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Journal of Molecular Catalysis A: Chemical 224 (2004) 61–70
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Water soluble ruthenium cyclopentadienyl and aminocyclopentadienyl PTA complexes as catalysts for selective hydrogenation of α,β-unsaturated substrates (PTA = 1,3,5-triaza-7-phosphaadamantane)

Sandra Bolaño[a], Luca Gonsalvi[a,**], Fabrizio Zanobini[a], Francesco Vizza[a], Valerio Bertolasi[b], Antonio Romerosa[c], Maurizio Peruzzini[a,*]

[a] *Istituto di Chimica del Composti Organometallici, Consiglio Nazionale delle Ricerche (ICCOM-CNR), Via Madonna del Piano, 50019 Sesto Fiorentino (Firenze), Italy*
[b] *Dipartimento di Chimica, Centro di Strutturistica Diffrattometrica, Università di Ferrara, Via L. Borsari 46, 44100 Ferrara, Italy*
[c] *Área de Química Inorgánica, Facultad de Ciencias Experimentales, Universidad de Almería, 04071 Almería, Spain*

Received 22 March 2004; received in revised form 8 June 2004; accepted 11 June 2004

Dedicated to Prof Jozef Ziolkowski on the occasion of his 70th birthday.

Abstract

A series of half-sandwich Ru-cyclopentadienyl derivatives containing the cage-like water soluble monodentate phosphine 1,3,5-triaza-7-phosphaadamantane (PTA) was synthesized and tested in aqueous phase or biphasic homogeneous hydrogenation of activated olefins via hydrogen transfer or under hydrogen pressure at mild conditions. The hydrogen transfer results show higher activity for the Cp* derivatives (Cp* = C_5Me_5) than for the corresponding Cp complexes (Cp = C_5H_5). Under H_2 pressure, all complexes show high selectivity to C=C double bond hydrogenation. The X-ray crystal structure featuring a protonated 2-aminoethylcyclopentadienyl Ru complex was also determined.

Keywords: 1,3,5-Triaza-7-phosphaadamantane; Water soluble phosphines; Homogeneous catalysis; Hydrogen transfer

1. Introduction

In recent years, environmental concerns have prompted a new approach to chemical reactions and technology, in order to reduce as much as possible the use of toxic reagents and/or volatile solvents. Nowadays, parameters such as *E*-factor [1], atom efficiency [2] and the "12 principles of Green Chemistry" [3] are often considered as essential driving forces in the quest for sustainable chemical processes. Within these aspects, the replacement of organic solvents with water has attracted interest both from academia and industry. The main advantage apart from the lower environmental impact, is the possibility to separate easily the products from the catalyst to allow its efficient and cost-effective recycling. The classic approach for homogeneously catalysed processes is to replace ancillary ligands (usually phosphines) with their water-soluble analogues, for example PPh_3 with the mono- or trisulfonated version, namely TPPMS and TPPTS [4].

The use of neutral water soluble monodentate phosphines such as 1,3,5-triaza-7-phosphaadamantane (PTA) has received renewed interest in the recent literature due to its properties to solubilize transition metal complexes in aqueous phase. This property has been used for application of Rh, Ru and Pd–PTA complexes in aqueous phase or biphasic homogeneous catalysis, in tests as new drugs for tumour inhibition (Ru– and Pt–PTA) and in photoluminescent devices (Au–PTA), as recently reviewed [5].

* Corresponding author. Tel.: +39 055 5225289; fax: +39 055 5225203.
** Co-corresponding author.
E-mail addresses: l.gonsalvi@iccom.cnr.it (L. Gonsalvi), mperuzzini@iccom.cnr.it (M. Peruzzini).

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doi:10.1016/j.molcata.2004.06.030

Regioselective hydrogenation of α,β-unsaturated substrates catalysed by transition metal complexes is a reaction of high interest for the synthesis of pharmaceutical intermediates and was successfully transferred to aqueous biphasic conditions. Examples of selective C=C double bond hydrogenation include substrates such as benzylidene acetone (BZA) and cinnamaldehyde (CNA) [6], unsaturated fatty acids esterified in lipids [7], fumaric, maleic and crotonic acids [8], 2-acetamidoacrylic acid methyl ester [9], etc. In general, hydrogenation at C=C double bond is catalysed by Rh complexes, whereas efficient reduction of C=O group is obtained by Ru-based catalysts [10]. Pioneering work done by Joó et al. [11] showed that the carbonyl group of a series of 2-keto acids can be selectively reduced by hydrogen in the presence of $[RuCl_2(TPPMS)_2]$ or $[Ru(H)Cl(TPPMS)_3]$ in water with high turnover numbers (1300 for the hydrogenation of pyruvic acid to lactic acid). Ru–TPPTS complexes were also found to be active catalysts for C=O reductions in water, as reviewed by Nomura [12].

Transfer hydrogenation of C=O groups by HCO_2Na/H_2O catalysed by Ru(II) water soluble complexes is also known. Unsaturated aldehydes, aromatic and aliphatic aldehydes were reduced in the presence of Ru, Rh, Ir and Pt complexes of TPPMS by hydrogen transfer using HCO_2Na/H_2O. Joó and Benyei reported that cinnamaldehyde, crotonaldehyde, 1-citronellal and citral are reduced under mild conditions (30–80 °C) exclusively to unsaturated alcohols by $[RuCl_2(TPPMS)_2]/HCO_2Na/H_2O$, without hydrogenation or hydrogenolysis of substituents on the aromatic rings [13]. Recent studies by the same authors have shown strong pH dependence of the molecular distribution of water soluble Ru–TPPMS hydrides and tested the effect on the selectivity of C=C versus C=O bond hydrogenation of cinnamaldehyde under H_2/H_2O [14]. At pH ≤3.3, the dominant species was found to be $[Ru(H)Cl(TPPMS)_3]$, able to catalyse C=C hydrogenation, whereas at pH ≥7 $[RuH_2(TPPMS)_4]$ was observed and found to be a selective catalyst for C=O bond reduction. The effect of hydrogen pressure was also tested in a later paper, showing that in water/chlorobenzene biphasic mixture buffered at pH 3, the hydrogenation of cinnamaldehyde catalysed by $[Ru(H)Cl(TPPMS)_3]$ produced a 61:39 mixture of cinnamyl alcohol and dihydrocinnamaldehyde at 14 psi H_2, but the selectivity increased to 93:7 by increasing the hydrogen pressure to 116 psi [15].

PTA complexes were also used as catalysts for selective hydrogenations although to a lower extent. In particular, under biphasic aqueous–organic solvent conditions using sodium formate as the hydrogen source, *cis*-$RuCl_2(PTA)_4$ accomplishes a 95.1% conversion of benzaldehyde into benzyl alcohol with a TOF of 22 h^{-1} at 80 °C [15b]. Ru–PTA complexes also found an efficient application in the water phase reduction of CO_2 and HCO_3^- to HCO_2^- [16].

