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From Ion Pairs to Ion Triples through a Hydrogen Bonding-Driven Aggregative Process

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Complexes [Ru(arene)(κ^3-dpk-OR]X (dpk = 2,2′-dipyridylketone) were synthesized, and their interionic structure was investigated through an integrated approach based on diffusion and NOE NMR experiments and X-ray single-crystal studies. PGSE NMR results indicated that the highest aggregation tendency occurred for complex **2**BF_4 (arene = *p*-cymene and R = OH) that showed aggregation numbers consistent with the main presence of $\mathbf{2}_2BF_4^+$ ion triples ($N^+ = 1.9$ and $N^- = 1.1$, in CD_2Cl_2 at 0.5 mM). X-ray investigations indicated that a [1 × 1] network of HBs is present involving the two OH moieties of the two cationic fragments belonging to the two independent ion pairs of the asymmetric unit. This dication is likely the central moiety of $\mathbf{2}_2BF_4^+$ ion triples. According to $^{19}F,^1H$-HOESY NMR interionic studies, the counterion was close to two pyridyl rings belonging to two different cations undergoing a $\pi-\pi$-stacking interaction in CD_2Cl_2 exactly as observed in the solid state. All of the other complexes having an alyphatic OR-tail showed a much smaller aggregation tendency, leading to ion pairs even when OR = OCH_2CH_2OH. In the latter case, X-ray studies showed that the terminal OH underwent an intracationic HB with the oxygen atom coordinated at the ruthenium.

Introduction

It is increasingly evident that noncovalent interactions may alter the structure and reactivity of organometallic compounds.[1,2] Ion pairing[3] has been deeply investigated, particularly by means of NOE[4] and diffusion NMR[5] experiments, because its effects on the chemistry of transition-metal salts are well-recognized.[6−8] Less attention has been dedicated to the aggregation of neutral "molecular entities" even if, in principle, they may play a role at least in two important catalytic reactions: the polymerization of olefins catalyzed by metallocene or post-metallocene ion pairs[9] and the transfer hydrogenation of ketones occurring through a bifunctional mechanism.[10,11] In the former case, ion pairs are the neutral "molecular entities" that have been demonstrated to aggregate forming ion quadruples; in the latter, monomers are the neutral "molecular entities" that, especially when they have peripheral functionalities suitable to undergo hydrogen bonding (HB), readily form dimers,[12,13] trimers, and, in favorable conditions, nanometric aggregates.[14]

The aggregation of transition-metal ion pairs to form ion quadruples usually occurs in solvent with a relative permittivity (ϵ_r) equal to or lower than that of chloroform mainly driven by the interaction between the permanent dipolar moments of ion pairs.[15,16] Consequently, a higher tendency to form ion quadruples is observed for large and least coordinating anions that, once paired with a given cation, lead to an ion pair having a higher dipole moment.[16] The association of neutral organometallics becomes relevant if HBs can establish in the second-coordination sphere. In such cases, dimers and higher aggregates can persist even in solvent with medium to high ϵ_r.[12,14] We thought that it could be of interest to investigate the aggregation tendency of ion pairs having a pendant peripheral group whose capability to undergo hydrogen bonding could be easily tuned.

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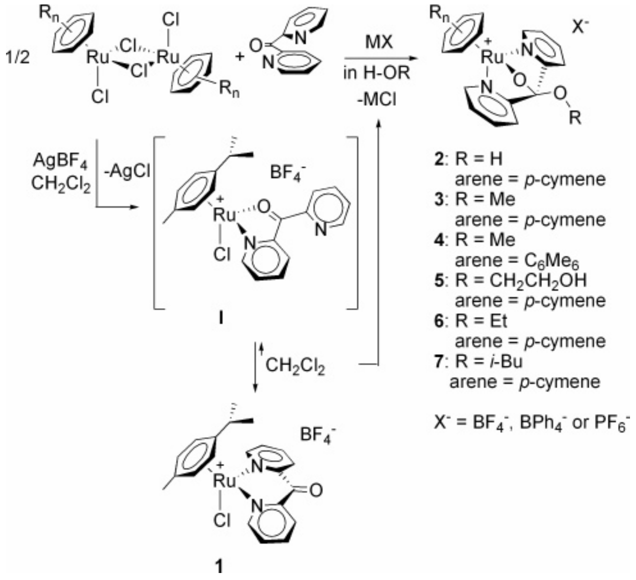
Scheme 1



