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Cationic half-sandwich Ru(II) complexes bearing (*S*)-2-pyridyl-imino-[2.2]paracyclophane ligands: Synthesis, intramolecular and interionic structure

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Abstract

(*S*)-2-Pyridyl-imino-[2.2]paracyclophane ligands **1** and **2** were synthesized by a condensation reaction of 2-COR-C_5H_4N (**1**: R = H; **2**: R = Me) with enantiopure (−)-*S*-amino-[2.2]-paracyclophane. The reactions of **1** and **2** with $[Ru(\eta^6\text{-cymene})Cl(\mu\text{-}Cl)]_2$ afforded complexes $[Ru(\eta^6\text{-cymene})Cl(N,N)]X$ (**3**: N,N = **1**; **4**: N,N = **2**; $X^- = BPh_4^-, PF_6^-, BF_4^-$) that were completely characterized in solution. For **4**PF_6 the solid state structure was determined by X-ray single-crystal diffractometric studies. Two diastereoisomers [(S_{Ru}, S_L) and (R_{Ru}, S_L)] were obtained in solution due to the presence of the planar chirality of paracyclophane (L) and the central chirality on ruthenium. ^{1}H-NOESY NMR experiments were used to determine the chirality of the metal center and, consequently, to identify (S_{Ru}, S_L) and (R_{Ru}, S_L) diastereoisomers. The cymene orientation, obtained by intramolecular ^{1}H-NOESY NMR investigations, and the relative anion–cation position, determined by interionic ^{1}H-NOESY or ^{19}F,^{1}H-HOESY NMR studies, depended on the nature of the diastereoisomer.

Keywords: Ruthenium compounds; N,N-paracyclophane ligands; ^{1}H-NOESY and ^{19}F,^{1}H-HOESY NMR; X-ray structure; Ion-pairs

1. Introduction

Half-sandwich ruthenium complexes bearing N,N-ligands are currently used as catalysts for organic reactions [1] and have recently been proposed as anticancer drugs [2]. In such applications a key role is played by weak interactions that can affect their catalytic performances in terms of reaction yield, chemio-, regio- and stereo-selectivity [3] and, in the biomedical applications, the recognition phenomena [2].

Valuable information about the intermolecular interactions in solution of transition-metal complexes can be obtained by NMR techniques. In particular, if salts are considered, the relative anion–cation orientations can be deduced by NOE (nuclear Overhauser effect) experiments [4]; orientations differing by less than 1 kcal/mol can be clearly and quantitatively discriminated [5]. The aggregation level can be determined by PGSE (pulsed field gradient spin-echo) techniques [6] that allow the average hydrodynamic radius and volumes of the species present in solution to be evaluated. In this context, a few half-sandwich Ru(II) complexes containing N-ligands have been investigated that show a remarkable tendency to aggregate in a variety of aprotic and protic solvents even those with moderate to high relative permittivity [7].

While [2.2]paracyclophane-based ligands are assuming a growing importance in asymmetric organometallic catalysis [8], they have rarely been used in reactions mediated by ruthenium complexes [9,10]. In the few existing cases, bisphoshino-[2.2]paracyclophane ligands have been employed [9] or the possibility of coordinating paracyclophane to the metal in a η^6-fashion has been utilized [10]. To the best of our knowledge, only one ruthenium complex bearing a nitrogen paracyclophane ligand has been synthesized [11]. In

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addition, only a few transition metal complexes bearing N,N-bidentate paracyclophane ligands have been previously prepared [12] and applied in catalysis [13].

Arene ruthenium complexes with central chirality at the metal center and central [14,15] or axial [16] chirality on the ligand have been extensively studied by Brunner and co-workers [17]. They deeply investigated the factors that affect the intercorversion of the various diastereoisomers in solution for several classes of ligands [18] including pyridine imines deriving from the condensation of pyridine 2-aldehyde and 2-acetylpyridine and optically active amines [16]. In addition, they showed that weak (arene)CH···X interactions (X = electronegative substituent) play a key role in determining 1:1 diastereoisomer co-crystallization and crystallization as a pure diastereoisomer [19].

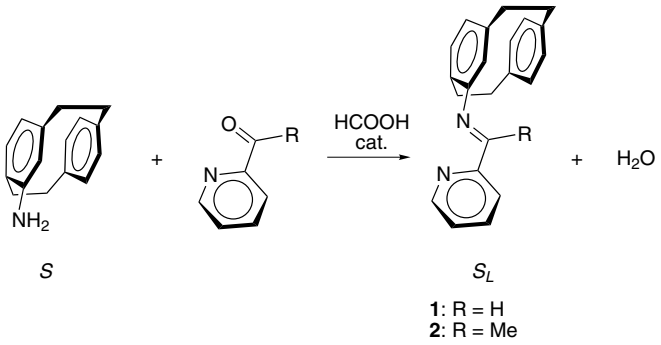
In this paper, we report the synthesis, intramolecular and interionic characterization of the first half-sandwich ruthenium complexes bearing an N,N-paracyclophane ligand. The synthesized complexes possess a planar chirality due to paracyclophane and a central chirality on ruthenium that has four different substituents. Since *S*-enantiopure paracyclophane ligands have been used, (S_{Ru}, S_L) and (R_{Ru}, S_L) diastereoisomers (where L stands for paracyclophane ligand) were obtained and identified in solution through ^{1}H-NOESY NMR studies. Furthermore, the orientation(s) of cymene and the relative anion–cation position(s) in solution were investigated by means of homo- and hetero-NOE experiments for both diastereoisomers.

2. Results and discussion

2.1. Synthesis of ligands 1–2 and complexes 3–4

2-Pyridyl-imino-(S)-[2.2]paracyclophane ligands **1**–**2** were synthesized by the condensation reaction of 2-pyridinecarboxyaldehyde and 2-acetylpyridine with the enantiopure (−)-*S*-amino-[2.2]-paracyclophane, respectively, in the presence of a catalytic amount of HCOOH (Scheme 1).

