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Ruthenium(II) complexes containing 2-diphenylphosphinobenzaldehyde: synthesis and catalytic activity in transfer hydrogenation§

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Dedicated to Professor J.J.R. Fraústo da Silva

Abstract

The reaction of dimers $[Ru(\eta^6\text{-arene})(\mu\text{-Cl})Cl]_2$ (arene = C_6H_6 (**2a**); 1-^{i}Pr-4-C_6H_4Me (**2b**); 1,2,4,5-$C_6H_2Me_4$ (**2c**); C_6Me_6 (**2d**)) with 2-diphenylphosphinobenzaldehyde (**1**) yields the neutral complexes $[Ru(\eta^6\text{-arene})Cl_2(\kappa^1\text{-}P\text{-}2\text{-}Ph_2PC_6H_4CH{=}O)]$ (**3a–d**). Treatment of compounds **3a–d** with one equivalent of $AgSbF_6$ leads to the formation of the monocationic derivatives $[Ru(\eta^6\text{-arene})Cl(\kappa^2\text{-}P,O\text{-}2\text{-}Ph_2PC_6H_4CH{=}O)][SbF_6]$ (**4a–d**). When **3a–d** are treated with two equivalents of $AgSbF_6$ in presence of acetone, the dicationic complexes $[Ru(\eta^6\text{-arene})(\kappa^1\text{-}O\text{-}Me_2C{=}O)(\kappa^2\text{-}P,O\text{-}2\text{-}Ph_2PC_6H_4CH{=}O)][SbF_6]_2$ (arene = C_6H_6 (**5a**); 1-^{i}Pr-4-C_6H_4Me (**5b**); 1,2,4,5-$C_6H_2Me_4$ (**5c**); C_6Me_6 (**5d**)) are obtained. Complexes **3–5a–d** have proven to be active catalysts in transfer hydrogenation of acetophenone by propan-2-ol.

Keywords: (η^6-Arene)–ruthenium(II) complexes; P,O-donor ligands; Transfer hydrogenation

1. Introduction

The reduction of carbonyl compounds is an important transformation in organic synthesis both from academic and industrial points of view [1]. Hydrogen transfer reactions are safer, highly selective and eco-friendly compared to the commonly used reduction processes which involve high hydrogen pressure or hazardous reducing reagents [2]. Although phosphines were historically the first type of ligands used in transition metal catalyzed transfer hydrogenations [3], it is now well-known that the use of nitrogen containing ligands leads to an increased activity [4]. Thus, a wide variety of ruthenium(II) derivatives bearing diamino or amino–alcohol ligands has been successfully used as catalysts precursors [2,4,5]. In addition, many ruthenium(II) complexes associated to a mixed nitrogen–phosphorus ligand have proven to be efficient in this type of catalytic transformations, i.e. bidentate or tridentate phosphinooxazolines [6], pyridylphosphines [7], imino- and aminophosphines [8], and iminophosphorane-phosphines [9]. In contrast, to the best of our knowledge only very few studies employed catalysts with tridentate P,N,O-donor ligands [7a,b,9b] and none with bidentate P,O-donor ligands.

The coordination chemistry of 2-diphenylphosphinobenzaldehyde (**1**) has been extensively studied with a large variety of Rh, Pt, Mn, Re, Ni and Co fragments [10], but, as far as we know, only the ruthenium(II) derivative *trans*,*cis*,*cis*-$[RuCl_2(\kappa^2\text{-}P,O\text{-}2\text{-}Ph_2PC_6H_4CH{=}O)_2]$ has been reported to date (isolated in 7% yield) [11]. With these precedents in mind, in this paper we describe the preparation and catalytic activity in transfer hydrogenation of ketones of novel neutral, monocationic and dicationic (η^6-arene)–ruthenium(II) complexes bearing 2-diphenylphosphinobenzaldehyde (**1**).

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2. Experimental

2.1. General information

The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds $[Ru(\eta^6\text{-arene})(\mu\text{-Cl})Cl]_2$ [12] and 2-$Ph_2PC_6H_4CH{=}O$ [13] were prepared by following the methods reported in the literature. Infrared spectra (Nujol) were recorded on a Perkin–Elmer 1720-XFT spectrometer; absorption frequencies are given in cm^{-1}. The C and H analyses were carried out with a Perkin–Elmer 2400 microanalyzer. Conductivities were measured at r.t. with approximately 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. Gas chromatographic measurements were made on a Hewlett–Packard HP6890 equipment; a HP-INNOWAX cross-linked poly(ethylene glycol) column (30 m, 250 μm) was used. NMR spectra were recorded on Bruker AV300 or 300DPX instrument at 300 MHz (^1H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments have been carried out for all the complexes. Coupling constants J are given in Hertz. Abbreviations used: s, singlet; d, doublet; sept, septuplet; m, multiplet; cym, 1-^{i}Pr-4-C_6H_4Me; C_q, quaternary carbon; Ar, aromatic; C_{arom}, aromatic carbons.