Herein, we report on the synthesis and characterization of complexes [Ru(arene)(κ^3-dpk-OR)]X (dpk = 2,2′-dipyridylketone, Scheme 1) having a suitable OR-tail for hydrogen bonding. Dpk has been used as ligand in several coordination compounds[17−22] because it is a versatile ligand that can afford κ^2-N,N-,[23] κ^2-N,O-,[24] and also anionic κ^3-N,N,O-[25] coordination at the metal. Addition of a nucleophile to the carbonyl of κ^2-N,N-coordinated dpk can be used to generate *gem*-diols κ^2-dpkH-OH[26] by the reaction with water or *semi*-acetal κ^2-dpkH-OR or κ^2-dpkH-NR by the reaction with alcohols,[27] amines,[28] or pyrazoles.[29] In the presence of an M−X (X = halogen) moiety, κ^3-N,N,O-coordination mode of dpk is obtained with a suitable −OR or −NR tail, through the elimination of HX.[25]

Results and Discussion

Synthesis. Complexes [Ru(arene)(κ^3-dpk-OR)]X (**2**BF$_4$, R = H, arene = *p*-cymene; **3**BPh$_4$, R = Me, arene = *p*-cymene; **3**PF$_6$, R = Me, arene = *p*-cymene; **4**PF$_6$, R = Me, arene = hexamethylbenzene; **5**BPh$_4$, R = CH$_2$CH$_2$OH, arene = *p*-cymene; **5**PF$_6$, R = CH$_2$CH$_2$OH, arene = *p*-cymene; **6**BPh$_4$, R = Et, arene = *p*-cymene; **7**BPh$_4$, R = *i*-Bu, arene = *p*-cymene) were synthesized by the reaction of [Ru$_2$(η^6-arene)$_2$Cl$_2$(μ-Cl)$_2$] with dpk in the appropriate protic solvent (H−OR), at room temperature, by adding a large excess of MX (NaBPh$_4$ or NH$_4$PF$_6$) that caused their precipitation (Scheme 1). Complexes **3**PF$_6$ and **5**PF$_6$ were preferably synthesized by the anion metathesis reaction of **3**BPh$_4$ and **5**BPh$_4$ and an equimolar amount of TlPF$_6$ in acetone, due to their higher solubility in methanol and HOCH$_2$CH$_2$OH. Complex [Ru(η^6-*p*-cymene)(κ^2-N,N-dpk)Cl]BF$_4$ (**1**BF$_4$) was isolated by the reaction of [Ru$_2$(η^6-*p*-cymene)$_2$Cl$_2$(μ-Cl)$_2$] with dpk in methylene chloride in the presence of 2 equiv of AgBF$_4$. The reaction of **1**BF$_4$ with H−OR, under the appropriate experimental conditions, afforded another pathway to obtain complexes **2**BF$_4$, **3**BPh$_4$, and **5**−**7**BPh$_4$ (Scheme 1). When the reaction of [Ru$_2$(η^6-*p*-cymene)$_2$Cl$_2$(μ-Cl)$_2$] with dpk was carried out in CD$_2$Cl$_2$, an intermediate (**I**) was observed that partial NMR characterization indicated to contain the κ^2-N,O-dpk moiety (Scheme 1). Consequently, complexes **I** and **1** seem to be the kinetic and thermodynamic products of the reaction, respectively, and it cannot be excluded that the transformation of **1** into **2**, **3**, and **5**−**7** proceeds through **I**. Dissolving complex **2** in methanol or HOCH$_2$CH$_2$OH did not lead to the conversion in complexes **3** and **5**; the latter complexes were stable for days in water.

