Inorganica Chimica Acta 362 (2009) 4486–4492

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis and characterization of Ru(arene) complexes of bispyrazolylazines: Catalytic hydrogen transfer of ketones ☆

M. Laura Soriano [a], Félix A. Jalón [a,*], Blanca R. Manzano [a], Miguel Maestro [b]

[a] Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Químicas-IRICA, UCLM, Avda. Camilo J. Cela 10, 13071 Ciudad Real, Spain
[b] Departamento de Química Fundamental, Universidade da Coruña, 15071 A Coruña, Spain

ARTICLE INFO

Article history:
Received 29 January 2009
Received in revised form 1 April 2009
Accepted 16 April 2009
Available online 23 April 2009

Dedicated to Prof. Jerry Trofimenko

Keywords:
Ruthenium
Pyrazole
Catalysis
Hydrogen transfer
N-donor ligands
Arene derivatives

ABSTRACT

The bis(pyrazol-1-yl)azine ligands 2,3-bis(pyrazol-1-yl)quinoxaline (bpzqnx), 2,3-bis(pyrazol-1-yl)pyrazine (bpzprz) and 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine (bpz*pdz) were prepared by the reaction of pyrazolate salts and the corresponding azine dichloride derivatives. The reaction of these ligands with Ru(arene) precursors led to the mononuclear complexes [RuCl(arene)(L)]BPh_4 (arene = *p*-cymene, L = bpzqnx, **1**, bpzprz, **5**, bpz*pdz, **7**; arene = C_6H_6, L = bpzqnx, **2**, bpzprz, **6**, bpz*pdz, **8**) with the N-donor ligand coordinated in a bidentate chelate way. In general, the ligands coordinate through one pyrazole ring and the azine, except in the cases of **1** and **2** where the two pyrazolyl rings are coordinated to the metal in a symmetrical way. When the reactions between the ruthenium precursors and bpzqnx are carried out in MeOH, the complexes [RuCl(arene)(OMepzqnx)]BPh_4 with partially methanolyzed ligands are isolated (arene = *p*-cymene, **3**; C_6H_6, **4**). In this process a methoxy group has replaced one of the pyrazole groups in the ligand. The X-ray structures of **6** and **7** have been determined. These compounds have a three-legged piano-stool structure with cations and anions packed through weak interactions. Complexes **1**–**8** are active in ketone hydrogenation transfer processes even in the absence of base.

1. Introduction

Ru(arene) derivatives constitute a family of interesting precursors in a variety of catalytic processes [1]. Noyori and other authors have designed very active systems with basic centres (N-donor mainly) in the asymmetric catalytic reduction of ketones using alcohols as the hydrogen source [2]. This situation has raised interest in the preparation of systems bearing N-donor centres that could participate in one or more steps of these hydrogenation processes [3]. However, the use of arene ruthenium derivatives with heterocyclic auxiliary ligands as polypyridines in catalytic hydrogenation processes has not been explored very much [4]. Our experience in the preparation of Ru(arene) complexes with N-donor ligands and their use in hydrogen transfer reactions [5] inspired the work described here, which focuses on the study of the effect that uncoordinated basic centres could have in hydrogen transfer catalytic processes. With this aim in mind, a family of bis(pyrazol-1-yl)azines, which are easily prepared, have been chosen. The preparation of mononuclear [RuCl(arene)(L)]BPh_4 derivatives was carried out and these compounds were used as precursors in hydrogen transfer reaction processes with and without a base as co-catalyst.

2. Experimental

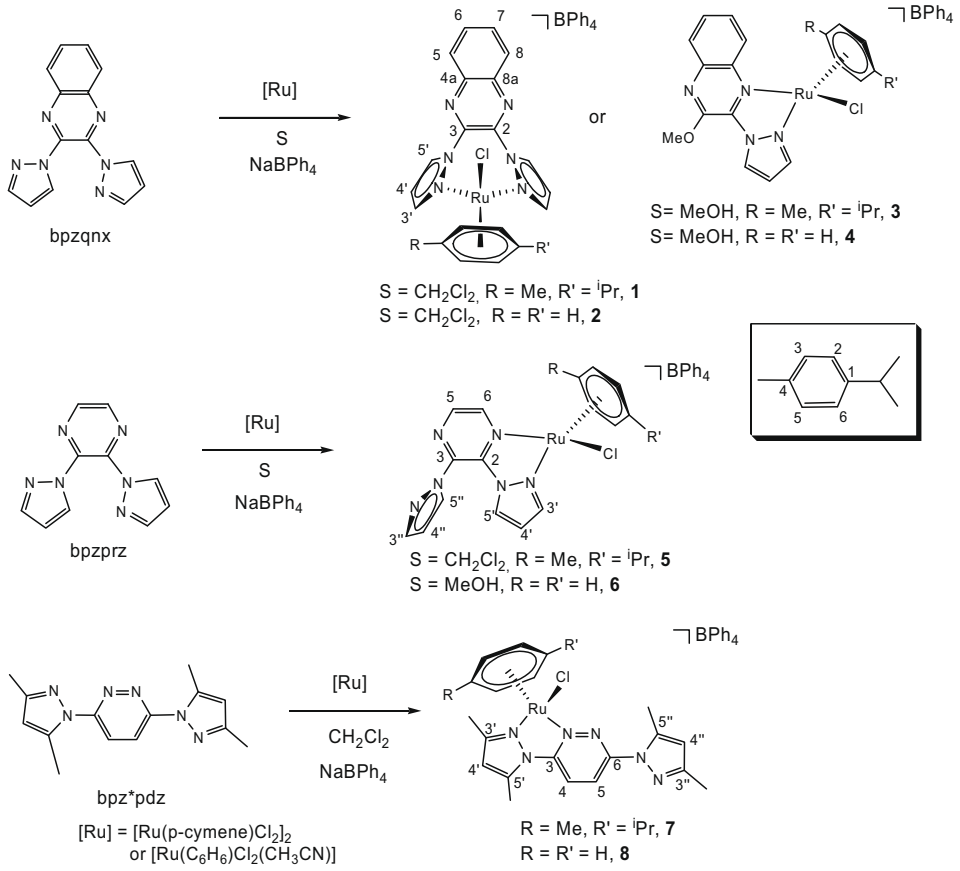
2.1. General procedures

All manipulations were carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Elemental analyses were performed with a Carlo Erba Instruments EA 1108 CHNS/O microanalyzer. IR spectra were recorded on a Shimadzu IRPRESTIGE-21 spectrophotometer deposing a pure solid sample over an ATR device (4000–700 cm^{-1} range). FAB+ mass spectra (position of the peaks in Da) were recorded with a VG Biotech Quattro Spectrometer. NMR spectra were recorded at room temperature (25 °C) on Varian Unity Inova-400 (400 MHz for ^1H; 100.6 MHz for ^{13}C) and Varian Inova FT-500 (500 MHz for ^1H; 125 MHz for ^{13}C) spectrometers. ^1H shifts (ppm) were recorded using the residual proton signal of the solvent as an internal standard (see numbering of protons and carbons in Scheme 1). For the acquisition of the COSY, *g*-HMBC and *g*-HMQC spectra the standard VARIAN pulse sequences were used (VNMR 6.1 C software). The following parameters were used for COSY: acquisition time 0.214 s, pulse width 10 μs, relaxation delay 1 s, 16 scans, 512 increments. For the *g*-HMBC and *g*-HMQC the spectra were acquired using 7996-Hz (^1H) and 25133.5-Hz (^{13}C) widths; 16 transients of 2048 data points were collected for each of the 128 increments. The nOe difference spectra were recorded with 5000 Hz, acquisition time 3.27 s, pulse width 90°, relaxation delay 4 s, and irradiation power 5–10 dB. All the $^{13}C\{^1H\}$ NMR resonances are singlets.

