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New neutral and cationic η^6-arene ruthenium complexes with phosphine and amine ligands: syntheses and molecular structures of $[(\eta^6\text{-}p\text{-cymene})Ru(NH_2CH_2C_6H_5)Cl_2]$, $[(\eta^6\text{-}C_6Me_6)Ru(PPh_2Py)Cl_2]$ and $[(\eta^6\text{-}C_6Me_6)Ru(PPh_2Py)Cl]^+$

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Abstract

The complex $[\{(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}Cl)Cl\}_2]$ (**1**) reacts with benzylamine to give a neutral N-coordinated complex of the type $[(\eta^6\text{-}p\text{-cymene})Ru(NH_2CH_2C_6H_5)Cl_2]$ (**2**). The complex $[(\eta^6\text{-}p\text{-cymene})Ru(PPh_3)Cl_2]$ (**3**) reacts with amine ligands to yield chiral complexes $[(\eta^6\text{-}p\text{-cymene})Ru(PPh_3)(NH_2\text{-}R)Cl]^+$ [R = $CH_2C_6H_5$ (**4a**), p-ClC_6H_4 (**4b**), p-$NO_2C_6H_4$ (**4c**)]. Complexes **1** and **3** react with N,N-donor chelating 1,2-phenylenediamine (PDA) giving cationic complexes **5** and **6**, respectively. The complex $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}Cl)Cl]_2$ (**7**) reacts with diphenyl-2-pyridylphosphine to yield a neutral P-coordinated ruthenium(II) complex $[(\eta^6\text{-}C_6Me_6)Ru(PPh_2Py)Cl_2]$ (**8**) as well as a cationic P,N-chelating complex $[(\eta^6\text{-}C_6Me_6)Ru(PPh_2Py)Cl]^+$ (**9**). The complex **9** undergoes substitution reactions with acetonitrile and 1,1-diphenyl-2-propyn-1-ol ligands. These complexes were characterized by FT-IR and FT-NMR spectroscopy as well as by analytical data. The molecular structures of the representative complexes $[(\eta^6\text{-}p\text{-cymene})Ru(NH_2CH_2C_6H_5)Cl_2]$ (**2**), $[(\eta^6\text{-}C_6Me_6)Ru(PPh_2Py)Cl_2]$ (**8**) and $[(\eta^6\text{-}C_6Me_6)Ru(PPh_2Py)Cl]BF_4$ (**9**) were established by single-crystal X-ray diffraction studies.

Keywords: Hexamethylbenzene; *p*-Cymene; Diphenyl-2-pyridylphosphine; Amines; Ruthenium complexes

1. Introduction

Arene ruthenium(II) complexes have been the subject of intense research in the field of organometallic chemistry during recent years [1]. The catalytic activity of these complexes ranges from hydrogen transfer [2] to ring closing metathesis [3]. Anti-tumor activity exhibited by some water-soluble arene ruthenium(II) complexes has also evoked interest in recent years [4]. We had earlier reported the reactivity differences of *p*-cymene ruthenium(II) and hexamethylbenzene ruthenium(II) dimers towards azide and pyrazoles [5,6]. Recent advances in catalytic amination have been based on the use of early transition metal and f-block element complexes [7]. However, catalytic additions of amines, H-NR_2, to non-activated double or triple bonds mediated by late-transition-metal complexes are still rare [7].

Diphenyl(2-pyridyl)phosphine (Fig. 1) is a versatile ligand which can coordinate to a metal in monodentate, chelating and bridging modes, depending on the requirements at the metal center [8,9]. Recently, we had conducted reactivity studies of this ligand with $[Cp^*MCl_2]_2$

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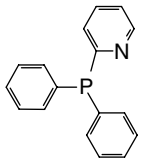


Fig. 1.

(M = Rh, Ir) dimers [10]. In a continuation of our previous work, we report in this communication the syntheses of neutral and chiral amine complexes of *p*-cymene ruthenium as well as hexamethylbenzene ruthenium complexes with the diphenyl(2-pyridyl)phosphine ligand.

2. Experimental

All the solvents were dried and distilled before use following the standard procedures. $RuCl_3 \cdot 3H_2O$ was purchased from Arora Matthey Ltd. and used as received. α-Phellandrene (Fluka), hexamethylbenzene (Acros Organics), benzylamine (Merck), diphenyl(2-pyridyl)phosphine (Aldrich) and 1,1-diphenyl-2-propyn-1-ol (Aldrich) were used as received. The precursor complexes [{(η^6-arene)Ru(μ-Cl)Cl}$_2$] [arene = *p*-cymene (**1**), hexamethylbenzene (**7**)] and [(η^6-*p*-cymene)Ru(PPh_3)Cl_2] (**3**) were prepared according to the literature procedures [11,12]. Elemental analyses were performed in a Perkin–Elmer 2400 CHN/O analyzer. Infrared spectra were recorded on a Perkin–Elmer Model 983 spectrophotometer with samples prepared as KBr and CsI pellets. Electronic spectra were recorded on a Hitachi-300 spectrophotometer. NMR spectra were taken on Bruker AMX-400 (400 MHz) and Bruker ACF-300 (300 MHz) spectrometers with tetramethylsilane as an internal standard. ^{31}P {^1H} NMR chemical shifts are reported relative to H_3PO_4 (85%).

2.1. Preparation of [(η^6-*p*-cymene)Ru($NH_2CH_2C_6H_5$)Cl_2] (**2**)

A mixture of [{(η^6-*p*-cymene)Ru(μ-Cl)Cl}$_2$] (**1**) (0.1 g, 0.163 mmol) and benzylamine (0.44 g, 0.408 mmol) in dichloromethane (20 ml) was stirred at room temperature for 3 h. The orange solution was concentrated under reduced pressure. The residue was extracted with dichloromethane and filtered through a short silica gel column. The resulting solution was reduced in volume to about 2 ml and hexane (20 ml) was added to give an orange-yellow compound, which was recrystallized from the mixture of dichloromethane and hexane to give orange crystals.