2.2. Preparations

2.2.1. *[Ru(η⁶-C₆H₆)Cl₂(κ¹-P-2-Ph₂PC₆H₄CH=O)] (**3a**)*

A slurry of **2a** (0.287 g, 0.57 mmol) and 1 (0.400 g, 1.38 mmol) in 50 ml of dichloromethane was stirred for 24 h at room temperature (r.t.). The reaction mixture was then filtered through Kieselguhr and the filtrate evaporated to dryness. The resulting residue was washed twice with 10 ml of a mixture of hexane + diethyl ether (1/1) and vacuum dried to afford a brown solid. Yield: 0.481 g (77%). *Anal.* Found (Calc. for $C_{25}H_{21}Cl_2OPRu$): C, 55.68 (55.57); H, 3.79 (3.92)%. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 29.4 (s). ^1H NMR, $CDCl_3$, δ: 10.45 (s, 1H, CH=O), 8.21–6.98 (m, 14H, ArH), 5.97 (s, 6H, C_6H_6). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 193.5 (d, $^3J_{PC} = 7.2$, CH=O), 139.4–128.0 (m, C_{arom}), 90.2 (d, $^2J_{PC} = 3.6$, C_6H_6). IR, $\nu_{C=O}$: 1684.

2.2.2. *[Ru(η⁶-1-ⁱPr-4-C₆H₄Me)Cl₂(κ¹-P-2-Ph₂PC₆H₄CH=O)] (**3b**)*

Following a similar procedure **3b** was prepared as a brown solid using 0.300 g (0.49 mmol) of **2b** and 0.343 g (1.18 mmol) of **1**. Reaction time: 2 h. Yield: 0.486 g (83%). *Anal.* Found (Calc. for $C_{29}H_{29}Cl_2OPRu$): C, 58.54 (58.39); H, 4.78 (4.90)%. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 27.8 (s). ^1H NMR, $CDCl_3$, δ: 10.31 (s, 1H, CH=O), 8.20–7.27 (m, 14H, ArH), 5.33 and 4.86 (both d, 2H each, $^3J_{HH} = 5.7$, CH of cym), 2.98 (sept, 1H, $^3J_{HH} = 6.8$, C*H*Me_2), 1.82 (s, 3H, ArMe), 1.24 (d, 6H, $^3J_{HH} = 6.8$, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR, $CDCl_3$, δ: 193.0 (d, $^3J_{PC} = 6.1$, CH=O), 138.6–128.1 (m, C_{arom}), 112.7 (d, $^2J_{PC} = 4.9$, C_q of cym), 97.9 (s, C_q of cym), 88.3 (d, $^2J_{PC} = 4.9$, CH of cym), 87.5 (d, $^2J_{PC} = 2.4$, CH of cym), 30.4 (s, *C*HMe$_2$), 22.0 (s, CH*Me*$_2$), 18.0 (s, Ar*Me*). IR, $\nu_{C=O}$: 1686.

2.2.3. *[Ru(η⁶-1,2,4,5-C₆H₂Me₄)Cl₂(κ¹-P-2-Ph₂PC₆H₄CH=O)] (**3c**)*

Following a similar procedure **3c** was prepared as a brown solid using 0.150 g (0.24 mmol) of **2c** and 0.170 g (0.59 mmol) of **1**. Reaction time: 1 h. Yield: 0.239 g (82%). *Anal.* Found (Calc. for $C_{29}H_{29}Cl_2OPRu$): C, 58.25 (58.39); H, 4.97 (4.90)%. $^{31}P\{^1H\}$ NMR, $CDCl_3$, δ: 28.8 (s). ^1H NMR, $CDCl_3$, δ: 10.19 (s, 1H, CH=O), 8.20–7.27 (m, 14H, ArH), 4.55 (s, 2H, $C_6H_2Me_4$), 1.92 (s, 12H, $C_6H_2Me_4$). $^{13}C\{^1H\}$ NMR, CD_2Cl_2, δ: 193.4 (d, $^3J_{PC} = 4.8$, CH=O), 138.8–128.5 (m, C_{arom}), 98.5 (s, CH of $C_6H_2Me_4$), 93.8 (d, $^2J_{PC} = 4.8$, C_q of $C_6H_2Me_4$), 16.6 (s, $C_6H_2Me_4$). IR, $\nu_{C=O}$: 1689.