☆ In memoriam of our friend and master Jerry Trofimenko.

* Corresponding author. Tel.: +34 926295300; fax: +34 926295318.
E-mail address: Felix.Jalon@uclm.es (F.A. Jalón).

0020-1693/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2009.04.011



Scheme 1.

2.2. Solvents and reagents

Solvents were supplied by SDS (reagent grade) and distilled from the appropriate drying agents and degassed before use. Starting materials $[RuCl_2(p\text{-cymene})]_2$ [6] and $[RuCl_2(C_6H_6)]_2$ [7] were prepared according to literature procedures. $NaBPh_4$, acetophenone and benzophenone were purchased from Aldrich.

2.3. Structure solution and refinement

Suitable single crystals of the title compounds for X-ray study were grown from the vapour transfer of pentane over a methanol solution of **6** or the slow evaporation of a methanol solution of **7**. Crystal data and refinement are summarized in Table S1 for compound **6** and in Table S2 for compound **7**. A yellow prism ($0.33 \times 0.29 \times 0.08$ mm) of compound **6** and a yellow irregular block ($0.33 \times 0.23 \times 0.20$ mm) of compound **7** were selected and mounted on a Bruker SMART-CCD area diffractometer. Unit cell parameters were determined from 1271 frames of intensity data covering 0.3° in ω over a hemisphere of the reciprocal space by combination of three exposure sets, and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) using the $\omega/2\theta$ scan-technique. A total of 40 592 reflections for **6** were measured in the range $1.21 \leqslant \theta \leqslant 26.37$ and 26 018 reflections for **7** were measured in the range $1.68 \leqslant \theta \leqslant 26.37$. Lorentz-polarization and absorption corrections were made.

The structures were solved by direct methods using the SHELXS computer program [8] and refined by the full-matrix least-squares method with the SHELX97 computer program [8], using 6786 reflections for **6** and 8471 reflections for **7**. The function minimized was $\sum w||Fo|^2 - |Fc|^2|^2$, where $w = [\sigma^2(I) + (0.0355P)^2 + 9.1687P]^{-1}$ for **6** and $w = [\sigma^2(I) + (0.0327P)^2 + 5.8723P]^{-1}$ for **7**, and $P = (|Fo|^2 + 2|Fc|^2)/3$. The values of f, f' and f'' were taken from International Tables of X-ray Crystallography [9]. All hydrogen atoms were computed and refined using a riding model. For compound **6**, the final R (on F) factor was 0.0354, wR (on $|F|^2$) = 0.0969 and goodness of fit = 1.243 for all observed reflections. The number of refined parameters was 442. Max. shift/esd = 0.002, Mean shift/esd = 0.00. Max. and Min. peaks in final difference synthesis were 0.871 and -0.592 eÅ^{-3}, respectively. For compound **7**, the final R (on F) factor was 0.0343, wR (on $|F|^2$) = 0.079 and goodness of fit = 1.021 for all observed reflections. The number of refined parameters was 514. Max. shift/esd = 0.001, Mean shift/esd = 0.00. Max. and Min. peaks in final difference synthesis were 1.517 and -1.092 eÅ^{-3}, respectively.

2.4. Preparation of ligands and complexes

2.4.1. Synthesis of 2,3-bis(pyrazol-1-yl)quinoxaline (bpzqnx)

A solution of pyrazole (729.1 mg, 10.71 mmol) in 10 ml of THF was added dropwise to a suspension of NaH (257.2 mg, 10.71 mmol) in 10 ml of THF. After 2 h of reaction at room temperature the solution was filtered and 2,3-dichloroquinoxaline (0.710 g, 3.57 mmol) was added to the solution. The mixture was refluxed during 4 h and then the solvent was removed under vacuum. The product was extracted with CH_2Cl_2 (3×10 ml), then the solvent was evaporated and finally the solid was washed with 2 ml of ethylacetate to remove the excess of pyrazole. Yield: 0.655 g (70%). *Anal.* Calc. for $C_{14}H_{10}N_6$: C, 64.10; H, 3.84; N, 32.04. Found: C, 63.94; H, 3.83; N, 31.92%. IR (Nujol, cm^{-1}): 1554 (m), 1526 (m). ^{1}H NMR ($CDCl_3$) δ (ppm): 8.08 (m, 2H, $H^{5,8}$), 7.77 (m, 2H,

$H^{6,7}$), 6.52 (dd, 2H, $H^{4'}$), 7.63 (d, J = 1.5 Hz, 2H, $H^{3'}$), 7.97 (d, J = 3.4 Hz, 2H, $H^{5'}$). $^{13}C\{^1H\}$ NMR (CD_3Cl): 142.8 ($C^{3'}$), 140.6 ($C^{2,3}$), 140.1 ($C^{4a,8a}$), 131.2 ($C^{6,7}$), 130.4 ($C^{5'}$), 128.8 ($C^{5,8}$), 108.3 ($C^{4'}$).

2.4.2. Synthesis of 2,3-bis(pyrazol-1-yl)pyrazine (bpzprz)

The synthesis of bpzprz is similar to that of bpzqnx. The amounts were as follows: pyrazole (959.6 mg, 14.10 mmol), NaH (338.2 mg, 14.10 mmol) and 2,3-dichloropyrazine (631.9 g, 4.24 mmol). The mixture was refluxed during 24 h and then the solvent was removed under vacuum. The product was extracted with toluene (3 × 10 ml), then the solvent was removed and finally the solid was washed (3 × 2 ml) with ethylacetate to remove the pyrazole in excess. Yield: 0.540 g (60%). *Anal.* Calc. for $C_{14}H_{10}N_6$: C, 56.60; H, 3.80; N, 39.60. Found: C, 56.47; H, 3.72; N, 39.10%. IR (Nujol, cm^{-1}): 1584 (m), 1526 (m). ^1H NMR (acetone-d_6) δ (ppm): 8.64 (s, 2H, $H^{5,6}$), 8.14 (dd, J = 2.2 Hz, 2H, $H^{5'}$), 7.55 (d, J = 1.8 Hz, 2H, $H^{3'}$), 6.47 (dd, 2H, $H^{4'}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 142.8 ($C^{3'}$), 141.5 ($C^{5,6}$), 130.3 ($C^{5'}$), 108.4 ($C^{4'}$).