Yield: 89.62% (0.12 g). Elemental *Anal*. Calc. (%) for $C_{17}H_{23}RuNCl_2$: C, 49.39; H, 5.61; N, 3.38. Found: C, 49.41; H, 5.94; N, 3.34%.

^1H NMR ($CDCl_3$, δ): 1.30 (d, 6H, J_{H-H} = 6.96 Hz, CH_3), 2.23 (s, 3H, CH_3), 2.98 (sep, 1H), 3.17 (b, 2H, NH_2), 4.14 (t, 2H, J_{H-H} = 7.64 Hz, CH_2), 5.22 (d, 2H, J_{H-H} = 5.88 Hz, cymene), 5.39 (d, 2H, J_{H-H} = 5.88 Hz, cymene), 7.31–7.38 (m, 5H, Ph).

IR (KBr pellets, cm^{-1}): *v*(N–H) 3287 (s), 3221 (s). IR (CsI pellets, cm^{-1}): *v*(Ru–Cl) 286 (s).

UV–vis (CH_2Cl_2): λ_{max} = 393 nm.

2.2. Preparation of chiral complexes

2.2.1. Preparation of [(η^6-*p*-cymene)Ru(PPh_3)($NH_2CH_2C_6H_5$)Cl]PF_6 (**4a**)

A mixture of [(η^6-*p*-cymene)Ru(PPh_3)Cl_2] (**3**) (0.1 g, 0.175 mmol), benzylamine (0.028 g, 0.263 mmol) and NH_4PF_6 (0.043 g, 0.263 mmol) in dichloromethane and methanol (2:1) (15 ml) mixture was stirred at room temperature for 2 h. The orange-yellow solution was concentrated to dryness. The residue was dissolved in dichloro-methane and filtered to remove NH_4Cl. The filtrate was concentrated to 2 ml, and addition of excess hexane gave an orange-yellow complex. The complex was filtered and washed with diethylether and dried under vacuum.

Yield: 71.01% (0.098 g). Elemental *Anal*. Calc. (%) for $C_{35}H_{38}RuNClP_2F_6$: C, 53.54; H, 4.87; N, 1.78. Found: C, 53.51; H, 4.66; N, 1.82%.

^1H NMR ($CDCl_3$, δ): 1.19 (d, 3H, J_{H-H} = 6.36 Hz, CH_3), 1.34 (d, 3H, J_{H-H} = 6.76 Hz, CH_3), 2.17 (s, 3H, CH_3), 2.72 (b, 2H, NH_2), 2.98 (sep, 1H, CH), 4.08 (t, 2H, J_{H-H} = 10.4 Hz, CH_2), 5.29 (d, 2H, J_{H-H} = 5.64 Hz, cymene), 5.42 (d, 2H, J_{H-H} = 5.64 Hz, cymene), 7.54–7.17 (m, 20H, Ph).

^{31}P {^1H} NMR ($CDCl_3$, δ): 36.05 (s).

IR (KBr pellets, cm^{-1}): *v*(N–H) 3287 (s), 3224 (s), *v*(P–F) 839 (s). IR (CsI pellets, cm^{-1}): *v*(Ru–Cl) 276 (s).

2.2.2. Preparation of [(η^6-*p*-cymene)Ru(PPh_3)($NH_2C_6H_4$-*p*-Cl)Cl]BF_4 (**4b**)

A mixture of [(η^6-*p*-cymene)Ru(PPh_3)Cl_2] (**3**) (0.1 g, 0.175 mmol), *p*-chloroaniline (0.044 g, 0.35 mmol) and NH_4BF_4 (0.037 g, 0.35 mmol) in methanol was refluxed for 2 h. The solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and then filtered. The solution was concentrated to 2 ml and an excess of hexane was added for precipitation. The orange compound was washed with diethylether and dried under vacuum.

Yield: 70.23% (0.092 g). Elemental *Anal*. Calc. (%) for $C_{34}H_{35}RuNCl_2PBF_4$: C, 54.64; H, 4.72; N, 1.87. Found: C, 54.61; H, 4.68; N, 1.84%.

^1H NMR ($CDCl_3$, δ): 1.10 (d, 3H, J_{H-H} = 6.92 Hz, CH_3), 1.25 (d, 3H, J_{H-H} = 6.92 Hz, CH_3), 2.16 (s, 3H, CH_3), 2.87 (sep, 1H, CH), 4.90 (s, 2H, NH_2), 4.98 (d, 2H, J_{H-H} = 5.84 Hz, cymene), 5.03 (d, 2H, J_{H-H} = 5.4 Hz), 5.08 (d, 2H, J_{H-H} = 5.84 Hz, cymene), 5.23 (d, 2H, J_{H-H} = 6.08 Hz), 7.31–7.88 (m, 15H, Ph).

^{31}P {^1H} NMR ($CDCl_3$, δ): 21.25 (s).

IR (KBr pellets, cm^{-1}): ν(N–H) 3429 (s), 3239 (s), ν(B–F) 1096 (s). IR (CsI pellets, cm^{-1}): ν(Ru–Cl) 273 (s).

2.2.3. Preparation of [(η^6-p-cymene)Ru(PPh_3)(NH_2-C_6H_4-p-NO_2)Cl]BF_4 (**4c**)

A mixture of [(η^6-*p*-cymene)Ru(PPh_3)Cl_2] (**3**) (0.1 g, 0.175 mmol), *p*-nitroaniline (0.048 g, 0.35 mmol) and NH_4BF_4 (0.037 g, 0.35 mmol) in methanol was stirred at room temperature for 14 h. A yellow colored product separated out. The complex was washed with diethylether and dried under vacuum.