2.2.4. *[Ru(η⁶-C₆Me₆)Cl₂(κ¹-P-2-Ph₂PC₆H₄CH=O)] (**3d**)*

Following a similar procedure **3d** was prepared as a red–brownish solid using 0.100 g (0.15 mmol) of **2d** and 0.100 g (0.34 mmol) of **1**. Reaction time: 1 h. Yield: 0.148 g (79%). *Anal.* Found (Calc. for $C_{31}H_{33}Cl_2OPRu$): C, 59.50 (59.62); H, 5.52 (5.33)%. $^{31}P\{^1H\}$ NMR, CD_2Cl_2, δ: 31.2 (s). ^1H NMR, CD_2Cl_2, δ: 10.17 (s, 1H, CH=O), 8.19–7.43 (m, 14H, ArH), 1.77 (s, 18H, C_6Me_6). The low solubility of **3d** prevented $^{13}C\{^1H\}$ NMR measurements. IR, $\nu_{C=O}$: 1683.

2.2.5. *[Ru(η⁶-C₆H₆)Cl(κ²-P,O-2-Ph₂PC₆H₄CH=O)][SbF₆] (**4a**)*

A slurry of **3a** (0.316 g, 0.59 mmol) and $AgSbF_6$ (0.20 g, 0.59 mmol) in 120 ml of dichloromethane was stirred in the dark at r.t. for 1 h. The reaction mixture was then filtered through Kieselguhr and the filtrate evaporated to dryness. The resulting residue was washed 3 times with 10 ml of diethyl ether and vacuum-dried to afford an orange solid. Yield: 0.304 g (78%). *Anal.* Found (Calc. for $C_{25}H_{21}ClF_6OPRuSb$): C, 40.65 (40.54); H, 2.88 (2.86)%. Conductivity: 105 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR, acetone-d_6, δ: 37.5 (s). ^1H NMR, acetone-d_6, δ: 9.97 (d, 1H, $^4J_{PH} = 3.4$, CH=O), 8.35–7.60 (m, 14H, ArH), 6.19 (d, 6H, $^3J_{PH} = 0.8$, C_6H_6). $^{13}C\{^1H\}$ NMR, acetone-d_6, δ: 204.6 (d, $^3J_{PC} = 5.3$, CH=O), 142.4–128.0 (m, C_{arom}), 91.4 (d, $^2J_{PC} = 3.0$, C_6H_6). IR, $\nu_{C=O}$: 1629.

*2.2.6. [Ru(η^6-1-^{i}Pr-4-C_6H_4Me)Cl(κ^2-P,O-2-$Ph_2PC_6H_4CH{=}O$)][SbF_6] (**4b**)*

Following a similar procedure **4b** was prepared as an orange solid using 0.220 g (0.37 mmol) of **3b** and 0.127 g (0.37 mmol) of $AgSbF_6$. Yield: 0.273 g (93%). *Anal.* Found (Calc. for $C_{29}H_{29}ClF_6OPRuSb$): C, 43.61 (43.72); H, 3.59 (3.67)%. Conductivity: 125 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR, acetone-d_6, δ: 36.0 (s). ^1H NMR, acetone-d_6, δ: 9.99 (d, 1H, $^4J_{PH} = 4.0$, CH=O), 8.32–7.45 (m, 14H, ArH), 6.39 and 6.21 (both d, 1H each, $^3J_{HH} = 6.5$, CH of cym), 6.05 and 5.78 (both d, 1H each, $^3J_{HH} = 5.2$, CH of cym), 2.46 (m, 1H, C*H*Me$_2$), 2.00 (s, 3H, ArMe), 1.10 and 0.79 (both d, 3H each, $^3J_{HH} = 6.8$, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR, acetone-d_6, δ: 204.8 (d, $^3J_{PC} = 5.3$, CH=O), 142.2–128.4 (m, C_{arom}), 109.7 (s, C_q of cym), 98.2 (d, $^2J_{PC} = 6.0$, CH of cym), 97.7 (s, C_q of cym), 92.8 (d, $^2J_{PC} = 6.8$, CH of cym), 89.5 (d, $^2J_{PC} = 1.5$, CH of cym), 87.4 (d, $^2J_{PC} = 3.0$, CH of cym), 31.4 (s, *C*HMe$_2$), 22.7 and 20.5 (both s, CH*Me*$_2$), 18.1 (s, Ar*Me*). IR, $\nu_{C=O}$: 1617.

*2.2.7. [Ru(η^6-1,2,4,5-$C_6H_2Me_4$)Cl(κ^2-P,O-2-$Ph_2PC_6H_4CH{=}O$)][SbF_6] (**4c**)*

Following a similar procedure **4c** was prepared as an orange solid using 0.513 g (0.86 mmol) of **3c** and 0.30 g (0.86 mmol) of $AgSbF_6$. Yield: 0.564 g (82%). Found (Calc. for $C_{29}H_{29}ClF_6OPRuSb$): C, 43.84 (43.72); H, 3.77 (3.67)%. Conductivity: 133 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR, acetone-d_6, δ: 37.4 (s). ^1H NMR, acetone-d_6, δ: 10.03 (d, 1H, $^4J_{PH} = 4.0$, CH=O), 8.32–7.41 (m, 14H, ArH), 5.96 (s, 2H, C_6H_2Me$_4$), 1.90 and 1.79 (both s, 6H each, C_6H_2*Me*$_4$). $^{13}C\{^1H\}$ NMR, acetone-d_6, δ: 205.0 (d, $^3J_{PC} = 5.3$, CH=O), 142.0–125.9 (m, C_{arom}), 100.6 (s, C_q of $C_6H_2Me_4$), 100.4 (d, $^2J_{PC} = 5.8$, C_q of $C_6H_2Me_4$), 95.8 (d, $^2J_{PC} = 5.3$, CH of $C_6H_2Me_4$), 16.4 and 16.3 (both s, C_6H_2*Me*$_4$). IR, $\nu_{C=O}$: 1622.