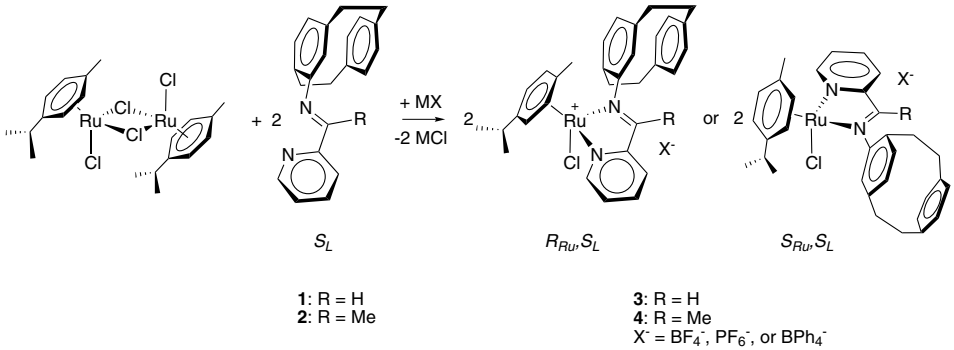
The reactions of **1** and **2** with the dimer [Ru(η^6-cymene)-Cl(μ-Cl)]$_2$ in methanol followed by the addition of a large excess of $NaBPh_4$ or NH_4PF_6 afforded complexes **3**X and **4**X ($X^- = BPh_4^-$ or PF_6^-), respectively (Scheme 2). Two diastereoisomers [(S_{Ru}, S_L) and (R_{Ru}, S_L)] were obtained for both complexes due to the presence of the planar chirality of paracyclophane and central chirality of ruthenium (Scheme 2). The ratio $(S_{Ru}, S_L)/(R_{Ru}, S_L)$ was 1.9 and 0.6 for **3**X and **4**X, respectively, and did not depend on the counterion. Anion methatesis of **3**BPh_4 and **4**BPh_4 with $AgBF_4$ afforded complexes **3** and **4** with BF_4^- counterion without altering the diastereoisomeric ratio.



Scheme 1.

A point that has provoked some controversy in the literature was the determination of the stability or lability of the metal configuration in chiral-at-metal half sandwich compounds [18]. In compounds **3** and **4** the two diastereoisomers did not exhibit any tendency to interconvert as deduced by the independence of the diastereoisomeric ratios of time and temperature and by the absence of exchange NOE peaks in the ^{1}H-NOESY NMR spectra. In fact, NMR tubes containing diastereoisomeric mixtures of **3** or **4** were maintained in solution for two weeks and warmed up to the solvent boiling point without the ^{1}H NMR spectra showing any significant alteration of the diastereoisomeric ratios. In addition, diastereoisomeric solutions enriched in one diastereoisomer by means of fractional crystallization did not exhibit any modification in the ^{1}H NMR spectrum recorded at 298 K in CD_2Cl_2 after 24 h. These observations lead one to conclude that the abovementioned ratios are likely kinetically determined and compounds **3**–**4** are configurationally stable at the metal in the investigated conditions.

Fractionated crystallizations allowed the major diastereoisomer [(S_{Ru}, S_L) and (R_{Ru}, S_L) for complexes **3** and **4**, respectively] to be obtained in a pure form.



Scheme 2.

2.2. Intramolecular characterization in solution

All compounds were characterized by ^{1}H, ^{13}C, ^{19}F, ^{1}H-COSY, ^{1}H-NOESY, ^{19}F, ^{1}H-HOESY, ^{1}H,^{13}C-HMQC and ^{1}H,^{13}C-HMBC NMR spectroscopies at 293 K in CD_2Cl_2. Numbering of atoms for **4**PF_6 is shown in Chart 1.

The complete assignment of the ^{1}H and ^{13}C NMR resonances of complexes **3**–**4** was obtained starting from H11, whose signal had the highest frequency [20], H7, the only septet, and H23, the only aromatic singlet, following the scalar and dipolar connectivity in the ^{1}H- or ^{1}H,^{13}C-COSY and NOESY spectra, respectively. Data are reported in Section 4.

The orientation of cymene and the consequent distinction of H3 and H2 from H5 and H6, respectively, were mainly deduced by analyzing the relative intensities of the H11 NOEs with cymene protons. Two different situations were encountered for (R_{Ru}, S_L) or (S_{Ru}, S_L) diastereoisomers of complexes **3** and **4** (Scheme 3). For the (R_{Ru}, S_L) diastereoisomer, the NOE intensities followed the order: H5/H11 $\gg$ H6/H11 $\approx$ H3/H11 $\approx$ H2/H11. In addition, given that a medium sized NOE was observed between H7 and H11, while a H10/H11 NOE was not and since H23 mainly interacted with H3, orientation A of cymene reported in the left side of Scheme 3 must be predominant in solution. The other orientation (B), that is thought to be derived from the rotation of the cymene in A by an angle slightly smaller than 180°, has to be present in order to justify the observations that H2/H11 and H3/H11 weak NOEs have the same intensities.

In the case of (S_{Ru}, S_L) diastereoisomer, H2 and H3 resonances were superimposed but the intensity of H6/H11 NOE was more than twice that of H5/H11. At the same time, the addition of the intensities of H5/H11 and H6/H11 NOEs was equal to that of H3/H11 and H2/H11. Similarly, the sum of the NOE intensities of H5–H6/H23 and H2–H3/H23 was equal. Furthermore, H10/H11 and H7/H11 contacts had comparable intensities. This clearly indicates that conformers A and B, shown in Scheme 3, are both present in solution in similar amounts. In this case, orientations A and B differ only with respect to a cymene rotation of 180°.

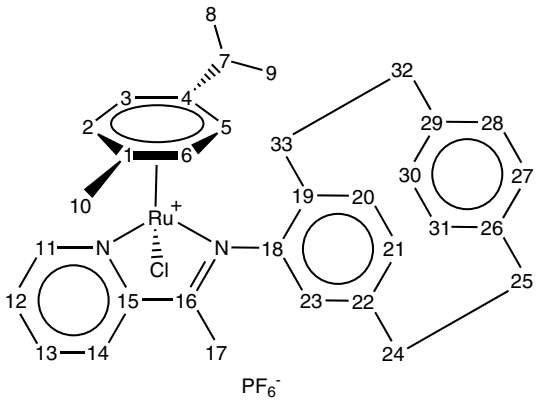
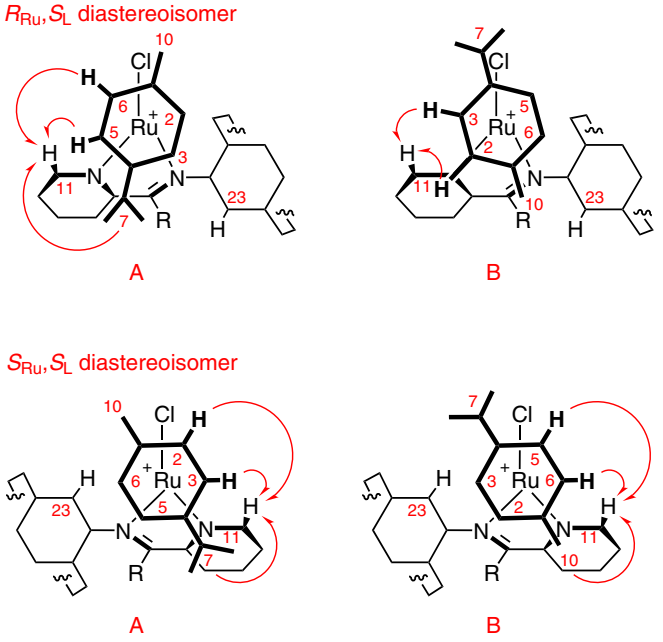


Chart 1.