Yield: 71.42% (0.095 g). Elemental *Anal*. Calc. (%) for $C_{34}H_{35}RuN_2O_2ClPBF_4$: C, 53.88; H, 4.65; N, 3.69. Found: C, 53.82; H, 4.56; N, 3.71%.

^{1}H NMR ($CDCl_3$, δ): 1.12 (d, 3H, J_{H-H} = 7.56 Hz, CH_3), 1.31 (d, 3H, J_{H-H} = 6.92 Hz, CH_3), 2.19 (s, 3H, CH_3), 2.95 (sep, 1H, CH), 4.40 (s, 2H, NH_2), 5.37 (d, 2H, J_{H-H} = 5.96 Hz), 5.50 (d, 2H, J_{H-H} = 5.88 Hz, cymene), 6.69 (d, 2H, J_{H-H} = 5.86 Hz, cymene), 7.68–7.34 (m, 15H, Ph), 8.10 (d, 2H, J_{H-H} = 8.96 Hz).

^{31}P {^{1}H} NMR ($CDCl_3$, δ): 26.54 (s).

IR (KBr pellets, cm^{-1}): ν(N–H) 3317 (s), 3246 (s), $\nu(NO_2)$ 1520 (s), 1341 (s), ν(B–F) 1096 (s). IR (CsI pellets, cm^{-1}): ν(Ru–Cl) 283 (s).

2.3. Preparation of [(η^6-p-cymene)Ru(PDA)Cl]BF_4 (**5**) (PDA = 1,2-phenylenediamine)

A suspension of the complex [{(η^6-*p*-cymene)Ru(μ-Cl)Cl}$_2$] (**1**) (0.1 g, 0.163 mmol) in methanol (20 ml) was treated with 1,2-phenylenediamine (0.035 g, 0.326 mmol) and NH_4BF_4 (0.05 g, 0.489 mmol) and allowed to stir at room temperature for 10 h. The solvent was removed under reduced pressure. The orange mass was dissolved in dichloromethane and filtered. The filtrate was concentrated to 2 ml and an excess of hexane added for precipitation. The orange-colored product was washed with diethylether and dried under vacuum.

Yield: 58.55% (0.089 g). Elemental *Anal*. Calc. (%) for $C_{16}H_{22}RuN_2ClBF_4$: C, 41.26; H, 4.76; N, 6.01. Found: C, 41.42; H, 4.93; N, 5.96%.

^{1}H NMR ($CDCl_3$, δ): 0.86 (d, 3H, J_{H-H} = 2.45 Hz, CH_3, cymene), 1.15 (d, 3H, J_{H-H} = 2.91 Hz, CH_3, cymene), 2.26 (s, 2H, CH_3, cymene), 3.00 (sep, 1H), 5.00 (d, 4H, J_{H-H} = 12.23 Hz, NH_2), 5.70 (d, 2H, J_{H-H} = 5.76 Hz, cymene), 5.93 (d, 2H, J_{H-H} = 5.76 Hz, cymene), 7.16 (dd, 2H, 2.27 Hz), 8.37 (d, 2H, 8.58 Hz).

IR (KBr pellets, cm^{-1}): ν(N–H) 3346 (s), 3232 (s), ν(B–F) 1082 (s).

2.4. Preparation of [(η^6-p-cymene)Ru(PPh_3)(PDA)](BF_4)$_2$ (**6**)

This complex was prepared by following the above-mentioned procedure (**5**), except that the complex [(η^6-*p*-cymene)Ru(PPh_3)Cl_2] (**3**) was used in place of complex [{(η^6-*p*-cymene)Ru(μ-Cl)Cl}$_2$] (**1**). The complex was isolated as an orange-red micro-crystalline solid.

Yield: 70.8% (0.097 g). Elemental *Anal*. Calc. (%) for $C_{34}H_{37}RuN_2PB_2F_8$: C, 52.40; H, 4.78; N, 3.59. Found: C, 52.06; H, 4.82; N, 3.37%.

^{1}H NMR ($CDCl_3$, δ): 0.93 (d, 3H, J_{H-H} = 6.69 Hz, CH_3), 1.11 (d, 3H, J_{H-H} = 6.67 Hz, CH_3), 2.20 (s, 3H, CH_3), 2.87 (sep, 1H), 4.61 (d, 4H, J_{H-H} = 10.74 Hz, NH_2), 5.63 (d, 2H, J_{H-H} = 5.85 Hz, cymene), 5.86 (d, 2H, J_{H-H} = 5.85 Hz, cymene), 6.92 (d, 2H, J_{H-H} = 6.46 Hz), 7.16–7.76 (m, 17H, Ph).

IR (KBr pellets, cm^{-1}): ν(N–H) 3326(s), 3192(s), ν(B–F) 1089(s).

2.5. Preparation of [(η^6-C_6Me_6)Ru(PPh_2Py)Cl_2] (**8**)

A mixture of [{(η^6-C_6Me_6)Ru(μ-Cl)Cl}$_2$] (**7**) (0.1 g, 0.149 mmol) and diphenyl(2-pyridyl)phosphine (PPh_2Py) (0.098 g, 0.374 mmol) in dichloromethane (20 ml) was stirred at room temperature for 1 h. The orange solution was concentrated to 3 ml and an excess of hexane was added for precipitation. The orange microcrystalline product was washed with diethylether and dried under vacuum.

Yield: 79.21% (0.141 g). Elemental *Anal*. Calc. (%) for $C_{29}H_{32}RuNCl_2P$: C, 58.29; H, 5.39; N, 2.34. Found: C, 58.32; H, 5.36; N, 2.39%.

^{1}H NMR ($CDCl_3$, δ): 1.76 (s, 18H, HMB), 7.13–8.11 (m, 13H), 8.57 (d, 1H, J_{H-H} = 6.24 Hz).

