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Synthesis and characterisation of new pyrazole–phosphinite ligands and their ruthenium(II) arene complexes

Rosa Tribó [a], Sergi Muñoz [a], Josefina Pons [a], Ramón Yáñez [a], Ángel Álvarez-Larena [b], Joan Francesc Piniella [b], Josep Ros [a,*]

[a] Departament de Química, Universitat Autònoma de Barcelona, 08193-Cerdanyola del Valles, Barcelona, Spain
[b] Departament de Geologia, Unitat de Cristal·lografía, Universitat Autònoma de Barcelona, 08193-Cerdanyola del Vallès, Barcelona, Spain

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Abstract

The new potentially bidentate pyrazole–phosphinite ligands [(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl diphenylphosphinite] ($\mathbf{L^1}$) and [2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethyl diphenylphosphinite] ($\mathbf{L^2}$) were synthesised and characterised. The reaction of $\mathbf{L^1}$ and $\mathbf{L^2}$ with the dimeric complexes $[Ru(\eta^6\text{-arene})Cl_2]_2$ (arene = *p*-cymene, benzene) led to the formation of neutral complexes $[Ru(\eta^6\text{-arene})Cl_2(L)]$ (L = $\mathbf{L^1}$, $\mathbf{L^2}$) where the pyrazole–phosphinite ligand is κ^1-*P* coordinated to the metal. The subsequent reaction of these complexes with $NaBPh_4$ or $NaBF_4$ produced the $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\mathbf{L^2})][BPh_4]$ and $[Ru(\eta^6\text{-benzene})Cl(\mathbf{L^2})][BF_4]$ compounds which contain the pyrazole–phosphinite ligand κ^2-*P,N* bonded to ruthenium. All the complexes were fully characterised by analytical and spectroscopic methods. The structure of the complex $[Ru(\eta^6\text{-}p\text{-cymene})Cl(\mathbf{L^2})][BPh_4]$ was also determined by a X-ray single crystal diffraction study.

Keywords: Pyrazole; Phosphinite; Arene ruthenium(II) complexes; X-ray structure

1. Introduction

The chemistry of transition-metal complexes containing hemilabile ligands have been the subject of many studies in recent years [1]. Along with the term first introduced by Jeffrey and Rauchfuss [2], hemilabile ligands contain both a strong donor group, fixing the ligand to the metal, and a weaker donor group, which can be easily replaced by another ligand. Ligands possessing both 'soft' and 'hard' donor atoms coordinated to the same metal centre have been found suitable for catalytic purposes since the stability of intermediate species is favoured [1]. Recently, many efforts have been made to improve the catalytic activity of some complexes by using hemilabile ligands [3–8]. Among 'soft' donor atoms, phosphorus is the most common in homogeneous catalysis and, for this reason, it is found in many ligands combined with a variety of 'hard' labile donor groups (i.e., N- or O-donor). Although hemilabile P–O-donor ligands have been widely studied [1a,1b], increased attention has recently been given to hemilabile P–N donor ligands [1e,5,7]. The preparation of new nitrogen–phosphinite ligands and their evaluation in the rhodium-catalysed hydroformylation of styrene have recently been undertaken, by Kostas [9].

In recent years our research group has reported the synthesis, characterisation and coordination properties of many N1-substituted pyrazolic ligands containing supplementary donor groups. The most characteristic ligands studied have been: (a) bidentate ligands N(pz)–N(amine) [10,11], N(pz)–O(alcohol, ether) [12–15], N(pz)–P(phosphine) [10,16–18], and N(pz)–S(thiolate)

* Corresponding author. Tel.: +34 93 581 1889; fax: +34 93 581 3101.
E-mail address: josep.ros@uab.es (J. Ros).

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[19,20]; (b) tridentate ligands $(N(pz))_2$–N(amine) [21,22], $(N(pz))_2$–O(ether) [23,24], $(N(pz))_2$–S(thioether) [25], $(N(pz))_2$–N(amine)–O(alcohol)groups [26]; (c) tetradentate ligands $(N(pz))_2$–$(S(thioether))_2$ [27]. These studies have shown that pyrazole, in general, is the stronger donor group of the ligand, but in the case of ligands containing third period donor atoms (P, S), the pyrazole group can also behave as a labile donor group [20]. This fact is apparent in the room temperature ^{1}H NMR spectrum of the complex $[PdCl_2(N_2S)]$ (N_2S = 1,5-bis(3,5-dimethyl-1-pyrazolyl)-3-thiapentane) which shows that the ligand alternates NN and NS coordination types [25]. With the aim of extending our studies towards pyrazole-derived ligands containing a strong P donor group we report here the synthesis and characterisation of new ligands: [(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl diphenylphosphinite] (**L^1**) and [2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethyl diphenylphosphinite] (**L^2**). This study was completed with the synthesis and full characterisation of neutral and cationic arene–ruthenium(II) complexes bearing these pyrazole–phosphinite ligands. A preliminary test on the catalytic activity in transfer hydrogenation of cyclohexanone by propan-2-ol is also reported.

2. Experimental

2.1. General details

All reactions were performed with the use of vacuum line and Schlenk techniques. All reagents were commercial grade and were used without further purification. All solvents were dried and distilled by standard methods.

The elemental analyses (C, H, N) were carried out by the staff of the Chemical Analyses Service of the Universitat Autònoma de Barcelona on a Carlo Erba CHNS EA-1108 instrument. Infrared spectra were run on a Perkin Elmer FT-2000 spectrophotometer as KBr pellets or in CH_2Cl_2 with NaCl mulls. The ^{1}H NMR, ^{13}C {^{1}H} NMR and ^{31}P{^{1}H} NMR spectra were run on a NMR-FT Bruker AC-250 spectrometer in $CDCl_3$ solutions at room temperature. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts (δ) were determined relative to internal TMS and are given in ppm. ^{31}P {^{1}H} NMR chemical shifts (δ) were determined relative to external 85% H_3PO_4 and are given in ppm. Electrospray mass spectra were obtained on an Esquire 3000 ion trap mass spectrometer from Bruker Daltonics. Quantitative gas chromatographic measurements were made on a Hewlett Packard HP-5890 apparatus equipped with a FID detector and a HP-5 (30 m, 0.32 mm) capillary column. Qualitative gas chromatographic measurements were run o a Hewlett Packard HP-G1800A equipment connected to a MS EID detector and using a HP-5 (30 m, 0.25 mm) capillary column. The precursor complexes $[Ru(benzene)Cl_2]_2$ [28] and $[Ru(p\text{-cymene})Cl_2]_2$ [29] compounds were prepared by using previously published procedures. The (3,5-dimethyl-1H-pyrazol-1-yl)methanol [30] and 2-(3,5-dimethyl-1H-pyrazol-1-yl)ethanol [31] were prepared as described in the literature.

