Aggregation tendency and reactivity toward AgX of cationic half-sandwich ruthenium(II) complexes bearing neutral N,O-ligands

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The aggregation tendency of complexes [Ru(η^6-cymene)(N,O)Cl]X [N,O = 2-benzoylpyridine (2-bzpy), **1**, and 2-acetylpyridine (2-acpy), **2**, X^- = BPh_4^- or PF_6^-] has been studied by means of PGSE NMR experiments. It was found that complexes with PF_6^- as counterion are mainly present in CD_2Cl_2 as ion pairs at low concentration, as a mixture of ion triples and free anions at medium concentration and as ion quadruples at elevated concentration. ^{19}F, ^1H-HOESY NMR experiments revealed that in ion triples and ion quadruples two cationic Ru-units pair up. Consistently, in the solid-state structure of **1**PF_6, determined through X-ray single-crystal investigation, two cationic Ru-units are held together by an intermolecular π–π stacking interaction between the pyridyl rings. Complexes having BPh_4^- as counterion are only present in solution as even aggregates, namely ion pairs at low concentration and ion quadruples at elevated concentration. In such a case a counteranion bridges two cationic Ru-units as observed in the solid-state structure of **1**BPh_4. The reactivity of complexes **1–2** toward AgX salts has been investigated in different solvents. Bicationic [Ru(η^6-cymene)(N,O)(MeCN)]X_2 (N,O = 2-bzpy, **3**, and 2-acpy, **4**) and [Ru$(MeCN)_4$(N,O)]X_2 (N,O = 2-bzpy, **5**, and 2-acpy, **6**) complexes were obtained by the reaction of **1** and **2** with AgX in the presence of three equivalents of acetonitrile or in acetonitrile, respectively. The reaction of **1** with $AgPF_6$ in acetone afforded complex [Ru(η^6-cymene)(N,O,O)]PF_6 (**7**, where N,O,O = 4-alcoxide-4-phenyl-4-(pyridin-2-yl)butan-2-one) from the C–C coupling of a deprotonated methyl group of the coordinated acetone and the C=O moiety of 2-bzpy ligand.

Introduction

The successful utilization of transition-metal organometallics in organic synthesis mainly stems from the alteration of the reactivity of organic substrates that are coordinated to the metal center.[1] Nevertheless, emerging evidence suggests that second-coordination-sphere interactions (H-bonding, π–π stacking, CH–π interaction, *etc*...) may play a significant role in such an activation process.[2] For example, it is now well-recognized that ion-pairing drastically affects the reactivity and structure of ionic organometallic catalysts.[3]

In a few cases, it has been proposed that organometallics catalyse organic reactions solely using second-coordination-sphere interactions. For instance, the Shvo[4] and Noyori[5] catalysts, bearing both a Y–H (Y = NR or O) proton donor and an M–H hydride donor, are thought to hydrogenate ketones in the second-coordination-sphere through a bifunctional mechanism that involves the interactions $Y–H^{\delta+}\cdots{}^{\delta-}O{=}C^{\delta+}\cdots{}^{\delta-}H–M$ and does not need the coordination of the ketone to the metal.

Second-coordination-sphere catalysis needs peripheral "anchor points" on the catalyst suitable for establishing favourable interactions with the organic substrate to be activated. Nevertheless, it seems reasonable that such "anchor points" can also lead to the self-aggregation of the catalyst itself. PGSE (Pulsed Field Gradient Spin-Echo) NMR experiments[6] have demonstrated that this indeed occurs in solution for the Shvo[7] and Noyori[8] catalysts. In particular, while Casey and co-workers have shown that [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)]$Ru(CO)_2H$ is a hydrogen bonded dimer in toluene,[7] in our laboratory it has been found that (η^6-arene)RuCl[N(Ts)CHPhCHPhNH_2] and other Ru(II) arene derivatives containing α-amino acid ligands have a remarkable tendency to form dimers, and even higher aggregates, in several solvents including isopropanol.[8] Cationic arene ruthenium complexes bearing diimine or diamine ligands were also found to undergo associative processes in several solvents leading to ion triples and ion quadruples held together by classical N–H···X or more unusual, and less energetic, CH···X H-bonds.[9,10]

Here we report PGSE and NOE (Nuclear Overhauser Effect) results on the aggregation and interionic structure in solution of novel [Ru(η^6-cymene)(N,O)Cl]X complexes that do not possess peripheral functionalities particularly suited to hydrogen bonding. The solution results are contrasted with those obtained in the solid state through X-ray single-crystal studies. Finally, the reactivity of such complexes toward silver salts is described.

Results and discussion

Syntheses and characterization of compounds 1–2

Complexes [Ru(η^6-cymene)(N,O)Cl]X [N,O = 2-benzoylpyridine (2-bzpy), **1**, and 2-aceylpyridine (2-acpy), **2**, X^- = BPh_4^- or PF_6^-] were synthesised by the reaction of [Ru_2(η^6-cymene)$_2Cl_2$(μ-Cl)$_2$] with the appropriate ligand in methanol at room temperature in the presence of a large excess of $NaBPh_4$ or NH_4PF_6 (Scheme 1). They were characterised in solution by FT-IR and ^1H, ^{13}C, ^{19}F, and ^{31}P NMR spectroscopies. Data are reported in the Experimental section. Numbering of carbon and proton resonances is illustrated

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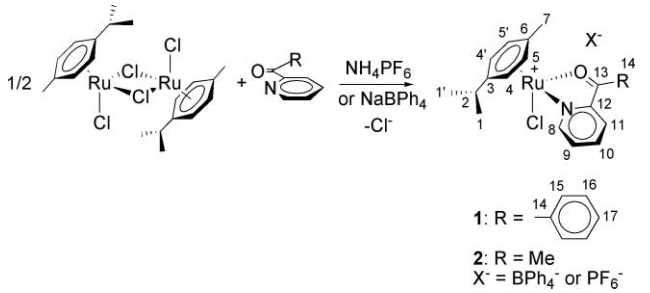
Table 1 Selected bond lengths (Å) and angles (°) of complexes **1**PF_6 and **1**BPh_4 with estimated standard deviation in parentheses

	1PF_6	**1**BPh_4
Ru–N	2.093(3)	2.102(2)
Ru–O	2.098(3)	2.091(2)
Ru–Cl	2.3890(9)	2.3755(10)
Ru–Cy[a]	1.671(5)	1.661(4)
O–Ru–N	75.77(12)	75.66(9)
Cl–Ru–N	84.60(8)	86.11(7)
Cl–Ru–O	84.56(6)	82.88(7)

[a] C13–C18 centroid.



Scheme 1

in Scheme 1. All the proton and carbon resonances were assigned (see Experimental) through ^{1}H, ^{13}C, ^{1}H-COSY, ^{1}H-NOESY, ^{1}H, ^{13}C-HMQC NMR, and ^{1}H, ^{13}C HMBC NMR spectroscopies. The solid-state structures for **1**PF_6 and **1**BPh_4 were determined by X-ray single-crystal diffractometry. An ORTEP view of cation **1** is shown in Fig. 1. Relevant bond lengths and angles are given in Table 1.

