, C. Massobrio, P. Rabu, G. Rogez, Eur. J. Inorg. Chem. (2010) 4450-4461.

[25] Other arene-ruthenium(II) complexes containing Schiff-base ligand stable against the hydrolytic decomposition have been reported previously. See reference 23c.

[26] For mechanistic considerations, see reference 9c.

[27] For positive effect of basic or acidic pH on the activity, see: (a) I. Nieto, M.S. Livings, J.B. Sacci III, L.E. Reuther, M. Zeller, E.T. Papish, Organometallics 30 (2011) 6339-6342; (b) C. Aliende, M. Pérez-Manrique, F.A. Jalón, B.R. Manzano, A.M. Rodríguez, G. Espino, Organometallics 31 (2012) 6106-6123.

[28] NaOH or HCO_2H was added to the aqueous sodium formate solution to reach the desired pH. In the absence of additive, the aqueous solution of HCO_2Na employed presents a pH of 8.3.

[29] For similar observations, see: M.A.N. Virboul, R.J.M. Klein Gebbink, Organometallics 31 (2012) 85-91

[30] Moreover NaOH and/or $NaHCO_3$ were formed during the first run, increasing also the pH of the medium. See: C. Wang, C.Q. Li, X.F. Wu, A. Pettman, J.L. Xiao, Angew. Chem. Int. Ed. 48 (2009) 6524-6528.

FOR GRAPHICAL ABSTRACT USE ONLY

Half-sandwich ruthenium(II) complexes with water-soluble Schiff base ligands: Synthesis and catalytic activity in transfer hydrogenation of carbonyl compounds

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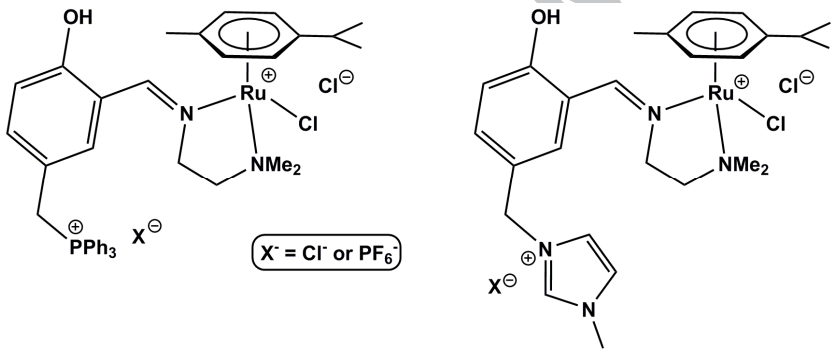
The preparation of novel water-soluble arene-ruthenium(II) complexes containing ionic Schiff base ligands is presented, along with their application as catalysts in the transfer hydrogenation of carbonyl compounds in aqueous medium.



Highlights

- Four new ionic Schiff-base ligands have been synthesized.
- Their selective coordination as *N,N*-chelates to an arene-ruthenium(II) fragment affords highly water-soluble complexes.
- The derivatives prepared have proved to be active in the transfer hydrogenation of ketones and aldehydes in aqueous media.