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Synthesis, crystal structure and spectroscopic characterization of new neutral and cationic (η^6-*p*-cymene)–ruthenium(II) complexes with phosphine–amide ligands

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Abstract

The dimeric starting material [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ reacts with the phosphino-amides *o*-Ph_2P–C_6H_4CO–NH–R [R = ^{i}Pr (**a**), Ph (**b**), 4-MeC_6H_4 (**c**), 4-FC_6H_4 (**d**)] to give the mononuclear compounds **1a**–**d** [RuCl(η^6-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–R)]Cl. The subsequent reaction of these complexes with KPF_6 produced the cationic species **2a**–**d** [RuCl(η^6-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–R)][PF_6] in which phosphino-amides also act as rigid *P*,*O*-chelating ligands. The molecular structures of **2b**–**d** were determined crystallographically. Amide deprotonation is achieved when complexes **2a**–**d** were made react with 1 M aqueous solution of KOH, affording the corresponding neutral species **3a**–**d** [RuCl(η^6-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–N–R)] in which a P,N-coordination mode is suggested.

Keywords: Phosphino-amides; Hemilabile ligands; Coordination modes; (η^6-*p*-cymene) complexes; Crystal structures; Ruthenium

1. Introduction

Hybrid ligands that contain distinct chemical functions [1–5], such as soft phosphine and hard (e.g., N or O) donor atoms, have attracted continuous interest during last years as a result of their versatile coordination behaviour [6,7] and its potential hemilability [3–5]. These properties have been exploited in several ways, as the ''weak-link approach'' for the synthesis of supramolecular structures [8] or the use of some ligands and its complexes in chemical sensing [9–11] and catalytic processes. It is in this last field that phosphine–amide ligands have received growing attention: the asymmetric 1,4-addition reaction of arylboronic acids with cycloalkenones is catalysed by an amidophosphine rhodium(I) complex [12], amide derived phosphines possessing various *N*,*N*-dialkyl aromatic amide scaffolds have shown to be highly effective in Suzuki cross-coupling reactions [13,14], and 2-diphenylphosphinobenzamido nickel complexes have found application in ethylene polymerization, showing that slight variations in the ligand frame produce drastic changes in the catalytic behaviour [15].

On the other hand, half-sandwich ruthenium(II) complexes bearing hemilabile ligands have been studied as efficient catalyst in hydrogen transfer reactions [16–21], and the hemilabile properties of several P,N- or P,O-donor ligands have been investigated synthesizing complexes in which these ligands adopt different coordination modes to the ruthenium atom [22–26]. No analogous studies concerning the phosphino-amides *o*-Ph_2P–C_6H_4–CO–NH–R have been reported and, as far as we are aware, the ligand 1,2-bis-N[2′-(diphenylphosphinobenzoyl)]diaminonaphthalene and its dimeric *p*-cymene ruthenium complex is the closest precedent described to date [26].

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We have recently studied the coordination properties of these mixed-donor bidentate ligands in their first described palladium(II) complexes, containing cyclometallated [27] or pentafluorophenyl co-ligands [28]. As a extension of our work on *o*-Ph_2P–C_6H_4–CO–NH–R ligands in this paper we present the preparation and characterization of new neutral and cationic (η^6-*p*-cymene)–ruthenium(II) complexes.

2. Experimental

2.1. Methods and materials

C, H, and N analyses were carried out with a Carlo Erba instrument. IR spectra were recorded on a Perkin–Elmer spectrophotometer 16F PC FT-IR, using Nujol mulls between polyethylene sheets. NMR data (^1H, ^{31}P) were recorded on Bruker Avance 200 and 300 spectrometers. Mass spectrometric analyses were performed on a Fisons VG Autospec double-focusing spectrometer, operated in positive mode. Ions were produced by fast atom bombardment (FAB) with a beam of 25 keV Cs atoms. The mass spectrometer was operated with an accelerating voltage of 8 kV and a resolution of at least 1000. All the solvents were dried by conventional methods.

The diphenylphosphinobenzamides *o*-Ph_2P–C_6H_4–CO–NH–R (R = ^{i}Pr (**a**), Ph (**b**), 4-MeC_6H_4 (**c**), 4-FC_6H_4 (**d**)) were prepared by a reported procedure [28]. The starting dinuclear dichloro complex [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ was prepared according to a published method [29].

2.2. Synthesis

2.2.1. Preparation of complexes [RuCl(η^6-p-cymene)-(o-Ph_2P–C_6H_4–CO–NH–R)]Cl (R = ^{i}Pr (**1a**); R = Ph (**1b**); R = 4-MeC_6H_4 (**1c**); R = 4-FC_6H_4 (**1d**))

The new complexes were obtained by treating [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ with previously prepared 2-diphenylphosphine benzamides in molar ratio 1:2, using CH_2Cl_2 as solvent and according to the following general method. To a dichloromethane solution (15 mL) of the precursor (250 mg; 0.40 mmol) was added solid 2-diphenylphosphinebenzamide (0.80 mmol). The resulting solution was stirred for 60 min. at room temperature and then concentrated to half volume under reduced pressure. Addition of diethyl ether caused precipitation of the new complexes, which were filtered off, air dried and recrystallized from dicholoromethane–ether.