Ru(II), Rh(I) and Rh(III) complexes of *N*-methyl-PTA (PTA-Me) such as *trans*-$[RuI_4(PTA\text{-}Me)_2]$, $[RuI_2(PTA\text{-}Me)_3(H_2O)]I_3$ and $[RhI_4(PTA\text{-}Me)_2]I$ are active catalysts for the hydrogenation of cinnamaldehyde [17] at the C=O bond for Ru, at the C=C double bond for Rh. Under biphasic conditions (water/toluene or chlorobenzene) with H_2 as the hydrogen source, average TOFs (h^{-1}) ranged from 40 to 190. Conversion of cinnamaldehyde using $[RhI_4(PTA\text{-}Me)_2]I$ was 95% with 84% selectivity to $PhCH_2CH_2CHO$, the best selectivity to $PhCH{=}CHCH_2OH$ was achieved with $[RuI_4(PTA\text{-}Me)_2]$ (84% yield at 89% conversion). Using sodium formate as the hydrogen source (chlorobenzene/water, 5 M $NaCO_2H$, [catalyst] 0.01 mmol, 75 °C) gave lower conversions, typically 2% conversion using $[RuI_4(PTA\text{-}Me)_2]$ and 13% with $[RhI_4(PTA\text{-}Me)_2]I$, with total selectivity to cinnamyl alcohol and dihydrocinnamaldehyde, respectively.

In a recent communication [18], we showed results on the catalytic activity of novel Ru–PTA complexes bearing cyclopentadienyl coligands, namely $[CpRuCl(PTA)_2]$ (**1**) and $[Cp^*RuCl(PTA)_2]$ (**2**). Under 450 psi of hydrogen at 80 °C in *n*-octane/water, these complexes catalyse the selective hydrogenation of BZA to 4-phenyl-butan-2-one at high catalytic ratio (1:200 to the substrate). In this paper, we report the synthesis of a new class of Ru–PTA cyclopentadienyl complexes, of general formula $[(C_5R_5)RuX_n(PTA)_m](PF_6)$ (R = H; X = Cl, I, $n = 1$, $m = 2$; X = MeCN; n, $m = 1$, 2; R = Me, X = MeCN, $n = 1$, $m = 2$) and of the complexes $[\{Cp(CH_2)_2NEt_2\}RuX(PTA)_2](PF_6)$ (X = Cl, MeCN, none) bearing a novel 2-(diethylamino)ethylcyclopentadienyl ligand. The complexes were tested as homogeneous catalysts for the hydrogenation of BZA under hydrogen pressure in biphasic conditions and in transfer hydrogenation of CNA using the HCO_2Na/H_2O protocol.

2. Experimental

2.1. General information

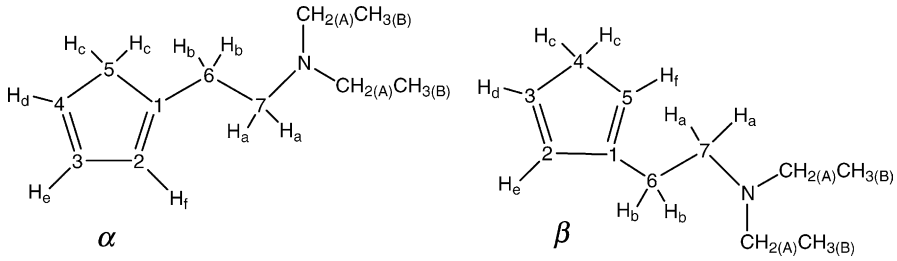
All synthetic procedures were carried out using standard Schlenk glassware under an inert atmosphere of dry nitrogen. The ligand PTA [19] and the ruthenium complexes $[RuCl_2(PPh_3)_3]$ [20], $[Cp^*Ru(MeCN)_3]PF_6$ [21], $[CpRuCl(PTA)_2]$ [18] and $[Cp^*RuCl(PTA)_2]$ [18] were prepared as described in the literature. Other reagents were obtained from the suppliers and used without further purification. The solvents were all degassed and distilled according to standard procedures [22]. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 1600 series FT-IR spectrometers between KBr plates. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker AC200 spectromers operating at 200.13 MHz and 50.32 MHz, respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (^1H) or the deuterated solvent multiplet (^{13}C). $^{31}P\{^1H\}$ NMR spectra were recorded on the same instrument operating at 81.01 MHz, respectively. Chemical shifts were measured relative to external 85% H_3PO_4, with downfield shifts considered positive. All the NMR spectra were recorded at room temperature (20 °C) unless otherwise stated. Batch reactions under a controlled

pressure of gas were performed with a stainless steel Parr 4565 reactor (100 ml) equipped with a Parr 4842 temperature and pressure controller. GC analyses were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionisation detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) SPB-1 Supelco fused silica capillary column. The crystal data were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα radiation and corrected for Lorentz, polarization and absorption effects [23]. All pH-metric measurements employed for the determination of protonation constants were carried out in aqueous 0.10 M NMe_4Cl solutions at 298.2 ± 0.1 K, by using a Crison Micro pH 2002 potentiometer fitted with a Metrohm combined glass electrode (model 6.0204.000). A Hamilton Microlab M motor-driven syringe under the control of an appropriate program running on an IBM PS/2 model 40 personal computer was used. The analytical methodology employed, has been previously described [24]. The computer program Hyperquad was used to calculate the equilibrium constants from emf data [25]. Elemental analyses (C, H) were performed using a Carlo Erba model 1106 elemental analyser by the Microanalytical Service of the Department of Chemistry at the University of Florence.

2.2. Synthetic procedures

2.2.1. 2-(Diethylamino)ethylcyclopentadiene

The compound was prepared similarly to the corresponding 2-(dimethyl)aminoethylcyclopentadiene [26]. A THF solution of sodium cyclopentadienylide (2 M, 157 ml, 0.314 mol) was slowly added through a dropping funnel with pressure equalizer to a stirred suspension of 2-(diethylamino)ethylchloride (32.71 g, 0.24 mol) in THF (100 ml). After the addition was complete, the resulting mixture was refluxed for 4 h and then concentrated to dryness under vacuum to leave a brown oily residue. Water (500 ml) was added to the crude residue which was then extracted with pentane (3 × 150 ml). The combined pentane extracts were concentrated under reduced pressure and the residue distilled (Kugelrohr), using a dry-ice cooling device at 0.5 Torr (b.p. 57–59 °C). Colourless distillates were collected to give 2-(diethylamino)ethylcyclopentadiene as a 4:3 mixture of the two isomers shown below). Yield 31.7 g (80%). ^{1}H NMR ($CDCl_3$): 6.52–6.38 (m, H_f-α + H_f-β); 6.32–6.24 (m, H_d-α + H_e-α); 6.23–6.17 (br m, H_e-β); 6.05 (dt, H_d-β, $^3J(H_dH_e)$ 3.2, $^3J(H_dH_c)$ 1.6 Hz); 3.00–2.94 (m, $2H_c$-α); 2.94–2.89 (m, $2H_c$-β); 2.65–2.75 (m, $2H_a$-α + $2H_b$-α + $2H_a$-β + $2H_b$-β); 2.58 (q, $4H_A$ + $4H_B$, $J(H_AH_B)$ 7.2 Hz, CH_2CH_3); 1.06 (t, $3H_A$ + $3H_B$, $J(H_AH_B)$ 7.2 Hz, CH_2CH_3). $^{13}C\{^1H\}$NMR ($CDCl_3$): 146.1 C1(β); 135.4 C2(α); 134.4 C2(β); 133.1 C3(α); 131.4 C3(β); 127.5 C4(α); 127.2 C4(β), 53.6 C7(α); 52.8 C7(β); 47.5 (CH_2CH_3); 44.2 C4(α); 42.0 C4(β); 28.7 C6(α); 27.9 C6(β); 12.4 (CH_3). Elemental analysis: $C_{11}H_{19}N$: Calcd C, 79.94; H, 11.59; N, 8.47. Found C, 79.7; H, 11.7; N, 8.4.