*2.4.3. Synthesis of [RuCl(p-cymene)(bpzqnx)](BPh$_4$) (**1**)*

To a suspension of $[RuCl_2(p\text{-cymene})]_2$ (68.8 mg, 0.11 mmol) in 20 ml of dry dichloromethane, bpzqnx (59.0 mg, 0.22 mmol) was added. The mixture was stirred at room temperature during 12 h and then $NaBPh_4$ (77.2 mg, 0.22 mmol) was added. After an hour of stirring the solvent was evaporated and the product was purified by extraction in dichloromethane (3 × 5 ml). The resulting product is soluble in acetone, dichloromethane and THF and insoluble in diethylether and alkanes. Yield: 159.3 mg (85%). This product can be recrystallised in dichloromethane/hexane. *Anal.* Calc. for $C_{48}H_{44}BClN_6Ru$: C, 69.69; H, 4.50; N, 9.38. Found: C, 69.99; H, 4.34; N, 9.21%. IR (ATR, cm^{-1}): 3047 (s), 2984 (s), 1576 (m), 1555 (m), 1520 (m), 1493 (s), 1031 (s). FAB$^+$ MS (NBA): m/z (%) = 533 (100) [M^+–(BPh_4)]. ^1H NMR ($CDCl_3$) δ (ppm): 8.19 (m, J = 2.9 Hz, 2H, $H^{6,7}$), 8.02 (d, J = 2.4 Hz, 2H, $H^{3'}$), 7.95 (m, J = 2.9, 2H, $H^{5,8}$), 7.90 (d, J = 2.9, 2H, $H^{5'}$), 6.52 (dd, 2H, $H^{4'}$), 4.98 (d, J = 5.9 Hz, 2H, $H^{2,6}_{cym}$), 4.31 (d, J = 6.4 Hz, 2H, $H^{3,5}_{cym}$), 2.24 (m, J = 6.4 Hz, 1H, C*H*Me$_2$ $_{cym}$), 1.26 (s, 3H, *Me*$_{cym}$), 1.14 (d, J = 7.3 Hz, 6H, CH*Me*$_2$ $_{cym}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 148.2 (2C, $C^{3'}$), 140.9 ($C^{4a,8a}$), 139 ($C^{2,3}$), 138.6 (2C, $C^{5'}$), 134 ($C^{5,8}$), 129.6 ($C^{6,7}$), 111.0 (2C, $C^{4'}$), 104.2 (C^1_{cym}), 102.0 (C^4_{cym}), 86.9 ($C^{2,6}_{cym}$), 82.4 ($C^{3,5}_{cym}$), 30.9 (*C*HMe$_2$ $_{cym}$), 22.4 (CH*Me*$_2$ $_{cym}$), 18.3 (Me$_{cym}$).

*2.4.4. Synthesis of [RuCl(benzene)(bpzqnx)](BPh$_4$) (**2**)*

The synthesis of **2** is similar to that of **1**. The amounts were as follows: bpzqnx (67.7 mg, 0.26 mmol), [RuCl(C_6H_6)(MeCN)] (75.1 mg, 0.26 mmol) and $NaBPh_4$ (88.3 mg, 0.26 mmol). The resulting product is a yellow solid and is purified by recrystallization in acetone/hexane. **2** is soluble in acetone and chloroform and insoluble in diethylether and alkanes. Yield: 169.7 mg (82%). *Anal.* Calc. for $C_{44}H_{36}BClN_6Ru$: C, 66.38; H, 4.56; N, 10.56. Found: C, 66.39; H, 4.42; N, 10.75%. IR (ATR, cm^{-1}): 3053 (s), 1567 (m), 1545 (m), 1529 (m), 1490 (s), 1030 (s). FAB$^+$ MS (NBA): m/z (%) = 477 (100) [M^+–(BPh_4)]. ^1H NMR ($CDCl_3$) δ (ppm): 8.63 (d, J = 2.6, 2H, $H^{5'}$), 8.39 (m, J = 3.3 Hz, 2H, $H^{6,7}$), 8.29 (d, J = 2.2, 2H, $H^{3'}$), 8.23 (m, J = 3.3 Hz, 2H, $H^{5,8}$), 6.33 (dd, 2H, $H^{4'}$), 5.77 (s, 6H, benzene). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 147.2 (2C, $C^{3'}$), 140.1 ($C^{4a,8a}$), 138.3 ($C^{2,3}$), 137.5 (2C, $C^{5'}$), 133.2 ($C^{5,8}$), 130.6 ($C^{6,7}$), 110.5 (2C, $C^{4'}$), 87.0 (C_6H_6).

*2.4.5. Synthesis of [RuCl(p-cymene)(OMepzqnx)](BPh$_4$) (**3**)*

The synthesis of **3** is similar to that of **1** but was carried out in MeOH as solvent. The amounts were as follows: $[RuCl_2(p\text{-cymene})]_2$ (37.7 mg, 0.06 mmol) in 15 ml of methanol, bpzqnx (32.3 mg, 0.12 mmol) and $NaBPh_4$ (42.1 mg, 0.12 mmol). The resulting product is a yellow-brownish solid and it was purified by recrystallization in acetone/hexane. **3** is soluble in acetone and THF, partially soluble in chloroform and insoluble in diethylether and alkanes. Yield: 78.4 mg (80%). *Anal.* Calc. for $C_{46}H_{44}BClN_4ORu$: C, 67.69; H, 5.43; N, 6.86. Found: C, 67.59; H, 5.35; N, 6.81%. IR (ATR, cm^{-1}): 3065 (s), 3002 (s), 1578 (m), 1526 (m), 1478 (s), 1044 (s). FAB$^+$ MS (NBA): m/z (%) = 497 (100) [M^+–(BPh_4)]. ^1H NMR ($CDCl_3$) δ (ppm): 8.82 (d, J = 3.4, 1H, $H^{5'}$), 8.33 (d, J = 8.6 Hz, 1H, H^5), 8.05 (d, J = 8.3 Hz, 1H, H^8), 7.90, 7.81 (2d, $J \approx$ 7.3 Hz, 2H, $H^{6,7}$), 7.65 (d, J = 2.0, 1H, $H^{3'}$), 6.62 (t, 1H, $H^{4'}$), 5.30 (d, J = 6.4 Hz, 1H, H^2_{cym}), 5.24 (d, J = 5.9 Hz, 1H, H^6_{cym}), 5.16 (d, J = 6.4 Hz, 1H, H^5_{cym}), 5.02 (d, J = 6.3 Hz, 1H, H^3_{cym}), 4.36 (s, 3H, MeO), 2.31 (m, J = 6.8 Hz, 1H, C*H*Me$_2$), 1.84 (s, 3H, Me$_{cym}$), 0.96, 0.90 (2d, J = 6.8 Hz, 6H, CH*Me*$_2$ $_{cym}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 150.4 ($C^{3'}$), 138.9 ($C^{5'}$), 132.2 (C^8), 130.4 (C^5), 128.5, 128.3 ($C^{6,7}$), 113.8 ($C^{4'}$), 87.7 (C^6_{cym}), 85.3 (C^3_{cym}), 84.2 ($C^{2,5}_{cym}$), 56.6 (O*Me*), 34.4 (*C*HMe$_2$ $_{cym}$), 22.7, 21.8 (2C, CH*Me*$_2$ $_{cym}$), 18.8 (Me $_{cym}$).

*2.4.6. Synthesis of [RuCl(benzene)(OMepzqnx)](BPh$_4$)·(MeOH)$_2$ (**4**)*

The synthesis of **4** is similar to that of **1** but it was carried out in MeOH as solvent. The amounts were as follows: bpzqnx (77.7 mg, 0.30 mmol) in 20 ml of methanol, [RuCl(C_6H_6)(MeCN)] (86.2 mg, 0.30 mmol) and $NaBPh_4$ (101.3 mg, 0.30 mmol). The resulting product is a yellow-brownish solid and it is purified by recrystallization in acetone/pentane. **4** is soluble in acetone and methanol, partially soluble in chloroform and insoluble in diethylether and alkanes. Yield: 187.9 mg (76%). *Anal.* Calc. for $C_{44}H_{44}BClN_4O_3Ru$: C, 64.12; H, 5.38; N, 6.80. Found: C, 64.19; H, 5.15; N, 6.85%. IR (ATR, cm^{-1}): 3003 (s), 1577 (m), 1525 (m), 1479 (s), 1043 (s). FAB$^+$ MS (NBA): m/z (%) = 441 (100) [M^+–(BPh_4)]. ^1H NMR ($CDCl_3$) δ (ppm): 8.80 (d, J = 2.9, 1H, $H^{5'}$), 8.24 (d, J = 8.6 Hz, 1H, H^5), 8.08 (d, J = 8.3 Hz, 1H, H^8), 7.90, 7.80 (2d, J = 7.1, 7.8 Hz, 2H, $H^{6,7}$), 7.71 (d, J = 2.0, 1H, $H^{3'}$), 6.65 (t, 1H, $H^{4'}$), 5.17 (s, 6H, C_6H_6), 4.35 (s, 3H, MeO). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 150.0 ($C^{3'}$), 138.1 ($C^{5'}$), 128.7, 128.0 ($C^{5,8}$), 132.3, 130.5 ($C^{6,7}$), 113.6 ($C^{4'}$), 86.9 (C_6H_6), 50.3 (O*Me*).