^{31}P {^{1}H} NMR ($CDCl_3$, δ): 25.88 (s). IR (CsI pellets, cm^{-1}): ν(Ru–Cl) 286 (s).

2.6. Preparation of [(η^6-C_6Me_6)Ru(PPh_2Py)Cl]BF_4 (**9**)

Method 1: A mixture of [{(η^6-C_6Me_6)Ru(μ-Cl)Cl}$_2$] (**7**) (0.1 g, 0.149 mmol), diphenyl(2-pyridyl)phosphine (PPh_2Py) (0.196 g, 0.748 mmol) and NH_4BF_4 (0.078 g, 0.748 mmol) in methanol were stirred at room temperature for 2 h. The yellow solution was concentrated under reduced pressure. The yellow residue was dissolved in dichloro-methane and filtered. The filtrate was concentrated to 2 ml and an excess of hexane was added for precipitation. The yellow-colored product was washed with diethylether and dried under vacuum.

Yield: 82.47% (0.16 g). Elemental *Anal*. Calc. (%) for $C_{29}H_{32}RuNClPBF_4$: C, 53.68; H, 4.97; N, 2.15. Found: C, 53.61; H, 5.01; N, 2.03%.

^{1}H NMR ($CDCl_3$, δ): 2.08 (s, 18H, HMB), 7.09–7.79 (m, 11H), 7.89 (t, 1H, J_{H-H} = 4.36 Hz), 8.01 (t, 1H, J_{H-H} = 4.42 Hz), 8.67 (d, 1H, J_{H-H} = 5.12 Hz).

^{31}P {^{1}H} NMR ($CDCl_3$, δ): −11.25 (s).

IR (KBr pellets, cm^{-1}): ν(B–F) 1089 (s). IR (CsI pellets, cm^{-1}): ν(Ru–Cl) 280 (s).

Method 2: A mixture of the complex [(η^6-C_6Me_6)Ru(PPh_2Py)Cl_2] (**8**) (0.1 g, 0.167 mmol) and NH_4BF_4 (0.052 g, 0.501 mmol) in methanol (15 ml) was stirred at room temperature for 4 h. The clear orange yellow

solution was then rotary evaporated. The residue was extracted with dichloromethane and filtered to remove insoluble material. The filtrate was then reduced to about 2 ml and addition of excess hexane gave a yellow solid.

Yield: 80.41% (0.156 g).

2.7. Preparation of $[(\eta^6\text{-}C_6Me_6)Ru(PPh_2Py)(NCCH_3)](BF_4)_2$ (**10**)

A mixture of complex **9** (0.06 g, 0.092 mmol) and NH_4BF_4 (0.019 g, 0.184 mmol) was refluxed in acetonitrile (15 ml) under a nitrogen atmosphere for 2 h, and the yellow solution turned light yellow in color. The solvent was rotary evaporated. The yellow solid was dissolved in CH_2Cl_2 and filtered. The filtrate was concentrated to 2 ml and an excess of hexane was added for precipitation. The light yellow product was washed with diethylether and dried under vacuum.

Yield: 78.07% (0.089 g). Elemental *Anal*. Calc. (%) for $C_{31}H_{35}RuN_2PB_2F_8$: C, 50.23; H, 4.75; N, 3.78. Found: C, 50.46; H, 4.57; N, 3.92%.

^{1}H NMR ($CDCl_3$, δ): 2.06 (s, 18H, HMB), 2.18 (s, 3H, CH_3), 7.69–8.01 (m, 13H, Ph), 8.76 (d, 1H).

^{31}P $\{^1H\}$ NMR ($CDCl_3$, δ): −13.57 (s).

IR (KBr pellets, cm^{-1}): ν(B–F) 1082 (s).

2.8. Preparation of $[(\eta^6\text{-}C_6Me_6)Ru(PPh_2Py)\{=C=C=C(Ph)_2\}](BF_4)_2$ (**11**)

A mixture of complex **9** (0.06 g, 0.092 mmol), 1,1-diphenyl-2-propyn-1-ol (0.048 g, 0.23 mmol) and NH_4BF_4 (0.029, 0.27 mmol) was refluxed in methanol (15 ml) under a nitrogen atmosphere for 3 h, the yellow suspension gradually turning brown in color. The solvent was removed under reduced pressure. The brown solid was dissolved in CH_2Cl_2 and filtered. The filtrate was concentrated to 2 ml and an excess of hexane was added for precipitation. The brown colored product was washed with diethylether and dried under vacuum.

Yield: 76.83% (0.063 g). Elemental *Anal*. Calc. (%) for $C_{44}H_{42}RuNPB_2F_8$: C, 59.35; H, 4.75; N, 1.57. Found: C, 59.43; H, 4.69; N, 1.59%.

^{1}H NMR ($CDCl_3$, δ): 1.83 (s, 18H, HMB), 7.15–7.71 (m, 14H), 8.05–8.08 (m, 6H), 8.29–8.31 (m, 3H), 8.95 (d, 1H, J_{H-H} = 5.97 Hz).

^{31}P $\{^1H\}$ NMR ($CDCl_3$, δ): −15.32 (s).

IR (KBr pellets, cm^{-1}): ν(C=C=C) 1964(s), ν(B–F) 1082(s).