[RuCl(η^6-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–^{i}Pr)]Cl (**1a**): (70% yield). *Anal.* Calc. for $C_{32}Cl_2H_{36}NOPRu$: C, 58.8; H, 5.5; N, 2.1. Found: C, 59.0; H, 5.7; N, 1.9%. FT-IR (Nujol mull cm^{-1}): *v*(NH) 3325(s); *v*(CO) 1608(vs). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm): 10.88 (s, 1H, NH), 8.52 (m, 1H, P–C_6H_4–CO–), 7.88–7.44 (m, 11H, 10H, PPh_2 + 1H P–C_6H_4–CO–), 7.24 (m, 1H, P–C_6H_4–CO–), 6.51 (m, 1H, P–C_6H_4–CO–), 5.85 (d, J_{HH} = 6.0 Hz, 1H, Cy), 5.74 (d, J_{HH} = 6.0 Hz, 1H, Cy), 5.39 (m, 1H, Cy), 5.19 (d, J_{HH} = 6.0 Hz, 1H, Cy), 4.15 (m, 1H, CH, N–^{i}Pr), 2.38 (m, 1H, CH, ^{i}Pr–Cy), 1.88 (s, 3H, Me–Cy), 1.46 (d, J_{HH} = 6.4 Hz, 3H, Me, N–^{i}Pr), 1.21 (d, J_{HH} = 6.4 Hz, 3H, Me, N–^{i}Pr), 1.15 (d, J_{HH} = 6.6 Hz, 3H, Me, ^{i}Pr–Cy), 0.54 (d, J_{HH} = 6.4 Hz, 3H, Me, ^{i}Pr–Cy). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm): 33.8 (s). FAB-MS (positive mode) *m*/*z*: 618 (M^+ − Cl), 583 (M^+ − 2Cl).

[RuCl(η^6-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–Ph)]Cl (**1b**): (71% yield). *Anal.* Calc. for $C_{35}Cl_2H_{34}NOPRu$: C, 61.1; H, 5.0; N, 2.0. Found: C, 60.9; H, 5.2; N, 2.0%. FT-IR (Nujol mull cm^{-1}): *v*(NH) 3405(s); *v*(CO) 1600(vs). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm): 12.99 (s, 1H, NH), 8.61 (m, 1H, P–C_6H_4–CO–), 7.92–7.31 (m, 15H, 10H PPh_2 + 5H N–Ph), 7.65 (m, 1H, P–C_6H_4–CO–), 7.21 (m, 1H, P–C_6H_4–CO–), 6.69 (m, 1H, P–C_6H_4–CO–), 5.86 (d, J_{HH} = 6.6 Hz, 1H, Cy), 5.79 (d, J_{HH} = 6.6 Hz, 1H, Cy), 5.28 (m, 1H, Cy), 4.89 (d, J_{HH} = 4.8 Hz, 1H, Cy), 1.89 (s, 3H, Me–Cy), 1.63 (m, 1H, CH, ^{i}Pr–Cy), 0.81 (d, J_{HH} = 6.0 Hz, 3H, Me, ^{i}Pr–Cy), −0.07 (d, J_{HH} = 6.9 Hz, 3H, Me,^{i}Pr–Cy). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm): 33.4 (s). FAB-MS (positive mode) *m*/*z*: 652 (M^+−Cl), 617 (M^+−2Cl).

[RuCl(η^6-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–C_6H_4– CH_3)]-Cl (**1c**): (81% yield). *Anal.* Calc. for $C_{36}Cl_2H_{36}NOPRu$: C, 61.6; H, 5.2; N, 2.1. Found: C, 61.8; H, 5.3; N, 2.1%. FT-IR (Nujol mull cm^{-1}): *v*(NH) 3402(s); *v*(CO) 1586(vs). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm): 12.99 (s, 1H, NH), 8.63 (m, 1H, P–C_6H_4–CO–), 7.90 (m, 2H, N–C_6H_4–CH_3), 7.65 (m, 1H, P–C_6H_4–CO–), 7.52–7.39 (m, 10H PPh_2), 7.33 (m, 1H, P–C_6H_4–CO–), 7.14 (m, 2H, N–C_6H_4–CH_3), 6.68 (m, 1H, P–C_6H_4–CO–), 5.85 (d, J_{HH} = 6.6 Hz, 1H, Cy), 5.79 (d, J_{HH} = 6.6 Hz, 1H, Cy), 5.28 (m, 1H, Cy), 4.89 (d, J_{HH} = 5.1 Hz, 1H, Cy), 2.32 (s, 3H, Me, N–C_6H_4–CH_3), 1.87 (s, 3H, Me–Cy), 1.66 (m, 1H, CH, ^{i}Pr–Cy), 0.83 (d, J_{HH} = 6.9 Hz, 3H, Me, ^{i}Pr–Cy), −0.05 (d, J_{HH} = 6.6 Hz, 3H, Me, ^{i}Pr–Cy). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm): 33.4 (s). FAB-MS (positive mode) *m*/*z*: 666 (M^+−Cl), 631 (M^+−2Cl).

[RuCl(η^6-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–C_6H_4–F)]-Cl (**1d**): (62% yield). *Anal.* Calc. for $C_{35}Cl_2FH_{33}NOPRu$: C, 59.6; H, 4.7; N, 2.0. Found: C, 59.4; H, 4.5; N, 2.3%. FT-IR (Nujol mull cm^{-1}): *v*(NH) 3372(s); *v*(CO) 1586(vs). ^1H NMR (300 MHz, $CDCl_3$): δ (ppm): 13.25 (s, 1H, NH), 8.69 (m, 1H, P–C_6H_4–CO–), 7.90 (m, 2H, N–C_6H_4–F), 7.67–7.48 (m, 11H, 10H PPh_2 + 1H P–C_6H_4–CO–), 7.35 (m, 1H, P–C_6H_4–CO–), 7.06 (m, 2H, N–C_6H_4–F), 6.69 (m, 1H, P–C_6H_4–CO–), 5.87 (d, J_{HH} = 6.9 Hz, 1H, Cy), 5.79 (d, J_{HH} = 6.6 Hz, 1H, Cy), 5.27 (m, 1H, Cy), 4.92 (d, J_{HH} = 5.4 Hz, 1H, Cy), 1.87 (s, 3H, Me–Cy), 1.67 (m, 1H, CH, ^{i}Pr–Cy), 0.87 (d, J_{HH} = 6.9 Hz, 3H, Me, ^{i}Pr- -Cy), 0.01 (d, J_{HH} = 6.6 Hz, 3H, Me, ^{i}Pr–Cy). ^{31}P NMR (300 MHz, $CDCl_3$): δ (ppm): 33.3 (s). ^{19}F NMR (200 MHz, $CDCl_3$): δ (ppm): −114.9 (s). FAB-MS (positive mode) *m*/*z*: 670 (M^+−Cl), 635 (M^+−2Cl).