2.2. Synthesis of the ligands

2.2.1. Synthesis of [(3,5-dimethyl-1H-pyrazol-1-yl) methyl diphenylphosphinite] (*L^1*)

PPh_2Cl (0.75 mL, 4.00 mmol) dissolved in 10 mL of THF were slowly added to a solution of (3,5-dimethyl-1H-pyrazol-1-yl)methanol (0.5 g, 4.00 mmol) and triethylamine (0.67 mL, 7.78 mmol) in 20 mL of THF at room temperature. The mixture was stirred for 12 h and the triethylammonium chloride was filtered off. Evaporation of the solvent in vacuo gave [(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl diphenylphosphinite] (**L^1**) as a yellowish oil in 98% yield.

2.2.2. *L^1: $C_{18}H_{19}N_2PO$ (310.0)*

Anal. Calc. C, 69.66; H, 6.17; N, 9.03. Found: C, 69.10; H, 6.37; N, 9.36%. IR: (NaCl, cm^{-1}) 3054 $(C–H)_{ar}$, 2950 $\nu(C–H)_{al}$, 1589, 1558 (ν(C=C), ν(C=N)), 1480, 1436 (δ(C=C), δ(C=N)), 1122 $\delta(C–H)_{ip}$, 1094 ν(P–C), 1053 ν(P–O–C), 743, 717, 694 $\delta(C–H)_{oop}$. MS (ESI): *m/z* (%) 311.0 [MH^+] (100%), 233.0 [$M^+ - C_6H_5$] (5%), 202.9 [$Ph_2PO + H^+$] (7%), 109.0 [pz-$CH_2 + H^+$] (43%). ^{1}H NMR ($CDCl_3$ solution, 250 MHz) δ: 7.75–7.10 (10H, m, C_6H_5), 5.65 (2H, s, pz-CH_2), 5.60 (1H, s, pz-C*H*), 2.15 (3H, s, pz-CH_3), 2.06 (3H, s, pz-CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$ solution, 63 MHz) δ: 148.4 (pz-*C*CH_3), 140.6 (pz-*C*CH_3), 135.8, 135.6 (d, $J_{P,C}$ = 7.2 Hz, C_6H_5), 135.4, 135.3 (d, $J_{P,C}$ = 7.2 Hz, C_6H_5), 133.3–128.2 (C_6H_5), 106.6 (pz-*C*H), 60.5, (pz-*C*H_2), 13.8 (pz-*C*H_3) 11.5 (pz-*C*H_3) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$ solution, 81 MHz) 115.9 (s, O–*P*–$(C_6H_5)_2$) ppm.

2.2.3. Synthesis of [2-(3,5-dimethyl-1H-pyrazol-1-yl) ethyl diphenylphosphinite] (*L^2*)

Method 1. PPh_2Cl (1.35 mL, 7.13 mmol) dissolved in 10 mL of THF were slowly added to a solution of 2-(3,5-dimethyl-1H-pyrazol-1-yl)ethanol (1.00 g, 7.14 mmol) and triethylamine (1.20 mL, 8.57 mmol) in 20 mL of THF at room temperature. The mixture was stirred for 12 h and the triethylammonum chloride was filtered off. Evaporation of the solvent in vacuo gave [2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethyl diphenylphosphinite] (**L^2**) as a yellowish oil in a 83% yield.

Method 2. A 1.6 M solution of *n*BuLi in hexane (2.34 mL, 3.74 mmol) was slowly added to a solution of 2-(3,5-dimethyl-1H-pyrazol-1-yl)ethanol (0.50 g, 3.57 mmol) in 30 mL of THF at 0 °C. After 1 h of stirring at this temperature, a solution of PPh_2Cl (0.67 mL, 3.55 mmol) in 10 mL of THF was slowly

added. The mixture was stirred at room temperature for 12 h, and then evaporated to dryness in vacuo. The residue was suspended in toluene (50 mL) and filtered. Evaporation of the solvent gave [2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethyl diphenylphosphinite] (**L²**) in 85% yield.

*2.2.4. **L²**: $C_{19}H_{21}N_2PO$ (324.4)*

Anal. Calc. C, 70.36; H, 6.52; N, 8.64. Found: C, 70.22; H, 6.78; N, 8.97%. IR: (NaCl, cm^{-1}) 3053 ($C–H)_{ar}$, 2926 $\nu(C–H)_{al}$, 1554 ($\nu(C{=}C)$, $\nu(C{=}N)$), 1481, 1435 ($\delta(C{=}C)$, $\delta(C{=}N)$), 1131 $\delta(C–H)_{ip}$, 1092 $\nu(P–C)$, 1047 $\nu(P–O–C)$, 739, 697 $\delta(C–H)_{oop}$. MS (ESI): *m/z* (%) 347.1 [MNa^+] (100%), 325.1 [MH^+] (87%), 247.0 [$M^+ - C_6H_5$] (11%), 203.0 [$Ph_2PO{+}H^+$] (4%), 123.1 [pz-CH_2–CH_2 + H^+] (41%). ^1H NMR ($CDCl_3$ solution, 250 MHz) δ: 7.31–7.17 (10H, m, C_6H_5), 5.66 (1H, s, pz-C*H*), 4.05 (4H, m, pz-CH_2–CH_2–O), 2.12 (3H, s, pz-CH_3), 2.04 (3H, s, pz-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$ solution, 63 MHz) δ: 148.1 (pz-*C*CH_3), 141.8, 141.5 (d, $J_{P,C}$ = 18.2 Hz, C_6H_5), 140.3 (pz-*C*CH_3), 134.5, 134.2 (d, $J_{P,C}$ = 16.8 Hz, C_6H_5), 131.5–128.5 (C_6H_5), 105.3 (pz-*C*H), 68.9, 68.6 (d, $^2J_{P,C}$ = 17.8, pz-CH_2–*C*H_2–O), 49.8, 49.7 (d, $^3J_{P,C}$ = 8.2, pz-*C*H_2–CH_2O), 14.0 (pz-*C*H_3), 11.5 (pz-*C*H_3) ppm. $^{31}P\{^1H\}$ NMR($CDCl_3$ solution, 81 MHz) 116.4 (s, O–*P*–$(C_6H_5)_2$) ppm.