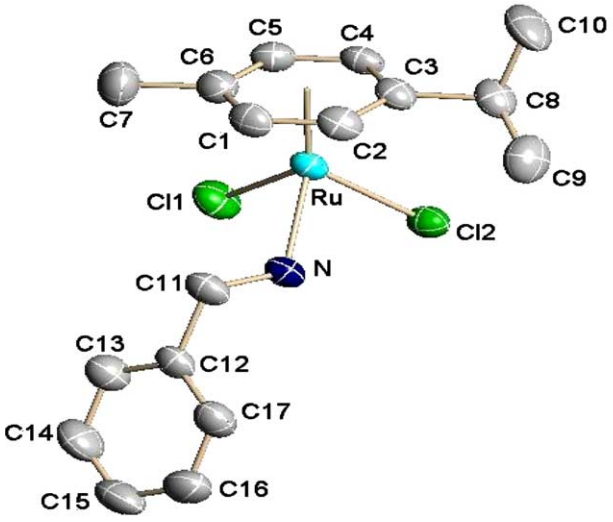
3. Crystallographic investigations

X-ray quality crystals of complex **2** were grown by slow diffusion of hexane into a dichloromethane solution of the complex, while those of complex **8** were grown by slow diffusion of diethyl ether into a dichloromethane solution. Crystals of complex **9** were grown by slow diffusion of hexane into an acetone solution. The orange crystals of complexes **2** and **8** and the yellow crystals of complex **9** were mounted on a Bruker Apex CCD diffractometer in a full reciprocal sphere equipped with a CCD detector, and were used for data collection.

Table 1
Crystal data and structure refinement details for complexes **2**, **8** and **9** acetone

Formula	$C_{17}H_{23}Cl_2NRu$	$C_{29}H_{32}Cl_2NPRu$	$C_{32}H_{38}BClF_4NOPRu$
M_r	413.33	597.5	706.93
T (K)	293 (2)	293 (2)	293 (2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1$
a (Å)	11.8414(7)	15.6052(19)	13.0710(11)
b (Å)	10.0786(6)	8.7978(11)	8.1669(7)
c (Å)	15.1580(8)	37.107(5)	15.2210(12)
β (°)	102.817 (1)	90.476 (2)	94.782 (1)
V (Å^3)	1763.95(17)	5094.4(11)	1619.2(2)
Z	4	8	2
Crystal size (mm)	0.5 × 0.3 × 0.2	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2
D_{calc} (g cm^{-3})	1.556	1.558	1.450
F(000)	840	2448	724
θ (°)	1.76–28.27	1.10–24.85	1.34–28.30
Reflections collected	14969	14468	14227
Independent reflections (R_{int})	4103 (0.0174)	4104 (0.0497)	7272 (0.0283)
Completeness to θ	28.27° – 93.8%	24.85° – 92.7%	28.30° – 95.0%
μ (Mo Kα) (mm)	1.185	0.908	0.665
Data/parameters	4103/0/173	4104/0/253	7272/1/327
Goodness-of-fit on F^2	1.033	1.257	1.077
R_1 [$I > 2\sigma(I)$], wR_2	0.0274, 0.0692	0.0661, 0.1498	0.0515, 0.1232
R_1, wR_2 (all data)	0.0299, 0.0705	0.0809, 0.1625	0.0594, 0.1278
Largest difference peak and hole (e Å^{-3})	0.856 and −0.695	1.152 and −0.795	1.249 and −0.451

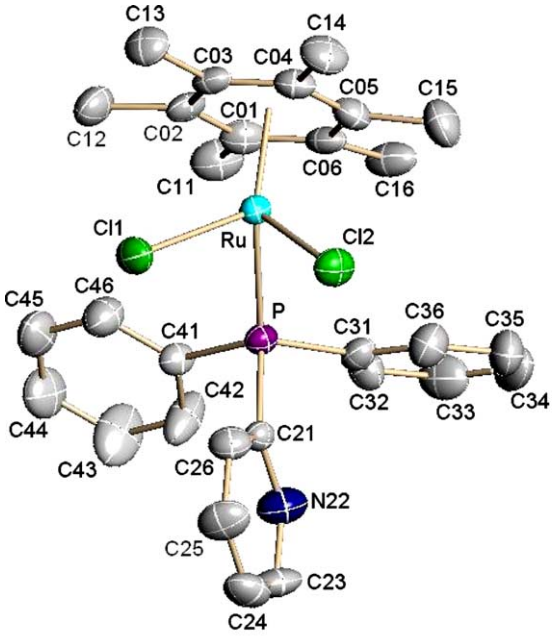
X-ray intensity data were collected with graphite monochromated Mo Kα radiation at 293(2) K, with the 0.3°ω scan mode and 10 s per frame. The intensity data were corrected for Lorentz and polarization effects. Absorption correction was done using the SAINT program [13]. A summary of the crystal data, data collection parameters and convergence results is compiled in Table 1. An empirical absorption correction was made by modeling a transmission surface by spherical harmonics employing equivalent reflections with $I > 3\sigma(I)$ (program SADABS) [14]. The structure was solved by direct methods [15]. All the non-hydrogen atoms were refined anisotropically using the full-matrix least-squares technique on F^2 using the SHELXL-97 software [16]. All the hydrogen atoms were found from difference Fourier synthesis after four cycles of an isotropic refinement and as per the ''riding'' model. Figs. 2–4 display the ORTEP [17] representations of the molecules with 50% probability thermal ellipsoids. Refinement converged at final R_1 values of 0.0274, 0.0661 and 0.0515 (for observed data F) for complexes **2**, **8** and **9**, respectively.



Selected bond lengths (Å) and bond angles (°)	
Bond lengths (Å)	
Ru–N	2.1445(18)
Ru–Cl(1)	2.4282(6)
Ru–Cl(2)	2.2497
N–C(11)	1.484(3)
Ru–C*	1.670
Bond angles (°)	
N–Ru–Cl(2)	80.65(5)
N–Ru–Cl(1)	80.97(6)
Cl(1)–Ru–Cl(2)	87.66(2)

*Ruthenium to centroid of *p*-cymene.

Fig. 2. ORTEP diagram of complex **2** with 50% probability thermal ellipsoids. Hydrogens are omitted for clarity.