*2.2.8. [Ru(η^6-C_6Me_6)Cl(κ^2-P,O-2-$Ph_2PC_6H_4CH{=}O$)][SbF_6] (**4d**)*

Following a similar procedure **4d** was prepared as an orange solid using 0.120 g (0.19 mmol) of **3d** and 0.066 g (0.19 mmol) of $AgSbF_6$. Yield: 0.134 g (86%). *Anal.* Found (Calc. for $C_{31}H_{33}ClF_6OPRuSb$): C, 44.96 (45.14); H, 4.21 (4.03)%. Conductivity: 128 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR, acetone-d_6, δ: 39.9 (s). ^1H NMR, acetone-d_6, δ: 9.95 (dd, 1H, $^4J_{PH} = 4.0$, $J_{HH} = 0.5$, CH=O), 8.21–7.49 (m, 14H, ArH), 1.96 (d, 18H, $^4J_{PH} = 0.8$, C_6Me$_6$). $^{13}C\{^1H\}$ NMR, acetone-d_6, δ: 204.8 (d, $^3J_{PC} = 4.3$, CH=O), 141.9–125.3 (m, C_{arom}), 100.4 (d, $^3J_{PC} = 2.9$, *C*$_6$Me$_6$), 15.7 (s, C_6*Me*$_6$). IR, $\nu_{C=O}$: 1613.

*2.2.9. [Ru(η^6-C_6H_6)(κ^1-O-$Me_2C{=}O$)(κ^2-P,O-2-$Ph_2PC_6H_4CH{=}O$)][SbF_6]$_2$ (**5a**)*

A slurry of **3a** (0.481 g, 0.89 mmol) and $AgSbF_6$ (0.672 g, 1.96 mmol) in 120 ml of dichloromethane was stirred in the dark at r.t. for 1 h. Then, 10 ml of acetone were added to the reaction mixture. After filtration through Kieselguhr, the filtrate was evaporated to approximately 3 ml and 10 ml of diethyl ether were added. The resulting precipitate was washed three times with 10 ml of diethyl ether and vacuum-dried to afford an ochre solid. Yield: 0.623 g (70%). Found (Calc. for $C_{28}H_{27}F_{12}O_2PRuSb_2$): C, 33.73 (33.66); H, 2.83 (2.72)%. Conductivity: 200 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR, acetone-d_6, δ: 41.0 (s). ^1H NMR, acetone-d_6, δ: 10.19 (dd, 1H, $^4J_{PH} = 3.4$, $J_{HH} = 0.7$, CH=O), 8.65–7.60 (m, 14H, ArH), 6.51 (d, 6H, $^3J_{PH} = 1.0$, C_6H_6). $^{13}C\{^1H\}$ NMR, acetone-d_6, δ: 205.0 (d, $^3J_{PC} = 6.8$, CH=O), 144.3–123.1 (m, C_{arom}), 91.2 (d, $^2J_{PC} = 3.0$, C_6H_6). ^1H and $^{13}C\{^1H\}$ NMR spectra (acetone-d_6): interchange between $(CH_3)_2C{=}O$ and the solvent prevented the observation of the signals corresponding to the coordinated acetone ligand. IR, $\nu_{C=O}$: 1635 (aldehyde), 1651 (acetone).

*2.2.10. [Ru(η^6-1-^{i}Pr-4-C_6H_4Me)(κ^1-O-$Me_2C{=}O$)(κ^2-P,O-2-$Ph_2PC_6H_4CH{=}O$)][SbF_6]$_2$ (**5b**)*