2.3. Synthesis of the complexes

*2.3.1. Complexes [Ru(p-cymene)Cl_2**L**] (**L** = **L¹** (**1**), **L²** (**2**)) and [Ru(benzene)Cl_2**L**](**L** = **L²** (**3**))*

The appropriate ligand (0.32 mmol: **L¹**, 0.101 g; **L²**, 0.106 g), dissolved in dichloromethane (5 mL) was added to a solution of the complex (0.16 mmol: [Ru(*p*-cymene)$Cl_2]_2$, 0.100 g; [Ru(benzene)$Cl_2]_2$, 0.080 g) in dichloromethane (20 mL). The solution was stirred at room temperature for 16 h. The resulting solution was concentred and the corresponding product was precipitated with cold diethylether and filtered off. Yields: 85% (**1**), 85% (**2**), 50% (**3**).

2.3.1.1. $C_{28}H_{33}Cl_2N_2OPRu$ (616.52). Anal. Calc. C, 54.55; H, 5.40; N, 4.54. Found: C, 54.16; H, 5.55; N, 4.23%. IR: (KBr, cm^{-1}) 3041 $\nu(C–H)_{ar}$, 2963 $\nu(C–H)_{al}$, 1552 ($\nu(C{=}C)$, $\nu(C{=}N)$), 1482, 1435 ($\delta(C{=}C)$, $\delta(C{=}N)$), 1093 $\nu(P–C)$, 1043 $\nu(P–O–C)$, 746, 696 $\delta(C–H)_{oop}$. ^1H NMR ($CDCl_3$ solution, 250 MHz) δ: 7.88–7.37 (10H, m, C_6H_5), 5.78 (1H, s, pz-C*H*), 5.63 (2H, d, $^3J_{P,H}$ = 4.4 Hz, pz-CH_2–O), 5.42 (4H, s(br), *p*-cym-C*H*), 2.60 (1H, sp, $^3J_{H,H}$ = 7.3 Hz, *p*-cym-C*H* $(CH_3)_2$), 2.21 (3H, s, pz-CH_3), 2.02 (3H, s, pz-CH_3), 1.84 (3H, s, *p*-cym-CH_3), 1.07 (6H, d, $^3J_{H,H}$ = 7.3 Hz, *p*-cym-CH(C$H_3)_2$) ppm. ^{13}C $\{^1H\}$ NMR ($CDCl_3$ solution, 63 MHz) δ: 176.9 (pz-*C*CH_3), 149.6 (pz-*C*CH_3), 141.1–128.1 (C_6H_5), 111.9 (*p*-cym-C_q), 106.6 (pz-*C*H), 98.6 (*p*-cym-C_q), 90.6 (*p*-cym-*C*H), 88.2 (*p*-cym-*C*H), 73.9 (pz-CH_2–O), 30.3 (*p*-cym-*C*H$(CH_3)_2$), 22.1 (*p*-cym-CH(*C*$H_3)_2$), 17.4 (*p*-cym-C*C*H_3), 13.7 (pz-*C*H_3), 10.7 (pz-*C*H_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$ solution, 81 MHz) 112.0 (s, O–*P*–$(C_6H_5)_2$) ppm.

2.3.1.2. $C_{29}H_{35}Cl_2N_2OPRu \cdot 0.5CH_3OH$ (646.57). Anal. Calc. C, 54.80; H, 5.77; N, 4.33. Found: C, 54.68; H, 5.70; N, 4.18%. IR: (KBr, cm^{-1}) 3040 $\nu(C–H)_{ar}$, 2920 $\nu(C–H)_{al}$, 1553 ($\nu(C{=}C)$, $\nu(C{=}N)$), 1482, 1435 ($\delta(C{=}C)$, $\delta(C{=}N)$), 1093 $\nu(P–C)$, 1043 $\nu(P–O–C)$, 746, 696 $\delta(C–H)_{oop}$. ^1H NMR ($CDCl_3$ solution, 250 MHz) δ: 7.79-7-36 (10H, m, C_6H_5), 5.83 (1H, s, pz-C*H*), 5.20 (2H, d, $^3J_{H,H}$ = 6.6 Hz, *p*-cym-C*H*), 5.10 (2H, d, $^3J_{H,H}$ = 6.6 Hz, *p*-cym-C*H*), 4.16 (2H, t, $^3J_{H,H}$ = 5.1 Hz, CH_2), 4.04 (2H, dt, $^3J_{H,H}$ = 5.1 Hz, $^3J_{P,H} \approx 4$ Hz, CH_2), 2.57 (1H, sp, $^3J_{H,H}$ = 6.6 Hz, *p*-cym-C*H* $(CH_3)_2$), 2.22 (3H, s, pz-CH_3), 2.20 (3H, s, pz-CH_3), 1.77 (3H, s, *p*-cym-CH_3), 1.04 (6H, d, $^3J_{H,H}$ = 7.3 Hz, *p*-cym-CH(C$H_3)_2$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$ solution, 63 MHz) δ: 147.7 (pz-*C*CH_3), 140.0 (pz-*C*CH_3), 136.6–127.9 (C_6H_5), 112.0 (*p*-cym-C_q), 105.3 (pz-*C*H), 98.4 (*p*-cym-C_q), 90.2 (d, $J_{P,C}$ = 3.7 Hz, *p*-cym-*C*H), 87.9 (d, $J_{P,C}$ = 7.4 Hz, *p*-cym-*C*H), 65.8 (O–CH_2), 48.9 (pz-*C*H_2), 30.3 (*p*-cym-*C*H$(CH_3)_2$), 22.0 (*p*-cym-CH(*C*$H_3)_2$), 17.4 (*p*-cym-C*C*H_3), 13.7 (pz-C*C*H_3), 11.4 (pz-C*C*H_3) ppm. $^{31}P\{^1H\}$ NMR($CDCl_3$ solution, 81 MHz) 114.1 (s, O–*P*–$(C_6H_5)_2$) ppm.