2.2.2. [{Cp(CH2)2NEt2}RuCl(PPh3)2] (3)

Complex **3** was prepared similarly to the analogue complex bearing the 2-(dimethylamino)ethylcyclopentadiene ligand [26]. A THF (30 ml) solution of KO^{t}Bu (0.17 g, 1.50 mmol) and $C_5H_5(CH_2)_2NEt_2$ (0.36 g, 2.20 mmol) was stirred at room temperature for 30 min. The resulting solution was then transferred to a THF (50 ml) solution of $[RuCl_2(PPh_3)_3]$ (1.00 g, 1.04 mmol) and additionally stirred for 1 h. Removal of the solvent in vacuo afforded **3** as an orange solid, which was recrystallized from diethyl ether/hexane. Yield: 0.73 g (85%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 40.37(s). ^{1}H NMR ($CDCl_3$: 7.00–7.50 (m, 30H, aromatic protons); 3.97 (br s, 2H, Cp); 3.34 (br s, 2H, Cp); 2.71 (t, 2H, J(HH) 7.0 Hz CH_2CH_2N); 2.59 (q, 4H, J(HH) 7.0 Hz, NCH_2CH_3); 2.43 (t, 2H, J(HH) 7.0 Hz, CH_2CH_2N); 1.05 (t, 6H, J(HH) 7.0 Hz, CH_2CH_3). Elemental analysis: $C_{47}H_{48}NClP_2Ru$: Calcd C, 68.40; H, 5.86; N, 1.70. Found C, 68.5; H, 6.1; N, 1.4.

2.2.3. [{Cp(CH2)2NEt2}RuCl(PTA)2] (4)

To a solution of $[\{Cp(CH_2)_2NEt_2\}RuCl(PPh_3)_2]$ (99 mg, 0.12 mmol) in 10 ml of toluene solid PTA (38 mg, 0.24 mmol) was added. The solution was refluxed under stirring for 2.5 h and then the solvent was evaporated under vacuum to about 5 ml. Addition of *n*-hexane (5 ml) while stirring yielded a canary yellow microcrystalline product, which was filtered on a sintered glass-frit and washed with *n*-hexane (2 × 3 ml) and vacuum dried. Yield 63 mg (85%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −25.30 (s, PTA). ^{1}H NMR ($CDCl_3$): 4.80–4.40 (m, 14H, $NCH_2N_{(PTA)}$ (12H), + Cp (2H), $^2J(HH_{(NCH_2N)})$ 13.3 Hz); 4.21–3.88 (14H, $PCH_2N_{(PTA)}$ (12H), + Cp (2H), $^2J(HH_{(PCH_2N)}) + {}^3J$(HP) 15.4 Hz; 2.69 (t, 2H, J(HH) 7.1 Hz, CH_2CH_2N); 2.57 (q, 4H, J(HH) 7.0 Hz, NCH_2CH_3); 2.22 (t, 2H, J(HH) 7.1 Hz, CH_2CH_2N); 1.04 (t, 6H, J(HH) 7.0 Hz, CH_2CH_3). Elemental analysis: $C_{23}H_{42}N_7ClP_2Ru$: Calcd C, 44.91; H, 6.88; N, 15.94. Found C, 44.6; H, 7.1; N, 15.6.

*2.2.4. [{Cp(CH$_2$)$_2$NEt$_2$}Ru(PTA)$_2$](PF$_6$) (**5**)*

Solid NH_4PF_6 (30 mg, 0.18 mmol) was added to a solution of **4** (100 mg, 0.16 mmol) in MeOH (10 ml) under stirring. After 30 min stirring, the solution was evaporated under a brisk current of nitrogen to yield pale yellow microcrystals of **5** which were collected on a glass frit and washed with cold MeOH (2 × 2 ml) and diethyl ether (2 × 3 ml). Yield 104 mg (90%). IR (cm^{-1}): ν(PF$_6$) 841 (vs). $^{31}P\{^1H\}$ NMR (D$_2$O): −24.29 (s, PTA); −144.27 (sept, *J*(PF) 708.6 Hz, PF$_6$). ^{1}H NMR (CDCl$_3$): 4.78 (br s, 2H, Cp); 4.45 (s, 12H, NCH$_2$N$_{(PTA)}$); 4.19 (br s, 2H, Cp); 3.95 (m, 12H, PCH$_2$N$_{(PTA)}$); 3.23 (m, 2H, CH$_2$*CH$_2$*N); 3.12 (q, 4H, *J*(HH) 6.9 Hz, N*CH$_2$*CH$_3$); 2.33 (br m, 2H, *CH$_2$*CH$_2$N); 1.19 (t, 6H, *J*(HH) 6.9 Hz, NCH$_2$*CH$_3$*). $^{13}C\{^1H\}$ NMR (D$_2$O): 108.6 (s, quaternary Cp); 74.8 (t, ^3J(CP) 4.3 Hz, Cp); 71.9 (br s, N*CH$_2$*N$_{(PTA)}$); 71.1 (s, Cp); 55.5 (t, *N* = ^1J(CP) + ^3J(CP) = 8.8 Hz, P*CH$_2$*N$_{(PTA)}$); 51.07 (s, CH$_2$*CH$_2$*N); 48.83 (s, N*CH$_2$*CH$_3$); 22.58 (s, *CH$_2$*CH$_2$N); 9.45 (s, CH$_2$*CH$_3$*). Elemental analysis: C$_{23}$H$_{42}$N$_7$F$_6$P$_3$Ru: Calcd C, 38.12; H, 5.84; N, 13.53. Found C, 37.6; H, 6.0; N, 13.3.

*2.2.5. [{Cp(CH$_2$)$_2$NEt$_2$}Ru(PTA)$_2$(MeCN)](PF$_6$) (**6**)*

[{Cp(CH$_2$)$_2$NEt$_2$}RuCl(PTA)$_2$] (100 mg, 0.16 mmol) was dissolved in 10 ml of MeCN, then NH_4PF_6 (35 mg, 0.21 mmol) was added. The solution was refluxed under stirring for 2 h, after which the volume of the solution was reduced under vacuum to about 5 ml and EtOH (5 ml) was added. The light yellow microcrystals which formed were isolated by filtration and washed with cold EtOH (2 × 3 ml) and pentane (2 × 3 ml). Yield 92 mg (75%). IR (cm^{-1}): ν(C≡N) 2256 (vw), ν(PF$_6$) 838 (vs). $^{31}P\{^1H\}$ NMR (D$_2$O): −23.64 (s, PTA); −144.27 (sept, *J*(PF) 708.5 Hz, PF$_6$). ^{1}H NMR (D$_2$O): 5.04 (t, 2H, *J*(HH) 1.8 Hz, Cp); 4.53 (br s, 12H, N*CH$_2$*N$_{(PTA)}$); 4.48 (br t, 2H, *J*(HH) 1.5 Hz, Cp); 4.03 (br s, 12H, P*CH$_2$*N$_{(PTA)}$); 3.32–3.08 (m, 6H, CpCH$_2$C*H$_2$*N(C*H$_2$*CH$_3$)$_2$); 2.50–2.31 (m, 2H, CpC*H$_2$*CH$_2$N); 2.30 (t, 3H, ^5J(HP) 1.5 Hz, CH$_3$CN); 1.19 (t, 6H, *J*(HH) 7.2 Hz, CH$_2$C*H$_3$*). Elemental analysis: C$_{25}$H$_{45}$N$_8$F$_6$P$_3$Ru: Calcd C, 39.22; H, 5.92; N, 14.63. Found C, 38.9; H, 6.1; N, 14.5.