Scheme 3.

The steric factor appears to determine the stability of a particular cymene orientation. In detail, the least hindered region that would be ideal for "locating" *i*-Pr and Me groups of cymene is on the top of the pyridine ring (Scheme 3). This definitely occurs in the (S_{Ru}, S_L) diastereoisomer, where this region is occupied by *i*-Pr or Me rather indifferently as indicated by the comparable abundance of A and B orientations. On the contrary, in the (R_{Ru}, S_L) diastereoisomer, the perfect orientation of the *i*-Pr or Me group on the top of the pyridine ring appears unlikely since the other one would come in contact with the methylene bridge (CH_2) of the paracyclophane moiety. Due to the fact that the *i*-Pr/CH_2 steric repulsion is higher than that of the Me/CH_2 one, the former is forced to rotate further away from CH_2. These considerations justify the main presence in solution of the two orientations A and B (Scheme 3), as deduced by NOE contacts. A results favored because it allows the most hindered cymene group to be located where there is more space. This, in fact, is the orientation observed in the solid state for (R_{Ru}, S_L)-**4**PF_6 (see below).

Interestingly enough, the chirality of the metal center for complexes **4** could be determined by a quantitative analysis of the NOEs between H17 and H23, H30 and H31. In fact, in the (R_{Ru}, S_L) diastereoisomer H17 is almost equidistant from all three protons and consequently three NOEs of comparable intensities were expected. On the contrary, H17 is closer to H30 in the diastereoisomer (S_{Ru}, S_L) and a stronger NOE contact was expected. These situations were observed for the diasteroisomers of **4** complexes whose chirality and, consequently, the diastereoisomeric ratio was established.

A quantitative analysis of ^{1}H-NOESY NMR spectra allowed us to find a probe to determine the chirality of the metal center also for complex **3**PF_6. In fact, H16 exhibited

a NOE with the aliphatic hydrogens of the paracyclophane only in the (S_{Ru}, S_L) isomer (Fig. 1).

2.3. Interionic characterization in solution

Relative anion–cation orientations were investigated by means of $^1H,^{19}F$-HOESY ($X^- = PF_6^-$) and ^1H-NOESY ($X^- = BPh_4^-$) NMR experiments. The spectra were collected at 293 K in CD_2Cl_2.

The intensities of the NOE contacts for (S_{Ru}, S_L)-**3**PF_6 and (R_{Ru}, S_L)-**4**PF_6, normalized for the number of equivalent protons through the parameter $f = [n_I \cdot n_S/(n_I + n_S)]$ (n_I = number of equivalent nuclei of the first type, that is ^1H, n_S = number of equivalent nuclei of the second type, that is ^{19}F) [21], are listed in Table 1. An analysis of the intensities of the interionic NOEs pertinent to imino-pyridyl protons allowed us to conclude that more than a single relative anion–cation orientation was present. The following intensity orders were found (Table 1): H11 > H14 ≈ H16 > H12 > H23 > H13, for (S_{Ru}, S_L)-**3**PF_6; H11 > H12 > H14 > H23 > H17 > H13, for (R_{Ru}, S_L)-**4**PF_6. It appears difficult to locate the anion in a particular position from which it can interact simultaneously with H11 and H23 having, in addition, the smallest NOE contact with H13. It is instead probable that the anion assumes two positions: one close to H11 as observed in the solid state for (R_{Ru}, S_L)-**4**PF_6 and the other close to the imino-moiety. The relative intensities of the interionic NOEs reported in Table 1 suggest that the former is more populated.

The interionic NOEs between PF_6^- and the cymene protons perfectly reflect the two different orientations of cymene in (R_{Ru}, S_L) or (S_{Ru}, S_L) diastereoisomers illustrated above (Scheme 3). In fact, in (R_{Ru}, S_L)-**4**PF_6 only H5, H6, H9 and H10 interacted with the counterion with the following order of intensities: H5 > H6 > H9 > > H10 (Table 1, Fig. 2). In contrast, for (S_{Ru}, S_L)-**3**PF_6 all cymene protons interacted with PF_6^- but, interestingly, the sum of

Table 1
Relative NOE intensities (I) determined by arbitrarily fixing at 1 the intensity of the NOE(s) between the cation resonances H11 and PF_6^-

	(S_{Ru}, S_L)-**3**PF_6			(R_{Ru}, S_L)-**4**PF_6		
	I	f	I/f	I	f	I/f
H2	0.39	0.857	0.46			
H3	0.15	0.857	0.18			
H5	0.59	0.857	0.69	0.56	0.857	0.65
H6				0.38	0.857	0.44
H7	0.14	0.857	0.16			
H8	0.22	2.00	0.11			
H9	0.34	2.00	0.17	0.50	2.00	0.25
H10	0.42	2.00	0.21	0.14	2.00	0.07
H11	1.00	0.857	1.17	1.00	0.857	1.17
H12	0.46	0.857	0.54	0.43	0.857	0.50
H13	0.24	0.857	0.28	0.11	0.857	0.13
H14	0.68	0.857	0.79	0.38	0.857	0.44
H16	0.61	0.857	0.71			
H17				0.44	2.00	0.22
H23	0.31	0.857	0.36	0.24	0.857	0.28
H29	0.11	0.857	0.13			
H30	0.21	0.857	0.25			

f equal to $n_I \cdot n_S/(n_I + n_S)$ (n_I = number of equivalent nuclei of the first type, that is ^1H, n_S = number of equivalent nuclei of the second type, that is ^{19}F), i.e., the factor that allows the number of equivalent nuclei to be taken into account.