2.3.1.3. $C_{25}H_{27}Cl_2N_2OPRu \cdot 0.5CH_2Cl_2$ (616.91). Anal. Calc. C, 49.65; H, 4.57; N, 4.54. Found: C, 50.01; H, 4.51; N. 4.50%. IR: (KBr, cm^{-1}) 3070 $\nu(C–H)_{ar}$, 2957 $\nu(C–H)_{al}$, 1550 ($\nu(C{=}C)$, $\nu(C{=}N)$), 1483, 1436 ($\delta(C{=}C)$, $\delta(C{=}N)$), 1095 $\nu(P–C)$, 1038 $\nu(P–O–C)$, 744, 698 $\delta(C–H)_{oop}$. ^1H NMR ($CDCl_3$ solution, 250 MHz) δ: 7.80–7.40 (10H, m, C_6H_5), 5.84 (1H, s, pz-CH), 5.34 (6H, s, C_6H_6), 4.21 (2H, br, CH_2), 4.15 (2H, br, CH_2), 2.25 (3H, s, pz-CH_3), 2.21 (3H, s, pz-CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$ solution, 63 MHz) δ: 147.7 (pz-*C*CH_3), 140.0 (pz-*C*CH_3), 132.3–128.1 (C_6H_5), 105.3 (pz-*C*H), 90.2 (C_6H_6), 66.3 (O-*C*H_2), 48.9 (pz-*C*H_2), 13.5 (pz-C*C*H_3), 11.3 (pz-C*C*H_3) ppm. $^{31}P\{^1H\}$ NMR($CDCl_3$ solution, 81 MHz) 114.1 (s, O–*P*–$(C_6H_5)_2$) ppm.

*2.3.2. Complexes [Ru(p-cymene)Cl**L²**][BPh_4] (**4**) and [Ru(benzene)Cl**L²**][BF_4] (**5**)*

0.18 mmol of **2** (0.113 g) or **3** (0.105 g) were dissolved in 10 mL of dichloromethane and 0.18 mmol of $NaBPh_4$ (0.062 g) or $NaBF_4$ (0.020 g) dissolved in 2 mL of methanol to this solution. The mixture was stirred at room temperature for 20 h and the solvent was evaporated to dryness in vacuo. The resulting solid was suspended in 10 mL of dichloromethane and filtered of to remove the NaCl. The addition of hexane resulted in the precipitation of the product. The solid was filtered off and dried in vacuo. Yields: 60% **4**, 60% **5**. Complexes can be crystallised in dichloromethane/methanol mixtures.

2.3.2.1. $C_{53}H_{55}BClN_2OPRu \cdot 0.25\,CH_2Cl_2$ (935.56). Anal Calc. C, 68.36; H, 5.98; N, 2.99. Found: C, 68.0; H, 5.64; N, 2.50%. IR: (KBr, cm^{-1}) 3055 ν(C–H)$_{ar}$, 2930 ν(C–H)$_{al}$, 1558 (ν(C=C), ν(C=N)), 1477, 1434 (δ(C=C), δ(C=N)), 1085 ν(P–C), 1034 ν(P–O–C), 746, 696 δ(C–H)$_{oop}$. ^{1}H NMR ($CDCl_3$ solution, 250 MHz) δ : 7.98–6.44 (10H, m, C_6 H_5), 6.16 (1H, s, pz-C*H*), 5.42 (1H, d, $^3J_{H,H}$ = 5.8 Hz, *p*-cym-C*H*), 4.93 (1H, d, $^3J_{H,H}$ = 5.8 Hz, *p*-cym-C*H*), 4.72 (2H, m, *p*-cym-C*H*), 3.88/3.55/3.21/2.99 (4H, 4ddd, CH_2H_2), 2.74 (3H, s, *p*-cym-CH_3), 2.49 (1H, sp, $^3J_{H,H}$ = 6.6 Hz, *p*-cym-C*H* $(CH_3)_2$), 1.73 (3H, s, pz-CH_3), 1.77 (3H, s, *p*-cym-CH_3), 1.20 (3H, d, $^3J_{H,H}$ = 7.3 Hz, *p*-cym-CH(CH_3)$_2$), 1.10 (3H, d, $^3J_{H,H}$ = 7.3 Hz, *p*-cym-CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$ solution, 63 MHz) δ: 165.3–121.9 (C_6H_5), 158.3 (pz-*C*CH_3), 147.9 (pz-*C* CH_3), 119.1 (*p*-cym-C_q), 110.1 (pz-*C* H), 101.5 (*p*-cym-C_q), 93.7, 91.5, 89.2, 85.4 (*p*-cym-*C* H), 65.7 (O–*C*H_2), 49.6 (pz-*C*H_2), 30.3 (*p*-cym-*C* H$(CH_3)_2$), 22.6 (*p*-cym-CH(C_3)$_2$) 21.4 (*p*-cym-CH(C_3)$_2$), 17.9 (*p*-cym-C*C*H_3), 17.3 (pz-C*C*H_3), 12.1 (pz-C*C*H_3) ppm. ^{31}P{^{1}H} NMR($CDCl_3$ solution, 81 MHz) 114.1 (s, O–*P*–$(C_6H_5)_2$) ppm.