*2.2.6. [CpRu(PTA)(MeCN)$_2$](PF$_6$) (**8**)*

[CpRu(MeCN)$_3$]PF$_6$ (100 mg, 0.23 mmol) and PTA (36 mg, 0.23 mmol) were dissolved in 15 ml of methanol. The solution was stirred for 2 h and then evaporated to dryness giving a yellow solid which was washed with Et$_2$O (2 × 3 ml) and dried under vacuum. Yield: 114 mg (90%). IR (cm^{-1}): ν(C≡N) 2267 (vw), ν(PF$_6$) 835 (vs). $^{31}P\{^1H\}$ NMR (CD$_2$Cl$_2$): −32.60 (s, PTA); −143.88 (sept, *J*(PF) 709.2 Hz, PF$_6$). ^{1}H NMR (CD$_2$Cl$_2$): 4.59 (br s, 12H, N*CH$_2$*N$_{(PTA)}$); 4.51 (s, 5H, Cp); 4.15 (s, 12H, P*CH$_2$*N$_{(PTA)}$); 2.37 (d, 6H, ^5J(HP) 1.5 Hz, CH$_3$CN). Elemental analysis: C$_{15}$H$_{23}$N$_5$F$_6$P$_2$Ru: Calcd C, 32.73; H, 4.21; N, 12.72. Found C, 32.5; H, 4.6; N, 12.6.

*2.2.7. [CpRu(PTA)$_2$(MeCN)](PF$_6$) (**9**)*

2.2.7.1. Method A. [CpRuCl(PTA)$_2$] (100 mg, 0.19 mmol) was dissolved in 15 ml of MeOH in a 50 ml round-bottomed flask. Solid TlPF$_6$ (74 mg, 0.21 mmol) and MeCN (10 μl, 0.26 mmol) were then added with continuous stirring. The off-white solid of TlCl slowly formed over 3 h was filtered off and the filtrate was evaporated to dryness giving **9** as a yellow solid. Yield 80 mg (63 %).

2.2.7.2. Method B. PTA (18 mg, 0.11 mmol) was added to a stirred solution of **8** (60 mg, 0.11 mmol) in MeOH (10 ml). After stirring 30 min, the solution was evaporated to dryness leaving **9** a yellow solid. Yield 70 mg (92%).

$^{31}P\{^1H\}$ NMR (acetone-d$_6$): −26.16 (s, PTA); −142.63 (sept, *J*(PF) = 709.1 Hz, PF$_6$). ^{1}H NMR (acetone-d$_6$): 4.98 (s, 5H, Cp); 4.56 (m, 12H, ^2J(HH) 13.6 Hz, N*CH$_2$*N$_{(PTA)}$); 4.17(m, 12H, ^2J(HH) 16 Hz, P*CH$_2$*N$_{(PTA)}$); 2.52 (t, 3H, ^5J(HP) 1.4 Hz, CH$_3$CN). Elemental analysis: C$_{19}$H$_{32}$N$_7$F$_6$P$_3$Ru: Calcd C, 34.24; H, 4.84; N, 14.71. Found C, 34.5; H, 4.6; N, 14.4.

*2.2.8. [Cp*Ru(PTA)$_2$(MeCN)](PF$_6$) (**10**)*

The synthesis of **10** was carried out as described above for [CpRu(PTA)$_2$(MeCN)](PF$_6$) (Method A), with the following quantities: [Cp*RuCl(PTA)$_2$] (100 mg, 0.17 mmol), MeOH (20 ml), TlPF$_6$ (70 mg, 0.20 mmol), and MeCN (20 μl, 0.40 mmol). Yield 70 mg (56%). $^{31}P\{^1H\}$ NMR (acetone-d$_6$): −37.36 (s, PTA); −142.61 (sept, *J*(PF) 708.6 Hz, PF$_6$,). ^{1}H NMR (acetone-d$_6$) 4.59 (m, 12H, N*CH$_2$*N$_{(PTA)}$), 4.20 (m, 12H, P*CH$_2$*N$_{(PTA)}$); 2.61 (t, 3H, ^5J(HP) 1.5 Hz, *CH$_3$*CN); 1.86 (t, 15H, ^3J(HP) 1.7, Cp*). Elemental analysis: C$_{24}$H$_{42}$N$_7$F$_6$P$_3$Ru: Calcd C, 39.13; H, 5.75; N, 13.31. Found C, 39.1; H, 5.9; N, 13.6.

*2.2.9. [CpRuI(PTA)$_2$] (**11**)*

[CpRuCl(PTA)$_2$] (100 mg, 0.19 mmol) and KI (332 mg, 2.0 mmol) were dissolved in 80 ml of methanol in a round-bottom flask wrapped with an aluminium foil and stirred at room temperature for 16 h. The orange solid which separated out was isolated via decantation, washed with *n*-hexane and dried under vacuum. Yield 60 mg (52%). $^{31}P\{^1H\}$ NMR (CDCl$_3$): −30.05 (s, PTA). ^{1}H NMR (CDCl$_3$, 200.13 MHz): 4.65 (s, 5H, Cp); 4.55 (m, 12H, ^2J(HH) 13.3 Hz, N*CH$_2$*N$_{(PTA)}$); 4.10 (m, 12H, ^2J(H$_A$H$_B$) 15.8 Hz, P*CH$_2$*N$_{(PTA)}$). Elemental analysis: C$_{17}$H$_{29}$N$_6$IP$_2$Ru: Calcd C, 33.62; H, 4.81; N, 13.84. Found C, 33.6; H, 5.0; N, 13.7.

*2.3. X-ray diffraction study of [{Cp(CH$_2$)$_2$NHEt$_2$}Ru(PTA)(MeCN)(μ-{PTA(H)PTA})(MeCN)(PTA)Ru[{Cp(CH$_2$)$_2$NHEt$_2$}](PF$_6$)$_5$·NH$_4$PF$_6$·4H$_2$O (**7**).*

Yellow crystals of [{Cp(CH$_2$)$_2$NHEt$_2$}Ru(PTA)(MeCN)(μ-{PTA(H)PTA})(MeCN)(PTA)Ru [{Cp(CH$_2$)$_2$NHEt$_2$}](PF$_6$)$_5$·NH$_4$PF$_6$·4H$_2$O (**7**) were obtained by slow crystallization from a solution of crude **6** in water. The structure was solved by direct methods [27] and refined using

Table 1
Crystal data parameters for **7**

Formula	$C_{25}H_{52.5}F_{18}N_{8.5}O_2P_5Ru$
M	1102.18
Space group	$P2_1/c$
Crystal system	Monoclinic
a (Å)	12.7320(2)
b (Å)	22.7376(4)
c (Å)	14.7337(3)
β (°)	102.126(1)
U (Å^3)	4170.2(1)
Z	4
D_c (g cm^{-3})	1.756
F(0 0 0)	2236
μ(Mo Kα) (cm^{-1})	6.88
Measured reflections	30991
Unique reflections	9349
R_{int}	0.053
Observed reflections [$I \geq 2\sigma(I)$]	7553
$\theta_{min} - \theta_{max}$ (°)	2.5–27.5
hkl ranges	−16,16;−29,29;−19,18
$R(F^2)$ (observed reflection)	0.0639
$wR(F^2)$ (all reflections)	0.1917
Number of variables	540
Goodness of fit	1.073
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (Åe^{-3})	−0.871, 0.753
CCDC deposition number	233549

full-matrix least-squares [28] with all non-hydrogen atoms anisotropic and hydrogens included on calculated positions, riding on their carrier atoms, except for the hydrogen atoms linked to N1 and N5 which were refined isotropically. The C8(H_2)–C9(H_3) and C10(H_2)–C11(H_3) moieties were found to be disordered and refined with two independent orientations with multiplicity of 0.5. The asymmetric unit of compound **7** contains a cationic Ru(II) complex protonated at N1 atom of *N*,*N*-diethylamino group and at N5 of a PTA ligand, two water molecules, three PF_6 anions and a NH_4 cation situated on a centre of symmetry. Crystal data are collected in Table 1.