*2.2.2. Preparation of complexes [RuCl(η⁶-p-cymene)-(o-Ph₂P–C₆H₄–CO–NH–R)][PF₆] (R = ⁱPr (**2a**); R = Ph (**2b**); R = 4-MeC₆H₄ (**2c**); R = 4-FC₆H₄ (**2d**))*

The new complexes were obtained by treating 0.145 mmol of the corresponding complexes [RuCl(η⁶-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–R)]Cl (R = ⁱPr (**1a**); R = Ph (**1b**); R = 4-MeC_6H_4 (**1c**); R = 4-FC_6H_4 (**1d**)) in acetone (20 ml) with stoichiometric KPF_6 (0.145 mmol). After 1/2 h stirring at room temperature, the mixture was filtered to remove KCl, and the resulting orange solution then concentrated to half volume under reduced pressure. Addition of diethyl ether caused precipitation of the new complexes, which were filtered off, air dried and recrystallized from acetone–ether.

[RuCl(η⁶-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–ⁱPr)][PF_6] (**2a**): (85% yield). *Anal.* Calc. for $C_{32}ClF_6H_{36}NOP_2Ru$: C, 50.4; H, 4.8; N, 1.8. Found: C, 50.2; H, 5.0; N, 1.9%. FT-IR (Nujol mull cm^{-1}): *ν*(NH) 3378(s); *ν*(CO) 1596(vs); *ν*(PF_6) 844(s). FAB-MS (positive mode) *m*/*z*: 618 ($M^+ - PF_6$), 583 ($M^+ - PF_6 - Cl$).

[RuCl(η⁶-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–Ph)][PF_6] (**2b**): (80% yield). *Anal.* Calc. for $C_{35}ClF_6H_{34}NOP_2Ru$: C, 52.7; H, 4.3; N, 1.8. Found: C, 52.9; H, 4.5; N, 1.9%. FT-IR (Nujol mull cm^{-1}): *ν*(NH) 3352(s); *ν*(CO) 1592(vs); *ν*(PF_6) 846(s). FAB-MS (positive mode) *m*/*z*: 652 ($M^+ - PF_6$), 617 ($M^+ - PF_6 - Cl$).

[RuCl(η⁶-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–C_6H_4–CH_3)]-[PF_6] (**2c**): (69% yield). *Anal.* Calc. for $C_{36}ClF_6H_{36}NOP_2Ru$: C, 53.3; H, 4.5; N, 1.7. Found: C, 53.6; H, 4.7; N, 2.0%. FT-IR (Nujol mull cm^{-1}): *ν*(NH) 3354(s); *ν*(CO) 1594(vs); *ν*(PF_6) 847(s). FAB-MS (positive mode) *m*/*z*: 666 ($M^+ - PF_6$), 631 ($M^+ - PF_6 - Cl$).

[RuCl(η⁶-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–C_6H_4–F)]-[PF_6] (**2d**): (67% yield). *Anal.* Calc. for $C_{35}ClF_7H_{33}NOP_2Ru$: C, 51.6; H, 4.1; N, 1.7. Found: C, 51.7; H, 4.3; N, 2.0%. FT-IR (Nujol mull cm^{-1}): *ν*(NH) 3354(s); *ν*(CO) 1592(vs); *ν*(PF_6) 845(s). FAB-MS (positive mode) *m*/*z*: 670 ($M^+ - PF_6$), 635 ($M^+ - PF_6 - Cl$).

*2.2.3. Preparation of complexes [RuCl(η⁶-p-cymene)-(o-Ph₂P–C₆H₄–CO–N–R)] (R = ⁱPr (**3a**); R = Ph (**3b**); R = 4-MeC₆H₄ (**3c**); R = 4-FC₆H₄ (**3d**))*

The new complexes were obtained by treating 0.145 mmol of the corresponding complexes [RuCl(η⁶-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–R)][PF_6] (R = ⁱPr (**2a**); R = Ph (**2b**); R = 4-MeC_6H_4 (**2c**); R = 4-FC_6H_4 (**2d**)) in acetone (30 ml) with stoichiometric amount of 1 M KOH aqueous solution. After 1 h stirring at room temperature, the mixture was concentrated to half volume under reduced pressure. Addition of diethyl ether caused precipitation of the new complexes, which were filtered off, washed with water, air dried and recrystallized from acetone–ether.