*2.4.7. Synthesis of [RuCl(p-cymene)(bpzprz)](BPh$_4$) (**5**)*

The synthesis of **5** is similar to that of **1**. The amounts were as follows: 2,3-bis(pyrazol-1-yl)pyrazine (32.4 mg, 0.15 mmol), $[RuCl_2(p\text{-cymene})]_2$ (46.8 mg, 0.08 mmol) and $NaBPh_4$ (52.4 mg, 0.15 mmol) in 15 ml of dichloromethane. The yellow product is purified by recrystallization in a mixture of dichloromethane/pentane. **5** is soluble in acetone, dichloromethane and chloroform and insoluble in diethylether and alkanes. Yield: 90.3 mg (75%). *Anal.* Calc. for $C_{44}H_{42}BClN_6Ru$: C, 65.88; H, 5.28; N, 10.48. Found: C, 65.83; H, 5.35; N, 10.56%. IR (ATR, cm^{-1}): 3036 (s), 2965 (s), 1580 (m), 1535 (m), 1520 (m), 1472 (s), 1030 (s). FAB$^+$ MS (NBA): m/z (%) = 483 (100) [M^+–(BPh_4)]. ^1H NMR (acetone-d_6) δ (ppm): 9.47 (d, 1H, H^6), 8.78 (dd, J = 2.2, 0.5 Hz, 1H, $H^{3'}$), 8.72 (d, J = 2.9 Hz, 1H, H^5), 8.39 (dd, J = 2.7, 1.7 Hz, 1H, $H^{5''}$), 7.96 (dd, J = 2.2, 1.7 Hz, 1H, $H^{3''}$), 7.17 (dd, J = 2.9, 0.5 Hz, 1H, $H^{5'}$), 6.84 (dd, 1H, $H^{4'}$), 6.75 (dd, 1H, $H^{4''}$), 6.27, 6.17 (d, J = 6.1 Hz, 2H, $H^{2,6}_{cym}$), 6.04, 5.95 (d, J = 6.1 Hz, 2H, $H^{3,5}_{cym}$), 2.86 (m, J = 6.8 Hz, 1H, C*H*Me$_2$ $_{cym}$), 2.25 (s, 3H, Me$_{cym}$), 1.22, 1.17 (2d, J = 6.8 Hz, 6H, CH*Me*$_2$ $_{cym}$). $^{13}C\{^1H\}$ NMR (acetone-d_6): 149.0 ($C^{3'}$), 147.5 (C^6), 144.0 ($C^{3''}$), 142.0 (C^5), 140.0 (C^2), 138.2 (C^3), 135.0 ($C^{5'}$), 132.6 ($C^{5''}$), 112.4 ($C^{4'}$), 110.0 ($C^{4''}$), 107.1 (C^1_{cym}), 103.9 (C^4_{cym}), 86.3, 85.5 ($C^{2,6}_{cym}$), 85.2, 84.6 ($C^{3,5}_{cym}$), 31.2 (*C*HMe$_2$ $_{cym}$), 21.7, 21.6 (2C, CH*Me*$_2$ $_{cym}$), 18.1 (Me$_{cym}$).

*2.4.8. Synthesis of [RuCl(benzene)(bpzprz)](BPh$_4$)·(MeOH)$_2$ (**6**)*

The synthesis of **6** is similar to that of **1** but it was carried out in MeOH as solvent. The amounts were as follows: 2,3-bis(pyrazol-1-yl)pyrazine (60.9 mg, 0.3 mmol), [RuCl(C_6H_6)(MeCN)] (83.6 mg, 0.3 mmol), $NaBPh_4$ (98.2 mg, 0.3 mmol) in 10 ml of methanol. The yellow product is soluble in acetone and methanol, partially soluble in dichloromethane and insoluble in diethylether and

alkanes. Yield: 175.0 mg (72%). Single crystals were obtained by recrystallization of the product in a mixture of MeOH/pentane. *Anal.* Calc. for $C_{42}H_{42}BClN_6O_2Ru$: C, 62.27; H, 5.23; N, 10.37. Found: C, 62.26; H, 5.38; N, 10.83%. IR (ATR, cm^{-1}): 3053 (s), 1593 (m), 1575 (m), 1526 (s), 1474 (s), 1034 (s). FAB^+ MS (NBA): *m*/*z* (%) = 427 (100) [M^+–(BPh_4)]. ^1H NMR (acetone-d_6) δ (ppm): 9.60 (d, 1H, H^6), 8.84 (dd, *J* = 2.2, 0.5 Hz, 1H, $H^{3'}$), 8.75 (d, *J* = 3.2 Hz, 1H, H^5), 8.42 (dd, *J* = 2.7, 1.7 Hz, 1H, $H^{5''}$), 7.98 (t, *J* = 1.7 Hz, 1H, $H^{3''}$), 7.14 (dd, *J* = 3.2, 0.5 Hz, 1H, $H^{5'}$), 6.85 (dd, 1H, $H^{4'}$), 6.79 (dd, 1H, $H^{4''}$), 6.29 (s, 6H, C_6H_6). $^{13}C\{^1H\}$ NMR (acetone-d_6): 149.2 ($C^{3'}$), 148.0 (C^6), 144.0 ($C^{3''}$), 141.8 (C^5), 140.1 (C_2), 138.2 (C_3), 134.9 ($C^{5'}$), 132.8 ($C^{5''}$), 112.4 ($C^{4'}$), 109.9 ($C^{4''}$), 87.6 (C_6H_6).