2.3.2.2. $C_{25}H_{27}BClF_4N_2OPRu \cdot 0.25CH_2Cl_2$ (647.03). Anal. Calc. C, 46.87; H, 4.28; N, 4.33. Found: C, 46.70; H, 4.45; N, 4.19%. IR: (KBr, cm^{-1}) 3070 ν(C–H)$_{ar}$, 2950 ν(C–H)$_{al}$, 1558 (ν(C=C), ν(C=N)), 1483, 1436 (δ(C=C), δ(C=N)), 1090 ν(P–C), 1040 ν(P–O–C), 1080 ν(B–F), 744, 700 δ(C–H)$_{oop}$. ^{1}H NMR ($CDCl_3$ solution, 250 MHz) δ: 8.05–6.53 (10H, m, C_6H_5), 6.21 (1H, s, pz-CH), 5.78 (6H, s, C_6 H_6), 4.64 (2H, br, CH_2), 4.21 (2H, br, CH_2), 2.87 (3H, s, pz-CH_3), 2.09 (3H, s, pz-CH_3) ppm.^{13}C{^{1}H} NMR ($CDCl_3$ solution, 63 MHz) δ: 158.1 (pz-*C* H_3), 148.2 (pz-*C*CH_3), 133.6–128.0 (C_6H_5), 110.0 (pz-*C*H), 92.6 (C_6H_6), 66.7 (O-*C*H_2), 51.4 (pz-*C*H_2), 17.4 (pz-C*C*H_3), 12.6 (pz-C*C*H_3) ppm. ^{31}P{^{1}H} NMR($CDCl_3$ solution, 81 MHz) 111.9 (s, O–*P*–$(C_6H_5)_2$) ppm.

2.4. Catalytic experiments

Under N_2 atmosphere, cyclohexanone (10 mmol, 0.981 g), the catalyst precursor (0.05 mmol), and 15 mL of a 0.094 M solution of NaOH (0.14 mmol, 5.6×10^{-3} g) in 2-propanol, were introduced in to a Schlenk flask fitted with a condenser and heated at 82 °C. The reaction was monitored by gas chromatography. Cyclohexanol and acetone were the only detected products.

2.5. X-ray crystal structure analysis of complex 4

Suitable crystals for X-ray diffraction of complex **4** were obtained by crystallisation in a dichloromethane/methanol mixture. Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) and a ω-2θ scan with an ω scan width = 0.80 + 0.35 tanθ, and an ω scan speed = 1.3–5.5°. Reflection ranges for the data collection: $1 < \theta < 25$; $-15 < h < 15$, $-16 < k < 15$, $-2 < l < 16$. Lp and empirical absorption corrections [32] were applied, T_{min} = 0.960, T_{max} = 1.000. 8498 unique reflections, 6988 with $I > 2\sigma(I)$, were used. The structure was solved by direct methods (SHELXS-86) [33] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97) [34]. One molecule of CH_2Cl_2 was found in the asymmetric unit. Restraints were applied in order to have sensible distances in phenyl groups and solvent. All non hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions with isotropic displacement factors 1.5 times (methyl H) or 1.2 times (the rest) times the U_{eq} values of corresponding carbons. The final weighting scheme was $w = 1/[\sigma^2(F_o^2) + 0.0806P^2 + 1.0526P]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. Crystal and other structure refinement data are displayed in Table 1.

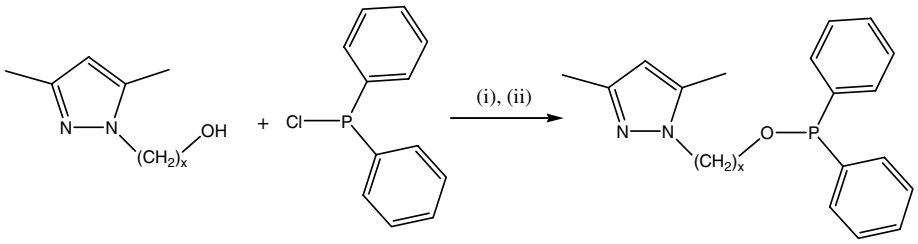
3. Results and discussion

3.1. Synthesis of the ligands

The synthetic procedure for the preparation of the ligands is shown in Scheme 1. Pyrazole–phosphinite ligands [(3,5-dimethyl-1*H*-pyrazol-1-yl)methyl diphenylphosphinite] (**L^1**) and [2-(3,5-dimethyl-1*H*-pyrazol-1-yl)ethyl diphenylphosphinite] (**L^2**) were synthesised by hydrogen

Table 1
Crystal data and structure refinement for **4**

Empirical formula	$C_{53}H_{55}BClN_2OPRu \cdot CH_2Cl_2$
Formula weight	999.22
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
A (Å)	12.965(2)
B (Å)	13.691(5)
c (Å)	14.269(5)
α (°)	100.80(3)
β (°)	99.68(2)
γ (°)	97.32(2)
V (Å^3)	2419.3(13)
Z	2
ρ_{calc} (g cm^{-3})	1.372
Absorption coefficient (mm^{-1})	0.564
F(000)	1036
θ Range for data collection (°)	1.48–24.97
Data/restraints/parameters	8498/38/568
Goodness-of-fit on F^2	1.092
R indices [$I > 2\sigma(I)$]	$R(F)$ = 0.044, $R_w(F^2)$ = 0.132
R indices (all data)	$R(F)$ = 0.057, $R_w(F^2)$ = 0.126
Largest difference peak and hole (e Å^{-3})	0.69 and −0.81