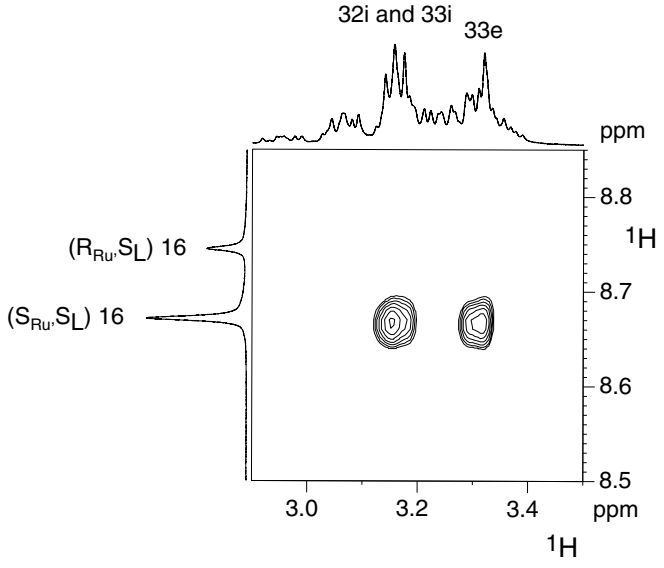


Fig. 1. A section of the ^1H-NOESY NMR spectrum (400.13 MHz, 293 K, CD_2Cl_2) for **3**PF_6 showing the interactions between 16 proton of only one diastereoisomer (assigned to (S_{Ru}, S_L)) and 32 and 33 paracyclophane protons. "i" and "e" indicate protons that point toward and in the opposite direction of the N,N-ligand, respectively.

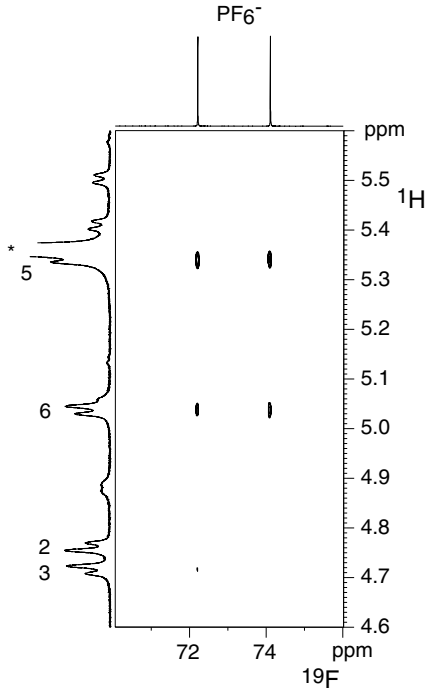
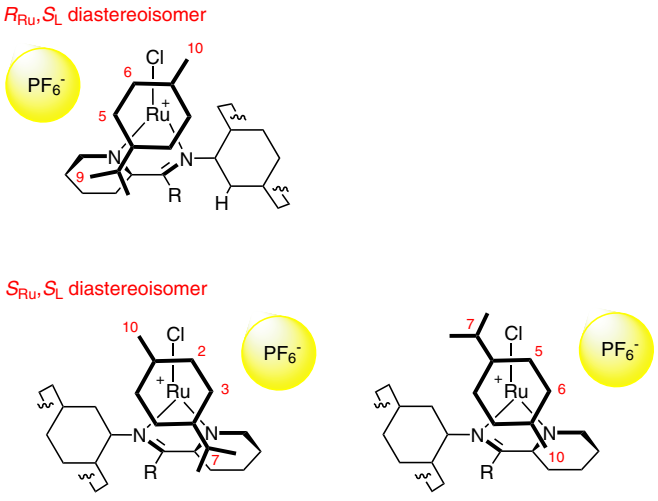


Fig. 2. A section of the $^{19}F,^1H$-HOESY NMR spectrum (376.65 MHz, 293 K, CD_2Cl_2) for **4**PF_6 showing the selective interactions of the anion with 5 and 6 cymene protons. Only the resonances pertinent to the (R_{Ru}, S_L) diastereoisomer are labeled. * denotes the signal due to the residual non-deuterated solvent.

the intensities of the H2 and H3 contacts was equal to that of H5 and H6 (Table 1). The contacts of the counterion with H7 and H10 also had comparable intensities (Table 1). All of the framework appears to be highly consistent: in the case of (R_{Ru}, S_L)-diastereoisomer, for which the cymene orientation A is predominant, the anion, that is mainly located close to H11, interacts exclusively with one side of the cymene (Scheme 4). In contrast, the anion can equivalently interact with the protons belonging to both sides of the cymene in (S_{Ru}, S_L) diastereoisomer which exhibit in solution both A and B cymene orientations (Scheme 4).



Scheme 4.

2.4. Solid state structure of $4PF_6$

Two ORTEP views of compound $4PF_6$ are shown in Fig. 3. The complex can be identified as a three-legged piano stool complex with a pseudo-octahedral geometry in which the arene ligand (cymene) occupies three adjacent sites of the octahedron as in other similar complexes reported in the literature [22].

The plane defined by C_1RuC_4, which bisects the cymene ligand along the direction of its two *para* substituents (methyl and isopropyl), and the plane defined by N_1RuN_2 form an angle of 62.65°. The cymene assumes an almost ideal staggered conformation with the methyl substituent of the cymene ligand that points in the same direction as Cl (Fig. 3). This cymene orientation corresponds to orientation A of Scheme 3 that was found to be predominant in solution.

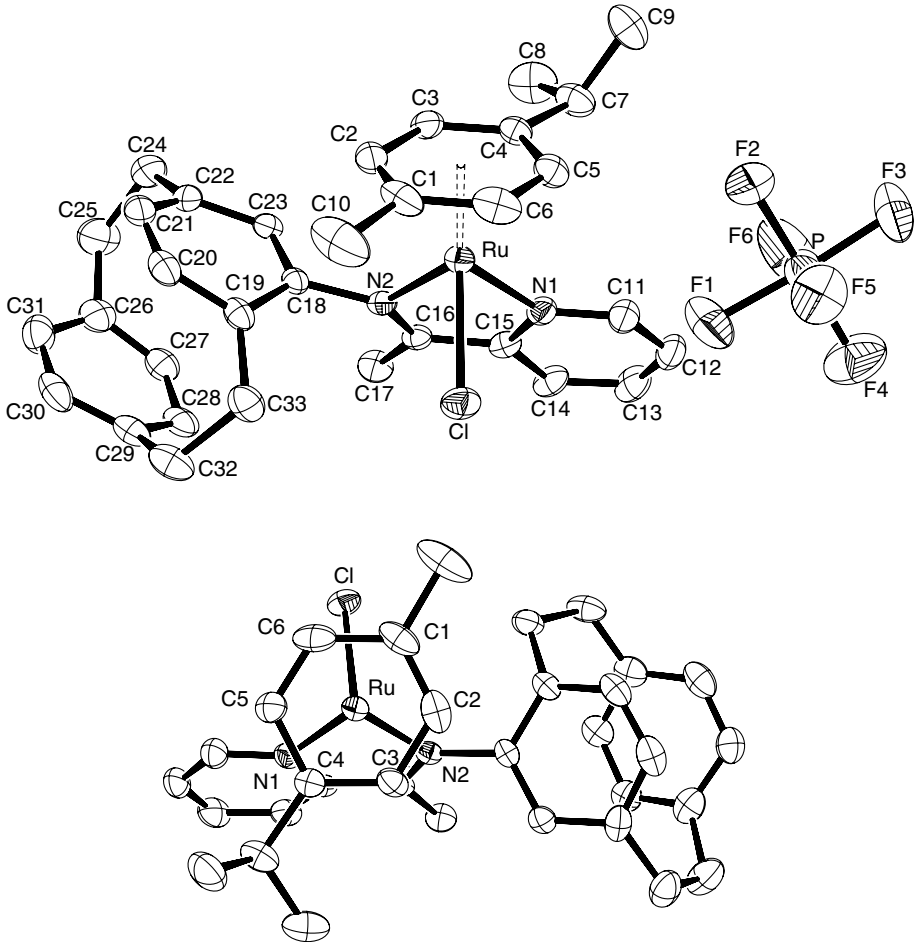


Fig. 3. Two ORTEP views (30% ellipsoid probability) of $4PF_6$.