2.4.9. Synthesis of [RuCl(p-cymene)(bpz*pdz)](BPh4)·(CH2Cl2) (7)

The synthesis of **7** is similar to that of **1**. The amounts were as follows: 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine (44.5 mg, 0.17 mmol) in 30 ml of dichloromethane, $[RuCl_2(p\text{-cymene})]_2$ (50.8 mg, 0.08 mmol) and $NaBPh_4$ (56.8 mg, 0.17 mmol). The product was isolated as a solvate with one molecule of CH_2Cl_2. The yellow product is soluble in acetone, dichloromethane and methanol and insoluble in diethylether and alkanes. Yield: 136.2 mg (85%). Single crystals were obtained by slow evaporation of a methanol solution of the product. *Anal.* Calc. for $C_{49}H_{52}BCl_3N_6Ru$: C, 62.40; H, 5.56; N, 8.91. Found: C, 62.60; H, 5.49; N, 9.09%. IR (ATR, cm^{-1}): 3053 (s), 3034 (s), 2968 (s), 1591 (m), 1578 (m), 1549 (m), 1479 (s), 1028 (s). FAB^+ MS (NBA): *m*/*z* (%) = 539 (100) [M^+-(BPh_4)]. ^1H NMR ($CDCl_3$) δ (ppm): 8.02 (d, 1H, H^5), 7.12 (d, *J* = 9.4 Hz, 1H, H^4), 6.12 (s, 1H, $H^{4''}$), 6.10 (s, 1H, $H^{4'}$), 5.52, 5.50 (2d, *J* = 6.2 Hz, 2H, $H^{3,5}_{cym}$), 5.33, 5.29 (2d, *J* = 6.1 Hz, 2H, $H^{2,6}_{cym}$), 2.68 (s, 1H, $Me^{5''}$), 2.46 (s, 1H, $Me^{3'}$), 2.55 (m, 1H, $CHMe_{2\ cym}$), 2.28 (s, 1H, $Me^{3''}$), 2.15 (s, 3H, Me_{cym}), 2.02 (s, 1H, $Me^{5'}$), 1.04, 1.03 (2d, *J* = 6.8 Hz, 6H, $CHMe_{2\ cym}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 157.4 ($C^{3'}$), 154.8 (C^5), 153.6 ($C^{3''}$), 149.5 (C^4), 145.7 ($C^{5'}$), 141.8 ($C^{5''}$), 120.1 (C^6), 114.6 ($C^{4'}$), 112.3 ($C^{4''}$), 107.3 (C^1_{cym}), 104.0 (C^4_{cym}), 86.9, 84.6 ($C^{2,6}_{cym}$), 84.3 ($C^{3,5}_{cym}$), 31.5 ($CHMe_{2\ cym}$), 22.7, 22.6 (2C, $CHMe_{2\ cym}$), 16.4 ($Me_{3'}$), 15.5 ($Me_{5''}$), 14.6 ($Me_{5'}$), 14.1 ($Me_{3''}$), 19.3 ($Me_{\ cym}$).

2.4.10. Synthesis of [RuCl(benzene)(bpz*pdz)](BPh4)·(CH2Cl2)2 (8)

The synthesis of **8** is similar to that of **1**. The amounts were as follows: 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine (52.7 mg, 0.2 mmol) in 20 ml of dichloromethane, $[RuCl(C_6H_6)(MeCN)]$ (57.2 mg, 0.2 mmol), $NaBPh_4$ (67.22 mg, 0.2 mmol). The product was isolated as a solvate with two molecules of CH_2Cl_2. The yellow product is soluble in acetone and methanol, partially soluble in dichloromethane and insoluble in diethylether and alkanes. Yield: 172.7 mg (89%). *Anal.* Calc. for $C_{46}H_{46}BCl_5N_6Ru$: C, 56.94; H, 4.77; N, 8.65. Found: C, 56.82; H, 4.73; N, 8.63%. IR (ATR, cm^{-1}): 3059 (s), 2980 (s), 1576 (m), 1553 (m), 1479 (s), 1030 (s). FAB^+ MS (NBA): *m*/*z* (%) = 483 (100) [M^+–(BPh_4)]. ^1H NMR ($CDCl_3$) δ (ppm): 8.08 (d, *J* = 9.8 Hz, 1H, H^5), 7.14 (d, *J* = 9.8 Hz, 1H, H^4), 6.13 (s, 1H, $H^{4''}$), 6.11 (s, 1H, $H^{4'}$), 5.29 (s, 6H, C_6H_6), 2.66 (s, 1H, $Me^{5''}$), 2.39 (s, 1H, $Me^{3'}$), 2.28 (s, 1H, $Me^{3''}$), 2.16 (s, 1H, $Me^{5'}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 157.4 ($C^{3'}$), 154.7 (C^5), 153.6 ($C^{3''}$), 149.3 (C^4), 145.1 ($C^{5'}$), 142.0 ($C^{5''}$), 120.0 (C^6), 114.6 ($C^{4'}$), 112.5 ($C^{4''}$), 86.9 (C_6H_6), 16.2 ($Me^{3'}$), 15.5 ($Me^{5''}$), 14.7 ($Me^{5'}$), 14.0 ($Me^{3''}$).

2.5. Catalysis experiments

Hydrogen transfer experiments for the hydrogenation of acetophenone or benzophenone were carried out using 2-propanol as the solvent and hydrogen source at the temperature of the refluxing solvent (82 °C). Each run was repeated three times to assure the reproducibility.

The general procedure was as follows: A solution of the ketone (1 mmol), KOH (0.2 ml of a 0.2 M solution in 2-propanol) and the corresponding catalyst (0.002 mmol) was heated under reflux in 10 ml of 2-propanol for 24 h. 2-Propanol was removed under vacuum and an aliquot of the remaining product was analysed by ^1H NMR in $CDCl_3$. The yield of the process was calculated considering the relative integrals of ketone and alcohol.

3. Results and discussion

3.1. Synthesis of ligands and complexes

The bis(pyrazol-1-yl)azine ligands used in this work (see Scheme 1) were prepared from the corresponding sodium pyrazolate (obtained in THF after the reaction of NaH with pyrazole or 3,5-dimethylpyrazole), which was reacted with the respective dichloroazine.

The ligands 2,3-bis(pyrazol-1-yl)quinoxaline, bpzqnx, and 2,3-bis(pyrazol-1-yl)pyrazine, bpzprz, were prepared in this study for the first time. The derivative 3,6-bis(3,5dimethylpyrazol-1-yl)pyridazine, bpz*pdz, has been described previously and prepared by different methods [10]. We used a method similar to that described by Thompson et al. [10c]. This compound has been used as a ligand with Cu(I) [11], Rh(I) [12], Cu(II) and Co(II) [10c,13]. The similar ligand 3,6-bis(pyrazol-1-yl)pyridazine was also previously prepared by a similar method [14] and used as a ligand in Cu coordination chemistry [13b,15].

All of these ligands can be considered as ditopic and suitable for a bisbidentate chelate coordination mode with potential coordination of the N-pyrazole and N-azine atoms. The ligands differ in the position of the pyrazole ring in the azine, with this ring being 1,2 in bpzqnx and bpzprz and 1,4 in bpz*pdz.

The cationic complexes **1**, **2**, **5**, **7** and **8** were easily prepared by the reaction of the respective ligands and $[Ru(p\text{-cymene})Cl_2]_2$ or $[Ru(C_6H_6)Cl_2(CH_3CN)]$ in CH_2Cl_2 in the presence of $NaBPh_4$ (Scheme 1). When the reactions of the Ru precursors with bpzqnx were carried out in MeOH as the solvent, complexes **3** and **4** were obtained as a consequence of the partial alcoholysis of the ligand bpzqnx. This reactivity can be attributed to the electrophilic character of the heterocyclic ring of the quinoxaline. The concomitant presence of alkoxy and heterocyclic groups as substituents in quinoxaline derivatives is uncommon [16], although (3-heterocycle)(4-alkoxy)quinoxaline systems have been described as herbicides [17] and other active pharmaceuticals drugs [18]. A different type of behaviour was observed for the ligand bpzprz because in this case, although the reaction with $[Ru(C_6H_6)Cl_2(CH_3CN)]$ was performed in MeOH, complex **6** was obtained and the alcoholysis of the ligand was not observed. All of these complexes were isolated in good yields, sometimes as solvate species, and the microanalysis data support their purity.

3.2. Structural characterization

The new complexes were analysed by IR, ^1H and $^{13}C\{^1H\}$ NMR, mass spectrometry and, for compounds **6** and **7**, by X-ray diffraction.