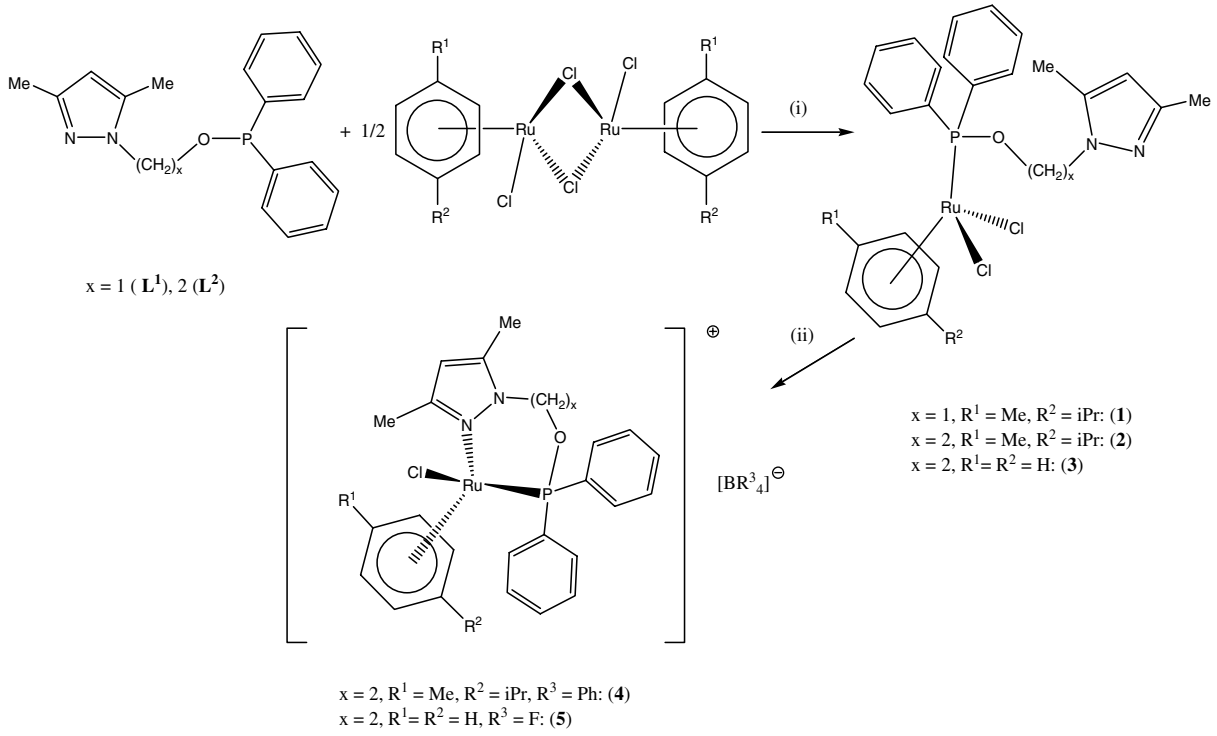
(i): NEt_3, THF, 12 h, room temperature; (ii) Alternatively for x = 2: nBuLi, THF, 12 h, 0 º C

Scheme 1.

abstraction of the previously described *N*1-hydroxyalkylpyrazoles $Me_2Pz(CH_2)_xOH$: (3,5-dimethyl-1H-pyrazol-1-yl)methanol ($x = 1$) [30] and 2-(3,5-dimethyl-1H-pyrazol-1-yl)ethanol ($x = 2$) [31], respectively, by a base (NEt_3) and the subsequent reaction with one equivalent of PPh_2Cl, in anhydrous THF and inert atmosphere (N_2). The ammonium salt was separated by filtration and the ligands were obtained by extracting the solvent in vacuo in good yields (98% and 83%, respectively). Alternatively, *n*BuLi was also used as a base in the synthesis of $\mathbf{L^2}$. These synthetic methodologies led to $\mathbf{L^1}$ and $\mathbf{L^2}$ ligands, as a yellowish oil, with enough purity to give good analytical and spectroscopic data (see Section 2). C, H, N elemental analyses and IR, ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR and MS spectroscopies are in agreement with the proposed structures for ligands. Singlets at $\delta = 115.9$ and 116.4 ppm, respectively, in the $^{31}P\{^1H\}$ NMR spectrum of ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ correspond to diphenylphosphinite groups [9]. The rest of NMR signals are consistent with those reported for related ligands [10,11].

3.2. Synthesis and characterisation of complexes

The whole of reactions with of $[Ru(\eta^6\text{-arene})Cl_2]_2$ with ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ are depicted in Scheme 2. The reactions of $[Ru(\eta^6\text{-arene})Cl_2]_2$ (arene = *p*-cymene, benzene) with an equimolar amount of $\mathbf{L^1}$ or $\mathbf{L^2}$ in dichloromethane at room temperature gave the red compounds **1**, **2** and **3** in moderate yields (85% (**1**), 85% (**2**), and 50% (**3**)). Elemental analyses of products **1**–**3** are consistent with the suggested molecular formulas containing solvent molecules. The absorption bands corresponding



(i): CH_2Cl_2, 16 h, room temperature; (ii): $NaBR^3{}_4$, CH_2Cl_2/MeOH, 20 h, room temperature

Scheme 2.