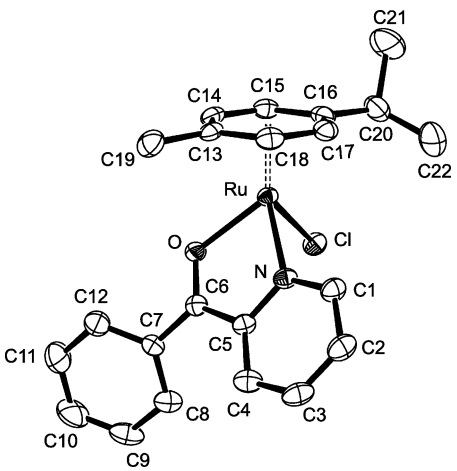


Fig. 1 An ORTEP diagram of the cation in **1**PF_6. Ellipsoids are drawn at the 30% probability level.

In solution, the coordination of the labile O-arm to ruthenium was indicated by a decrease in the C=O stretching frequency of 67 and 81 cm^{-1} for 2-bzpy and 2-acpy complexes, respectively, with respect to the uncoordinated ligand.[11] At the same time, a deshielding of C13 was observed that passed from 194.7 and 200.8 ppm in the free ligands to 205.0 and 211.6 ppm in **1**X and **2**X, respectively.

In the solid state, the Ru–O bond lengths found for **1**PF_6 (2.098 Å) and **1**BPh_4 (2.091 Å) were similar to those reported for *cis*-$RuCl_2$(dppb)(2-bzpy) [2.035 Å, dppb = 1,4-bis-(diphenylphosphino)butane][12] and [Ru(2,2′-bipy)$_2$(2-bzpy)]$(PF_6)_2$ (2.058 Å, 2,2′-bipy = 2,2′-bipyridine)[13] but were significantly shorter than that of *trans*-[Ru$(PMe_3)_2$(CO)(COMe)(2-bzpy)]BPh_4 (2.226 Å).[14]

Aggregation and relative anion–cation orientations through PGSE and NOE NMR experiments

PGSE measurements were performed for all complexes in CD_2Cl_2 at 296 K as a function of the concentration (Table 2). In the case of complex **1**PF_6, the effect of changing the solvent was also investigated (Table 2). From the measured self-diffusion coefficients (D_t), the average hydrodynamic radius (r_H) and volume (V_H) of the diffusing particles were derived taking advantage of the Stokes–Einstein eqn (1), where k is the Boltzmann constant, T is the temperature, c is a numerical factor and η is the solution viscosity.

$$D_t = \frac{kT}{c\pi\eta r_H} \quad (1)$$

TMSS [tetrakis(trimethylsilyl)silane], whose dimensions are known from the literature, was used as internal standard.[15] The methodology to obtain accurate r_H and V_H values has been described elsewhere.[10] The average hydrodynamic volumes for cation (V_{H^+}) and anion (V_{H^-}), determined from ^{1}H- and

Table 2 Diffusion coefficients ($10^{10}D_t/m^2\ s^{-1}$), hydrodynamic radii (r_H/Å) and aggregation number (N) for compounds **1** and **2** as a function of solvent (ε_r at 25 °C) and concentration (C/mM)

		D_t^+	D_t^-	r_H^+	r_H^-	N^+	N^-	C
1PF_6 (V_{ip} = 368 Å^3)								
1	CD_2Cl_2 (8.93)	11.6	12.5	4.5	4.3	1.0	0.9	5
2	CD_2Cl_2 (8.93)	9.8	11.0	5.4	4.9	1.8	1.3	15
3	CD_2Cl_2 (8.93)	9.3	10.9	5.6	4.9	2.0	1.3	41
4	CD_2Cl_2 (8.93)	8.7	9.31	5.7	5.4	2.1	1.8	70
5	CD_2Cl_2 (8.93)	7.8	8.53	5.9	5.5	2.3	1.8	113[b]
6	$CDCl_3$ (4.81[a])	7.5	7.7	5.7	5.6	2,1	2.0	1
7	$CDCl_3$ (4.81[a])	7.2	7.3	5.8	5.8	2.2	2.2	6[b]
8	C_6D_5Cl (5.61)	5.6	5.7	5.0	4.9	1.4	1.4	1
9	C_6D_5Cl (5.61)	5.1	5.2	5.6	5.6	2.0	2.0	6[b]
1BPh_4 (V_{ip} = 600 Å^3)								
10	CD_2Cl_2 (8.93)	8.6	8.7	6.1	6.0	1.6	1.6	9
11	CD_2Cl_2 (8.93)	7.6	7.7	6.2	6.1	1.7	1.6	34
12	CD_2Cl_2 (8.93)	7.5	7.7	6.4	6.3	1.9	1.8	43[b]
2PF_6 (V_{ip} = 322 Å^3)								
13	CD_2Cl_2 (8.93)	10.2	10.4	4.2	4.2	1.0	1.0	6
14	CD_2Cl_2 (8.93)	9.8	10.0	5.3	4.9	1.9	1.5	12
15	CD_2Cl_2 (8.93)	9.7	9.7	5.3	5.3	2.0	2.0	31
16	CD_2Cl_2 (8.93)	8.6	8.6	5.7	5.7	2.4	2.4	80[b]
2BPh_4 (V_{ip} = 554 Å^3)								
17	CD_2Cl_2 (8.93)	8.5	8.6	6.0	5.9	1.6	1.6	7
18	CD_2Cl_2 (8.93)	7.1	7.1	6.5	6.5	2.1	2.1	24[b]

[a] 20 °C. [b] Saturated solution.

^{19}F-PGSE experiments, respectively, were contrasted with the van der Waals volume of the ion-pair (V_{IP}) known from single-crystal X-ray investigations or derived from them. The cationic and anionic aggregation numbers (N^+ and N^-) were calculated as the ratios $V_H{}^+/V_{IP}$ and $V_H{}^-/V_{IP}$, respectively (Table 2).

Complex **1**PF_6 was mainly present as ion-pair in CD_2Cl_2 at the lowest concentration considered (5 mM). In fact, N^+ and N^- were both equal to 1 (entry 1) within the experimental error that was estimated to be *ca.* 10%. An increase of the concentration led to a rapid increment of N^+ that passed from 1.0 (5 mM) to 1.8 (15 mM, entry 2) and then up to 2.3 in the saturated solution (113 mM, entry 5). N^- also increased but in a less accentuated manner and it only approached the value 2 at concentrations higher than 70 mM (entries 4 and 5). These results indicate that an increase in concentration initially causes the transformation of ion pairs into ion triples and free anions. For a solution of **1**PF_6 containing 50% of PF_6^- and 50% of **1**$_2PF_6^+$, N^+ and N^- are expected to be 1.8 and 1.1, respectively, in good agreement with the observed values for 15 and 41 mM solutions (entries 2 and 3). A further concentration increase led to the presence of mainly ion quadruples in solution (entries 4 and 5). In $CDCl_3$, **1**PF_6 was already present as ion quadruples at 1 mM concentration (entry 6) and it remained as ion quadruples in the saturated solution (entry 7). Complex **2**PF_6 showed a greater tendency to aggregate than **1**PF_6 in CD_2Cl_2 (entries 13–16). While the former afforded ion quadruples at 31 mM, the latter needed a concentration higher than 70 mM. The PGSE measurements for **2**PF_6 also indicated that ion pairs were formed at low concentration, ion triples and free anions at intermediate concentration and ion quadruples at high concentration.

The relative anion–cation orientations for complexes **1**X in CD_2Cl_2 were studied by detecting dipolar interionic interactions in the ^{19}F, ^{1}H-HOESY (X$^-$ = PF_6^-) and ^{1}H-NOESY (X$^-$ = BPh_4^-) NMR spectra at room temperature (296 K).