[RuCl(η⁶-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–N–ⁱPr)] (**3a**): (78% yield). *Anal.* Calc. for $C_{32}ClH_{35}NOPRu$: C, 62.4; H, 5.6; N, 2.3. Found: C, 62.5; H, 5.8; N, 2.5%. FT-IR (Nujol mull cm^{-1}): *ν*(CO) 1586(vs). ^1H NMR (300 MHz, $CDCl_3$): *δ* (ppm): 8.36 (m, 1H, P–C_6H_4–CO–), 7.97 (m, 1H, P–C_6H_4–CO–), 7.60–7.27 (m, 10H, PPh_2), 7.04 (m, 1H, P–C_6H_4–CO–), 6.55 (m, 1H, P–C_6H_4–CO–), 5.68 (d, $J_{HH} = 6.2$ Hz, 1H, Cy), 5.46 (d, $J_{HH} = 6.2$ Hz, 1H, Cy), 5.35 (m, 1H, Cy), 4.99 (d, $J_{HH} = 5.6$ Hz, 1H, Cy), 4.10 (m, 1H, CH, N–ⁱPr), 2.48 (m, 1H, CH, ⁱPr–Cy), 1.89 (s, 3H, Me–Cy), 1.26 (d, $J_{HH} = 6.4$ Hz, 3H, Me, N–ⁱPr), 1.12 (d, $J_{HH} = 6.4$ Hz, 3H, Me, N–ⁱPr), 1.03 (d, $J_{HH} = 7.0$ Hz, 3H, Me,ⁱPr–Cy), (d, $J_{HH} = 7.0$ Hz, 3H, Me, ⁱPr–Cy). ^{31}P NMR (300 MHz, $CDCl_3$): *δ* (ppm): 30.2 (s). FAB-MS (positive mode) *m*/*z*: 617 (M^+), 580 ($M^+ - Cl$).

[RuCl(η⁶-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–N–Ph)] (**3b**): (52% yield). *Anal.* Calc. for $C_{35}ClH_{33}NOPRu$: C, 64.6; H, 5.1; N, 2.1. Found: C, 64.9; H, 5.3; N, 2.2%. FT-IR (Nujol mull cm^{-1}): *ν*(CO) 1596(vs). ^1H NMR (300 MHz, $CDCl_3$): *δ* (ppm): 8.46 (m, 1H, P–C_6H_4–CO–), 8.01-7.36 (m, 11H, 10H PPh_2 + 1H P–C_6H_4–CO), 7.24 (m, 2H, N–Ph), 7.08 (m, 3H, N–Ph), 6.92 (m, 1H, P–C_6H_4–CO–), 6.66 (m, 1H, P–C_6H_4–CO–), 5.35 (m, 2H, Cy), 5.16 (m, $1H_B$, Cy), 4.66 (d, $J_{HH} = 5.7$ Hz, 1H, Cy), 1.66 (s, 3H, Me–Cy), 1.60 (m, 1H, CH, ⁱPr–Cy), 0.77 (d, $J_{HH} = 6.9$ Hz, 3H, Me, ⁱPr–Cy), 0.23 (d, $J_{HH} = 6.9$ Hz, 3H, Me, ⁱPr–Cy). ^{31}P NMR (300 MHz, $CDCl_3$): *δ* (ppm): 28.9 (s). FAB-MS (positive mode) *m*/*z*: 651 (M^+), 61 ($M^+ - Cl$).

[RuCl(η⁶-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–N–C_6H_4–CH_3)] (**3c**): (61% yield). *Anal.* Calc. for $C_{36}ClH_{35}NOPRu$: C, 65.0; H, 5.3; N, 2.1. Found: C, 64.8; H, 5.5; N, 2.3%. FT-IR (Nujol mull cm^{-1}): *ν*(CO) 1572(vs). ^1H NMR (300 MHz, $CDCl_3$): *δ* (ppm): 8.47 (m, 1H, P–C_6H_4–CO–), 8.00 (m, 2H, P–C_6H_4–CO–), 7.57–7.37 (m, 10H PPh_2), 7.02 (m, 4H, N–C_6H_4–CH_3), 6.66 (m, 1H, P–C_6H_4–CO–), 5.41 (m, 2H, Cy), 5.20 (m, 1H, Cy), 4.64 (d, $J_{HH} = 5.6$ Hz, 1H, Cy), 2.31 (s, 3H, Me N–C_6H_4–CH_3), 2.17 (s, 3H, Me–Cy), 1.60 (m, 1H, CH, ⁱPr–Cy), 0.79 (d, $J_{HH} = 7.2$ Hz, 3H, Me, ⁱPr–Cy), 0.21 (d, $J_{HH} = 6.8$ Hz, 3H, Me, ⁱPr–Cy). ^{31}P NMR (300 MHz, $CDCl_3$): *δ* (ppm): 29.1 (s). FAB-MS (positive mode) *m*/*z*: 666 (M^+), 631 ($M^+ - Cl$).

[RuCl(η⁶-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–N–C_6H_4–F)] (**3d**): (54% yield). *Anal.* Calc. for $C_{35}ClFH_{32}NOPRu$: C, 62.8; H, 4.8; N, 2.1. Found: C, 62.9; H, 4.9; N, 2.2%. FT-IR (Nujol mull cm^{-1}): ν(CO) 1586(vs). ^1H NMR (300 MHz, $CDCl_3$): *δ* (ppm): 8.47 (m, 1H, P–C_6H_4–CO–), 8.00 (m, 2H, P–C_6H_4–CO–), 7.60–7.34 (m, 10H, PPh_2), 7.14–6.91 (m, 4H, N–C_6H_4–F), 6.68 (m, 1H, P–C_6H_4–CO–), 5.38 (m, 2H, Cy), 5.20 (m, 1H, Cy), 4.71 (d, $J_{HH} = 5.8$ Hz, 1H, Cy), 1.71 (m, 1H, CH, ⁱPr–Cy), 1.24 (s, 3H, Me–Cy), 0.83 (d, $J_{HH} = 7.2$ Hz, 3H, Me, ⁱPr–Cy), 0.29 (d, $J_{HH} = 7.2$ Hz, 3H, Me, ⁱPr–Cy). ^{31}P NMR (200 MHz, $CDCl_3$): *δ* (ppm): 29.1 (s). ^{19}F NMR (300 MHz, $CDCl_3$): *δ* (ppm): −124.1 (s). FAB-MS (positive mode): *m*/*z*: 670 (M^+), 635 ($M^+ - Cl$).