The cymene plane, defined by the $C_1C_3C_5$ atoms is bent of 57.84° with respect to the N_1RuN_2 plane. The paracyclophane moiety shows a pseudo-perpendicular configuration with respect to the pyridyl moiety. In fact, the angles between the planes described by $C_{19}C_{22}C_{26}C_{29}$ (the four atoms bound to the two ethyl groups) and those containing N_1RuN_2 and the pyridyl moiety are 94.62° and 96.95°, respectively. Furthermore, if we consider the average of the two possible planes that described the paracyclophane moiety, $C_{18}C_{20}C_{21}C_{23}$ and $C_{27}C_{28}C_{30}C_{31}$, they are bent at about 153° with respect to the cymene plane, defined by the $C_1C_3C_5$ atoms (the methyl substituent of the cymene ligand is on the same part of the paracyclophane moiety) and are bent at about 63° with respect to the N_1RuN_2 plane.

The PF_6^- anion is positioned between the chloride ligand and the pyridyl ring as illustrated in Fig. 3 (top) and observed in solution. The P–Ru distance is of 5.597 Å.

3. Conclusions

Cationic arene Ru(II) complexes **3** and **4** bearing (*S*)-2-pyridyl-imino-[2.2]paracyclophane ligands, possessing both planar chirality in the ligand and central chirality at the metal, were synthesized and completely characterized in solution and in the solid state. ^{1}H-NOESY NMR experiments were used to determine the chirality of the metal center and cymene orientation in solution. ^{19}F,^{1}H-HOESY NMR investigation allowed us to elucidate the interionic structure, i.e., the relative anion–cation orientations, in solution. The solid state structure of **4**PF_6 was obtained through X-ray single crystal studies and compared from intramolecular and interionic points of view with that in solution. Anion mainly locates close to H11 in both diastereoisomers. Arene orientation is determined by steric factors and results to be sensitive to the nature of the diastereoisomer. In (S_{Ru}, S_L) diastereoisomer this corresponds to orienting *i*-Pr (A) and Me (B) groups of cymene on the top of the pyridine and the two orientations are equally present in solution. In (R_{Ru}, S_L) diastereoisomer, *i*-Pr and Me steric interactions with the methylene bridge of the paracyclophane slightly alter A and B conformations and favor A over B.

4. Experimental

4.1. General methods

All reactions were carried out in dry, oxygen-free nitrogen atmosphere, using standard Schlenk techniques. All solvents were dried and purified by standard methods, that is, sodium/benzophenone for diethyl ether, phosphorus pentoxide for methylene chloride and calcium hydride for methanol, and freshly distilled before use. All commercial reagents were used as received, without any further purification. Complex [Ru(η^6-cymene)Cl(μ-Cl)]$_2$ [23] and (−)-*S*-amino [2.2]paracyclophane [24] were prepared as reported in the literature. One- and two-dimensional ^{1}H, ^{13}C, ^{19}F NMR spectra were measured on a Bruker DRX 400 spectrometer, using TMS as reference for ^{1}H and ^{13}C experiments. NMR samples were prepared dissolving about 20 mg of compound in 0.5 ml of methylene chloride-d_2. Two-dimensional ^{1}H-NOESY and ^{19}F, ^{1}H-HOESY spectra were recorded with a mixing time of 500–800 ms. IR spectra were measured at room temperature (CH_2Cl_2, NaCl cell) on a FT-IR 1725 X Perkin–Elmer spectrophotometer. Optical rotations were taken using a JASCO DIP-360 polarimeter.

4.2. Synthesis and characterization of **1**

2.254 g of (−)-*S*-amino [2.2]paracyclophane (10.09 mmol), 1.8 mL of 2-pyridinecarboxaldehyde (18.92 mmol) and 0.05 mL of formic acid were added to 30 mL of methanol. The resulting heterogeneous dispersion was kept under stirring for 2 h, at the end of which the solid turned from white to yellow. The solid was filtered off, washed with cold methanol (2 × 5 mL) and crystallized from methanol in the refrigerator at −18 °C. The needle-shaped, bright yellow crystals were dried under vacuum, yielding 1.840 g of (−)-*S*-Py–C(H)=N–($C_{16}H_{15}$) (**1**, 5.88 mmol, yield: 58.3 %). M.p. 137–138 °C. $[\alpha]_D^{25} = -371.8$ ($c = 0.77$; $CHCl_3$). IR (CH_2Cl_2, cm^{-1}): 3016.2 (s), 2932.4 (s), 1588.2 (s, C=O), 1568.0 (m), 897,9 (m). ^{1}H NMR (CD_2Cl_2, 293 K): δ 8.69 (d, $J = 5.6$ Hz, 1H, 11), 8.37 (d, $J = 7.9$ Hz, 1H, 14), 8.32 (s, 1H, 16), 7.87 (t, $J = 7.5$ Hz, 1H, 13), 6.79 (d, $J = 7.8$ Hz, 1H, 12), 6.82 (d, $J = 6.9$ Hz, 1H, 30), 6.57 (m, 4H, 20-21-27-28), 6.39 (d, $J = 6.9$ Hz, 1H, 31), 6.06 (s, 1H, 23), 3.30 (m, 1H, 32i), 3.10 (m, 6H), 2.78 (m, 1H, 33e). ^{13}C NMR (CD_2Cl_2, 293 K): 158.0 (16), 155.7 (15), 149.8 (11), 149.0 (19), 141.8 (26), 140.6 (29), 139.4 (22), 137.1 (13), 136.3 (18), 135.0 (27 or 28), 133.8 (20 or 21), 133.2 (20 or 21), 132.3 (31), 132.1 (27 or 28), 130.2 (30), 125.2 (12), 124.9 (23), 121.7 (14), 35.1 (32), 35.7 (24 or 25), 35.4 (24 or 25), 33.0 (33). *Anal.* Calc. for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 85,20; H, 6.68; N, 8.12%.