In the 5 mM solution of **1**PF_6 where ion pairs were mainly present ($N^+ = 1.0$ and $N^- = 0.9$, entry 1 of Table 2), strong NOEs were observed between the F-atoms of the counterion and proton 8 and the aromatic cymene protons (Table 3). Interactions of moderate intensity were detected with 9, 10, 11 and 15 resonances. Weak interactions were observed with the methyl and isopropyl groups of cymene. Only 2, 16 and 17 did not show any NOE with the anion. These observations are consistent with a single relative anion–cation orientation, where PF_6^- is located above the pyridyl moiety in agreement with our previous findings.[14,16]

The formation of ion triples (15 mM solution, $N^+ = 1.8$ and $N^- = 1.3$) had little effect on the relative intensities of interionic NOEs (Table 3) with the exception of weak interionic NOEs between 2 and 16 and the anion that became visible in the ^{19}F, ^{1}H-HOESY spectrum (Fig. 2). For the 70 mM solution in CD_2Cl_2 (entry 4, Table 2) and the 6 mM saturated solution in $CDCl_3$ (entry 7, Table 2), which contained mainly ion quadruples, the relative intensities of the contacts between 5/5′, 9 and 15 and PF_6^- increased.

In the solid state, complex **1**PF_6 showed sinusoidal chains of cations that lay parallel to the *bc* plane. The chains consisted of pairs of cations of alternating chirality: *R*,*R*,*S*,*S*,*R*,*R*, etc... The cations of opposite chirality exhibited face to face π–π stacking interactions involving the pyridyl groups (Fig. 3). These were completely coplanar, while the mean slip angle between the normal

Table 3 Relative NOE intensities in CD_2Cl_2 determined by arbitrarily fixing the intensity of the NOE(s) between the anion resonances (*o*-H in the case of BPh_4^-) and the aromatic proton 8 of pyridyl at 1. Quantification was carried out by taking into account that the volumes of the NOE cross peaks are proportional to $(n_I n_S/n_I + n_S)$ where n_I and n_S are the number of equivalent I and S nuclei, respectively[17]

	1PF_6	**1**PF_6	**1**PF_6	**1**PF_6	**1**PF_6[a]	**1**BPh_4
	5 mM	15 mM	41 mM	70 mM	6 mM	34 mM
	$N^+ = 1.0$	$N^+ = 1.8$	$N^+ = 2.0$	$N^+ = 2.1$	$N^+ = 2.2$	$N^+ = 1.7$
	$N^- = 0.9$	$N^- = 1.3$	$N^- = 1.3$	$N^- = 1.8$	$N^- = 2.2$	$N^- = 1.6$
1,1′	0.12	0.14	0.06	0.09	0.12	0.20
2	—	0.12	0.13	0.10	0.39	0.30
4	0.57	0.52	0.57	0.63	1.12	0.62
4′						0.77
5	0.57	0.52	0.74	0.91		1.01
5′						0.85
7	0.22	0.19	0.17	0.19	0.32	0.35
8	1	1	1	1	1	1
9	0.38	0.45	0.54	0.64	0.99[b]	1.23
10	0.22	0.27	0.27	0.29	0.46	1.02
11						0.54
15	0.26	0.26	0.42	0.42	0.99[b]	0.68
16	—	0.04	0.05	0.06	—	0.33
17	—	—	—	—	—	—

[a] In $CDCl_3$, [b] 9 and 15 are superimposed.

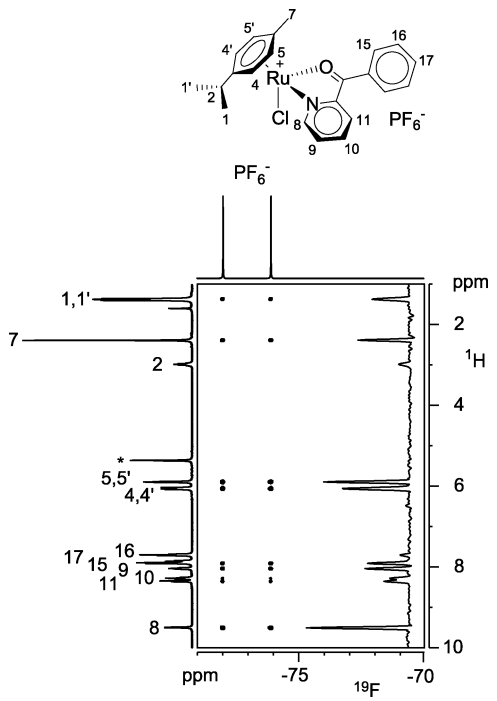


Fig. 2 ^{19}F, ^{1}H-HOESY NMR spectrum (376.65 MHz, 296 K, CD_2Cl_2) of complex **1**PF_6 at 15 mM; *denotes the residue of non-deuterated solvent.

of one pyridine plane and the centroid vector was 31.5° and the centroid to centroid distance was 4.10 Å. The latter values are higher than the mean ones of 20° and 3.80 Å[18,19] but similar to those of other complexes.[13,18] Kol and co-workers previously showed an analogous chiral recognition, based on π-stacking interactions,

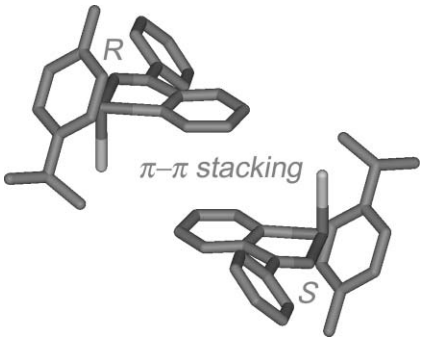


Fig. 3 Chiral recognition observed in the solid state for **1**PF_6 due to a π–π stacking interaction between two pyridyl rings.

in both solid state and solution for octahedral Ru(II) and Os(II) complexes of eilatin.[20]

The cations with the same chirality did not show any specific interaction between them. Only very weak π–π stacking interactions between the cymene group and a benzylic moiety could be observed. The two planes made a 31.8° angle with an interplane minimum and maximum separation of 3.51 and 4.90 Å, respectively, and a centroid to centroid distance of 4.16 Å. The mean slip angle between the normal of the cymene plane and the centroid vector was 29.9°. π–π Stacking interactions were also observed between the benzylic groups of two different sinusoidal cation chains. The benzyls were completely coplanar, while the mean slip angle between the normal of the benzylic plane and the centroid vector was 38.2° and the centroid to centroid distance was 4.91 Å.

The PF_6^- anions were distributed as bridges between different cations and formed linear chains that lay parallel to the *ab* faces and form the diagonals of these with alternated slopes. Each cationic unit was surrounded by four anions. The closest two were at a Ru···P distance of 5.825 and 5.883 Å, respectively (orientations A and B in Fig. 4).

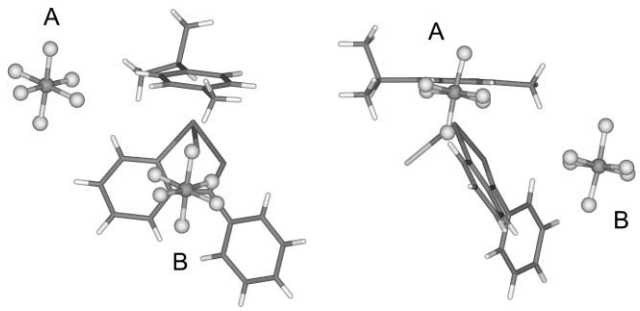


Fig. 4 Two views of two ion pairs (A and B) present in the solid state for compound **1**PF_6 (the PF_6 A and B are represented as balls and sticks).