All complexes **1**−**7** were characterized in solution by ^{1}H, ^{13}C, ^{31}P, ^{19}F NMR spectroscopies (Experimental Section). The solid-state structures of complexes **2**BF$_4$ and **5**BPh$_4$ were solved by X-ray diffractometric studies.

Intramolecular NMR Characterization in Solution. The assignment of all ^{1}H and ^{13}C NMR resonances of complexes **1**−**7** was carried out by crossing together the information coming from ^{1}H, ^{13}C, ^{1}H-COSY, ^{1}H-NOESY, ^{1}H,^{13}C-HMQC, and ^{1}H,^{13}C-HMBC NMR experiments. Data are reported in the Experimental Section. In the ^{13}C NMR spectrum of complex **1**, the resonance of the carbonyl moiety fell at a chemical shift value (185.46 ppm) lower than that of the free dpk ligand (192.95 ppm); this is consistent with a carbonyl moiety not coordinated at the metal center. In contrast, when dpk coordinates at the metal as an N,O-ligand, a deshielding of the carbon nucleus of C=O is observed; the latter resonates above 200 ppm in similar complexes.[30,31] In **2**−**7**, no carbon resonance at ppm values higher than 165 ppm was observed, while a new quaternary carbon appeared at ca. 105 ppm. This carbon showed long-range correlation with proton 14 (Figure 1) that, in turn, correlates with carbon 12, in perfect agreement with the proposed structure.

X-ray Studies. (a) Intramolecular Structure. The solid-state structures of compounds **2**BF$_4$ and **5**BPh$_4$ were determined through single-crystal X-ray diffractometric investigations. Both complexes exhibit a three-legged piano stool pseudo-octahedral geometry where the arene occupies three adjacent sites of the octahedron and dpk-OR$^-$ the other three. Intramolecular bond lengths and angles fall in the typical ranges observed for analogous compounds and will not be discussed here.[32] Both complexes contain two independent anion/cation pairs in the asymmetric unit; in addition, two solvent molecules (CH$_2$Cl$_2$) are present in **2**BF$_4$ and one in **5**BPh$_4$. In the latter complex, each cation exhibits an intramolecular H bonding between the Ru-coordinated oxygen atom and the terminal OH group with

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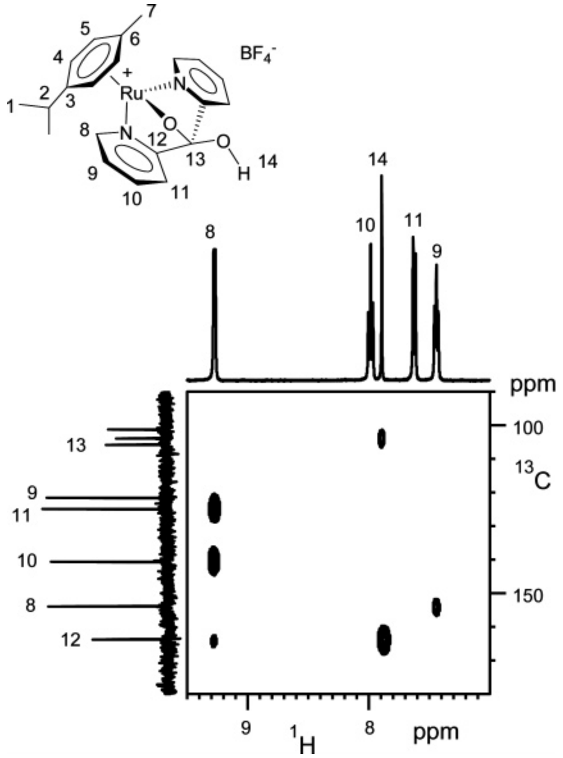

Figure 1. A section of the long-range $^{1}H,^{13}C$-HMBC NMR correlation recorded for **2**BF_4 in CD_2Cl_2, showing the scalar coupling of H14 with C13 and C12.