*2.3. Crystal structure determination of **2b–2d***

Crystals suitable for a diffraction study were prepared by slow diffusion of hexane into their dichloromethane solutions. Data collection was performed at −173 °C on

Table 1
Crystal data and structure refinement for compounds **2b–d**

	2b	**2c** · $1/2CH_2Cl_2$	**2d**
Empirical formula	$C_{35}H_{34}ClF_6NOP_2Ru$	$C_{36.5}H_{37}Cl_2F_6NOPRu$	$C_{35}H_{33}ClF_7NOPRu$
Formula weight	797.09	853.58	784.11
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P*21/*n*	*P*21/*n*	*P*21/*n*
Unit cell dimensions			
a (Å)	9.6313(4)	9.5651(4)	9.6494(7)
b (Å)	24.0527(10)	24.4322(9)	24.0892(18)
c (Å)	15.6647(6)	15.7079(6)	15.6671(12)
β (°)	93.0390(10)	92.8620(10)	93.0320(10)
V (Å^3)	3623.8(3)	3666.3(2)	3636.7(5)
Z	4	4	4
D_{calc} (Mg m^{-3})	1.461	1.546	1.432
Absorption coefficient (mm^{-1})	0.654	0.722	0.612
F(000)	1616	1732	1588
Crystal size (mm)	0.29 0.17 × 0.10	0.24 × 0.10 × 0.09	0.32 × 0.22 × 0.14
θ Range for data collection (°)	1.55–28.23	1.67–28.23	1.55–28.07
Index ranges	$-12 \leqslant h \leqslant 12$, $-31 \leqslant k \leqslant 30$, $-20 \leqslant l \leqslant 20$	$-12 \leqslant h \leqslant 12$, $-32 \leqslant k \leqslant 31$, $-20 \leqslant l \leqslant 20$	$-12 \leqslant h \leqslant 12$, $-31 \leqslant k \leqslant 30$, $-20 \leqslant l \leqslant 20$
Reflections collected	42063	42722	41122
Independent reflections [R_{int}]	8456 [0.0285]	8586 [0.0460]	8395 [0.0282]
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/parameters	8456/424	8586/443	8395/433
R^a, Rw^b [I>2σ(I)]	$R_1 = 0.0500$, $wR_2 = 0.1625$	$R_1 = 0.0496$, $wR_2 = 0.1097$	$R_1 = 0.0791$, $wR_2 = 0.2310$
R^a, Rw^b [all data]	$R_1 = 0.0555$, $wR_2 = 0.1675$	$R_1 = 0.0603$, $wR_2 = 0.1146$	$R_1 = 0.0827$, $wR_2 = 0.2335$
S^c	1.738	1.117	1.141
Maximum, minimum Δ*ρ* (e Å^{-3})	4.849, −0.603	1.321, −0.726	6.095, −1.009

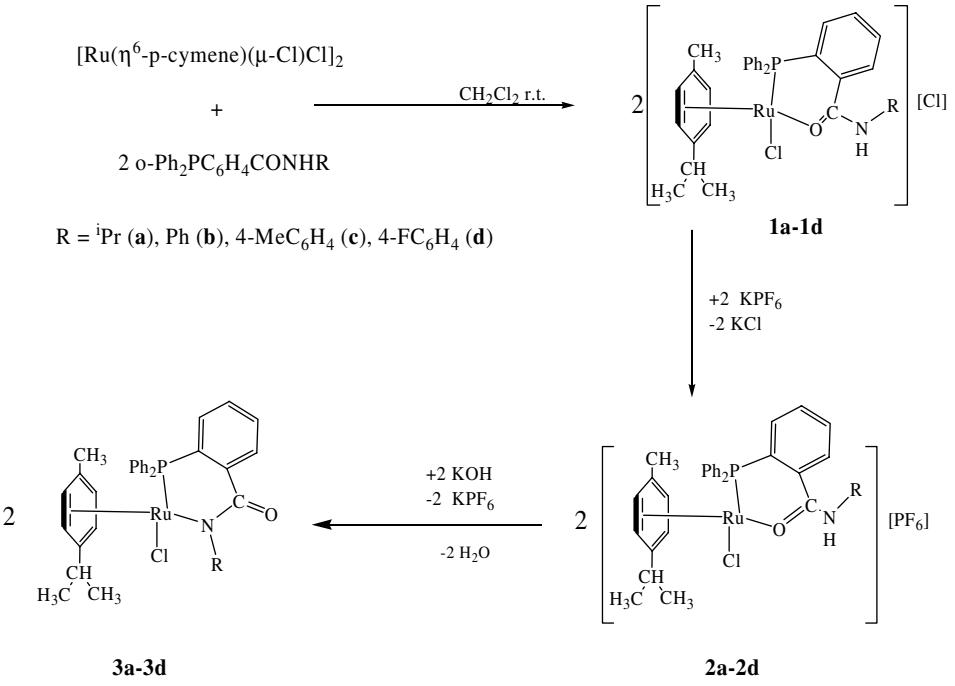
[a] $R = \sum |F_0| - |F_C| / \sum |F_0|$.
[b] $Rw = \{\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]\}^{1/2}; w = 1/\sigma^2(|F_0^2|)$.
[c] $S = \left[\sum [w(F_0^2 - F_c^2)^2] / (N_{obs} - N_{param})\right]^{1/2}$.

a Bruker Smart CCD diffractometer with a nominal crystal to detector distance of 6.2 cm. Diffraction data were collected based on a ω scan run. A total of 2524 frames were collected at 0.3° intervals and 10 s per frame. The diffraction frames were integrated using the SAINT package [30] and corrected for absorption with SADABS [31].