Selected bond lengths (Å) and bond angles (°)	
Bond lengths (Å)	
Ru–Cl(1)	2.417(2)
Ru–Cl(2)	2.422(2)
Ru–P	2.3573(19)
P–C(31)	1.825(3)
P–C(41)	1.834(3)
P–C(21)	1.845(3)
C(21)–N(22)	1.3900
Ru–C*	1.740
Bond angles (°)	
Cl(1)–Ru–Cl(2)	86.41(8)
P–Ru–Cl(1)	88.51(7)
P–Ru–Cl(2)	88.2(7)

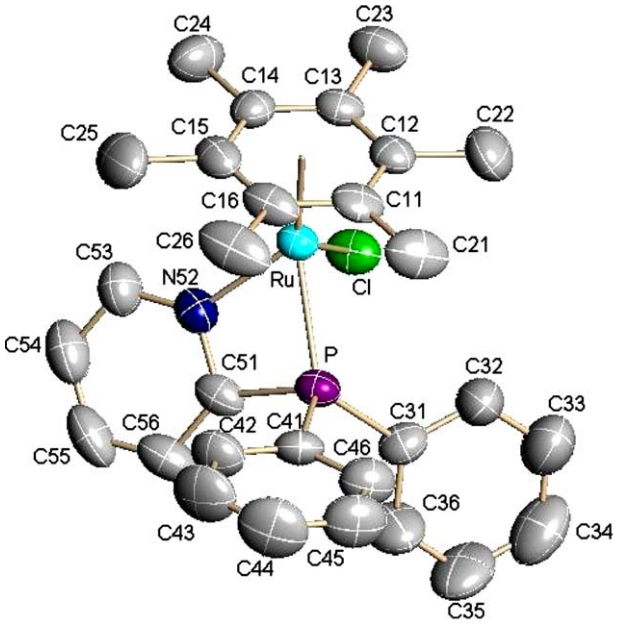
*Ruthenium to centroid of HMB.

Fig. 3. ORTEP diagram of complex **8** with 50% probability thermal ellipsoids. Hydrogens are omitted for clarity of the figure.

4. Results and discussion

4.1. Amine complexes

The dinuclear complex $[\{(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-}Cl)Cl\}_2]$ (**1**) undergoes a bridge cleavage reaction with benzylamine to yield neutral complex **2** (Scheme 1). The complex $[(\eta^6\text{-}p\text{-cymene})Ru(PPh_3)Cl_2]$ (**3**) reacts with amines resulting in the formation of chiral complexes (Scheme 2). Complexes **1** and **3** also react with 1,2-phenylenediamine (PDA) giving the cationic complexes $[(\eta^6\text{-}p\text{-cymene})Ru(PDA)Cl]^+$ (**5**) and $[(\eta^6\text{-}p\text{-cymene})Ru(PPh_3)(PDA)]^{2+}$ (**6**) (Scheme 1, reaction (1)). These complexes are stable in air and are soluble in polar solvents such as dichloromethane and acetone, but insoluble in non-polar solvents such as pentane and hexane. The infrared spectra of these complexes show strong bands in the range 3221–3429 cm^{-1} for the ν_{N-H} mode of the amine group [5b] and a strong band in the range 273–286

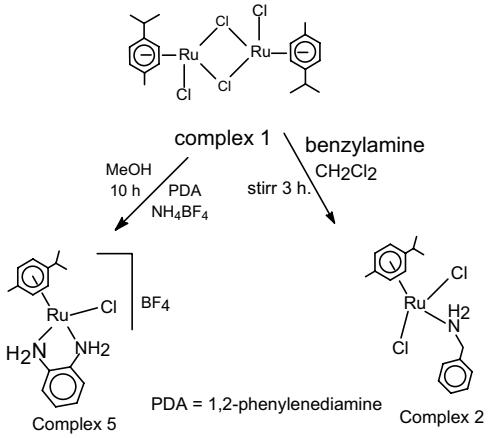


Selected bond lengths (Å) and bond angles (°)	
Bond lengths (Å)	
Ru–Cl	2.3981(14)
Ru–P	2.3412(13)
Ru–N(52)	2.107(2)
P–C(31)	1.818(2)
P–C(41)	1.828(2)
P–C(51)	1.792(2)
N(52)–C(53)	1.3900
Ru–C*	1.705
Bond angles (°)	
P–Ru–Cl	86.97(5)
N(52)–Ru–Cl	82.95(7)
N(52)–Ru–P	67.72(6)

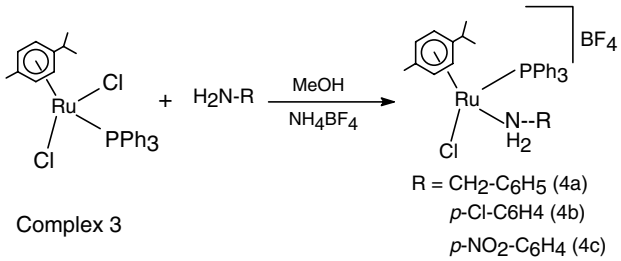
*Ruthenium to centroid of HMB.

Fig. 4. ORTEP diagram of complex **9** with 50% probability thermal ellipsoids. Hydrogens are omitted for clarity.

cm^{-1} for the ν_{Ru-Cl} mode [5b]. All these complexes (**4–6**) exhibit a strong band at 1089 cm^{-1} due to the ν_{B-F} mode of the BF_4 group.

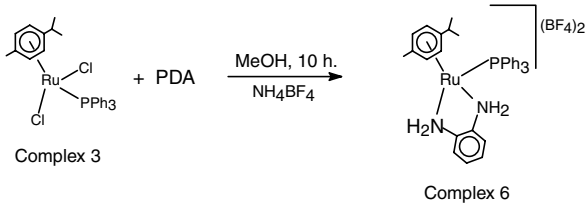


Scheme 1.