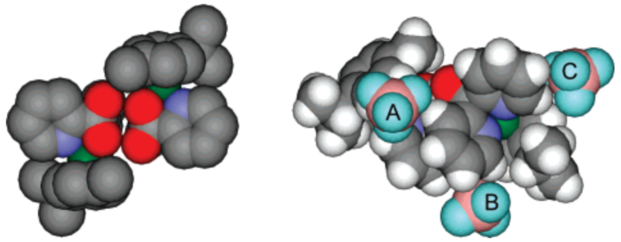

Figure 2. Left: CPK representation of two $\mathbf{2}^+$ cationic moieties in the solid state showing O···O proximities (hydrogen atoms are omitted for clarity). Right: CPK representation of some counterion orientations observed in the solid-state structure of **2**BF_4. Coloring: Ru, green; O, red; H, light gray; N, blue; F, light blue; B, pink; C, gray.

donor···acceptor distances ranging around 2.7 Å. The cymene assumes an eclipsed conformation and orients the *i*-Pr and Me groups in a way of perfectly dividing the dpk ligand into two parts.

(b) Supramolecular Structure. The supramolecular structure of complexes **2**BF_4 and **5**BPh_4 was analyzed focusing the attention on the possible role of the peripheral OH moiety. In complex **2**BF_4, a [1 × 1] network of HBs is present involving the two OH moieties of the two cationic fragments belonging to the two independent ion pairs of the asymmetric unit with O···O distances equal to 2.62 and 2.69 Å (Figure 2). Analogous dimeric structures held together by HBs have been observed by Puddephatt and co-workers for Pt(II) complexes,[33] while also in *fac*-$[Mn(CO)_3(\kappa^3\text{-dpk-OH})]$ complexes[25] a network of hydrogen bonds was observed. In addition to HBs, two cationic moieties also undergo a $\pi-\pi$-stacking interaction between two pyridyl rings in **2**BF_4; a 21.5° mean slip angle between the normal of one pyridyl plane and 3.67 Å centroid−centroid distance were observed (Figure 2). With reference to these two cationic moieties, involved both in the HBs and in the $\pi-\pi$-stacking interaction, three BF_4^- counterions are located in the next proximities. Two of them (orientations A and B in Figure 2) are located close to the pyridyl rings that undergo the $\pi-\pi$-stacking interaction (A, Ru−B 5.26 and 8.30 Å; B, Ru−B, 5.41 and 8.53 Å). The other one (orientation C in Figure 2) is between a pyridyl ring and a cymene moiety of one ruthenium atom (Ru−B, 5.35 and 11.47 Å).

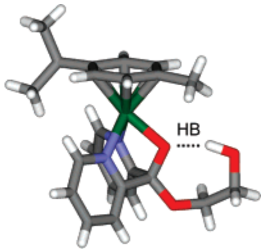

Figure 3. Stick representation of the cation $\mathbf{5}^+$ in the solid state showing the intracationic O···H hydrogen bond (HB).

Complex **5**BPh_4 shows Ru···B contacts of 6.55 and 6.23 Å, respectively, for the two ionic pairs in the asymmetric unit, a value quite similar to that found in *cis*-$[Ru(PMe_3)(CO)_2(COMe)(\kappa^2\text{-}pz_2\text{-}CH_2]BPh_4$.[34] Considering the whole crystal packing, the same interaction is significantly longer on the average (8.05 Å): that is, the two closest packed ion pairs were chosen as the crystallographic asymmetric unit.

In the same complex, in contrast to what was observed for complex **2**BF_4, no intercationic HB is present, while an intracationic HB between the OH functionality and the oxygen atom coordinated at the ruthenium is present with an O···O distance equal to 2.70 Å (Figure 3).