2.4. Catalytic tests

2.4.1. Autoclave experiments

Typically, 45 ml of a 1:3 (v:v) mixture of *n*-octane/water was introduced by suction into a 120 cm^3 autoclave, which contained 9×10^{-3} mmol of the precatalyst and 200 equivalents of benzylidene acetone (BZA, 263 mg). The autoclave was pressurized with the required pressure of hydrogen at room temperature and then heated to 80 or 130 °C. As soon as the reaction mixture in the autoclave reached the desired temperature, stirring (1200 rpm) was applied for the desired time. The reaction was stopped by cooling the autoclave to room temperature with an ice-water bath. The pressure was then released. THF and methanol were added to the biphasic system, in order to obtain one phase, which was analysed by GC and GC/MS. Each test was repeated twice to check for reproducibility.

2.4.2. Transfer hydrogenation tests

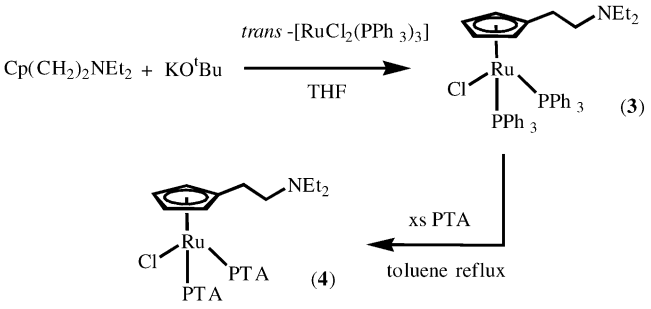
The reactions were carried out in Schlenk tubes under rigorously inert atmosphere with degassed solvents. For hydrogen transfer of BZA, the substrate (0.75 mmol) was dissolved into 5 ml of a H_2O/MeOH mixture (2:3) together with HCO_2Na (7.0 mmol), and the resulting solution was transferred via cannula to a solution of the catalyst (7.5×10^{-3} mmol) and HCO_2Na (0.5 mmol in 1 ml H_2O) pre-heated to 70 °C. The resulting solution was left stirring for 6 h at 90 °C. At the end of the reaction, the mixture was analysed by GC. For hydrogen transfer of cinnamaldehyde (CNA), the catalyst (0.03 mmol) was placed in a Schlenk tube with a HCO_2Na solution in water (2 ml, 1 M). The solution was stirred under nitrogen and heated to 80 °C for 2–3 min, after which a mixture of CNA (2 mmol) and aqueous HCO_2Na (4 ml, 5 M) was added by cannula. The resulting solution was left stirring for 5 h at 80 °C. At the end of the reaction, the mixture was extracted with CH_2Cl_2 and the organic phase was analysed by GC. Each test was repeated twice to check for reproducibility.

3. Results and discussion

3.1. Synthesis of cyclopentadienyl Ru(II)–PTA complexes

In a previous communication [18] we showed that the water soluble neutral complexes [CpRuCl(PTA)$_2$] (**1**) and [Cp*RuCl(PTA)$_2$] (**2**) are active catalysts for the selective hydrogenation of activated olefins such as BZA to the saturated ketone (C=C double bond reduction) at 80 °C, 435 psi H_2. Further investigations suggested however that phosphine dissociation may occur during the catalytic runs, leading to less efficient performance upon recycling. Although PTA-free Ru species after catalysis were not identified, Dyson et al. showed that for the hydrogenation of arenes under slightly harsher reaction conditions (90 °C, 870 psi H_2) catalysed by [Ru(*p*-cymene)Cl_2(PTA)] and [Ru(*p*-cymene)Cl(PTA)$_2$]$^+$, formation of the trinuclear cluster [Ru_3(*p*-cymene)$_3$(μ_3-Cl)]$^+$ was detected as the resting state of the catalyst [29].

We reasoned that higher catalytic performance could in principle be obtained using more stable analogues of **1** and **2**. The complexes were modified by introducing a hemilable arm bearing a tertiary amine group on the cyclopentadienyl ring. Therefore, the new 2-(diethylamino)ethylcyclopentadiene ligand, Cp(CH_2)$_2$$NEt_2$, was prepared following the method described by Wang et al. for the 2-(dimethylamino)ethyl analog with minor modifications [26]. The aminocyclopentadienyl ligand was then reacted with a suitable Ru(II) precursor, such as [$RuCl_2$(PPh_3)$_3$], to obtain [{Cp(CH_2)$_2$$NEt_2$}RuCl($PPh_3$)$_2$] (**3**). Metathesis with excess PTA in refluxing toluene afforded the hydrosoluble species [{Cp(CH_2)$_2$$NEt_2$}RuCl(PTA)$_2$] (**4**) in good yield as showed in Scheme 1.

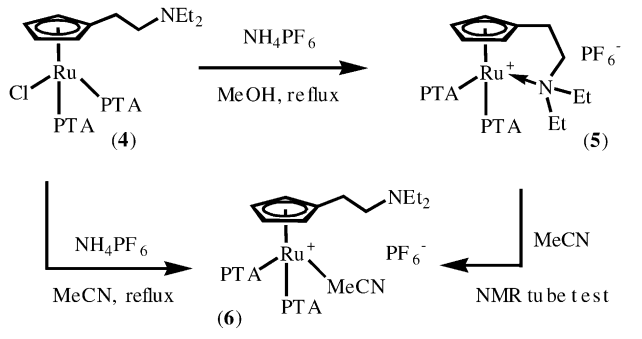


Scheme 1.

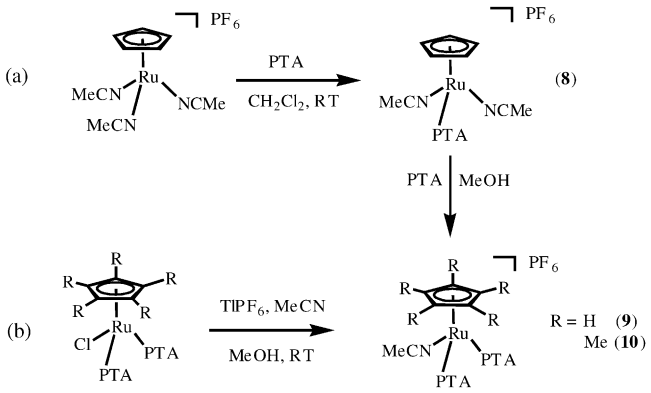
Reaction of **4** with NH_4PF_6 in MeOH afforded the *N*-coordinated $[\{Cp(CH_2)_2NEt_2\}Ru(PTA)_2]PF_6$ (**5**) via removal of the coordinated chloride which is highly favoured in polar solvents such as methanol. The hemilability of the *N*-arm was shown by reaction of **4** with NH_4PF_6 in the presence of a coordinating solvent such as MeCN, which in turn yielded the complex $[\{Cp(CH_2)_2NEt_2\}Ru(MeCN)(PTA)_2]PF_6$ via decoordination of the pending 2-(diethylamino)ethyl substituent of the Cp ring (**6**, Scheme 2). Alternatively, complex **6** was straightforwardly obtained in quantitative yield by treating **5** with MeCN in MeOH (NMR tube test).