4.3. Synthesis and characterization of **2**

2.314 g of (−)-*S*-amino [2.2]paracyclophane (10.36 mmol), 2.5 mL of 2-acetylpyridine (26.28 mmol) and 0.05 mL of formic acid were added to 30 mL of methanol. A heterogeneous dispersion was obtained, due to the low solubility of the white amine, that was kept under stirring for 2 h, at the end of which the solid turned from white to yellow. The solid was filtered off and washed with cold methanol (2 × 5 mL). The resulting yellow solid was crystallized from methanol in the refrigerator at −18 °C. Pale yellow crystals were dried under vacuum, yielding 1.979 g of (−)-*S*-Py–C(Me)=N–($C_{16}H_{15}$) (**2**, 6.06 mmol, yield: 58.5 %). M.p. 197–199 °C. $[\alpha]_D^{25} = -484.0$ ($c = 0.96$; $CHCl_3$). IR (CH_2Cl_2, cm^{-1}): 3017.8 (s), 2931.7 (s), 1641.9 (s, C=O), 1587.9 (m), 897,7 (m). ^{1}H NMR (CD_2Cl_2, 293 K): δ 8.70 (d, $J = 4.8$ Hz, 1H, 11), 8.54 (d, $J = 7.9$ Hz, 1H, 14), 7.90 (t, $J = 7.6$ Hz, 1H, 13), 7.41 (t, $J = 6.8$ Hz, 1H, 12), 7.25 (d, $J = 7.8$ Hz, 1H, 30), 6.63 (d, $J = 7.8$ Hz, 1H, 27), 6.53 (d, $J = 7.8$ Hz, 1H,

28), 6.48 (d, $J = 7.8$ Hz, 1H, 20), 6.44 (m, 2H, 21 and 31), 5.62 (s, 1H, 23), 3.29 (m, 2H, 32i and 33i), 3.10 (m, 4H, 24e, 25 and 33e), 2.95 (m, 1H, 24i), 2.64 (m, 1H, 32e), 2.24 (s, 3H, 17). ^{13}C NMR (CD_2Cl_2, 293 K): 164.6 (16), 157.6 (15), 148.9 (11), 148.9 (18), 140.9 (22), 140.3 (29), 139.4 (26), 136.7 (13), 135.0 (20), 133.7 (28), 133.0 (27), 132.4 (31), 131.9 (19), 130.0 (30), 128.9 (21), 126.1 (23), 125.1 (12), 121.7 (14), 35.8 (25), 35.4 (24), 34.3 (33), 33.3 (32), 16.9 (17). Anal. Calc. for $C_{23}H_{22}N_2$: C, 84.63; H, 6.79; N, 8.58. Found: C, 84,90; H, 7.02; N, 8.08%.

4.4. Synthesis and characterization of *3*PF_6

0.1928 g of **1** (0.6171 mmol) and 0.1922 g of [Ru(η^6-cymene)Cl(μ-Cl)]$_2$ (0.3138 mmol) were added to 5 mL of methanol. A heterogeneous dispersion was obtained, due to the low solubility of the ligand, that was kept under magnetic stirring for 4 h. A solution of NH_4PF_6 in methanol was added drop by drop to the resulting solution. An orange solid immediately precipitated. It was filtered off, washed with cold methanol (2×1 mL), with *n*-hexane (2×3 mL) and dried under vacuum, yielding 0.338 g of **3**PF_6 (0.4641 mmol, yield: 75.2%). ^{1}H NMR (CD_2Cl_2, 293 K, (S_{Ru}, S_L)): δ 9.33 (d, $J = 5.6$ Hz, 1H, 11), 8.67 (s, 1H, 16), 8.34 (d, $J = 7.6$ Hz, 1H, 14), 8.23 (t, $J = 7.6$ Hz, 1H, 13), 7.83 (t, $J = 6.4$ Hz, 1H, 12), 6.81 (m, 2H, 20 and 21), 6.71 (m, 3H, 23, 27 and 28), 6.62 (d, $J = 8.4$ Hz, 1H, 31), 6.45 (d, $J = 8.0$ Hz, 1H, 30), 5.36 (m, 2H, 2 and 3), 5.23 (d, $J = 6.0$ Hz, 1H, 5), 5.06 (d, $J = 6.0$ Hz, 1H, 6), 3.32 (m, 24i and 33e), [25] 3.30 (m, 25i), 3.28 (m, 33i), 3.26 (m, 32e or 25e), 3.17 (m, 24e, 32i and 33i), 3.09 (32e or 25e), 2.57, (sept, $J = 7.2$ Hz, 1H, 7), 2.10 (s, 3H, 10), 1.03 (d, $J = 7.2$ Hz, 3H, 9), 0.86 (d, $J = 6.8$ Hz, 3H, 8); ^{13}C NMR (CD_2Cl_2, 293 K) δ: 164.17 (16), 155.94 (11), 155.72 (15), 149.42 (18), 142.53 (20), 140.64 (29), 140.01 (13), 139.13 (22), 136.80 (27 or 28), 135.69 (23), 133.90 (20 or 21), 133.70 (20 or 21), 133.03 (30), 130.30 (14), 129.73 (12), 129.57 (31), 128.20 (19), 125.78 (27 or 28), 107.33 (4), 102.27 (1), 87.26 (5 or 6), 87.01 (3), 86.90 (2), 86.10 (5 or 6), 36.57 (32), 35.23 (24), 35.04 (33), 31.79 (25), 31.23 (7), 22.39 (9), 21.35 (8), 18.60 (10); ^{19}F NMR (CD_2Cl_2, 293 K) δ: −72.67 (d, $J = 762$ Hz, 6F). ^{1}H NMR (CD_2Cl_2, 293 K, (R_{Ru}, S_L)): δ 9.26 (d, $J = 5.4$ Hz, 1H, 11), 8.75 (s, 1H, 16), 8.41 (d, $J = 5.4$ Hz, 1H, 14), 8.21 (t, $J = 8.7$ Hz, 1H, 13), 7.79 (t, $J = 6.2$ Hz, 1H, 12), 6.85 (m, 2H), 6.70 (m, 3H), 6.56 (m, 2H), 5.71 (d, $J = 6.0$ Hz, 1H, 5), 5.30 (d, $J = 6.2$ Hz, 1H, 6), 5.17 (d, $J = 6.0$ Hz, 1H, 2), 5.02 (d, $J = 5.9$ Hz, 1H, 3), 3.18 (m, 6H), 2.96 (m, 1H), 2.86 (m, 1H), 2.36 (sept, $J = 6.7$ Hz, 1H, 7), 2.15 (s, 3H, 10), 0.99 (d, $J = 6.9$ Hz, 3H, 8 or 9), 0.95 (d, $J = 6.9$ Hz, 3H, 8 or 9). Anal. Calc. for $C_{32}H_{34}ClF_6N_2PRu$: C, 52.79; H, 4.71; N, 3.85. Found: C, 53.04; H, 4.92; N, 3.55%.