The C=C and C=N stretching vibrations of the heterocycles appear in the 1500–1600 cm^{-1} region. In general, these bands are shifted to higher frequencies with respect to those in the free ligands as a result of the coordination, and sometimes a higher number of signals are observed. The ν(CH) and δ(CH) vibrations are also observed for the heterocycles and the BPh_4^- counteranion (see Section 2 for details).

The ^1H and $^{13}C\{^1H\}$-NMR resonances were assigned on the basis of literature information and taking into account the information from ^1H–^1H-COSY and heteronuclear *g*-HMBC and *g*-HMQC spectra. As one example, the corresponding spectra for complex **8** can be found in the Supplementary material (Figs. S2–S5). The ^1H

and $^{13}C\{^1H\}$ NMR spectra are indicative of the symmetry of the complexes. For example, the spectra of **1** and **2** show the resonances for only one type of pyrazole ring whereas two distinct pyrazoles are observed for the rest of the complexes due to the existence of one uncoordinated ring. In general, this uncoordinated pyrazole exhibits resonances with chemical shifts comparable to those of the free ligands, while a shift is usually observed in the signals of the coordinated pyrazole and azine heterocycles as a consequence of the coordination to the metal. The resonances of the *p*-cymene ring also reflect the symmetry of the complex. In complex **1**, two resonances are observed for the aromatic CH groups, whereas the rest of the complexes (**3**, **5** and **7**) present four resonances. The ^{i}Pr methyl groups also reflect this asymmetry and appear as two doublets in the asymmetric complexes and one doublet in **1**. In complexes **1** and **5**, the nOe effect observed between the $H^{3'}$ pyrazole resonances and the methyl resonances of the ^{i}Pr group was conclusive for the differentiation of the $H^{3'}$ and $H^{5'}$ protons. For **5** an nOe is also observed between the methyl (^{i}Pr) resonances and H^6 of the pyridazine. The observed differences in the coupling constants of the pyrazole protons ($J_{4'5'} > J_{4'3'}$) were also used to differentiate the $H^{3'}$ and $H^{5'}$ resonances [19]. NOe studies also proved important in the assignment of the *p*-cymene resonances. The benzene ring gives rise to a singlet in the 5–6 ppm region and the MeO group appears around 4.30 ppm.

Mass spectra (FAB^+) were obtained for all of the complexes and in all cases the peak corresponding to the cation complex was observed ($M–BPh_4$).

3.3. X-ray diffraction

The molecular structures of complexes **6** and **7** were determined by X-ray diffraction. In the analysed samples solvate molecules were not found. The corresponding ORTEP diagrams are shown in Fig. 1. A selection of bond distances and angles is compiled in Table 1 and the crystallographic information is included in the Supplementary material.

Both compounds crystallize in the monoclinic system with *P*2(1)/c space groups. The two complexes have a three-legged piano-stool structure with centroid(*p*-cymene)–Ru–Cl and centroid(*p*-cymene)–Ru–N angles not far from 130°. The N-donor ligands are coordinated in a bidentate chelate manner through one nitrogen atom of a pyrazole and other of the azine. As expected, one of the pyrazoles is not coordinated to the Ru centre. In **7** the dihedral angle between the coordinated heterocycles is quite small (9.52°) and that of the pyridazine and the uncoordinated pyrazole rings is even lower (8.94°), indicating an approximate coplanar disposition of the heterocycles, which facilitates the electronic delocalization. The uncoordinated pyrazole is oriented in such a way that the expected repulsion between the lone electron pairs of the nitrogen atoms (pyrazole and azine) is avoided. This coplanarity is not observed in **6**. In this complex the two coordinated rings are nearly coplanar (as in **7**) with a dihedral angle of 1.39°, but the value for this angle is 62.94° for the uncoordinated pyrazole and the pyrazine rings. The out-of-plane orientation of the uncoordinated pyrazole is very probably due to the steric repulsion between the two pyrazoles in a contiguous position of the azine. The Ru–C, Ru–N and Ru–Cl distances in both derivatives are similar to those in comparable complexes [20]. The Ru–N bond distances follow the expected order considering the pK_a values of the heterocycles: $Ru–N_{pyrazine} > Ru–N_{pyridazine} > Ru–N_{pyrazole}$. Unexpectedly, the $Ru–N_{pz^*}$ (pz^* = 3,5-dimethylpyrazole) distance is longer than that of the $Ru–N_{pyrazole}$, probably due to steric repulsion between $Me^{3'}$ and the ^{i}Pr group of the *p*-cymene ligand.

Cations and counteranions are packed in the crystal through weak interactions between one another. On the one hand, there are CH–π interactions between CH bonds of the *p*-cymene, Me

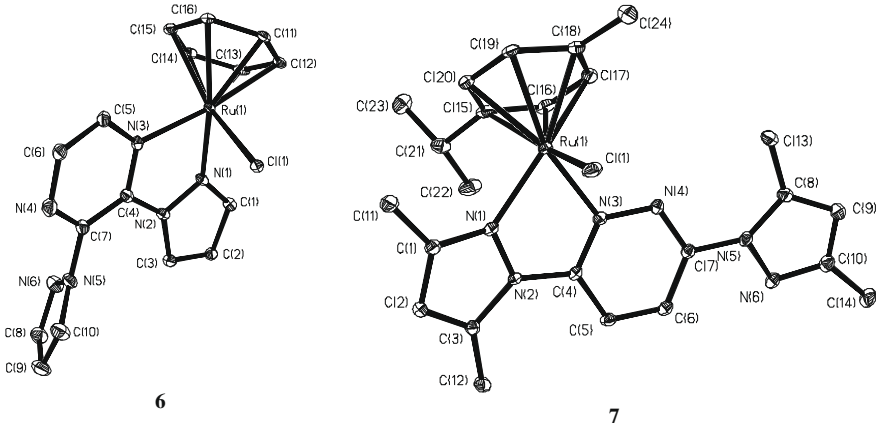


Fig. 1. ORTEP representation (ellipsoids at a 30% level) and labelling for the cations of complexes **6** and **7**. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for complexes **6** and **7**.

6				**7**			
Bond lengths (Å)		Angles (°)		Bond lengths (Å)		Angles (°)	
Ru(1)–N(1)	2.029(3)	N(1)–Ru(1)–N(3)	74.27(10)	Ru(1)–N(3)	2.0652(19)	N(3)–Ru(1)–N(1)	77.63(7)
Ru(1)–N(3)	2.091(3)	N(1)–Ru(1)–Cl(1)	81.48(8)	Ru(1)–N(1)	2.0796(19)	N(3)–Ru(1)–Cl(1)	86.66(6)
Ru(1)–C(13)	2.175(3)	N(3)–Ru(1)–Cl(1)	82.34(7)	Ru(1)–C(16)	2.164(3)	N(1)–Ru(1)–Cl(1)	85.95(6)
Ru(1)–C(11)	2.186(3)	cym_{cent}–Ru(1)–Cl(1)	130.26	Ru(1)–C(15)	2.192(2)	cym_{cent}–Ru(1)–Cl(1)	128.20
Ru(1)–C(12)	2.203(3)	cym_{cent}–Ru(1)–N(3)	131.64	Ru(1)–C(17)	2.192(2)	cym_{cent}–Ru(1)–N(3)	130.16
Ru(1)–C(16)	2.206(3)	cym_{cent}–Ru(1)–N(1)	133.57	Ru(1)–C(19)	2.205(2)	cym_{cent}–Ru(1)–N(1)	132.22
Ru(1)–C(15)	2.237(3)	N(1)–N(2)–C(4)–N(3)	1.39	Ru(1)–C(20)	2.210(2)	N(1)–N(2)–C(4)–N(3)	9.52
Ru(1)–C(14)	2.236(3)	N(6)–N(5)–C(7)–N(4)	62.94	Ru(1)–C(18)	2.226(2)	N(6)–N(5)–C(7)–N(4)	8.94
Ru(1)–Cl(1)	2.4579(7)			Ru(1)–Cl(1)	2.4028(7)		
Ru(1)–Cym_{cent}	1.461			Ru(1)–cym_{Cent}	1.440		