Recrystallization from a diluted water solution of the crude product obtained from the mother liquor of the reaction to synthesize complex **6**, gave pale yellow crystals suitable for X-ray data diffraction (vide infra). The complex crystallized as *N*-protonated at the amine group and on one PTA ligand for each dimeric unit (vide infra) with half molecule of NH_4PF_6 and two H_2O interspersed in the lattice. The protonation is possibly due to the presence of ammonium salt in solution. This result is consistent with potentiometric titration data which show that the first protonation equilibrium L + H = HL (L = $[\{Cp(CH_2)_2NEt_2\}Ru(MeCN)(PTA)_2]PF_6$) occurs at basic pH 9.5, at values expected for the quaternization of the free tertiary amine [30].

A series of cationic mono- or bis-PTA ruthenium complexes was also synthesized as shown in Scheme 3. The Cp mono-PTA complex $[CpRu(MeCN)_2(PTA)]PF_6$ (**8**) was obtained via ligand substitution (Scheme 3a) from the *tris*-acetonitrile precursor $[CpRu(MeCN)_3]PF_6$ [21] using the



Scheme 2.



Scheme 3.

stoichiometric amount of phosphine. The corresponding bis-PTA complexes $[(C_5R_5)Ru(MeCN)(PTA)_2]PF_6$ (R = H, **9**; R = Me, **10**) were obtained by halogen abstraction from **1** and **2** with $TlPF_6$ in the presence of MeCN, respectively (Scheme 3b). Addition to **8** of a second equivalent of PTA in MeOH is a simple way to generate **9** in quantitative yield. Finally, the iodo derivative $[CpRuI(PTA)_2]$ (**11**) was obtained by halogen exchange between **1** and a suspension of KI in MeOH at RT. Separation from KCl was possible due to the low solubility of **11** which crystallized out from the solution on standing overnight at room temperature.

3.2. X-ray crystal structure of $[\{Cp(CH_2)_2NHEt_2\}Ru(PTA)(MeCN)(\mu\text{-}\{PTA(H)PTA\})(MeCN)(PTA)Ru\{Cp(CH_2)_2NHEt_2\}](PF_6)_5\cdot NH_4PF_6\cdot 4H_2O$ (7)

The structure of **7** consists of ruthenium(II) cations coordinated by a η^5-2-(diethylammonium)ethylcyclopentadienyl ligand, the N8 nitrogen of a molecule of acetonitrile and one P-bonded PTA ligand. A second PTA ligand, also coordinated to ruthenium with the P-atom, is in addition connected to another PTA ligand from a second complex cation by a shared proton laying on a special position, equally distant from the two N atoms (vide infra). An ORTEP plot of **7** is shown in Fig. 1, while selected bond angles and distances are given in Table 2. A molecule of NH_4PF_6, with the ammonium ion located in a special position, and two clathrates H_2O molecules complete the asymmetric unit.

The H5N hydrogen bonded to N5 atom lays on a centre of symmetry and is shared with another N5 atom of a second Ru complex forming a centrosymmetric dimer by means of a very strong intermolecular N5···H5N···N5 hydrogen bond with N5···N5 distance of 2.775(6) Å. (Fig. 2). Accordingly each Ru complex displays a positive 2.5+ charge. The sharing of a proton between two equivalent nitrogens is typical for organic cations as proton sponges and medium-ring bridgehead bi- or tricyclic bi- or triamines [31], but is unprecedented in the vast series of X-ray authenticated PTA derivatives [5]. The coordination geometry about ruthenium can be described as a three-legged piano stool with L–Ru–L basal angles in the range 86.98(1)–97.66(4)°. Alternatively,

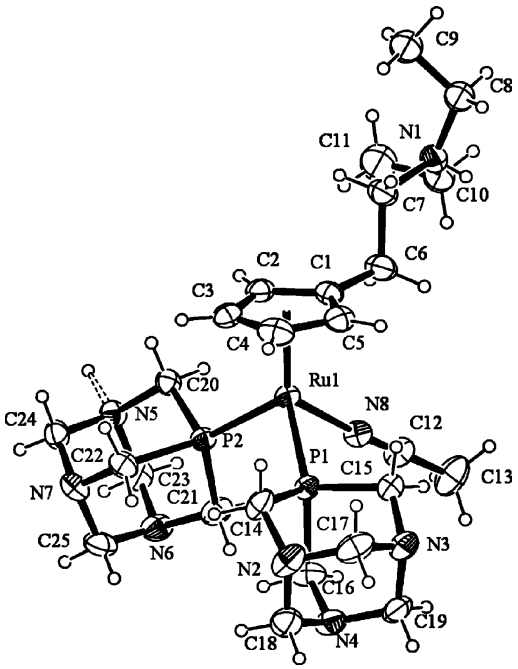


Fig. 1. An ORTEP view of complex **7** showing thermal ellipsoids at 30% probability. NH_4 cation, PF_6 anions and H_2O molecules have been omitted for sake of clarity.

it may be viewed either as distorted octahedral if cyclopentadienyl ring is allowed three facial coordination sites or as distorted tetrahedral if Cp is considered to occupy one coordination site.

The Ru–P bond lengths of 2.286(1) and 2.274(1) Å fall in the range of distances of 2.25–2.38 Å observed in structures of Ru–PTA complexes [4b,15,16b,18,32] and $[CpRu(L)(PR_3)_2]$ compounds [33]. The distances between Ru and Cp ring [Ru–C in the range 2.187(5)–2.243(5) Å and Ru–Cp(centroid) of 1.857(2) Å] are typical for Ru–cyclopentadienyl complexes and, similarly to the metrical parameters of the pending 2-(diethylammonium)ethyl arm, do not deserve additional comments. The Ru–N(acetonitrile) distance of 2.061(4) Å compares well with those in $[CpRu(CH_3CN)(PPh_3)_2]^+$ [33c] and in $[CpRu(\eta^4\text{-}CH_2{=}C(CH_3){-}CH{=}CH_2)(CH_3CN)]^+$ [34] of 2.040(3) and 2.059(3) Å, respectively.

Table 2
Selected bond distances (Å) and angles (°) for **7**

Ru1—P1	2.286(1)
Ru1—P2	2.274(1)
Ru1—N8	2.061(4)
Ru1—C1	2.243(5)
Ru1—C2	2.226(5)
Ru1—C3	2.187(5)
Ru1—C4	2.191(5)
Ru1—C5	2.218(5)
Ru1—Cp	1.857(5)
P1—Ru1—P2	97.66(4)
P1—Ru1—N8	86.9(1)
P2—Ru1—N8	91.6(1)
P1—Ru1—Cp	123.5(1)
P2—Ru1—Cp	122.7(1)
N8—Ru1—Cp	125.1(1)

Cp is the centroid of the cyclopenadienyl ring C1–C5.