The structures were solved by direct methods [32] and refined by full-matrix least-squares techniques using anisotropic thermal parameters for non-H atoms [32] (Table 1). Hydrogen atoms were introduced in calculated positions and refined during the last stages of the refinement.

3. Results and discussion

In dichloromethane, the precursor [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ reacts at room temperature with *o*-Ph_2P–C_6H_4–CO–NH–R: (R = ^{i}Pr (**a**); R = Ph (**b**); R = 4-MeC_6H_4 (**c**); R = 4-FC_6H_4 (**d**)) (see Section 2 for details) yielding the orange compounds of general formula [RuCl(η^6-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–R)]Cl (R = ^{i}Pr (**1a**); R = Ph (**1b**); R = 4-MeC_6H_4 (**1c**); R = 4-FC_6H_4 (**1d**)) in which an κ^2-*P*,*O* coordination mode for diphenylphosphine–benzamide ligands is observed. The characterizing spectroscopic and analytical data are in agreement with the proposed structures presented in Scheme 1. The appearance of the *ν*(CO) absorptions lowered by approximately 30 cm^{-1} with respect to those of the free ligands gives a first support to the formation of a P^O chelate around the Ru centre [27,28]. A medium *ν*(NH) vibration, shifted towards higher wavenumbers than free ligands, is the other remarkable aspect found in the IR spectra. The FAB mass spectrometry displays fragments corresponding to ($M^+ - Cl$) and ($M^+ - 2Cl$). The presence of diphenylphosphine–benzamide ligands is also confirmed by $^{31}P\{^1H\}$ NMR spectroscopy, the spectra consisting of singlets around 33 ppm. This range of chemical shift is typical of a P^O coordination of these ligands to palladium [27] (P-monodentate around 40 ppm) and is coincidental with the one shown later for **2a–d** ruthenium complexes. Further evidence of the proposed coordination comes from the ^1H NMR spectroscopy. It has been reported that heterobidentate P^X chelates produce chiral metal centers when bound to arene–ruthenium complexes, and such chirality in *p*-cymene complexes produces diasterotopic methyls in the isopropyl fragment, which serve as detector of the chirality at the metal [17,33]. Also four different aromatic CH



Scheme 1. Preparation of phosphino-amide derivatives.

groups are usually seen when P^X chelates are present, whereas only two CH's and one isopropylic methyl resonance are observed if the ligand acts as P-monodentate. In our case, the ^{1}H NMR spectra of complexes **1a**–**d** display two doublets attributed to diasterotopic methyl groups in the isopropyl of *p*-cymene, as well as four CH aromatic resonances.

It is worth it to mention that no evidence of equilibrium between coordination isomers [RuCl(η^6-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–R)]Cl and [$RuCl_2$(η^6-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–R)] was observed. The strong chelating ability of diphenylphosphine–benzamide ligands towards ruthenium is emphasized by the fact that our attempts to open the chelate ring with pyridine or bipyridine produced mixtures of compounds in which the arene had been removed.

This result is in contrast to our previous studies on the behaviour of these ligands coordinating palladium(II) [27], since κ^1-*P* binding mode was adopted when chloride ion was in competition for a position around the metal center. Only forcing the chloride exit with a silver salt that provided an appropriate counteranion the chelating coordination was achieved. Regarding ruthenium(II) arene complexes with potentially N̂P or ÔP hemilabile ligands, most of the studies reported lately starting from [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ show that direct reaction with this precursor yields neutral complexes where the ligand is κ^1*P*-coordinated to the metal [16–25]. Once again the subsequent treatment with halide abstractors such silver or sodium salts (mostly BF_4^-, BPh_4^-, $CF_3SO_3^-$, PF_6^- or SbF_6^-) preferably in polar solvents provided a route to the chelating cationic compounds. Strong dependence with the solvent has been reported in the preparation of complexes [Ru(η^6-arene)(κ^1-*P*-N*)Cl_2]/[Ru(η^6-arene)(κ^2-*P*-*N**)Cl]Cl [34]. Thus, neutral complexes were obtained in dichloromethane while same reactions in methanol afforded the corresponding chelate complexes, that also were prepared by adding small amounts of methanol to solutions of [Ru(η^6-arene)(κ^1-*P*-N*)Cl_2] in chloroform. A mixture of neutral and cationic complexes has been reported when the P^N ligand was 2-(diphenylphosphinomethyl)pyridine [35]. In complexes **1a**–**d** even working in dichloromethane the chelating mode of diphenylphosphine–benzamides is preferred. Such behaviour has been previously found for chiral ruthenium complexes of bidentate bisphosphine monoxide ligands [Ru(η^6-arene)(κ^1-Ph_2PC(R)P(O)Ph_2)Cl_2]/[Ru(η^6-arene)(κ^2-Ph_2PC(R)P(*O*)Ph_2)Cl]Cl [33], for which an equilibrium in dichloromethane between the κ^1-*P* complexes and their respective κ^2-*P*,*O* coordination isomers is reported. The steric bulk in the ligands backbones seems to drive the chelation, and cationic κ^2-complexes were obtained with bulkier ligands, the κ^1-*P* complex with the lighter and mixtures of two coordination isomers for middle sized. In this previous study, as happens for complexes **1a**–**d**, conversion of the chloride salts to those with another counteranion allowed the preparation of crystals suitable for X-ray diffraction.