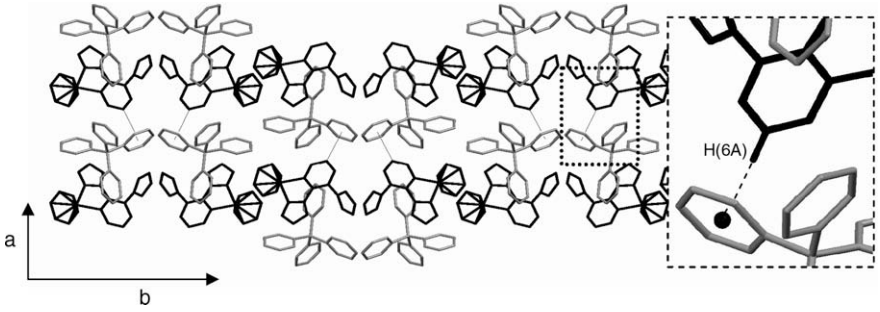


Fig. 2. Partial view of the crystal network of complex **6** down the *c*-axis, showing the alternate rows of cations (black) and anions (grey) and the penetration of one of the Ph groups of the BPh_4 into the alignment of the cations. Narrow lines represent the CH–π interactions. Inset shows the CH–π interaction of H(6A) and one of the Ph rings of the anion.

(pz) or phenyl (BPh_4) groups and the neighbouring aromatic rings [21]. An illustrative example of such contacts is the interaction in complex **6** between H(6A) and one of the Ph rings of the counteranion, with a CH–centroid distance of 2.286 Å and a very similar CH–plane distance of 2.262 Å. The CH–centroid angle is 160.11° (See Fig. 2). Weak hydrogen bonds also exist between the chloride atoms of the cations and Me(pz) groups in **7** and H(pz) and H(C_6H_6) atoms in **6**.

In the crystal network of **6** the formation of rows of cationic molecules along the *b* axis is observed. The counteranions, which are intercalated between these rows, penetrate the cationic alignments through one of the Ph groups (Fig. 2). Similar rows of cations are formed in complex **7** along the *a* axis (see Fig. S1 in the Supplementary Information) with the intercalation of the BPh_4 anions.

3.4. Catalytic behaviour of complexes ***1–8***

Hydrogen transfer reactions of acetophenone and benzophenone, using 2-propanol as the hydrogen source, were carried out. The reaction products were analysed by ^{1}H NMR spectroscopy. The experimental conditions are indicated in Section 2.5. Reactions with or without the addition of KOH were explored for all of the isolated halide precursors. A notable result is that the prior preparation of a hydride derivative was not necessary to obtain the activities shown in Table 2, even in the absence of base as a co-catalyst.

The activity of these complexes in the hydrogenation of ketones is moderate, with better results obtained for acetophenone than for benzophenone – although the difference is not marked. This suggests that the size of substituents on the ketone is of little importance.

In the reactions performed in the presence of base (KOH) the derivatives with benzene generally show higher activity than those containing *p*-cymene and of the nitrogenated ligands the following order of activity was found: bpz*pdz > bpzprz > bpzqnx > OMe-pzqnx, with poor results obtained for the complexes containing the methoxy group in the ligand (**3** and **4**). The highest activity levels were thus found with complexes **7** and **8**.

It is remarkable that these complexes are active in the hydrogenation process in the absence of base. The addition of a base is usually necessary in transfer hydrogenations [22] except if a hydride, which is usually unstable, is used as the starting material [23] or some sort of activation of the precursor is previously necessary [24]. In any case, for our complexes, lower activities are generally observed without base although it is worth noting that for complexes **3** and **4** (both containing OMe groups in the ligands) the activity is higher in the absence of base and comparable results to those obtained for other derivatives in the presence of base were found. The best result was achieved with **3** and this also reflects the general trend that *p*-cymene complexes are more active when base is not added to the medium.

Although, the mechanism of these reactions was not studied in the work described here, a prior step involving the formation of hydrides was thought to be necessary. It is reasonable that these hydrides can be formulated as $[Ru(arene)H(L)]^+$. The partial decoordination of the N-donor ligand is also necessary in order to allow the coordination of the ketone. In such an unsaturated intermediate, the transitory coordination of the OMe group is probably possible and this could favour the deprotonation of the alcohol, which in turn leads to the formation of the alkoxide in the proximity of the metal and promotes the β-elimination and the concomitant formation of the desired hydride. This proposed role of the MeO group would be comparable to the role of the C=O group of a cyclopentadienone experimentally determined by Casey et al. [25] for the formation of Ru-hydrides in Shvo's catalyst [26].

Table 2
Yields and TON of the hydrogen transfer reactions of complexes **1–8** with benzophenone and acetophenone (reaction conditions are given in experimental Section 2.5).

Catalyst	With base		Without base	
	Yield (%)	TON	Yield (%)	TON
Benzophenone				
1	14	70	9	45
2	23	115	2	10
3	14	70	74	370
4	7	35	22	110
5	49	245	36	180
6	92	460	25	125
7	100	500	57	285
8	74	370	25	125
Acetophenone				
1	19	95	13	65
2	24	120	9	45
3	20	100	87	435
4	0	–	52	260
5	73	365	61	305
6	84	420	26	130
7	78	390	42	210
8	100	500	37	185

Acknowledgements

We are grateful to the Spanish Ministerio de Ciencia e Innovacion MICINN (Project No. CTQ2008-03783) and the Consejería de Educación y Ciencia of JCCM (PCI08-0054) for financial support.

Appendix A. Supplementary material

CCDC 717640 and 717641 contain the supplementary crystallographic data for complexes **6** and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre

via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.04.011.

References

[1] Recent and selected articles: (a) V. Cadierno, J. Victorio, J. Francos, J. Gimeno, Chem. Eur. J. 14 (2008) 6601;
(b) D. Carmona, M.P. Lamata, F. Viguri, R. Rodriguez, F.J. Lahoz, I.T. Dobrinovitch, L.A. Oro, Dalton Trans. (2008) 3328;
(c) D. Gnanamgari, E.L.O. Sauer, N.D. Schley, Ch. Butler, Ch.D. Incarvito, R.H. Crabtree, Organometallics 28 (2009) 321;
(d) B.C. Boren, S. Narayan, L.K. Rasmussen, L. Zhang, H. Zhao, Z. Lin, G. Jia, V.V. Fokin, J. Am. Chem. Soc. 130 (2008) 8923;
(e) N. Pannetier, J.-B. Sortais, P.S. Dieng, L. Barloy, C. Sirlin, M. Pfeffer, Organometallics 27 (2008) 5852;
(f) Sh. Oi, H. Sasamoto, R. Funayama, Y. Inoue, Chem. Lett. 37 (2008) 994;
(g) Sh.M. Ashraf, I. Berger, A.A. Nazarov, Ch.G. Hartinger, M.P. Koroteev, E.E. Nifant'ev, B.K. Keppler, Chem. Biodiversity 5 (2008) 1640;
(h) X. Wu, J. Liu, D. Di Tommaso, J.A. Iggo, C.R.A. Catlow, J. Bacsa, J. Xiao, Chem. Eur. J. 14 (2008) 7699;
(i) R. Castarlenas, C. Fischmeister, Ch. Bruneau, P.H. Dixneuf, J. Mol. Catal. A: Chem. 213 (2004) 31;
(j) H. Nagashima, H. Kondo, T. Hayashida, Y. Yamaguchi, M. Gondo, S. Masuda, K. Miyazaki, K. Matsubara, K. Kirchner, Coord. Chem. Rev. 245 (2003) 177;
(k) F.Ch. Pigge, J.J. Coniglio, Curr. Org. Chem. 5 (2001) 757;
(l) Ch. Bruneau, P.H. Dixneuf, Chem. Commun. (1997) 507;
(m) T. Higuchi, M. Hirobe, J. Mol. Catal. A: Chem. 113 (1996) 403.