In solution, the NOE measurements indicated that within an ion pair the counterion is located between the pyridyl ring and cymene ligand, *i.e.* in an intermediate position with respect to A and B orientations. In such a position, the anion is affected little by the formation of the ion triple that probably occurs through a π-stacking interaction of the other face of the pyridyl ring as observed in the solid state (Fig. 3). On passing from ion pairs to ion triples and, finally, to ion quadruples, the average anion position changes a little becoming more similar to the orientation B observed in the solid state, as indicated by the increased intensities of the PF_6^-/9 and 15 interionic NOEs.

PGSE measurements were made of **1**PF_6 in C_6D_5Cl to corroborate the hypothesis that ion triples and ion quadruples in solution are held together by pyridyl π-stacking. C_6D_5Cl has a relative permittivity (ε_r) comparable to that of $CDCl_3$ (Table 1) but it can compete with another molecule of **1**PF_6 in π-stacking interactions and, consequently, it should reduce the aggregation tendency. Consistently, at 1 mM the aggregation in C_6D_5Cl was significantly lower than that in $CDCl_3$ (compare entries 8 and 6 in Table 2) and, more importantly, the values of N^+ and N^- were identical indicating that ion quadruples dissociate into two ion pairs and not into ion triples and anions.

PGSE measurements carried out for complexes **1**BPh_4 and **2**BPh_4 in CD_2Cl_2 showed that at the lowest concentrations a mixture of ion pairs and ion quadruples was present (Table 2, entries 10–11 and 17). Ion quadruples were observed almost exclusively in saturated solutions (Table 2, entries 12 and 18). Interestingly, in all cases, N^+ was equal to N^- indicating that only even aggregates (ion pairs and ion quadruples) were present in solution. This is in marked contrast with the results obtained for **1**PF_6 and **2**PF_6 for which ion triples and free ions formed (compare entries 10–12 with 1–3 and 13–14 with 17–18 in Table 2). The quantitative analysis of NOE measurements carried out for a 34 mM solution of complex **1**BPh_4 in CD_2Cl_2 (Table 3) showed that the counterion interacted with all protons except 17.

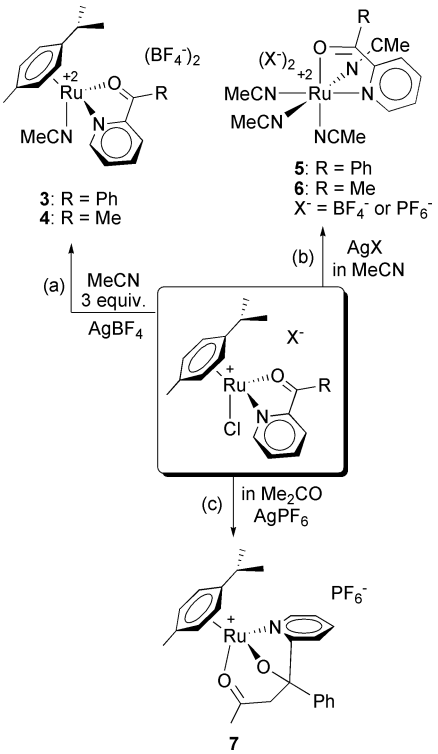
In contrast to **1**PF_6, the solid-state structure of **1**BPh_4 did not exhibit any intercationic proximity; on the contrary, there was a perfect alternation of cations and anions in all three directions. Although NMR does not afford any direct evidence, based on the solid-state structure, we propose that, in solution, ion quadruples are constituted by an alternation of cations and anions.

Reactivity of complexes 1–2 with AgX salts

The reactivity of complexes **1–2** toward AgX salts was investigated in different solvents. The species formed were completely characterised in solution by means of multinuclear and multidimensional NMR experiments. The results are summarised in Scheme 2.

By the reaction of complexes **1** or **2** with a stoichiometric amount of $AgBF_4$, in methylene chloride in the presence of *ca.* 3 equivalents of acetonitrile (MeCN), the bicationic **3** or **4** complexes formed [Scheme 2, pathway (a)]. The coordination of a Me–C≡N unit was ascertained by the presence in the ^{1}H NMR spectra of a resonance at 2.34 and 2.38 ppm for **3** and **4**, respectively, integrating for three protons. Two resonances were present in the ^{13}C NMR spectra at 129.5 and 4.3 ppm for **3** and at 128.6 and 4.3 ppm for **4** due to CN and Me moieties, respectively. The O-arm remained coordinated to the metal as indicated by the high-frequency value of C=O that fell to 207.4 and 216.0 ppm for **3** and **4**, respectively.

When the reactions of **1** and **2** with AgX (X^- = BF_4^- and PF_6^-) were carried out in MeCN, in addition to the Cl^-/MeCN substitution reaction, cymene was also replaced by three MeCN molecules and complexes **5** and **6** were formed [Scheme 2, pathway (b)]. Three resonances were observed for the carbons and hydrogens of *Me*CN in both the ^{1}H and ^{13}C NMR spectra. Due



Scheme 2

to the equivalence of the MeCN ligands in relative *trans* position, one of these integrated twice as much as the other two. The O-arm appeared to be still coordinated to ruthenium since the resonance due to C=O fell to 210.4 and 217.0 ppm for **5** and **6**, respectively. Complexes **5** and **6** were also obtained by dissolving **3** and **4** in acetonitrile.

To the best of our knowledge, these are the first bicationic solvento-complexes of ruthenium bearing a neutral N,O-ligand. Since these complexes can be prepared in good yield and contain up to five labile ligands they may be good starting materials for the syntheses of other compounds. Monocationic cycloruthenated $[Ru(N,C)(CH_3CN)_4]PF_6$ and $[Ru(\eta^2\text{-amidinate})(CH_3CN)_4]PF_6$ complexes were synthesised by Pfeffer and co-workers[21] and Hayashida and Nagashima,[22] respectively, and it has been demonstrated that acetonitrile ligands can be easily replaced by other σ-donor ligands such as pyridines, phosphines, and isocyanides.[22]

In an attempt to synthesise a complex similar to **3** with acetone coordinated to ruthenium instead of MeCN,[23] the reactions of **1** with $AgPF_6$ were carried out in acetone [Scheme 2, pathway (c)]. Interestingly enough, the monocationic complex **7** was obtained in good yield from the C–C coupling of a deprotonated methyl group of the coordinated acetone molecule and the C=O moiety of the N,O-ligand. All NMR information was consistent with the formation of complex **7**. In particular, an AB spin-system attributed to 18 protons was observed in the ^{1}H NMR spectrum and only one singlet integrating for three protons (20) was observed besides that due to 7. The 18 protons showed NOEs with 20 and with the aromatic protons 15 and 11 (Fig. 5). They also exhibited scalar correlation with carbon 18, 13, 14, 12 and 19, as shown in Fig. 6.

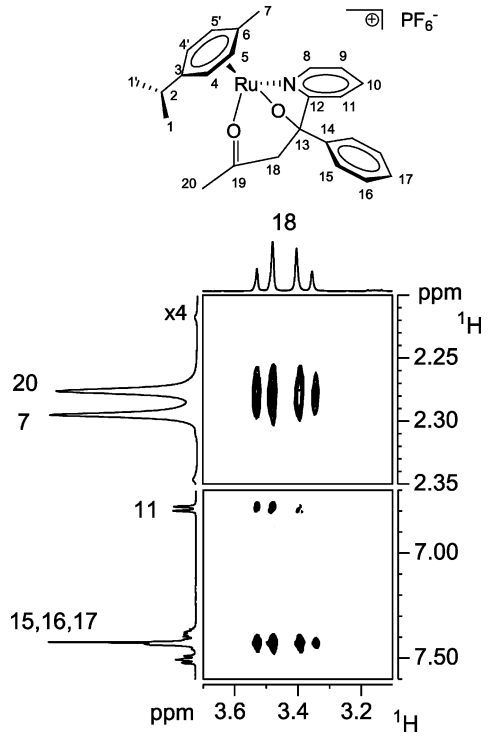


Fig. 5 Two sections of the ^{1}H-NOESY NMR spectrum (400.13 MHz, 296 K, CD_2Cl_2) of complex **7** showing the proximity of 18 with 20, 15 and even 11.