The reaction in acetone of compounds **1a**–**d** with stoichiometric KPF_6 under the mild conditions described in the experimental section yielded complexes [RuCl(η^6-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–NH–R)][PF_6] (R = ^{i}Pr (**2a**); R = Ph (**2b**); R = 4-MeC_6H_4 (**2c**); R = 4-FC_6H_4 (**2d**)) (Scheme 1). The presence of a P,O-chelate is supported by the appearance of the *ν*(CO) vibration in the same range

mentioned above for complexes **1a**–**d**. Other features of IR spectra are a sharp NH absorption around 3355 cm^{-1} and a single band at ca. 845 cm^{-1} that indicates the presence of PF_6^- also detected by ^{19}F and ^{31}P NMR. The rest of NMR data confirm the proposed formulae and, as expected, are quite similar to those of precursor complexes in chemical shift, number and multiplicity of signals and therefore have not been included in experimental section. Thus, again the asymmetry of the MLL′L″ three-legged fragment and consequent chirality at Ru centre raised diasterotopic isopropylic methyl groups and differentiated aromatic CH resonances.

As mentioned above, changing chloride by PF_6^- made possible to grow X-ray quality crystals that after diffraction study have confirmed the structures of **2b**–**d**. Each of them consisted of a cationic complex [RuCl(η^6-*p*-cymene)-(*o*-Ph_2P–C_6H_4–CO–NH–R)]$^+$ (Figs. 1–3, respectively) and an anion $[PF_6]^-$. While **2c** crystallizes with 1/2 molecule of dichoromethane, **2b** and **2d** also contain some unrefined solvent that causes high values of maximum $\Delta\rho$. As can be inferred from data in Table 1 the three complexes are isomorphous. Selected bond lengths and angles listed in Table 2 are very similar. Moreover, molecular conformation in the three compounds are similar, the phenyl ring bonded to the iminic group is oriented towards the isopropyl group from the η^6-arene, with distances from the centroid to the (Me)$_2$C–*H* hydrogen atom of 3.081, 2.948 and 3.010 Å for complexes **2b**, **2c**, and **2d**, respectively. The molecules displayed a pseudooctahedral three-legged piano-stool geometry around the ruthenium atom with the arene, the corresponding diphenylphosphine–benzamide ligand and the chloride completing the coordination. The distortion of the octahedral geometry is shown by the values of the O(1)–Ru(1)–P(1), O(1)–Ru(1)–Cl(1), and P(1)–Ru(1)–Cl(1) angles, in the range 82.49(8)–88.02(5)° (see Table 2).

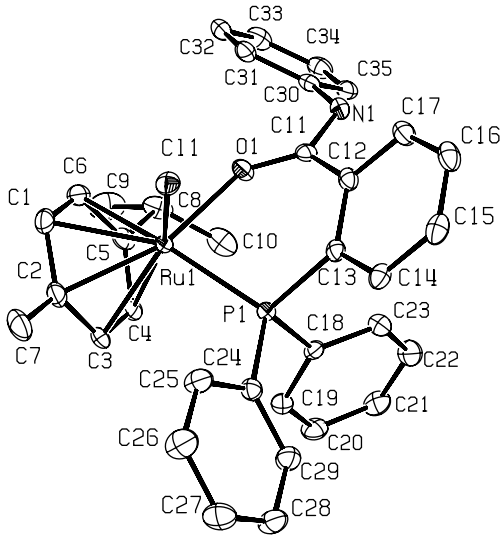


Fig. 1. ORTEP diagram of cation complex **2b** with the atom numbering scheme; thermal ellipsoids are drawn at the 50% probability level.

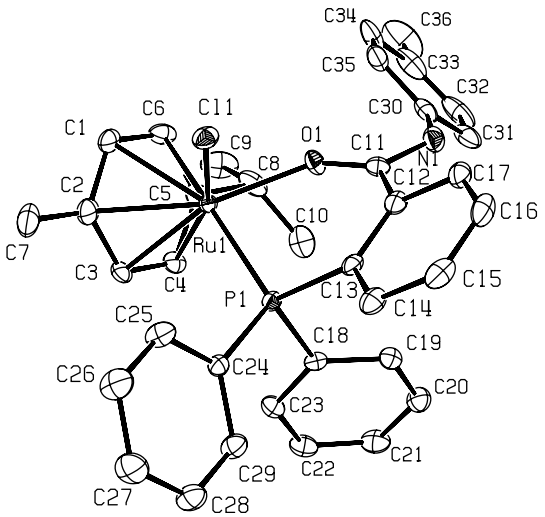


Fig. 2. ORTEP diagram of cation complex **2c**; thermal ellipsoids are drawn at the 50% probability level.

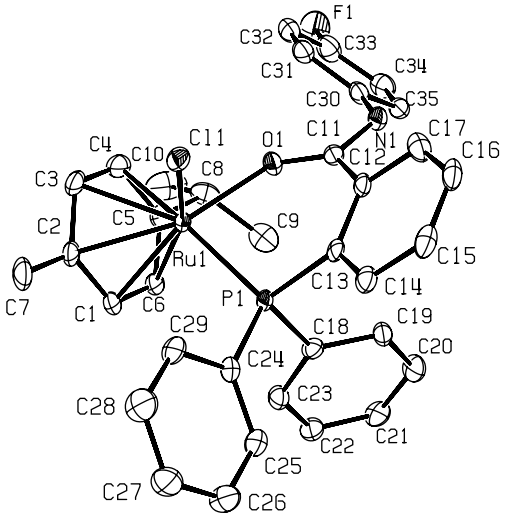


Fig. 3. ORTEP diagram of cation complex **2d**. Thermal ellipsoids are drawn at 50% probability.