3.3. Hydrogenation catalytic tests.

All complexes tested are active in regioselective hydrogenation of BZA to 4-phenyl-butan-2-one (**12**) in H_2O/*n*-octane. By-products 4-phenyl-but-3-en-2-ol (**13**) and 4-phenyl-butan-2-ol (**14**) were formed in small amount or traces, as summarized in Table 3. Catalytic tests with **1** at 80 °C, 450 psi of H_2, showed very high selectivity to **12**

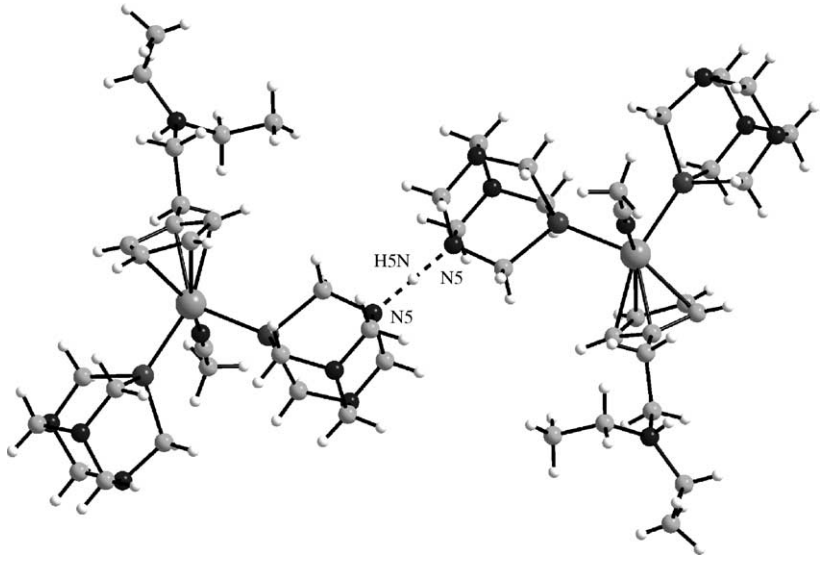


Fig. 2. A view of $[\{Cp(CH_2)_2NHEt_2\}Ru(PTA)(MeCN)(\mu\text{-}\{PTA(H)PTA\})(MeCN)(PTA)Ru\{Cp(CH_2)_2NHEt_2\}]^{5+}$ cation highlighting that the dimer is held together through a centre of symmetry by N5···H5N···N5 hydrogen bond.

Table 3
Catalyst screening for aqueous biphasic hydrogenation of BZA[a]

Catalyst	% conversion[b]	% **12**[b]	% **13**[b]
–	<1	<1	0.0
1	76.3	76.0	0.3
2	20.9	20.9	0.0
5	19.4	19.4	0.0
6	26.5	26.5	0.0
8	75.7	75.0	0.7
9	49.3	48.7	0.6
10	50.8	50.8	0.0

[a] Conditions: BZA, 1.8 mmol; catalyst, 9×10^{-3} mmol; $p(H_2)$ 450 psi; 80 °C; 16 h; *n*-octane, 10 ml; H_2O, 35 ml.
[b] GC values based on pure samples. **12** = 4-phenyl-butan-2-one; **13** = 4-phenyl-but-3-en-2-ol.

(>99%) at high conversion (76%) after 16 h. The activity of **2** was much lower under the same conditions, with conversion reaching ca. 21%, again with complete selectivity to C=C hydrogenation. Complexes **5** and **6** showed very similar catalytic performance (complete selectivity to 12, 19 and 26% conversion at 16 h, respectively). These results may reflect the lability of the amino group which is likely to be dangling under the catalytic conditions as a *N*-protonated β-ethylammonium salt, with H_2O completing the coordination sphere of Ru for **5**.

Complex **8** showed very similar activity and selectivity to **1** for the hydrogenation of BZA, which in turn suggests that both **1** and **8** may generate the same (or very similar) catalytic active species, in the case of **1** by fast dissociation of one PTA molecule. Indeed, catalytic tests with **1** in the presence of an excess of free PTA showed a decrease in conversion rate [18]. Cationic bis-PTA complexes **9** and **10** showed again comparable activity, indicating little effect of Cp or Cp* on the hydrogenation of BZA.

The effects of H_2 pressure and temperature on the hydrogenation of BZA were screened using **1** as catalyst. By reducing the pressure from 450 to 200 psi at 80 °C, the conversion actually raised from 76% to almost complete after 16 h. A possible explanation for this puzzling behaviour could be that higher hydrogen pressure may stabilize catalytically inactive species thus reducing the activity. Lowering the temperature to 40 °C did not affect activity or selectivity which were found to be greater than 99% after 6 h at 200 psi H_2 (optimized conditions). At 25 °C and 200 psi H_2, moderate conversion was observed (46%), which raised to 88% after 16 h in a separate experiment (Table 4). In all cases high selectivity to the saturated ketone was maintained.

We tried to expand the scope of the reaction by testing different substrates for hydrogenation. Diphenyl acetylene was reduced at 80 °C, 200 psi H_2 in *n*-octane/H_2O with low conversion (9.5%) to *cis*-stilbene (2.9%) and 1,2-diphenylethane (6.6%). Under the same conditions, *trans*-stilbene was converted to 1,2-diphenylethane with 10.8% conversion. Styrene was hydrogenated to ethylbenzene (12.3%) after 6 h at 80 °C using 200 psi H_2 or alternatively in 1 h at 450 psi H_2 (12.9% conversion). Acetophenone was recovered unchanged after

Table 4
Pressure and temperature screening for aqueous biphasic hydrogenation of BZA[a]

pH_2 (psi)	*T* (°C)	% conversion (h)[b]	% **12**[b]	% **13**[b]
450	80	76.3(16)[c]	76.0	0.3
200	80	99.9(16)[c]	99.5	0.4
200	40	99.7(6)	99.1	0.6
200	25	46.4(1)	46.4	0.0
200	25	88.5(16)	88.2	0.3

[a] Conditions: BZA, 1.8 mmol; **1**, 9×10^{-3} mmol; *n*-octane, 10 ml; H_2O, 35 ml.
[b] GC values based on pure samples. **12** = 4-phenyl-butan-2-one; **13** = 4-phenyl-but-3-en-2-ol.
[c] Repeated three times to check for reproducibility.

6 h at 120 °C, 200 psi H_2. These data confirm the high specificity of these catalytic systems for C=C double bond hydrogenation for activated substrates under the conditions stated.

3.4. Hydrogen transfer catalytic tests

The Ru(II) complexes were tested in transfer hydrogenation catalysis using HCO_2Na as reducing agent in water. The regioselectivity of the catalysts was checked using both BZA and CNA as substrates. In the former case, addition of MeOH was needed due to the insolubility of BZA in water. All Cp-based complexes tested for the reduction of BZA at moderate catalytic ratio (1:100) at 90 °C, gave moderate conversions (ca. 30%) after 6 h, showing good selectivity to the saturated ketone. Almost complete conversion and selectivity was observed using **2** under the same experimental conditions (Table 5).

The transfer hydrogenation of CNA to dihydrocinnamaldehyde (**15**), cinnamol (**16**) and 3-phenyl-1-propanol (**17**) was carried out at lower catalytic ratio (1:66) as described for a comparable study using *cis*-[$RuCl_2(PTA)_4$] [13a]. The results summarized in Table 6 confirm a remarkable difference in activity between Cp and Cp* complexes.