Following a similar procedure **5b** was prepared as a yellow solid using 0.300 g (0.50 mmol) of **3b** and 0.688 g (1.11 mmol) of $AgSbF_6$. Yield: 0.502 g (95%). *Anal.* Found (Calc. for $C_{32}H_{35}F_{12}O_2PRuSb_2$): C, 36.38 (36.43); H, 3.24 (3.34)%. Conductivity: 193 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR, acetone-d_6, δ: 37.0 (s). ^1H NMR, acetone-d_6, δ: 10.21 (d, 1H, $^4J_{PH} = 3.4$, CH=O), 8.50–7.74 (m, 14H, ArH), 6.88 (d, 1H, $^3J_{HH} = 6.3$, CH of cym), 6.62 (d, 1H, $^3J_{HH} = 5.7$, CH of cym), 6.48 (d, 1H, $^3J_{HH} = 6.3$, CH of cym), 5.99 (d, 1H, $^3J_{HH} = 5.7$, CH of cym), 2.69 (m, 1H, C*H*Me$_2$), 2.11 (s, 3H, ArMe), 1.25 and 0.95 both (d, 3H each, $^3J_{HH} = 6.8$, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR, acetone-d_6, δ: 205.7 (d, $^3J_{PC} = 6.8$, CH=O), 144.3–124.5 (m, C_{arom}), 108.7 (s, C_q of cym), 100.3 (s, C_q of cym), 94.3 (d, $^2J_{PC} = 6.0$, CH of cym), 93.4 (d, $^2J_{PC} = 3.0$, CH of cym), 91.5 (d, $^2J_{PC} = 3.0$, CH of cym), 86.2 (d, $^2J_{PC} = 1.5$, CH of cym), 31.7 (s, *C*HMe$_2$), 22.9 and 20.6 (both s, CH*Me*$_2$), 17.9 (s, ArMe). ^1H and $^{13}C\{^1H\}$ NMR spectra (acetone-d_6): interchange between $(CH_3)_2C{=}O$ and the solvent prevented the observation of the signals corresponding to the coordinated acetone ligand. IR, $\nu_{C=O}$: 1626 (aldehyde), 1652 (acetone).

*2.2.11. [Ru(η^6-1,2,4,5-$C_6H_2Me_4$)(κ^1-O-$Me_2C{=}O$)(κ^2-P,O-2-$Ph_2PC_6H_4CH{=}O$)][SbF_6]$_2$ (**5c**)*

Following a similar procedure **5c** was prepared as a yellow solid using 0.250 g (0.42 mmol) of **3c** and 0.320 g (0.93 mmol) of $AgSbF_6$. Yield: 0.386 g (87%). *Anal.* Found (Calc. for $C_{32}H_{35}F_{12}O_2PRuSb_2$): C, 36.39 (36.43); H, 3.48 (3.34)%. Conductivity: 200 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR, acetone-d_6, δ: 38.6 (s). ^1H NMR, acetone-d_6, δ: 10.32 (d, 1H, $^4J_{PH} = 2.9$, CH=O), 8.54–7.55 (m, 14H, ArH), 6.33 (s, 2H, C_6H_2Me$_4$),

2.15 (d, 6H, $^4J_{PH} = 1.1$, $C_6H_2Me_4$), 1.91 (s, 6H, $C_6H_2Me_4$). $^{13}C\{^1H\}$ NMR, acetone-d_6, δ: 206.1 (d, $^3J_{PC} = 6.4$, CH=O), 144.1–124.2 (m, C_{arom}), 105.1 (d, $^2J_{PC} = 2.9$, C_q of $C_6H_2Me_4$), 96.8 (s, C_q of $C_6H_2Me_4$), 95.5 (d, $^2J_{PC} = 4.3$, CH of $C_6H_2Me_4$), 16.3 and 16.2 (both s, $C_6H_2Me_4$). ^1H and $^{13}C\{^1H\}$ NMR spectra (acetone-d_6): interchange between $(CH_3)_2C=O$ and the solvent prevented the observation of the signals corresponding to the coordinated acetone ligand. IR, $\nu_{C=O}$: 1624 (aldehyde), 1646 (acetone).

2.2.12. [Ru(η⁶-C₆Me₆)(κ¹-O-Me₂C=O)(κ²-P,O-2-Ph₂PC₆H₄CH=O)][SbF₆]₂ (5d)

Following a similar procedure **5d** was prepared as an ochre solid using 0.200 g (0.32 mmol) of **3d** and 0.242 g (0.70 mmol) of $AgSbF_6$. Yield: 0.270 g (78%). *Anal.* Found (Calc. for $C_{34}H_{39}F_{12}O_2PRuSb_2$): C, 37.58 (37.70); H, 3.71 (3.63)%. Conductivity: 200 Ω^{-1} cm^2 mol^{-1}. $^{31}P\{^1H\}$ NMR, acetone-d_6, δ: 38.0 (s). ^1H NMR, acetone-d_6, δ: 10.40 (d, 1H, $^4J_{PH} = 2.9$, CH=O), 8.62–7.43 (m, 14H, ArH), 1.90 (s, 18H, C_6Me_6). ^1H and $^{13}C\{^1H\}$ NMR spectra (acetone-d_6): interchange between $(CH_3)_2C=O$ and the solvent prevented the observation of the signals corresponding to the coordinated acetone ligand. The low solubility of **5d** prevented $^{13}C\{^1H\}$ NMR measurements. IR, $\nu_{C=O}$: 1625 (aldehyde), 1643 (acetone).