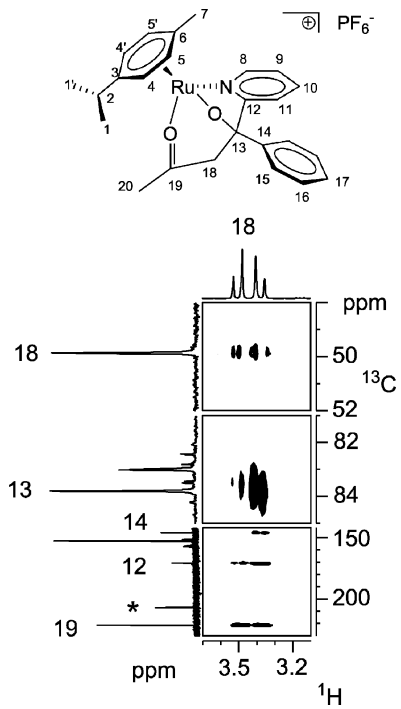


Fig. 6 Scalar correlations of 18 protons with 18 ($^1J_{HC}$), 13 ($^2J_{HC}$), 14 ($^3J_{HC}$), 12 ($^3J_{HC}$) and 19 ($^2J_{HC}$) carbons; * indicates the C=O resonance of free acetone.

It is known that Rh(III)[24] and Au(III)[25] can activate a C–H bond of coordinated acetone. It is also known that coordinated acetone may undergo C–C coupling in metalloaromatic complexes

of Ir(I).[26,27] To the best of our knowledge, this is the first example of both processes occurring in the same reaction.[28]

Conclusions

PGSE NMR investigations indicate that arene ruthenium complexes **1–2** aggregate in solution affording ion quadruples at the highest concentration levels even though they do not possess peripheral functionalities particularly suited to hydrogen bonding. Combining the results coming from the investigations in solution (NOE NMR) and in the solid state (X-Ray) it is deduced that the structure of the quadruples depends on the nature of the counterion. While −+−+ quadruples were observed for BPh_4^-, in the case of PF_6^- counterion −++− quadruples were more probable. These deductions are in perfect agreement with our previous findings for arene ruthenium diimine[9] and diamine complexes.[10] These different types of ion quadruples undergo different equilibria as the concentration is decreased. −+−+ dissociates into two −+ ion pairs, while −++− initially dissociates into a free anion − and a ++− ion triple. A further decrease in concentration leads to two ion pairs. In the solid-state structure of **1**PF_6 two cationic units of opposite chirality are held together by a π–π stacking interaction between two pyridyl rings; this also seems to be responsible for the formation of ion quadruples and ion triples in solution for complexes with PF_6^- as counterion.

Experimental

All preparations and manipulations were carried out under nitrogen atmosphere using standard Schlenk techniques. The compounds were prepared using freshly distilled solvents (hexane with Na, Et_2O with Na/benzophenone, MeOH with CaH_2, CH_2Cl_2 and CH_3CN with P_2O_5). The solvents were also degassed by many gas-pump-nitrogen cycles before use. IR spectra were measured at room temperature in CH_2Cl_2 solution on a FT-IR 1725 X Perkin-Elmer spectrophotometer. One- and two-dimensional ^1H, ^{13}C, ^{31}P and ^{19}F NMR spectra were measured on Bruker DPX 200 and DRX 400 spectrometers. Referencing is relative to TMS (^1H and ^{13}C), and CCl_3F (^{19}F). Complex $[Ru(\eta^6\text{-cymene})Cl_2]_2$ was prepared according to Benneth *et al.*[29]

Synthesis of complexes 1–7

Complex 1BPh$_4$. 2-Bzpy (120 mg, 0.64 mmol) was added to a suspension of $[Ru(\eta^6\text{-cymene})Cl_2]_2$ (100 mg, 0.16 mmol) in methanol (15 mL) at room temperature. The suspension became a red–brown solution; after 1 h $NaBPh_4$ (438 mg, 1.28 mmol) was added and a yellow precipitate was obtained. The suspension was stirred for 2 h and the precipitate became red–brown (complex **1**BPh_4); it was filtered off, washed with methanol, and dried under vacuum. Yield: 87%. ^1H NMR (CD_2Cl_2, 298 K): δ 8.90 (d, $^3J_{8,9}$ = 4.8, 8), 8.13 (d, $^3J_{11,10}$ = 7.2, 11), 7.92 (ddd, $^3J_{10,11}$ = $^3J_{10,9}$ = 7.8, $^4J_{10,8}$ = 1.3, 10), 7.87 (t, $^3J_{17,16}$ = 7.5, 17), 7.79 (d, $^3J_{15,16}$ = 7.2, 15), 7.68 (dd, $^3J_{16,15}$ = $^3J_{16,17}$ = 7.6, 16), 7.57 (ddd, $^3J_{9,10}$ = 7.7, $^3J_{9,8}$ = 5.5, $^4J_{9,11}$ = 1.3, 9), 7.38 (br, *o*), 7.03 (dd, $^3J_{m,p}$ = $^3J_{m,o}$ = 7.3, *m*), 6.89 (t, $^3J_{p,m}$ = 7.2, *p*), 5.70 (d, $^3J_{4,5}$ = 6.0, 4), 5.59 (d, $^3J_{4',5'}$ = 6.0, 4′), 5.47 (d, $^3J_{5,4}$ = 6.1, 5), 5.36 (d, $^3J_{5',4'}$ = 6.0, 5′), 2.80 (sept, $^3J_{2,1(1')}$ = 6.9, 2), 2.21 (s, 7), 1.31 (d, $^3J_{1,2}$ = 7.0, 1), 1.29 (d, $^3J_{1',2}$ = 7.0, 1′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 204.8 (s, 13), 165.4 (q, $^1J_{C11B}$ = 49.5, C_{ipso}), 155.7 (s, 8), 150.3 (s, 12), 140.7 (s, 17), 136.4 (s, 10 and *o*), 133.7 (s, 11), 133.4 (s, 14), 132.5 (s, 9), 130.6 (s, 15), 130.0 (s, 16), 126.1 (s, *m*), 122.3 (s, *p*), 105.4 (s, 3), 100.2 (s, 6), 85.0 (s, 4′), 84.5 (s, 5), 83.5 (s, 4), 82.3 (s, 5′), 31.8 (s, 2), 22.4 (s, 1 or 1′), 22.3 (s, 1 or 1′), 19.0 (s, 7). Anal. Calc. for $C_{45}H_{40}BClNORu$: C, 71.29; H, 5.32; N, 1.85. Found: C, 71.45; H, 5.42; N, 1.78%.