A strong influence of the degree of methyl substitution in the ancillary ligands on the regioselectivity of hydrogenation of α,β-unsaturated substrates was observed by Lopez-Linares et al. for the transfer hydrogenation of CNA using $[Ir(COD)Cl]_2$ stabilized by hydro(pyrazolyl)borate ligands [6a]. When hydrotris(pyrazolyl)borate (Tp) or dihydrobis(3,4,5-trimethylpyrazolyl)borate (Bp*) were

Table 5
Hydrogen transfer tests for the reduction of BZA using HCO_2Na/H_2O/MeOH[a]

Catalyst	% conversion[b]	% **12**[b]	% **13**[b]	% **14**[b]
1	36.1	33.9	2.19	0.0
2	97.4	96.9	0.0	0.5
8	29.0	28.5	0.4	0.1
11	34.9	34.3	0.4	0.2

[a] Conditions: BZA, 0.75 mmol; catalyst, 7.5×10^{-3} mmol; HCO_2Na, 7.5 mmol; MeOH, 3 ml; H_2O, 3 ml; 90 °C, 6 h.
[b] GC values based on pure samples. **12** = 4-phenyl-butan-2-one; **13** = 4-phenyl-but-3-en-2-ol; **14** = 4-phenyl-butan-2-ol.

Table 6
Hydrogen transfer tests for the reduction of CNA using HCO_2Na/H_2O[a]

Catalyst	% conversion (h)[b]	% **15**[b]	% **16**[b]	% **17**[b]
1	11.1(5)	9.5	0.8	0.8
2	76.7(1/4)	26.5	26.7	23.6
2	93.4(1)	20.0	24.5	48.9
2	99.4(5)	5.6	7.3	86.5
2[c]	86.3(1)	27.2	30.4	28.7
2[d]	47.1(1)	13.9	27.0	6.2
2[e]	8.2(1)	3.4	4.4	0.4
2[f]	45.4(1)	21.8	9.9	22.9
8	5.7(5)	5.7	0.0	0.0
9	5.8(5)	5.8	0.0	0.0
10	77.2(5)	26.5	16.9	33.8
11	11.5(5)	9.8	0.8	0.9

[a] Conditions: CNA, 2 mmol; catalyst, 3×10^{-2} mmol; HCO_2Na, 22 mmol; H_2O, 6 ml, 80 °C.
[b] GC values based on pure samples. **15** = dihydrocinnamaldehyde; **16** = cinnamol; **17** = 3-phenyl-1-propanol.
[c] 60 °C.
[d] 40 °C.
[e] 25 °C.
[f] CNA, 1.5 mmol; **2**, 7.5×10^{-3} mmol; HCO_2Na, 15 mmol; H_2O, 3 ml, 80 °C.

used, the selectivity shifted to dihydrocinnamaldehyde, whereas using hydrotris(3,5-dimethylpyrazolyl)borate (Tp*) or hydrotris(3,4,5-trimethylpyrazolyl) borate (Tp^{3Me}), the main product was observed to be cinnamol.

In our systems, the difference is rather in the activity of the catalysts, from moderate (Cp, complexes **1**, **7**, **9**, **11**) to excellent (Cp*, complexes **2**, **10**) under the same experimental conditions. Interestingly, high regioselectivity to C=C double bond hydrogenation using HCO_2Na/H_2O is usually featured by Rh–PTA complexes, such as $[Rh(PTAH)(PTA)_2Cl]Cl$, as reported by Darensbourg et al. [35]. At 80 °C in the presence of **2**, 76.7% CNA is converted into a ca. equimolar distribution to the three possible products after 15 min. After 1 h, 93% conversion is reached with over-hydrogenation to the fully saturated product (**17**) being observed (**15**:**16**:**17** = 1:1.2:2.4). Product **17** becomes dominant after 5 h (99.4% conversion, **15**:**16**:**17** = 1:1.3:15.4), as shown in Fig. 3.

The effect of the temperature was also tested. At 60 °C, an almost equimolar distribution is observed after 1 h, 86% conversion; at 40 °C a higher amount of cinnamol was obtained, namely **15**:**16**:**17** = 1:1.9:0.46, although conversion dropped to 47%. At 25 °C, only 8% CNA is converted, with a distribution of **15**:**16**:**17** = 1:1.3:0.12. These data suggest that at higher temperature the hydrogenation of cinnamol (**16**) is faster than for dihydrocinnamaldehyde (**15**), confirming the preference of our catalytic system to C=C bond reduction. Higher catalytic ratios (1:200) can also be used. At 80 °C, 45.4% CNA is converted in a ratio **15**:**16**:**17** = 1:0.45:1.05, suggesting that the larger effect on the selectivity is played by the temperature.

Although we cannot propose a comprehensive rationale for the different behaviour of these systems based only on catalytic data at this time, studies in progress on Ru–PTA hydride formation suggest that under hydrogen pressure, a stable

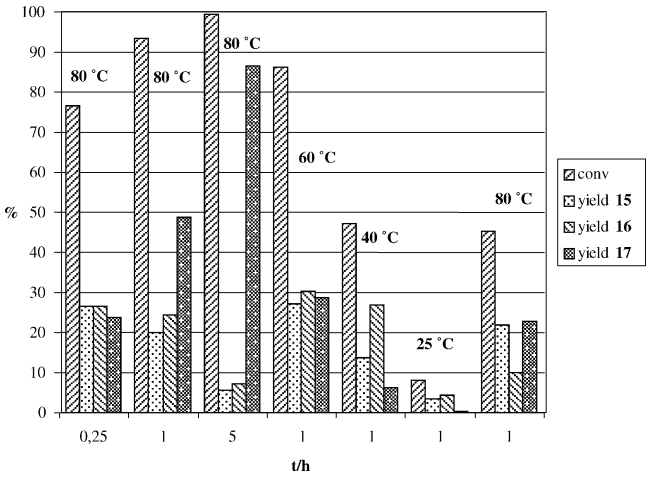


Fig. 3. Reduction of CNA using HCO_2Na/H_2O in the presence of **2** (1:66 except last bars, 1:200).

Ru(IV)–dihydride complex $[Cp^*Ru(H)_2(PTA)_2]X$ (X = Cl, PF_6) are formed, whereas $[CpRu(H)(PTA)_2]$ is obtained under the same conditions [18]. The data are supported by DFT calculations which will be published in due course [36]. The nature and stability of these intermediates may be crucial to the different catalytic activity of the corresponding precursors. Conversely, stable $[CpRu(H)(PTA)_2]$ is formed by reaction of **1** with HCO_2Na, whereas formation of highly reactive $[Cp^*Ru(H)(PTA)_2]Cl$ was observed by reaction of **2** with HCO_2Na under the same conditions [36].

4. Conclusions

In this study, new Ru(II) complexes containing the water soluble phosphine PTA and (modified) η^5-cyclopentadienyl rings were synthesized and tested as catalysts for regioselective hydrogenation of α,β-unsaturated compounds. Under an atmosphere of hydrogen and mild conditions, all complexes have shown almost complete selectivity towards C=C hydrogenation. The best activity (almost comparable) was shown by complexes $[CpRuCl(PTA)_2]$ (**1**), and $[CpRu(MeCN)_2(PTA)](PF_6)$ (**8**), while lower activity was shown by $[Cp^*RuCl(PTA)_2]$ (**2**). The opposite trend was observed under hydrogen transfer conditions, where Cp* complexes are generally much more active than the Cp analogues. The regioselectivity of CNA hydrogenation is influenced mainly by the temperature in our systems.

Acknowledgements

We acknowledge the contribution of EC through COST (WGD29/009-03) and MRTN-CT2003-503864 (AQUACHEM) for promoting this scientific activity. SB thanks also Xunta de Galicia (Spain) for a postdoctoral grant.

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