to pyrazole–phosphinite ligands in the infrared spectra of compounds **1**–**3** do not show significant differences with respect to those of the free ligands. ^{1}H and ^{13}C NMR spectra of compounds **1**–**3** display all the signals of coordinated ligands. In the ^{1}H NMR of **1** the methylene CH_2 protons of $\mathbf{L^1}$ appear at 5.63 ppm as a doublet ($J_{P,H}$ = 4.4 Hz) and the *p*-cymene C*H* protons are observed as a broad singlet, that integrates 4H, at 5.42 ppm. The ^{1}H NMR of **2** shows the CH_2H_2 signals of $\mathbf{L^2}$ ligand as two separated resonances: a triplet at 4.16($J_{H,H}$ = 5,1 Hz) and a double triplet at 4.04 ppm ($J_{H,H}$ = 5,1 and $J_{H,P} \approx 4$ Hz). This spectrum also displays the *p*-cymene C*H* protons as two doublets at 5.20 and 5.10 ppm ($^{3}J_{H,H}$ = 6.6 Hz). The presence of one (broad) or two signals corresponding to C*H* *p*-cymene hydrogens in the ^{1}H NMR spectra of **1** and **2** is consistent with a C_s symmetry of complexes and with a free rotation of the arene ligand [35,36]. The proton NMR spectrum of complex **3** displays the CH_2H_2 resonances of $\mathbf{L^2}$ ligand as two broad signals at 4.21 and 4.10 ppm and the C_6H_6 protons as a singlet at 5.34 ppm (6H). The proton signals corresponding to pyrazolyl group of coordinated $\mathbf{L^1}$ and $\mathbf{L^2}$ in complexes **1**–**3** do not differ significantly from those of free ligand spectra, which is in agreement with a free orientation of this group. The most relevant signals of $^{13}C\{^{1}H\}$ NMR spectra of complexes **1**–**3** are those corresponding to arene ligands (*p*-cymene **1**, **2**), C_6H_6 (**3**) and to $(C_2)_x$ (x = 1 (**1**), 2 (**2**, **3**)) chain. Carbon atoms of the arene ring in *p*-cymene ligand are observed as two singlets at 90.6 and 88.2 ppm in compound **1** and as a two doublets at 90.2 and 87.9 ppm ($J_{C,P}$ = 3.7 and 7.4 Hz, respectively). A similar pattern of signals was observed in the $^{13}C\{^{1}H\}$ NMR spectra of [$RuCl_2$ (*p*-cymene)(PR_3)] (*R* = Ph, OMe, OPh) complexes [37]. The signal corresponding to the *C*H_2 link of complex **1** is observed at 73.9 ppm, whereas the signals of the CH_2CH_2 fragment are found at: (a) 65.8 ppm (O*C*H_2) and 48.9 ppm (*C*H_2Pz) for complex **2**, and (b) 66.3 ppm (O*C*H_2) and 48.9 ppm (*C*H_2Pz) for complex **3**. Regarding $^{31}P\{^{1}H\}$ NMR spectra, singlets at 112.0, 114.1 and 114.1 ppm are found for complexes **1**, **2** and **3**, respectively, which are in the expected range for coordinated phenylphosphinite ligands [7,30,38,39]. All these data are in agreement with [$RuCl_2$-(η^6-arene)(κ^1-*P*-pyrazole–phosphinite)] type structures for compounds **1**–**3**.

The reaction in CH_2Cl_2 of complexes **2** and **3** with equimolar amounts of Na[PPh_4] or Na[BF_4], respectively, yielded complexes **4** and **5**, which showed a κ^2-*PN* mode of coordination of the pyrazole–phosphinite ligand $\mathbf{L^2}$. Yields were of 60% for both complexes. Elemental analyses of orange products **4** and **5** agree with the molecular formula [$RuCl_2$(η^6-arene)($\mathbf{L^2}$)][BR_4] · 0.25 CH_2Cl_2 (*R* = Ph (**4**), F (**5**)). The infrared spectra of these ionic compounds **4** and **5** show a similar pattern of bands to that in neutral complexes **1**–**3** but with the expected absorptions due to the presence of the anions $[BPh_4]^-$ and $[BF_4]^-$, respectively. The room temperature ^{1}H NMR spectra of compounds **4** and **5** display complex multiplets, corresponding to the OCH_2H_2Pz fragment, characteristic of pairs of diastereotopic hydrogen atoms in a rigid ethylene alkyl chain [25]. In complex **4**, four multiplets (ddd) at 3.88, 3.55, 3.21 and 2.99 ppm (1H each) are observed, but, in complex **5**, two broad unresolved multiplets centred at 4.64 (2H) and 4.21 (2H) are observable. Although the proton NMR signals for the OCH_2H_2Pz agreed with a rigid conformation of the chain, the two broad resonances observed for complex **5** would suggest some degree of flexibility, probably attributable to the smaller steric requirement of the benzene ligand compared with that of the *p*-cymene. The proton spectrum of complex **4** exhibited the C*H* *p*-cymene signals as three signals: two doublets at 5.42 (1H) and 4.93 (1H) ppm ($J_{H,H}$ = 5.8 Hz), and a multiplet at 4.72 (2H) ppm. The appearance of separated signals for C*H* *p*-cymene hydrogens was consistent with a C_1 symmetry of the complex, which was expected for a [(η^6-arene)R-u$L^1L^2L^3$] complex core [7,35,36]. In addition, the bulk of the pyrazole–phosphinite $\mathbf{L^2}$ chelated ligand seems to prevent a free rotation of the *p*-cymene ligand around the arene–Ru axis. This phenomenon is common in [(η^6-arene)RuCl(**L**–**L**)]$^+$(**L**–**L** = neutral bidentate ligand) complexes [35,36]. With reference to complex **5**, the C_6H_6 proton signal is observed at 5.78 ppm as a singlet (6H). The $^{13}C\{^{1}H\}$ NMR spectra of complexes **4** and **5** display signals of the OC_2C_2Pz chain at 65.7, 66.7 ppm (O*C*H_2) and 49.6, 51.4 ppm (*C*H_2Pz), respectively. In concordance with the proton spectrum of **4**, the *C*H *p*-cymene signals are observed as four signals at 93.7, 91.5, 89.2 and 85.4 ppm. The C_6H_6 carbon resonance occurred at 92.6 (s) ppm. Concerning the $^{31}P\{^{1}H\}$ NMR spectra of complexes **4** and **5**, expected singlets at 114.1 and 111.9 ppm are observed. It is significant to remark that ^{31}P NMR signals of ligands and complexes do not differ significantly [38,39].

3.3. Catalysis

In a preliminary study, some of the synthesised complexes were evaluated as a precursor for the catalytic transfer hydrogenation of cyclohexanone by 2-propanol (Table 2). The activity of ruthenium(II) arene complexes is well known in this catalytic process [7, (and references therein)]. In a typical experiment, 0.05 mmol of the complex and 10 mmol of cyclohexanone were added to a 0.094 M solution of NaOH in 2-propanol (0.14 mmol of NaOH in 15 mL of 2-propanol) and refluxed at 82 °C, the reaction being monitored by GC. With a complex/NaOH ratio of 1/24, complexes **1**–**4** are rather active in the transfer hydrogenation. Complex **3** is the most active one which leads to a quantitative transfor-

mation of the ketone in 2 h, with a moderate TOF_{50} of 152 h^{-1}. From these preliminary results, it can be seen that neutral complexes are more active than cationic compound **4** and that the η^6-benzene ruthenium(II) complex **4** is more effective than η^6-*p*-cymene derivatives. These results are consistent with those reported in the literature [7,40]. The decrease of the quantity of base leads to the deactivation of the catalyst. It should be pointed out that complexes **1**–**4** are more active catalysts than the corresponding precursors: $[Ru(p\text{-cymene})Cl_2]_2$ (41% maximum yield in 24 h) and $[Ru(benzene)Cl_2]_2$ (37% maximum yield in 24 h) with a 1/14 complex/NaOH ratio.