Complex 1PF$_6$. Complex **1**PF_6 was obtained with the same procedure as **1**BPh_4 using NH_4PF_6 (208 mg, 1.28 mmol) instead of $NaBPh_4$. Yield: 76%. ^1H NMR (CD_2Cl_2, 298 K): δ 9.51 (dd, $^3J_{8,9}$ = 4.8, $^4J_{8,10}$ = 0.7, 8), 8.36 (dd, $^3J_{11,10}$ = 7.2, $^4J_{11,9}$ = 0.8, 11), 8.28 (ddd, $^3J_{10,11}$ = $^3J_{10,9}$ = 7.7, $^4J_{10,8}$ = 1.3, 10), 8.03 (ddd, $^3J_{9,10}$ = 7.8, $^3J_{9,8}$ = 5.4, $^4J_{9,11}$ = 1.5, 9), 7.90 (dd, $^3J_{15,16}$ = 7.2, $^4J_{15,17}$ = 1.3, 15), 7.85 (t, $^3J_{17,16}$ = 7.5, 17), 7.69 (dd, $^3J_{16,15}$ = $^3J_{16,17}$ = 8.1, 16), 6.06 (d, $^3J_{4',5'}$ = 5.6, 4′), 6.04 (d, $^3J_{4,5}$ = 5.6, 4), 5.89 (d, ^3J = 5.6, 5 or 5′), 5.87 (d, ^3J = 5.6, 5 or 5′), 2.97 (sept, $^3J_{2,1(1')}$ = 6.9, 2), 2.37 (s, 7), 1.37 (d, $^3J_{1,2}$ = 6.9, 1), 1.34 (d, $^3J_{1',2}$ = 6.9, 1′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 205.1 (s, 13), 156.5 (s, 8), 150.6 (s, 12), 140.6 (s, 17), 136.2 (s, 10), 133.8 (s, 11), 133.6 (s, 14), 132.5 (s, 9), 130.8 (s, 15), 129.9 (s, 16), 105.4 (s, 3), 100.5 (s, 6), 85.5 (s, 4′), 84.6 (s, 5), 83.7 (s, 4), 82.6 (s, 5′), 31.8 (s, 2), 22.4 (s, 1 or 1′), 22.3 (s, 1 or 1′), 18.9 (s, 7). ^{19}F NMR (CD_2Cl_2, 298 K): δ −71.6 (d, $^1J_{FP}$ = 711.0). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ −141.0 (sept, $^1J_{PF}$ = 711.0). Anal. Calc. for $C_{22}H_{23}ClF_6NOPRu$: C, 44.12; H, 3.87; N, 2.34. Found: C, 44.25; H, 3.95; N, 2.28%.

Complex 2BPh$_4$. Complex **2**BPh_4 was obtained with the same procedure as **1**BPh_4. Yield: 76%. ^1H NMR ($CDCl_3$, 298 K): δ 8.41 (d, $^3J_{8,9}$ = 4.7, 8), 7.43 (br, 10 and *o*), 7.19 (dd, $^3J_{9,10}$ = 8.0, $^3J_{9,8}$ = 4.7, 9), 7.15 (d, $^3J_{11,10}$ = 7.7, 11), 6.99 (dd, $^3J_{m,p}$ = $^3J_{m,o}$ = 7.4, *m*), 6.88 (t, $^3J_{p,m}$ = 7.2, *p*), 5.38 (d, $^3J_{4,5}$ = 6.0, 4), 5.31 (d, $^3J_{4',5'}$ = 5.8, 4′), 5.11 (br, 5 and 5′), 2.66 (sept, $^3J_{2,1(1')}$ = 5.4, 2), 2.03 (s, 14), 1.55 (s, 7), 1.24 (d, $^3J_{1,2}$ = 5.4, 1), 1.23 (d, $^3J_{1',2}$ = 5.4, 1′). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): δ 211.5 (s, 13), 164.3 (q, $^1J_{C11B}$ = 49.5, C_{ipso}), 154.7 (s, 8), 150.3 (s, 12), 141.2 (s, 10), 136.6 (s, *o*), 132.7 (s, 9), 131.4 (s, 11), 126.3 (s, *m*), 122.6 (s, *p*), 104.7 (s, 3), 99.2 (s, 6), 84.8 (s, 4′), 84.2 (s, 5), 82.7 (s, 4), 82.3 (s, 5′), 31.7 (s, 2), 26.4 (s, 14), 22.6 (s, 1 or 1′), 22.5 (s, 1 or 1′), 19.0 (s, 7). Anal. Calc. for $C_{41}H_{41}BClNORu$: C, 69.25; H, 5.81; N, 1.97. Found: C, 69.35; H, 5.91; N, 1.83%.

Complex 2PF$_6$. $TlPF_6$ (161 mg, 0.46 mmol) was added to a solution of complex **2**BPh_4 (329 mg, 0.46 mmol) in CH_2Cl_2 (15 mL) at room temperature. $TlBPh_4$ formed as a white solid that was filtered off. *n*-Hexane was added to the remaining solution and a red–brown precipitate was obtained; it was filtered off, washed with *n*-hexane, and dried under vacuum. Yield: 96%. ^1H NMR (CD_2Cl_2, 298 K): δ 9.34 (dd, $^3J_{8,9}$ = 5.4, $^4J_{8,10}$ = 0.6, 8), 8.35 (dd, $^3J_{11,9}$ = 7.8, $^4J_{11,10}$ = 0.9, 11), 8.28 (ddd, $^3J_{10,9}$ = $^3J_{10,11}$ = 7.7, $^4J_{10,8}$ = 1.4,10), 7.97 (ddd, $^3J_{9,10}$ = 7.7, $^3J_{9,8}$ = 5.4, $^4J_{9,11}$ = 1.5, 9), 6.01 (d, $^3J_{4',5'}$ = 6.2, 4′), 5.94 (d, $^3J_{4,5}$ = 6.2, 4), 5.80 (d, $^3J_{5',4'}$ = 6.2, 5′), 5.78 (d, $^3J_{5,4}$ = 6.2, 5), 2.98 (s, 14), 2.97 (sept, $^3J_{2,1(1')}$ = 6.9, 2), 2.33 (s, 7), 1.37 (d, $^3J_{1,2}$ = 6.9, 1), 1.36 (d, $^3J_{1',2}$ = 6.9, 1′). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 211.6 (s, 13), 155.4 (s, 8), 151.2 (s, 12), 141.0 (s, 10), 132.7 (s, 9), 131.0 (s, 11), 104.9 (s, 3), 100.3 (s, 6), 85.3 (s, 4′), 83.6 (s, 5), 83.5 (s, 4), 82.1 (s, 5′), 31.7 (s, 2), 26.3 (s, 14), 22.5 (s, 1 or 1′), 22.4 (s, 1 or 1′), 18.7 (s, 7). ^{19}F NMR (CD_2Cl_2, 298 K): δ −71.6 (d, $^1J_{FP}$ = 711.0). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ −141.0 (sept, $^1J_{PF}$ = 711.0). Anal. Calc. for $C_{17}H_{21}ClF_6NOPRu$: C, 38.03; H, 3.94; N, 2.61. Found: C, 38.13; H, 4.00; N, 2.54%.