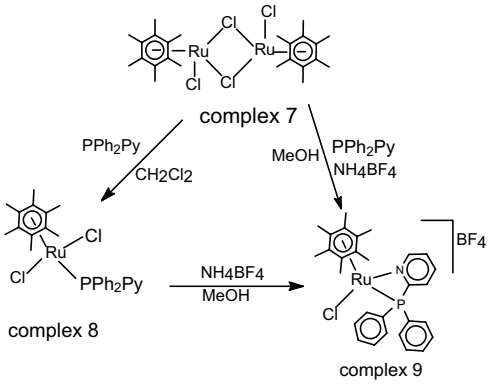
Scheme 2.

The ^{1}H NMR spectrum of complex **2** exhibits a doublet at 1.30 ppm (J = 6.96 Hz) while a septet at 2.98 ppm is observed for the isopropyl group protons. The two doublets observed at 5–6 ppm correspond to the aromatic *p*-cymene ring CH protons. The phenyl group of the benzylamine ligand gives multiplets in the range 7.31–7.40 ppm. The ^{1}H NMR spectra of the mononuclear complexes **4** exhibit two doublets for the methyl protons of the isopropyl group. This is due to the diastereotopic nature of these complexes (**4a–c**) (Scheme 2) since the ruthenium metal is a chiral center. The complexes **5** and **6** also exhibit two doublets for the methyl groups of the *p*-cymene ligand due to the steric nature of the bulky 1,2-phenylenediamine ligand.



(1)

The ^{1}H NMR spectrum of complex **5** exhibits two doublets at 7.16 and 8.23 ppm for the ring protons of 1,2-phenylenediamine. In the case of complex **6**, the signals for these protons merge with those for the phenyl group protons of the triphenylphosphine ligand, thereby exhibiting multiplets in the range 6.93–7.76 ppm. Both



Scheme 3.

the complexes show broad peaks around 4.5–5.0 ppm due to the coordinated NH_2 group. The structure of complex **2** is shown in Fig. 2.

The electronic spectrum of complex **2** in dichloromethane features a UV–vis pattern similar to the analogous ruthenium polypyridyl complexes [18], which arises from the metal-to-ligand charge transfer at 393 nm.

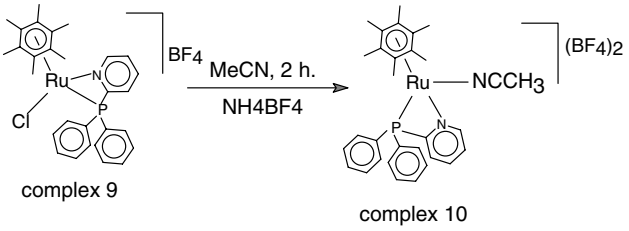
4.2. Complexes of diphenyl-2-pyridylphosphine (*8–11*)

The reaction of $[\{(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}Cl)Cl\}_2]$ (**7**) with diphenyl(2-pyridyl)phosphine in dichloromethane yields the neutral P-coordinated complex **8**. However, in methanol, the P,N-chelated cationic complex $[(\eta^6\text{-}C_6Me_6)Ru(PPh_2Py)Cl]^+$ (**9**) is isolated as the tetrafluoroborate salt **9**$[BF_4]$. Complex **8** with an excess of NH_4BF_4 in methanol gives the complex **9**$[BF_4]$ (Scheme 3). These complexes are stable in air and soluble in polar solvents such as chloroform and dichloromethane, but are insoluble in non-polar solvents such as hexane and pentane.

The spectroscopic data clearly suggests the coordination of the ligand to the metal as evident from the shift of the phosphorus and proton resonance compared to the starting complex **7**. The ^1H NMR spectrum of complex **8** shows a singlet at 1.76 ppm for the hexamethylbenzene protons (an upfield shift compared to the starting compound) and also in the aromatic region at 7.13–8.11 ppm for the phosphine ligand. The ^{31}P NMR shows one singlet at 25.88 ppm for the phosphine ligand, where a significant downfield shift is observed after coordination to the metal as compared to the free ligand (−3.43 ppm). The far IR spectrum shows a strong band at 286 cm^{-1} for the Ru–Cl stretching vibration mode.

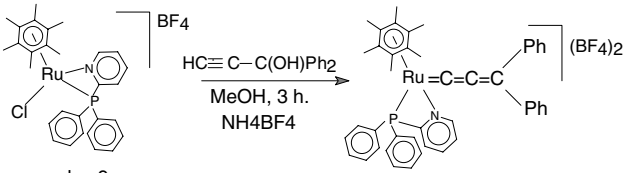
The ^1H NMR spectrum of complex **9** shows a pattern of signals different from the spectrum of complex **8**. The pyridine ring protons appear as two triplets at 7.89 and 8.01 ppm and one doublet at 8.67 ppm. The phenyl group protons appear as a multiplet in the aromatic region at 7.09–7.79 ppm. The singlet at 2.08 ppm for the hexamethyl-benzene protons indicates a downfield shift compared to complex **8**. The ^{31}P $\{^1H\}$ NMR spectrum of complex **9** exhibits a singlet at −11.25 ppm (upfield compared to complex **8**). The far IR spectrum shows a band at 280 cm^{-1}, which is assigned to the terminal stretching vibration of ν_{Ru-Cl}. In addition, the IR spectrum contains a strong band at 1089 cm^{-1} due to the ν_{B-F} mode of the BF_4 group. However, we do not observe formation of a pyridylphosphine-coordinated complex of the type $[Ru(PPh_2Py)_2Cl_2]$ in these reactions, as was the case for the *p*-cymene ruthenium dimer [19].