2.3. General procedure for catalytic transfer hydrogenation of acetophenone

Under inert atmosphere acetophenone (0.60 g, 5 mmol), the ruthenium catalyst precursor (0.01 mmol, 0.2 mol%), and 45 ml of propan-2-ol were introduced in a Schlenk tube fitted with condenser and heated at 82 °C for 15 min. Then NaOH was added (5 ml of a 0.048 M solution in propan-2-ol, 4.8 mol%) and the reaction monitored by gas chromatography. GC measurements are effectued each 5 min till conversion reachs 50% in order to obtain the half-reaction time and the TOF_{50} values with the better precision. TOF_{50} values are given with a precision of ± 10 h^{-1}. Acetone and 1-phenylethanol were the only products detected in all cases.

3. Results and discussion

3.1. Synthesis and characterization of complexes [Ru(η⁶-arene)Cl₂(κ¹-P-2-Ph₂PC₆H₄CH=O)] (3a–d)

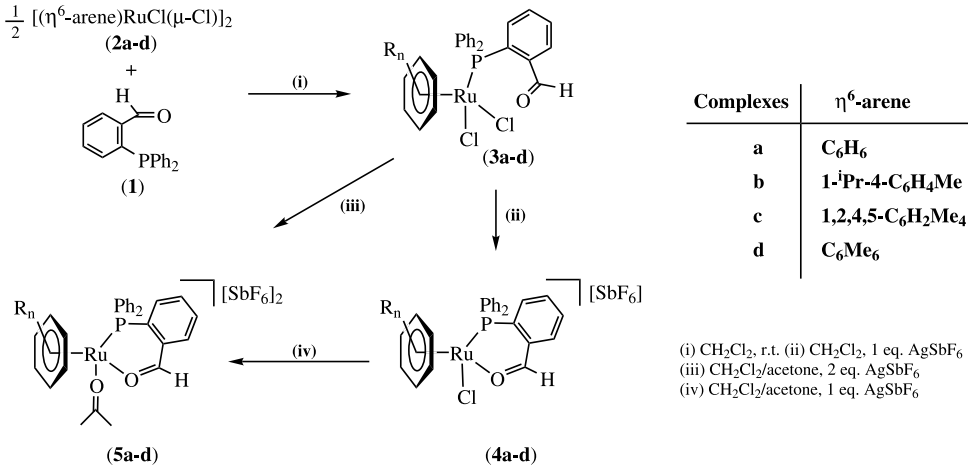
Dimers $[Ru(\eta^6\text{-arene})(\mu\text{-Cl})Cl]_2$ (**2a**–**d**) react with two equivalents of 2-diphenylphosphinobenzaldehyde (**1**), in dichloromethane at room temperature, to afford neutral complexes $[Ru(\eta^6\text{-arene})Cl_2(\kappa^1\text{-}P\text{-}2\text{-}Ph_2PC_6H_4CH=O)]$ (arene = C_6H_6 (**3a**); 1-^{i}Pr-4-C_6H_4Me (**3b**); 1,2,4,5-$C_6H_2Me_4$ (**3c**); C_6Me_6 (**3d**)) in 77–83% yield (Scheme 1). Compounds **3a**–**d** have been characterized by elemental analyses, IR, and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy being all the data fully consistent with the proposed structures. In particular, the coordination of the phosphine is readily assessed in the $^{31}P\{^1H\}$ NMR spectra by a downfield shift of the Ph_2P resonance with respect to the free ligand (δ = 29.4 (**3a**); 27.8 (**3b**); 28.8 (**3c**); 31.2 (**3d**) vs. −11.2 (**1**) ppm). The IR spectra exhibit an absorption band in the range 1683–1689 cm^{-1}, characteristic of a non-coordinated aldehyde group [10f]. In addition, the free CH=O function gives rise in the ^1H NMR spectra to a singlet signal at approximately 10.2 ppm and in the $^{13}C\{^1H\}$ NMR spectra to a doublet at approximately 193 ppm due to the coupling with the phosphorus nuclei. These chemical shifts are similar to those observed for the free ligand **1**. ^1H NMR ($CDCl_3$) δ: 10.52 (d, 1H, $^4J_{PH} = 5.5$, C*H*=O); $^{13}C\{^1H\}$ NMR, δ: 191.7 (d, $^4J_{PC} = 18.9$, *C*H=O). As far as we know, complexes **3a**–**d** represent the first examples of ruthenium derivatives containing a phosphino–aldehyde ligand coordinated in a monodentate manner.