Complex 3. $AgBF_4$ (176 mg, 0.90 mmol) and CH_3CN (0.060 mL, 1.1 mmol) were added to a solution of complex **1**BPh_4 (264 mg, 0.34 mmol) in CH_2Cl_2 (15 mL) at room temperature. The resulting suspension was stirred for 16 h. The formed AgCl and $AgBPh_4$ were filtered off. *n*-Hexane was added to the remaining solution and a red–brown precipitate was obtained; it was filtered off, washed with *n*-hexane, and dried under vacuum. Yield: 65%. ^{1}H NMR (CD_2Cl_2, 298 K): δ 9.58 (dd, $^3J_{8,9} = 4.8$, $^4J_{8,10} = 1.4$, 8), 8.52 (dd, $^3J_{11,10} = 7.2$, $^4J_{11,9} = 1.4$, 11), 8.41 (ddd, $^3J_{10,11} = {}^3J_{10,9} = 7.2$, $^4J_{10,8} = 1.4$, 10), 8.14 (ddd, $^3J_{9,10} = 7.2$, $^3J_{9,8} = 4.8$, $^4J_{9,11} = 1.4$, 9), 8.04 (dd, $^3J_{15,16} = 7.3$, $^4J_{15,17} = 1.3$, 15), 7.89 (td, $^3J_{17,16} = 7.5$, $^4J_{17,15} = 1.3$, 17), 7.71 (dd, $^3J_{16,15} = 7.3$, $^3J_{16,17} = 7.6$, 16), 6.34 (d, $^3J_{4,5} = 5.6$, 4), 6.26 (d, $^3J_{4',5'} = 5.6$, 4′), 6.15 (d, $^3J_{5',4'} = 5.6$, 5′), 6.14 (d, $^3J_{5,4} = 5.6$, 5), 2.98 (sept, $^3J_{2,1(1')} = 6.9$, 2), 2.37 (s, 7), 2.34 (s, 19), 1.39 (d, $^3J_{1,2} = 6.9$, 1), 1.36 (d, $^3J_{1',2} = 6.9$, 1′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): δ 207.4 (s, 13), 157.4 (s, 8), 150.9 (s, 12), 141.9 (s, 10), 136.9 (s, 17), 135.5 (s, 11), 133.7 (s, 9), 133.2 (s, 14), 131.8 (s, 15), 129.9 (s, 16), 129.5 (s, 18), 108.2 (s, 6), 103.6 (s, 3), 87.0 (s, 4′), 86.7 (s, 4), 85.3 (s, 5′), 85.0 (s, 5), 31.7 (s, 2), 22.5 (s, 1), 22.3 (s, 1′), 18.4 (s, 7), 4.3 (s, 19). ^{19}F NMR (CD_2Cl_2, 298 K): δ −152.32 (br, $^{10}BF_4$), −152.37 (br, $^{11}BF_4$). Anal. Calc. for $C_{24}H_{26}B_2F_8N_2ORu$: C, 45.53; H, 4.14; N, 4.42. Found: C, 45.64; H, 4.20; N, 4.32%.

Complex 4. Complex **4** was obtained with the same procedure as complex **3**. Yield: 62%. ^{1}H NMR (CD_2Cl_2, 298 K): δ 9.55 (dd, $^3J_{8,9} = 4.9$, $^4J_{8,10} = 1.4$, 8), 8.47 (dd, $^3J_{11,10} = 7.6$, $^4J_{11,9} = 1.4$, 11), 8.39 (ddd, $^3J_{10,11} = {}^3J_{10,9} = 7.6$, $^4J_{10,8} = 1.4$, 10), 8.11 (ddd, $^3J_{9,10} = 7.6$, $^3J_{9,8} = 4.9$, $^4J_{9,11} = 1.4$, 9), 6.28 (m, 4 and 4′), 6.09 (m, 5 and 5′), 3.11 (s, 14), 3.00 (sept, $^3J_{2,1(1')} = 6.9$, 2), 2.38 (s, 16), 2.31 (s, 7), 1.43 (m, 1 and 1′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): δ 216.0 (s, 13), 156.3 (s, 8), 152.0 (s, 12), 142.0 (s, 10), 133.6 (s, 9), 132.3 (s, 11), 128.6 (s, 15), 108.1 (s, 3), 104.5 (s, 6), 89.3 (s, 4′ or 4), 87.4 (s, 4′ or 4), 84.5 (s, 5′ or 5), 83.7 (s, 5′ or 5), 31.8 (s, 2), 26.6 (s, 14), 22.7 (s, 1 or 1′), 22.2 (s, 1 or 1′), 18.4 (s, 7), 4.3 (s, 16). ^{19}F NMR (CD_2Cl_2, 298 K): δ −152.32 (br, $^{10}BF_4$), −152.37 (br, $^{11}BF_4$). Anal. Calc. for $C_{19}H_{24}B_2F_8N_2ORu$: C, 39.96; H, 4.24; N, 4.91. Found: C, 40.02; H, 4.29; N, 4.84%.

Complex 5. $AgBF_4$ (63 mg, 0.32 mmol) was added to a solution of complex **1**PF_6 (149 mg, 0.24 mmol) in CH_3CN (15 mL) at room temperature. The formed AgCl was filtered off. Diethyl ether was added to the remaining solution and a red–brown precipitate was obtained; it was filtered off, washed with *n*-hexane, and dried under vacuum. Yield: 73%. ^{1}H NMR (CD_2Cl_2, 298 K): δ 9.36 (dd, $^3J_{6,5} = 4.8$, $^4J_{6,4} = 1.4$, 6), 8.55 (dd, $^3J_{3,4} = 7.4$, $^4J_{3,5} = 1.4$, 3), 8.30 (ddd, $^3J_{4,5} = {}^3J_{4,3} = 7.7$, $^4J_{4,6} = 1.4$, 4), 8.10 (ddd, $^3J_{5,4} = 7.7$, $^3J_{5,6} = 4.8$, $^4J_{5,3} = 1.4$, 5), 8.03 (dd, $^3J_{9,10} = 8.2$, $^4J_{9,11} = 1.2$, 9), 7.87 (td, $^3J_{11,10} = 7.6$, $^4J_{11,9} = 1.2$, 11), 2.79 (s, 17), 2.73 (s, 15), 2.38 (s, 13). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): δ 210.38 (s, 7), 156.8 (s, 6), 153.4 (s, 2), 139.2 (s, 4), 135.99 (s, 11), 134.3 (s, 3), 133.9 (s, 8), 132.6 (s, 5), 130.8 (s, 9), 130.5 (s, 16), 129.8 (s, 10), 127.0 (s, 14), 125.5 (s, 12), 4.8 (s, 17), 4.6 (s, 15), 4.2 (s, 13). ^{19}F NMR (CD_2Cl_2, 298 K): δ −72.1 (d, $^1J_{FP} = 711$), −152.32 (br, $^{10}BF_4$), −152.37 (br, $^{11}BF_4$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): δ −143.2 (sept, $^1J_{PF} = 711$). Anal. Calc. for $C_{22}H_{25}BF_{10}N_6OPRu$: C, 36.58; H, 3.49; N, 11.63. Found: C, 36.66; H, 3.54; N, 11.55%.

Complex 6. Complex **6** was obtained with the same procedure as complex **5**. Yield: 73%. ^{1}H NMR (CD_2Cl_2, 298 K): δ 9.22 (dd, $^3J_{6,5} = 5.4$, $^4J_{6,4} = 1.4$, 6), 8.53 (dd, $^3J_{3,4} = 7.8$, $^4J_{3,5} = 1.4$, 3), 8.28 (ddd, $^3J_{4,5} = {}^3J_{4,3} = 7.8$, $^4J_{4,6} = 1.4$, 4), 8.17 (ddd, $^3J_{5,4} = 7.8$, $^3J_{5,6} = 5.4$, $^4J_{5,3} = 1.4$, 5), 3.15 (s, 8), 2.76 (s, 12), 2.71 (s, 14), 2.37 (s, 10). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): δ 217.0 (s, 7), 155.8 (s, 6), 154.3 (s, 2), 139.5 (s, 4), 132.5 (s, 5), 131.8 (s, 3), 130.12 (s, 11), 126.9 (s, 13), 125.6 (s, 9), 26.4 (s, 8), 4.8 (s, 12), 4.5 (s, 14), 4.2 (s, 10). ^{19}F NMR (CD_2Cl_2, 298 K): δ −152.32 (br, $^{10}BF_4$), −152.37 (br, $^{11}BF_4$). Anal. Calc. for $C_{17}H_{23}B_2F_8N_6ORu$: C, 33.91; H, 3.85; N, 13.96. Found: C, 34.02; H, 3.95; N, 13.84%.