4.5. Synthesis and characterization of *3*BPh_4

Complex **3**BPh_4 was synthesized with the same procedure as that used for **3**PF_6, adding $NaBPh_4$ instead of NH_4PF_6 as precipitating agent. Yield : 80.4%. ^{1}H NMR (CD_2Cl_2, 293 K, (S_{Ru}, S_L)) δ: 8.85 (d, $J = 5.1$ Hz, 1H), 8.50 (s, 1H), 7.94 (m, 2H), 7.49 (m, 1H), 7.32 (br, 8H, *o*-BPh_4), 7.00 (t, $J = 7.0$ Hz, 8H, *m*-BPh_4), 6.86 (7, $J = 7.1$ Hz, 4H, *p*-BPh_4), 6.69 (m, 4H), 6.48 (m, 2H), 6.37 (d, $J = 8.1$ Hz, 1H), 5.06 (br, 2H), 5.00 (d, $J = 5.91$ Hz, 1H), 3.01 (m, 8H), 2.42 (sept, $J = 6.9$ Hz, 1H), 1.92 (s, 3H), 0.93 (d, $J = 7.0$ Hz, 3H), 0.81 (d, $J = 6.9$ Hz, 3H). Anal. Calc. for $C_{56}H_{54}BClN_2Ru$: C, 74.54; H, 6.03; N, 3.10. Found: C, 74.71; H, 6.13; N, 3.00%.

4.6. Synthesis and characterization of *3*BF_4

71.21 mg of **1**BPh_4 (0.0789 mmol) and 16.31 mg of $AgBF_4$ (0.0838 mmol) were dissolved in methylene chloride. The mixture was kept under magnetic stirring for 2 h. The color of the mixture changed from orange to brown, and $AgBPh_4$, that precipitated from the solution as a colorless solid, was filtered off through celite. The addition of *n*-hexane to the solution led to the product that was crystallized from a (1:1) mixture of diethyl ether and dichloromethane. The yellow powder was dried under vacuum, yielding 29.61 mg of **3**BF_4 (0.0442 mmol, yield: 56%). ^{1}H NMR (CD_2Cl_2, 293 K, (S_{Ru}, S_L)) δ: 9.51 (d, $J = 5.2$ Hz, 1H), 8.80 (s, 1H), 8.34 (d, $J = 7.6$ Hz, 1H), 8.14 (t, $J = 8.0$ Hz, 1H), 7.75 (t, $J = 6.4$ Hz, 1H), 6.64 (m, 7H), 5.79 (d, $J = 6.0$ Hz, 1H), 5.68 (d, $J = 6.0$ Hz, 1H), 5.11 (d, $J = 6.0$ Hz, 1H), 4.88 (d, $J = 6.0$ Hz, 1H), 2.93 (m, 8H) 2.12 (m, 4H), 0.83 (d, $J = 6.8$ Hz, 3H), 0.69 (d, $J = 6.8$ Hz, 3H); ^{19}F NMR (CD_2Cl_2, 293 K) δ: −149.10 (br, $^{10}BF_4$), −149.16 (br, $^{11}BF_4$). *Anal.* Calc. for $C_{32}H_{34}BClF_4N_2Ru$: C, 57.37; H, 5.12: N, 4.18. Found: C, 57.71; H, 5.23; N, 3.92%.

4.7. Synthesis and characterization of *4*PF_6

Complex **4**PF_6 was synthesized with the same procedure used for **3**PF_6, starting with **2** instead of **1**. Yield: 83.0%. ^{1}H NMR (CD_2Cl_2, 293 K, (R_{Ru}, S_L)) δ: 9.23 (d, $J = 5.2$ Hz, 1H, 11), 8.23 (t, $J = 7.6$ Hz, 1H, 13), 8.16 (d, $J = 7.2$ Hz, 1H, 14), 7.81 (t, $J = 7.2$ Hz, 1H, 12), 6.92 (dd, $J_1 = 7.6$ Hz, $J_2 = 7.8$ Hz, 2H, 27–28), 6.73 (d, $J = 8.0$ Hz, 1H, 20), 6.60 (d, $J = 8.0$ Hz, 1H, 21), 6.54 (d, $J = 8.4$ Hz, 1H, 31), 6.47 (d, $J = 8.4$ Hz, 1H, 30), 6.40 (s, 1H, 23), 5.04 (d, $J = 6.0$ Hz, 1H, 6), 4.77 (d, $J = 6.0$ Hz, 1H, 2), 4.72 (d, $J = 6.0$ Hz, 1H, 3), 3.42 (m, 33i), 3.38 (m, 24e), 3.30 (m, 25i), 3.25 (m, 32i), 3.22 (s, 17), 3.18 (m, 33e), 3.17 (m, 32e), 3.08 (m, 24i), 3.02 (m, 25e), 2.46 (sept, $J = 7.2$ Hz, 1H, 7), 2.10 (s, 3H, 10), 1.03 (d, $J = 7.2$ Hz, 3H, 9), 0.97 (d, $J = 6.8$ Hz, 3H, 8); ^{13}C NMR (CD_2Cl_2, 293 K) δ: 173.76 (16), 155.93 (11), 155.72 (15), 151.30 (18), 140.73 (29), 140.57 (22), 140.06 (13), 140.01 (26), 137.72 (20), 135.36 (19), 134.47 (22), 133.69 (27–28), 133.10 (27–28), 131.82 (30), 131.60 (31), 129.24 (12), 128.41 (14), 120.94 (23), 107.20 (4), 103.69 (1), 86.61 (3), 86.47 (5), 86.20 (6), 86.00 (2), 35.842, 35.44, 35.27, 35.13, 22.62 (9), 21.82, 19.89 (17), 18.84 (10), 14,29 (8); ^{19}F

NMR (CD_2Cl_2, 293 K) δ: −73.16 (d, $J = 755.6$, 6F). ^1H NMR (CD_2Cl_2, 293 K, (S_{Ru}, S_L)) δ: 9.29 (d, $J = 5.6$, 1H, 14), 8.25 (t, $J = 8.0$, 1H, 12), 8.19 (d, $J = 7.6$, 1H, 11), 7.84 (t, $J = 6.8$, 1H, 13), 6.98 (dd, $J_1 = 7.6$, $J_2 = 11.4$, 2H, 27–28), 6.78 (d,$J = 7.2$, 1H, 20), 6.66 (d, $J = 8.0$, 1H, 31), 6.61 (d, $J = 7.6$, 1H, 21), 6.44 (d, $J = 8.8$, 1H, 30), 6.29 (s, 1H, 23), 5.50 (d, $J = 6.0$, 1H, 2), 5.41 (d, $J = 6.4$, 1H, 5), 5.05 (d, $J = 6.4$, 1H, 3), 4.87 (d, $J = 6.4$, 1H, 6), 3.221 (m, 8H), 2.65 (sept, $J = 7.2$, 1H, 7), 1.56 (s, 3H, 10), 1.02 (d, $J = 7.2$, 3H, 9), 0.82 (d, $J = 6.8$, 3H, 8). Anal. Calc. for $C_{33}H_{36}ClF_6N_2PRu$: C, 53.41; H, 4.89; N, 3.77. Found: C, 53.6; H, 5.21; N, 3.50%.