3.2. Synthesis and characterization of complexes [Ru(η⁶-arene)Cl(κ²-P,O-2-Ph₂PC₆H₄CH=O)][SbF₆] (4a–d)

Treatment of dichloromethane solutions of **3a**–**d** with one equivalent of $AgSbF_6$ yields (78–93%) the cationic derivatives $[Ru(\eta^6\text{-arene})Cl(\kappa^2\text{-}P,O\text{-}2\text{-}Ph_2PC_6H_4CH=O)][SbF_6]$ (arene = C_6H_6 (**4a**); 1-^{i}Pr-4-C_6H_4Me (**4b**); 1,2,4,5-$C_6H_2Me_4$ (**4c**); C_6Me_6 (**4d**)), which are readily formed *via* abstraction of one chloride ligand and O-coordination of the aldehyde group (Scheme 1). Characterization of compounds **4a**–**d** was achieved by means of standard spectroscopic techniques as well as elemental analyses and conductance measurements. The $^{31}P\{^1H\}$ NMR spectra of complexes **4a**–**d** display a singlet signal at 37.5 (**4a**), 36.0 (**4b**), 37.4 (**4c**) and 39.9 (**4d**) ppm which appear at lower fields (ca. 10 ppm) when compared to their neutral precursors **3a**–**d**. The coordination of the aldehyde group on the ruthenium centre is evidenced by: (i) (IR) the ν(C=O) absorptions (in the range 1613–1629 cm^{-1}) which are red-shifted in comparison with those observed for complexes **3a**–**d** and that of the free ligand 1, and (ii) ($^{13}C\{^1H\}$ NMR spectra) the downfield shifting of the C=O resonance (δ ca. 205 ppm). In addition, conductance measurements in acetone confirm that compounds **4a**–**d** are 1:1 electrolytes (Λ_M between 105 and 133 Ω^{-1} cm^2 mol^{-1}).

3.3. Synthesis and characterization of complexes [Ru(η⁶-arene)(κ¹-O-Me₂C=O)(κ²-P,O-2-Ph₂PC₆H₄CH=O)][SbF₆]₂ (5a–d)

The treatment of complexes $[Ru(\eta^6\text{-arene})Cl_2(\kappa^1\text{-}P\text{-}2\text{-}Ph_2PC_6H_4CH=O)]$ (**3a**–**d**) with a twofold excess of $AgSbF_6$, in dichloromethane and further addition of



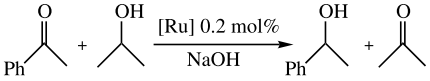
Complexes	η6-arene
a	C_6H_6
b	1-^{i}Pr-4-C_6H_4Me
c	1,2,4,5-$C_6H_2Me_4$
d	C_6Me_6

Scheme 1.

acetone, leads to the formation of the dicationic derivatives [Ru(η6-arene)(κ1-*O*-Me_2C=O)(κ2-*P*,*O*-2-$Ph_2PC_6H_4CH$=O)][SbF_6]2 (arene = C_6H_6 (**5a**); 1-^{i}Pr-4-C_6H_4Me (**5b**); 1,2,4,5-$C_6H_2Me_4$ (**5c**); C_6Me_6 (**5d**)) (75–95% yield; Scheme 1). Alternatively, complexes **5a**–**d** can be prepared in similar yields starting from **4a**–**d** and one equivalent of $AgSbF_6$ in a mixture dichloromethane/acetone as solvent. These compounds have been obtained as yellow–brownish air stable solids, being slightly soluble in chloroform or dichloromethane but highly soluble in acetone. Analytical and spectroscopic data support the proposed formulation. In particular, the presence of the coordinated acetone is assessed by an IR absorption at approximately 1650 cm^{-1}. The spectroscopic features corresponding to the coordinated ligand 2-$Ph_2PC_6H_4CH$=O are very similar to those observed for the complexes **4a**–**d**, confirming once again the chelate coordination of the 2-diphenylphosphinobenzaldehyde ligand. Remarkable features are: (i) (^{1}H NMR) a doublet signal at approximately 10.2 ppm attributable to the aldehydic proton, (ii) ($^{13}C\{^1H\}$ NMR) a doublet resonance at approximately 205 ppm assignable to the aldehydic carbon, and (iii) (IR) an absorption band for the CH=O group between 1624 and 1635 cm^{-1}. Conductance measurements in acetone confirm that compounds **5a**–**d** are 1:2 electrolytes (Λ_M ca. 200 Ω^{-1} cm^2 mol^{-1}).

3.4. Catalytic transfer hydrogenation of acetophenone

The catalytic activity of complexes **3a**–**d**, **4a**–**d** and **5a**–**d** in transfer hydrogenation of acetophenone by propan-2-ol has been investigated (Scheme 2). In a typical experiment, the ruthenium(II) catalyst precursor (0.2 mol%) and NaOH (4.8 mol%) were added to a 0.1 M solution of acetophenone in propan-2-ol at reflux temperature, the reaction being monitored by gas chromatography. The results are summarized in Table 1.



Scheme 2.