The angles between the centroid of the arene ring, Ru, O, P, and Cl atoms are in the 125–133° range. The Ru–Cl bond distances fall within the range of reported values [16,24]. The average Ru–C bond distance is around 2.209 Å, whereas the distance between the ruthenium atom and the centroid of the ring is 1.693 Å for the three compounds. As has been previously reported [17 and references therein] a heterogeneous distribution of the Ru–C(*p*-cymene) bond distances was observed in the sense that distances *trans* to the more strongly donating phosphine group are longer that those *trans* to the chlorine atoms.

The diphenylphosphine–benzamide ligands are κ^2-*P*,*O* bonded to ruthenium forming a six-membered metallacycle that in the three compounds display a 10° distorted *screw–boat* conformation, according to the classification of Allen and Taylor [36].

Table 2
Selected distances (Å) and angles (°) of the new complexes

	2b	2c	2d
Ru(1)–O(1)	2.114(3)	2.114(2)	2.109(4)
Ru(1)–P(1)	2.3191(10)	2.3167(8)	2.3194(15)
Ru(1)–Cl(1)	2.3930(9)	2.3926(8)	2.3936(15)
Ru(1)–C(1)	2.237(4)	2.235(3)	2.166(6)
Ru(1)–C(2)	2.195(4)	2.189(3)	2.199(6)
Ru(1)–C(3)	2.169(4)	2.171(3)	2.232(6)
Ru(1)–C(4)	2.201(4)	2.205(3)	2.243(6)
Ru(1)–C(5)	2.209(4)	2.207(3)	2.205(6)
Ru(1)–C(6)	2.243(4)	2.240(6)	2.206(6)
Ru(1)–$C_{(average)}$	2.209	2.208	2.209
Ru(1)–$Cent_{(p-cimeno)}$	1.693	1.693	1.693
O(1)–C(11)	1.256(5)	1.250(4)	1.258(7)
O(1)–Ru(1)–P(1)	82.49(8)	82.56(7)	82.73(12)
O(1)–Ru(1)–Cl(1)	87.09(8)	87.41(7)	86.96(12)
P(1)–Ru(1)–Cl(1)	87.85(3)	87.75(3)	88.02(5)
O(1)–Ru(1)–Centr	125.73	125.30	125.62
P(1)–Ru(1)–Centr	132.29	132.34	132.04
Cl(1)–Ru(1)–Centr	126.32	126.49	126.46

The most significant difference between the solid state conformation of the free ligand **b** and the coordinated ligand in **2b** is the angle between planes O(1)–C(11)–C(12) and C(12)–C(13)–P(1) (53.11(13)° and 30.9(4)°, respectively). Similar values are found for complexes **2c** 30.6(3)° and **2d** 30.0(6)°. This value also diminishes slightly once the ligand is complexed to Ni or Pd: 38.4(2)°, 33.3(2)° and 41.3(2)° [28]. The relative position of the phenyl rings bonded to the N–CO-moiety stays without major variation upon coordination. In the free ligand both rings are nearly perpendicular (81.7°) and so happens in **2b** (79.8°), **2c** (81.8°) and **2d** (81.3°) while in the reported Ni complex the phenyl bonded to N rotated, becoming both rings parallels (10.2°) [28].

The new complexes exhibit intermolecular hydrogen bonding between F from PF_6^- and N(1) atoms (distance N(1)···F ranges 2.912–2.916 Å and angle N(1)–H···F ranges 152.37–155.01°).

In order to induce amide deprotonation in the ligands, and a likely κ^2-*P*,*N* coordination mode according to our previous studies with other metals, compounds **2a**–**d** were treated with KOH(aq) in acetone, as explained in the experimental section, to yield neutral complexes [RuCl(η^6-*p*-cymene)(*o*-Ph_2P–C_6H_4–CO–N–R)] (R = ^{i}Pr (**3a**); R = Ph (**3b**); R = 4-MeC_6H_4 (**3c**); R = 4-FC_6H_4 (**3d**)) (Scheme 1). The loss of both *ν*(NH) and *ν*(PF) bands in their IR spectra with regards to precursor compounds confirmed that the proposed reactions took place. The characterization in solid state was completed with the FAB mass spectrometry, that shows fragments at [M^+] and [$M^+ - Cl$]. A singlet shifted at ca. 7 ppm highfield compared to P^O-chelated compounds characterizes the $^{31}P\{^1H\}$ NMR spectra, and the expected pattern is observed in the ^1H NMR with significant absence of amidic proton resonance at low field. The solutions of new complexes turned black after 48 h thus preventing the obtention of crystals suitable for a diffraction analysis and a conclusive assertion about the coordination mode. Absence of arene was observed in the subsequent decomposition products.

4. Conclusion

Twelve new (η^6-*p*-cymene)–ruthenium(II) complexes with diphenylphosphine–benzamide ligands exhibiting different coordination modes have been prepared and characterized by spectroscopic techniques and single crystal X-ray diffraction analysis. Stronger κ^2-*P*,*O* chelating ability towards ruthenium can be attributed to these ligands in comparison with our previous results dealing with nickel and palladium. Also if compared with other potentially hemilabile P,O- or P,N-ligands in its reaction with the precursor [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$, that usually yields P- monodentate compounds.

Acknowledgements

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Appendix A. Supplementary material

CCDC 631104, 631105 and 631106 contain the supplementary crystallographic data for **2b**, **2c** and **2d**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +(44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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