4.8. Synthesis and characterization of *4*BPh_4

Complex **4**BPh_4 was synthesized with the same procedure used for **4**PF_6, using $NaBPh_4$ instead of NH_4PF_6 as precipitating agent. Yield: 83.5%. ^1H NMR (CD_2Cl_2, 293 K, (R_{Ru}, S_L)) δ: 8.88 (d, $J = 4.8$ Hz, 1H), 7.97 (t, $J = 8.0$ Hz, 1H), 7.70 (d, $J = 7.6$ Hz, 1H), 7.54 (t, $J = 6.4$ Hz, 1H), 7.39 (br, 8H, *o*-BPh_4), 7.06 (t, $J = 7.6$ Hz, 8H, *m*-BPh_4), 6.97 (m, 2H), 6.92 (br, 4H, *p*-BPh_4), 6.71 (d, $J = 8.0$ Hz, 1H), 6.59 (d, $J = 7.2$ Hz, 1H), 6.48 (d, $J = 8.0$ Hz, 1H), 6.21 (s, 1H), 5.13 (d, $J = 6.0$ Hz, 1H), 4.88 (d, $J = 6.0$ Hz, 1H), 4.59 (d, $J = 6.0$ Hz, 1H), 4.47 (d, $J = 6.0$ Hz, 1H), 3.21 (m, 8H), 2.89 (s, 3H), 2.34 (sept, $J = 6.8$ Hz, 1H), 2.05 (s, 3H), 0.99 (d, $J = 6.8$ Hz, 3H), 0.89 (d, $J = 6.8$ Hz, 3H). Anal. Calc. for $C_{57}H_{56}BClN_2Ru$: C, 74.71; H, 6.16; N, 3.06. Found: C, 75.02; H, 6.40; N, 2.87%.

4.9. Synthesis and characterization of *4*BF_4

Complex **4**BF_4 was synthesized with the same procedure used for **3**BF_4, starting with **4**BPh_4 instead of **3**BPh_4. Yield: 54.0%. ^1H NMR (CD_2Cl_2, 293 K, (R_{Ru}, S_L)) δ: 9.31 (d, $J = 5.2$ Hz, 1H), 8.23 (t, $J = 8.0$ Hz, 1H), 8,17 (d, $J = 8.0$ Hz, 1H), 7.84 (t, $J = 6.4$ Hz, 1H), 6,91 (br, 2H), 6.72 (d, $J = 7.6$ Hz, 1H), 6.59 (d, $J = 7.2$ Hz, 1H), 6.53 (d, $J = 8.0$ Hz, 1H), 6.47 (d, $J = 8.4$ Hz, 1H), 6.41 (s, 1H), 5.40 (d, $J = 6.0$ Hz, 1H), 5.07 (d, $J = 6.0$ Hz, 1H), 4.76 (t, $J = 6.8$ Hz, 2H), 3.24 (m, 11H), 2.44 (sept, $J = 7.2$ Hz, 1H), 2.09 (s, 3H), 1.02 (d, $J = 6.8$ Hz, 3H), 0.96 (d, $J = 7.2$ Hz, 3H). ^{19}F NMR (CD_2Cl_2, 293 K) δ: −149.09 (br, $^{10}BF_4$), −149.15 (br, $^{11}BF_4$). Anal. Calc. for $C_{33}H_{36}BClF_4N_2Ru$: C, 57.95; H, 5.31; N, 4.10. Found: C, 58.3; H, 5.54; N, 3.90%.

4.10. X-ray crystallography

A single crystal of **4**PF_6 suitable for X-ray diffraction (a red block with approximate dimensions of 0.20 mm × 0.15 mm × 0.10 mm) was obtained by crystallization from methyl alcohol and diethyl ether. Data were collected on a XCALIBUR (Kuma4CCD) diffractometer using Mo Kα graphite-monochromated radiation ($\lambda = 0.71069$ Å), ω scans and the frame data were acquired with the CRYSALIS (CCD 169) software. The crystal-to-detector distance was 65.77 mm. The structure was solved using direct methods and refined against $|F|^2$. The Laue symmetry was determined to 1.541 g cm^{-3} ($Z = 2$ and $FW = 742.13$) and the investigation of the observed systematic absences are consistent with the monoclinic space group $P21$ (no. 4). The data were collected at room temperature. The lattice parameters found were: $a = 8.015(1)$, $b = 14.316(1)$ and $c = 14.349(1)$ Å, $\beta = 103.750(10)°$, and $V = 1599.3(3)$ Å^3. Data were collected to $2\theta_{max}$ of 57.20° in the index ranges $-5 \leqslant h \leqslant 10$, $-18 \leqslant k \leqslant 19$, and $-19 \leqslant l \leqslant 18$ with a total of 11 372 reflections collected, of which 53 were rejected and 7263 were unique reflections, independent $R_{int} = 0.0178$, up to a resolution of 0.74 Å. The frames were then processed using the CRYSALIS (RED 169) software to give the *hkl* file corrected for scan speed, background, and Lorentz and polarization affects. Standard reflections, measured periodically, showed no apparent variation in intensity during data collection and so, no correction for crystal decomposition was necessary. The data were corrected for absorption using the SADABS [26] program. The structure was solved by the direct method using the SIR97 [27] program and refined by the full-matrix least-squares method on F^2 using the SHELXL-97 [28], WinGX [29] version. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added at the calculated positions and refined using a riding model. The final cycle of full-matrix least-squares refinement against $|F|^2$ was based on 6116 observed reflections [$F_0 > 4\ \sigma\ (F_0)$] and 404 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.0366$ and $R_w = 0.0767$, and GOF = 1.030 $\quad (w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3)$.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 269352. 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.ccdc.cam.ac.uk/data_request/cif).

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