All the complexes are active leading to nearly quantitative conversions to 1-phenylethanol. Both in the neutral and the monocationic series the benzene (**3a**,**b**) and *p*-cymene (**4a**,**b**) derivatives are the most active (entries 1, 2, 5 and 6). Nevertheless, this trend is no longer observed for the dicationic complexes, being **5c** (1,2,4,5-$C_6H_2Me_4$) the faster catalyst. This seems to indicate that the catalytic activity does not depend exclusively on the steric or electronic properties of the arene ligand.

Different types of the active catalytic species have been proposed in the literature, the requirements being a metal–hydride function and a free coordination site [14]. In our case, no mechanistic studies have been performed. Nevertheless, we can propose that the hydride formation results probably from the substitution of a chloride ligand (**3a**–**d**, **4a**–**d**), or the coordinated acetone (**5a**–**d**),[1] by the isopropoxide anion,[2] followed by β-elimination. The generation of a vacancy can be provided by (i) substitution of the arene [15] or (ii) partial dissociation of the chelate ligand [8d], as proposed previously for similar catalyst precursors. The former proposition can be discarded here since

[1] Treatment of complex [Ru(η6-1-^{i}Pr-4-C_6H_4Me)Cl(κ2-*P*,*O*-2-$Ph_2PC_6H_4CH$=O)][SbF_6] with 24 equiv. of NaOH in refluxing 2-propanol leads after 5 min to the formation of three new species ($^{31}P\{^1H\}$ NMR, in 2-propanol/capilar D_2O, δ: 49.8, 52.8 and 54.8 ppm) which can tentatively be attributed to [Ru(η6-1-^{i}Pr-4-C_6H_4Me)H(κ2-*P*,*O*-2-$Ph_2PC_6H_4CH$=O)][SbF_6], [Ru(η6-1-^{i}Pr-4-C_6H_4Me)H_2(κ1-*P*-2-$Ph_2PC_6H_4CH$=O)] and [Ru(η6-1-^{i}Pr-4-C_6H_4Me)ClH(κ1-*P*-2-$Ph_2PC_6H_4CH$=O)]. The mixture rapidly decomposes avoiding further characterization.

[2] The isopropoxide anion is generated from 2-propanol and base. No activity is observed in absence of base.

Table 1
Transfer hydrogenation of acetophenone

Entry	Catalyst	Yield [a] after 1 h (%)	Yield [a] (time)	TOF_{50} (h^{-1}) [b]
[Ru(η⁶-arene)Cl₂(κ¹-P-2-Ph₂PC₆H₄CH=O)]				
1	**3a**	60	97 (10)	370
2	**3b**	64	98 (10)	370
3	**3c**	14	96 (9)	100
4	**3d**	17	97 (8)	110
[Ru(η⁶-arene)Cl(κ²-P,O-2-Ph₂PC₆H₄CH=O)][SbF₆]				
5	**4a**	58	94 (10)	350
6	**4b**	64	97 (9)	380
7	**4c**	17	96 (9)	120
8	**4d**	9	98 (22)	70
[Ru(η⁶-arene)(κ¹-O-Me₂C=O)(κ²-P,O-2-Ph₂PC₆H₄CH=O)][SbF₆]₂				
9	**5a**	49	96 (22)	240
10	**5b**	62	96 (6)	410
11	**5c**	61	96 (10)	430
12	**5d**	49	95 (22)	240

Conditions: reactions were carried out at 82 °C using 5 mmol of acetophenone (0.1 M in propan-2-ol). Ketone/catalyst/NaOH: 500/1/24.

[a] Yield of 1-phenylethanol, GC determined.

[b] Turnover frequencies ((mol product/mol catalyst)/time) were calculated at 50% conversion.

the addition of free arene to the catalytic medium (100 equiv. per Ru) does not affect the rate of the reaction.

4. Conclusions

We have prepared in high yields new ruthenium(II) complexes containing 2-diphenylphosphinobenzaldehyde of the type $[Ru(\eta^6\text{-arene})Cl_2(\kappa^2\text{-}P,O\text{-}2\text{-}Ph_2PC_6H_4CH{=}O)]$, $[Ru(\eta^6\text{-arene})Cl(\kappa^2\text{-}P,O\text{-}2\text{-}Ph_2PC_6H_4CH{=}O)][SbF_6]$ and $[Ru(\eta^6\text{-arene})(\kappa^1\text{-}O\text{-acetone})(\kappa^2\text{-}P,O\text{-}2\text{-}Ph_2PC_6H_4CH{=}O)][SbF_6]_2$ (arene = C_6H_6, 1-^{i}Pr-4-C_6H_4Me, 1,2,4,5-$C_6H_2Me_4$, C_6Me_6). All the compounds have proved to be active in transfer hydrogenation of acetophenone by propan-2-ol leading to almost quantitative conversions. The catalytic efficiency of these complexes is moderate and comparable to that observed for similar (η^6-arene)-ruthenium(II) derivatives [6a,g,8d,9,15,16].

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