Treatment of the complex $[(\eta^6\text{-}C_6Me_6)Ru(PPh_2Py)Cl]BF_4$ (**9**) with acetonitrile and 1,1-diphenyl-2-propyn-1-ol ligands generated the cationic complexes **10** and **11** (reactions (2) and (3)), which can be isolated in good yield as their BF_4 salts. Formation of the allenylidene complex **11** is confirmed by the appearance of the ν(C═C═C) absorption mode (asymmetric stretching vibration) as a strong band at 1964 cm^{-1} [20]. The ^1H NMR spectrum of complex **10** shows a singlet for the acetonitrile methyl protons at 2.18 ppm. The phenyl protons appear in the aromatic region in the range of 7.15–8.95 ppm for both complexes. HMB protons are observed at 2.06 ppm for complex **10** and at 1.83 ppm for complex **11**. The ^{31}P $\{^1H\}$ NMR spectrum of complexes exhibits a sharp peak at 13.57 ppm for complex **10** and at 15.32 ppm for complex **11**.



complex 9 complex 10

(2)



complex 9 complex 11

(3)

5. Molecular structures

In order to confirm the structures suggested by the spectroscopic data, molecular structures of complexes **2**, **8** and **9** were determined using single-crystal X-ray diffraction studies. The summary of the single-crystal X-ray structure analyses is shown in Table 1. ORTEP drawings of the complexes **2**, **8** and **9** are shown in Figs. 2–4, respectively.

The structure of complex **2** consists of a ruthenium atom η^6-coordinated to a *p*-cymene molecule, two chlorine atoms and one benzylamine ligand (through the N atom) leading to the usual 'three-legged piano stool' structure. The complex $[(\eta^6\text{-}p\text{-cymene})Ru(NH_2CH_2C_6H_5)Cl_2]$ (**2**) crystallizes in the monoclinic space group $P2_1/c$ (Fig. 2). The average Ru–C bond distance is 2.1726 Å, whereas the distance between the ruthenium atom and the centroid of the ring is 1.670 Å at the axis $x = 0.3938$, $y = 0.3638$ and $z = 0.1334$. These bond lengths are closely related to those in other reported complexes [21]. The Ru–N bond length involving benzylamine is 2.1445(18) Å, which is within the usual range of Ru–N bond distances [22]. The Ru–Cl bond lengths are 2.4282(6) and 2.4297(6) Å, well in accord with the

literature values [23]. The geometry of the complex is octahedral with a piano-stool structure and is marked by the nearly 90° value for the bond angles between the non-*p*-cymene ligands at the metal centre, viz., Cl(1)–Ru–Cl(2) (87.66(2)°), N–Ru–Cl(1) (80.97(6)°) and N–Ru–Cl(2) (80.65(5)°).

Complex **8** crystallizes in the monoclinic space group *C*2/*c*. The geometry around the ruthenium atom in complex **8** is octahedral where the hexamethylbenzene occupies three-coordination positions. Complex **8** also has a 'three-legged piano stool' type structure. Fig. 3 shows an ORTEP representation of complex **8**. The Ru–Cl(1) and Ru–Cl(2) bond distances (2.417(2) and 2.422(2) Å) are closely related to other reported values (2.4299 Å) [24]. The Ru–P bond distance 2.3573(19) Å is within the range of the literature values [24a]. The average bond distance between ruthenium and hexamethylbenzene is 2.227 Å, and the distance between ruthenium and the centroid of the ring is 1.740 Å. The bond angles P–Ru–Cl(1), P–Ru–Cl(2) and Cl(1)–Ru–Cl(2) are 88.51(7)°, 88.20(7)° and 86.41(8)°, respectively, indicating a piano stool type structure.

Complex **9** crystallizes with one molecule of acetone; the complex cation and the BF_4^- anion are joined by coulombic forces. Complex **9** contain a ruthenium atom η^6-coordinated to a hexamethylbenzene ring and bonded to a chlorine atom and a bidentate PPh_2Py ligand through the P and N atoms. Fig. 4 is an ORTEP representation of complex **9**. Complex **9** crystallizes in the monoclinic space group $P2_1$. The Ru–P bond distance 2.3412(13) Å is shorter than in complex **8**. This is because the diphenyl(2-pyridyl)phosphine ligand restricts the bite angle of the four-membered chelating ring using both the P and N atoms. The Ru–Cl and Ru–N(52) bond distances 2.3981(14) and 2.107(2) Å fall within the range of reported values [25]. The bond angles around the ruthenium are P–Ru–Cl 86.97(5)° and N(52)–Ru–Cl 82.95(7)°. The rigid bond distance between the nitrogen and phosphorus atoms (P∩N) of pyridylphosphine is approximately 3.1 Å, whereas the rigid narrow angle N(52)–Ru–P in complex **9** is 67.72(6)°. The average bond distance between ruthenium and the hexamethylbenzene carbons is 2.204 Å, while that between the centroid of the arene and the metal atom is 1.705 Å.

6. Concluding remarks

We have prepared some new η^6-arene ruthenium(II) complexes containing amines and diphenyl(2-pyridyl)phosphine ligands. The *p*-cymene ruthenium dimer $[(\eta^6\text{-}C_{10}H_{14})RuCl_2]_2$ with diphenyl(2-pyridyl)phosphine in the presence of methanol under refluxing conditions yields two types of products – one having an organic fragment, viz., $[(\eta^6\text{-}p\text{-cymene})Ru(PPh_2Py)Cl]BF_4$, and the other without an organic fragment, viz., $[RuCl_2(PPh_2Py)_2]$ [19]. The hexamethylbenzene ruthenium(II) dimer $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ under the same conditions gave only one product having an organic fragment, viz., $[(\eta^6\text{-}C_6Me_6)Ru(PPh_2Py)Cl]BF_4$. This is a clear indication that hexamethylbenzene binds to the metal quite strongly for the latter case due to the high electron-donating ability of the $\eta^6\text{-}C_6Me_6$ moiety relative to the η^6-*p*-cymene in these ruthenium complexes.

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Appendix A. Supplementary data

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre (CCDC), CCDC No. 246203 for complex **2**, CCDC No. 246204 for complex **8**, and CCDC No. 246205 for complex **9**. 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; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.poly.2004.09.031.

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