[2] Selected papers: (a) T. Ohkuma, K. Tsutsumi, N. Utsumi, N. Arai, R. Noyori, K. Murata, Org. Lett. 9 (2007) 255;
(b) T. Ohkuma, N. Utsumi, K. Tsutsumi, K. Murata, Ch. Sandoval, R. Noyori, J. Am. Chem. Soc. 128 (2006) 8724;
(c) Ch.A. Sandoval, T. Ohkuma, N. Utsumi, K. Tsutsumi, K. Murata, R. Noyori, Chem. Asian J. 1 (2006) 102;
(d) R. Noyori, M. Yamakawa, Sh. Hashiguchi, J. Org. Chem. 66 (2001) 7931;
(e) M. Yamakawa, I. Yamada, R. Noyori, Angew. Chem., Int. Ed. 40 (2001) 2818;
(f) J. Takehara, Sh. Hashiguchi, A. Fujii, Sh.-i. Inoue, T. Ikariya, R. Noyori, Chem. Commun. (1996) 233.

[3] (a) M. Poyatos, W. McNamara, Ch. Incarvito, E. Clot, E. Peris, R.H. Crabtree, Organometallics 27 (2008) 2128;
(b) K.N. Kumar, G. Venkatachalam, R. Ramesh, Y. Liu, Polyhedron 27 (2007) 157;
(c) M. Gómez, S. Jansat, G. Muller, G. Aullón, M.A. Maestro, Eur. J. Inorg. Chem. (2005) 4341;
(d) R. Rakesh, N. Munirathiam, A.R. Chakravarty, Polyhedron 20 (2001) 2735.

[4] (a) Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, H. Arakawa, K. Kasuga, Stud. Surf. Sci. Catal. 153 (2004) 263;
(b) Y. Himeda, N. Onosawa, H. Sugihara, H. Arakawa, K. Kasuga, Jpn. Kokai Tokkyo Koho (2004) 19.

[5] M.C. Carrión, F.A. Jalón, B.R. Manzano, A.M. Rodríguez, F. Sepúlveda, M. Maestro, Eur. J. Inorg. Chem. (2007) 3961.

[6] (a) M.A. Bennett, T.N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74;
(b) M.A. Bennett, A.K. Smith, J. Chem. Soc., Dalton Trans. (1974) 233.

[7] H. Takahashi, K. Kobayashi, M. Osawa, Anal. Sci. 16 (2000) 777.

[8] G.M. Sheldrick, A Computer Program for the Determination of Crystal Structure, University of Göttingen, Germany, 1997.

[9] International Tables of X-ray Crystallography, vol. IV, Kynoch Press, 1974, p. 99.

[10] (a) J. Elguero, R. Jacquier, S. Mondon, Bull. Soc. Chim. Fr. (1970) 1346;
(b) G.L. Rusinov, R.I. Ishmetova, N.I. Latosh, I.N. Ganebnych, O.N. Chupakhin, V.A. Potemkin, Russ. Chem. Bull. 49 (2000) 355;
(c) L.K. Thompson, T.C. Woon, D.B. Murphy, E.J. Gabe, F.L. Lee, Y. Le Page, Inorg. Chem. 24 (1985) 4719.

[11] B.R. Manzano, F.A. Jalón, I.M. Ortiz, M.L. Soriano, F. Gómez de la Torre, J. Elguero, M.A. Maestro, K. Mereiter, T.D.W. Claridge, Inorg. Chem. 47 (2008) 413.

[12] R. Uson, L.A. Oro, M. Esteban, D. Carmona, R.M. Claramunt, J. Elguero, Polyhedron 3 (1984) 213.

[13] (a) H. Gao, Z.-H. Zhang, P. Jiang, X-.R. Li, Trans. Met. Chem. 31 (2006) 1088;
(b) L.K. Thompson, S.S. Tandon, M.E. Manuel, Inorg. Chem. 34 (1995) 2356.

[14] (a) P.J. Steel, E.C. Constable, J. Chem. Res., Synop. (1989) 189;
(b) A.W. Addison, P.J. Burke, J. Heterocycl. Chem. 18 (1981) 803.

[15] (a) M.-X. Peng, C.-L. Li, J. Jang, M.-L. Tong, J. Mol. Struct. 798 (2006) 149;
(b) D. Sabari, S. Subhash, F. Ahmed, F. Sarkar, Inorg. Chim. Acta 358 (2005) 3617;
(c) P. Hubberstey, C.E. Russell, J. Chem. Soc., Chem. Commun. (1995) 959;
(d) S.S. Tandon, L.K. Thompson, M.E. Manuel, J.N. Bridson, Inorg. Chem. 33 (1994) 5555.

[16] L.M. Gad, Mansoura J. Pharm. Sci. 10 (1994) 237.

[17] M.T. Clark, Brit. CODEN: BRXXAA GB 1574429 19800910, 1980, p. 9.

[18] H.M.A. Hamid, Carbohyd. Res. 338 (2003) 2301.

[19] (a) L.A. Oro, M. Esteban, R.M. Claramunt, J. Elguero, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 276 (1984) 79;
(b) J. Elguero, R. Jacquier, D. Tizane, Bull. Soc. Chim. Fr. 5 (1969) 1687;
(c) G. Minghetti, M.A. Cinellu, A.L. Bandini, G. Banditelli, F. Demartin, M. Manassero, J. Organomet. Chem. 315 (1986) 387.

[20] A. Singh, N. Sing, D.S. Pandey, J. Organomet. Chem. 642 (2002) 48.

[21] M. Nishio, Cryst. Eng. Commun. 6 (2004) 30.

[22] W. Baratta, K. Siega, P. Rigo, Chem. Eur. J. 13 (2007) 7479.

[23] (a) T. Ohkuma, M. Koizumi, K. Muniz, G. Hilt, C. Kabuto, R. Noyori, J. Am. Chem. Soc. 124 (2002) 6508;
(b) K. Abdur-Rashid, S.E. Clapham, A. Hadzovic, J. Harvey, A.J. Lough, R.H. Morris, J. Am. Chem. Soc. 124 (2002) 15104;
(c) Z.R. Dong, Y.Y. Li, J.S. Chen, B.Z. Li, Y. Xing, J.X. Gao, Org. Lett. 7 (2005) 1043.

[24] (a) R. Castarlenas, M.A. Esteruelas, E. Oñate, Organometallics 27 (2008) 3240;
(b) R. Corberan, E. Peris, Organometallics 27 (2008) 1954.

[25] C.P. Casey, S.W. Singer, D.R. Powell, R.K. Hayashi, M. Kavana, J. Am. Chem. Soc. 123 (2001) 1090.

[26] N. Menasche, Y. Shvo, Organometallics 10 (1991) 3885.