Complex 7. $AgBF_4$ (50 mg, 0.23 mmol) was added to a solution of complex **1**PF_6 (119 mg, 0.19 mmol) in acetone (15 mL) at room temperature. The suspension was stirred for 16 h. The formed AgCl was filtered off. *n*-Hexane was added to the remaining solution and complex **7** was obtained as a brown–green precipitate; it was filtered off, washed with *n*-hexane, and dried under vacuum. Yield: 65%. ^{1}H NMR (CD_2Cl_2, 298 K): δ 9.40 (d, $^3J_{8,9} = 5.6$, 8), 7.72 (ddd, $^3J_{10,11} = {}^3J_{10,9} = 7.8$, $^4J_{10,8} = 1.4$, 10), 7.50 (ddd, $^3J_{9,10} = 7.8$, $^3J_{9,8} = 5.6$, $^4J_{9,11} = 1.3$, 9), 7.39 (m, aromatic proton 15, 16, 17), 6.78 (d, $^3J_{11,10} = 7.8$, 11), 5.89 (d, $^3J_{4,5} = 5.8$, 4), 5.77 (s, 4′ and 5′), 5.47 (d, $^3J_{5,4} = 5.8$, 5), 3.49 (d, $^2J_{18B,18A} = 19.6$, 18B), 3.37 (d, $^2J_{18A,18B} = 19.6$, 18A), 2.87 (sept, $^3J_{2,1(1')} = 6.9$, 2), 2.29 (s, 7), 2.27 (s, 20), 1.37 (d, $^3J_{1,2} = 6.9$, 1), 1.28 (d, $^3J_{1',2} = 6.9$, 1′). ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K): δ 221.6 (s, 19), 170.5 (s, 12), 152.5 (s, 8), 145.6 (s, 14), 140.4 (s, 10), 129.1, 128.8, 126.3 (s, aromatic carbon 15, 16, 17), 125.5 (s, 9), 123.27 (s, 11), 99.0 (s, 3), 97.8 (s, 6), 85.3 (s, 4), 83.8 (s, 5′ and 13), 83.0 (s, 4′), 79.8 (s, 5), 49.8 (s, 18), 33.1 (s, 20), 31.3 (s, 2), 22.7 (s, 1), 22.4 (s, 1′), 18.1 (s, 7). ^{19}F NMR (CD_2Cl_2, 298 K): δ −72.1 (d, $^1J_{FP} = 711$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K): δ −143.2 (sept, $^1J_{PF} = 711$). Anal. Calc. for $C_{25}H_{28}F_6NO_2PRu$: C, 48.39; H, 4.55; N, 2.26. Found: C, 48.50; H, 4.63; N, 2.20%.

NOE measurements

The ^{1}H-NOESY[30] NMR experiments were acquired by the standard three-pulse sequence or by the PFG version.[31] Two-dimensional ^{19}F, ^{1}H-HOESY NMR experiments were acquired using the standard four-pulse sequence or the modified version.[32] The number of transients and the number of data points were chosen according to the sample concentration and to the desired final digital resolution. Semi-quantitative spectra were acquired using a 1 s relaxation delay and 800 ms mixing times. Quantitative ^{1}H-NOESY and ^{19}F, ^{1}H-HOESY NMR experiments were carried out with a relaxation delay of 10 s and a mixing time of 150 ms (initial rate approximation).[33]

PGSE Measurements

^{1}H and ^{19}F PGSE NMR measurements were performed by using the standard stimulated echo pulse sequence[34] on a Bruker AVANCE DRX 400 spectrometer equipped with a GREAT 1/10 gradient unit and a QNP probe with a Z-gradient coil, at 296 K without spinning. The shape of the gradients was rectangular, their duration (δ) was 4–5 ms, and their strength (G) was varied during the experiments. All the spectra were acquired using 32 K points, a spectral width of 5000 (^{1}H) and 18000 (^{19}F) Hz, and processed with a line broadening of 1.0 (^{1}H) and 1.5 (^{19}F) Hz. The semi-logarithmic plots of $\ln(I/I_0)$ *vs.* G^2 were fitted using a standard linear regression algorithm; the R factor was always higher than 0.99. Different values of Δ (delay between the midpoints of the gradients), "nt" (number of transients) and number of different

Table 4 Crystallographic data

	$1PF_6$	$1BPh_4$
Formula	$C_{23}H_{27}ClNO_2RuPF_6$	$C_{46}H_{43}BClNORu$
M	630.94	773.14
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a/Å	30.0777(18)	12.498(2)
b/Å	9.1795(5)	9.869(2)
c/Å	22.0930(12)	30.431(2)
β/°	121.318(6)	93.523(5)
V/Å^3	5211.1(6)	3746.5(10)
Z	8	4
D_c/g cm^{-3}	1.598	1.371
μ(Mo-Kα)/mm^{-1}	0.832	0.527
Total data collected	22062	32151
Unique obs. data	5121	7234
Criterion for obs.	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$
Unique data used (N_o)	3434	4910
No. params refined (N_v)	342	470
R_{int}	0.0380	0.0467
$wR(F^2)$	0.1079	0.0892
GOF	0.999	1.004
θ Range/°	3.25–26.27	2.91–26.49

gradient strengths (G) were used for different samples. The methodology for treating the data was previously described.[10] The uncertainty of the measurements was estimated by determining the standard deviation of D_t by performing experiments with different Δ values. Experimental error was found to be approximately 3% on D_t and hydrodynamic radii and 10% on hydrodynamic volumes and aggregation numbers N.

X-Ray crystallography

Single crystals of $1BPh_4$ and $1PF_6$, suitable for X-ray diffraction, were obtained by crystallisation from methylene chloride–methanol–diethyl ether solutions. Data were collected at room temperature on a XCALIBUR (CCD areal) diffractometer of the OXFORD Instrument using Mo-Kα graphite-monochromated radiation ($\lambda = 0.71069$ Å); ω-scans and the frame data were acquired with the CRYSALIS (CCD 171) software. The structure was solved using direct methods and refined against $|F|^2$. The frames were then processed using the CRYSALIS (RED 171) software to give the *hkl* file corrected for scan speed, background, and Lorentz and polarization effects. Standard reflections, measured periodically, in both complexes, showed that there was no apparent variation in intensity during data collection and so, no correction for crystal decomposition was necessary. The data were corrected for absorption using semi-empirical multi-scan[35] methods.

The structures were solved by the direct method using the Sir97[36] program and refined by the full-matrix least-squares method on F^2 using the SHELXL-97,[37] WinGX[38] version. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added at the calculated positions and refined using a riding model. Unfortunately, the crystal of $1PF_6$ that was examined had an internal disorder due to molecules of methyl alcohol that co-crystallised with the complex. Data concerning the cell parameters and the structure refinements are reported in Table 4.

CCDC reference numbers 272774 and 272775.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514269e

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