3.4. Crystal and molecular structure of complex *4*

The structure of complex **4** was confirmed by a single-crystal X-ray diffraction study. Complex **4** consisted of a cationic complex $[Ru(p\text{-cymene})Cl(L^2)]^+$ and an anion $[BPh_4]^-$ with a solvent molecule (CH_2Cl_2). A view of the molecular structure of the cation complex is shown in Fig. 1. Selected bond lengths and angles of the structure are displayed in Table 3. The molecule displayed a pseudooctahedral three-legged piano-stool geometry around the ruthenium atom with the arene, the $\mathbf{L^2}$ ligand and the chloro ligand completing the coordination around the metal. The distortion of the octahedral geometry was evident from the values of the P–Ru–N(82) (89.69(9)°), P–Ru–Cl (84.31(4)°) and N(82)–Ru–Cl (91.18(9)°) angles. It is interesting to note that the flexibility of the bidentate $\mathbf{L^2}$ ligand makes possible a nearly equal distribution of the N, P, Cl donor atoms around the metal. The angles between the centroid of the arene ring (C*), the metal and the N, P and Cl atoms

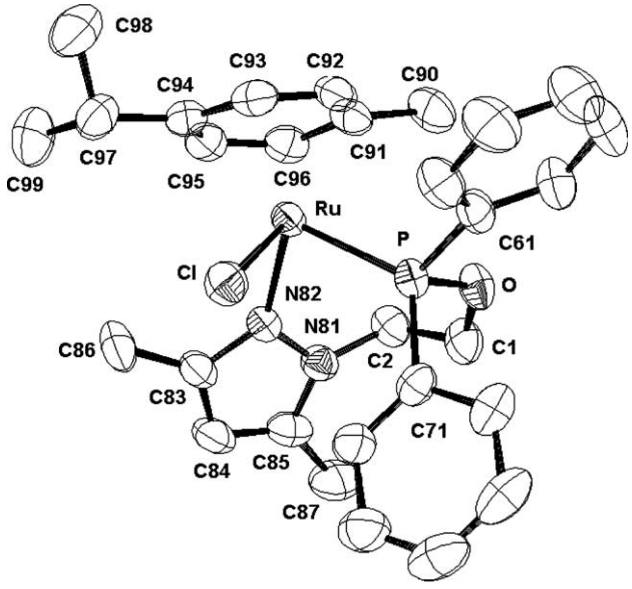


Fig. 1. Molecular structure of the cation complex of **4**.

Table 2
Catalytic transfer hydrogenation of cyclohexanone[a]

Entry	Catalyst	Yield (%)[b,c]	TOF_{50} (h^{-1})[d]
1	**1**	55 (>99)[e]	55
2	**2**	25 (75)[c]	10
3	**3**	98 (>99)[f]	152
4	**4**	23 (60)[c]	16
5	**3**[g]	10 (12)[c]	[h]

[a] Reaction conditions: 82 °C, 2-propanol (15 mL), NaOH (0.14 mmol), catalyst (0.05 mmol) and cyclohexanone (10 mmol). Ketone/catalyst/NaOH ratio: 200/1/24 Yields were determined by GC.
[b] Yield of cyclohexanol after 2 h.
[c] Yield after 24 h in parenthesis.
[d] Turnover frequencies [(mol cyclohexanol/mol catalyst)/time] at 50% conversion.
[e] Yield after 12 h in parenthesis.
[f] Yield after 3 h in parenthesis.
[g] Catalyst/NaOH ratio: 1/14.
[h] Maximum yield of 12%.

Table 3
Selected bond distances (Å) and angles (°) for **4**

Ru–Cl	2.407(1)
Ru–P	2.305(1)
P–O	1.614(3)
O–C(1)	1.434(5)
Ru–N(82)	2.141(3)
Ru–C(92)	2.195(4)
Ru–C(94)	2.329(4)
Ru–C(96)	2.202(4)
Ru–C(91)	2.250(4)
Ru–C(93)	2.181(4)
Ru–C(95)	2.293(5)
Ru–C*	1.745(5)
Cl–Ru–N(82)	91.18(9)
P–Ru–N(82)	89.69(9)
C*–Ru–N(82)	127.0(1)
C*–Ru–P	128.7(1)
Cl–Ru–P	84.31(4)
Ru–P–O	114.0(1)
C*–Ru–Cl	123.2(1)
P–O–C(1)	121.6(2)

C* = centroid ring

are in the 123–129° range. The Ru(II) atom is η^6-bonded to a *p*-cymene ring, to $\mathbf{L^2}$ in a κ^2-*P,N* coordination mode and to a Cl atom. The Ru–Cl bond length of 2.407(1) Å was consistent with those reported in the literature [35]. The Ru–C(*p*-cymene) bond lengths average 2.242(4) Å and the Ru–C* distance is of 1.745(5) Å (C* = centroid ring). The coordination of *p*-cymene to metal was slightly unsymmetrical, with Ru–C(94) (2.329(4) Å) and Ru–C(95) (2.293(4) Å) bond lengths significantly long. This distortion possibly comes from the steric constraint imposed by the pyrazole ring, whose methyl C(86) points directly to C(94) and C(95) atoms. The $\mathbf{L^2}$ ligand is κ^2-bonded to metal forming a seven-membered metallacycle with Ru–P and Ru–N(82) distances of 2.305(1) and 2.141(3) Å, respectively. These values are of the same order as those found in the related

[Ru(*p*-cymene)Cl(Me_2HPz)(PPh_2OH)] complex [16]. The P–O bond length of 1.614(3) Å is coherent with others reported in the literature [41].

Acknowledgement

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Appendix A. Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 266007 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336 033, email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.uk. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.05.047.

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