NMR Interionic Structure in Solution. (a) PGSE Measurements. The aggregation tendency of complexes **2**−**5** with fluorinated counterions was investigated by ^{1}H- and ^{19}F-PGSE measurements using TMSS [tetrakis-(trimethylsilyl)silane] as internal standard. PGSE measurements allowed the translational self-diffusion coefficients (D_t) for both cationic (D_t^+) and anionic (D_t^-) moieties (Table 1) to be determined. By applying (Experimental Section) the Stokes−Einstein equation $D_t = kT/c\pi\eta r_H$, where k is the Boltzman constant, T is the temperature, c is a numerical factor, and η is the solution viscosity, the average hydrodynamic radii for the cationic (r_H^+) and anionic (r_H^-) moieties were measured (Table 1).[35] From the average hydrodynamic radii of the aggregates, assumed to be spherical, their volumes (V_H^+ and V_H^-) were obtained. To have an immediate idea of the level of aggregation, V_H^+ and V_H^- can be contrasted with the expected volume of the ion pair. We have recently shown that the latter is well-described by the van der Waals volume of the ion pair, easily derived from X-ray or theoretical data, only for molecules not having inlets.[36] In other cases, it is preferable to use the hydrodynamic volume measured at very low concentration or extrapolated at infinite dilution (V_H^0).

The trend of V_H versus the salt concentration (C) was obtained for **4**PF_6 (Table 1, entries 7−12) to determine the hydrodynamic volume of $\mathbf{4}^+$ at infinite dilution (V_H^{+0}).[37] **4**PF_6 was selected

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Table 1. Diffusion Coefficients ($10^{10}D_t$, m^2 s^{-1}), Hydrodynamic Radii (r_H, Å), Hydrodynamic Volumes (V_H, Å^3), and Aggregation Number for Cation (N^+) and Anion (N^-) of Compounds 2−5X in CD_2Cl_2 as a Function of Concentration (C, mM)

		D_t^+	D_t^-	r_H^+	r_H^-	V_H^+	V_H^-	N^+	N^-	C
1	**2**BF_4 ($V_H^0 = 471$)	8.9	10.9	6.0	5.1	900	542	1.9	1.1	0.5
2		8.2	9.3	6.3	5.7	1040	780	2.2	1.7	1.7[a]
3	**3**PF_6 ($V_H^0 = 512$)	11.4	15.4	5.0	4.0	523	268	1.0	0.5	0.1
4		10.6	12.4	5.2	4.6	578	405	1.1	0.8	0.6
5		9.7	11.0	5.3	4.8	619	470	1.2	0.9	3
6		9.5	10.7	5.4	4.9	659	504	1.3	1.0	21
7	**4**PF_6 ($V_H^0 = 556$)	11.2		4.9		495		0.9		0.008
8		11.6	16.7	4.9	3.7	483	217	0.9	0.4	0.07
9		10.9	13.3	5.2	4.4	575	361	1.0	0.7	0.6
10		9.9	11.9	5.3	4.6	637	415	1.1	0.7	10
11		10.7	11.8	5.3	4.9	610	477	1.1	0.8	28
12		8.5	10.0	5.4	4.9	663	467	1.2	0.8	63
13	**5**PF_6 ($V_H^0 = 541$)	9.8	11.4	5.3	4.7	610	427	1.1	0.8	1
14		9.4	10.4	5.6	5.2	750	575	1.4	1.1	24

[a] Saturated solution.

because the presence of the hexamethylbenzene reduces the aggregation tendency and furnishes an intense resonance due to the six equivalent methyl groups that allowed PGSE experiments at micromolar concentration to be performed. V_H^{-0} for small counterions was considered equal to the van der Waals volume.[16,36] Consequently, V_H^0 of **4**PF_6 ion pair was derived by adding the volumes of the single ions (Table 1). It can be seen that the determined V_H^0 of **4**$^+$ is ca. 1.46 times higher than that of the V_{vdW} one. Because **4**$^+$ has a shape similar to that of other complexes, their V_H^0 values were derived by scaling V_{vdW} by the same factor (Table 1).

From the ratio between the hydrodynamic volumes (V_H) at a particular concentration and the volumes of ion pairs at infinite dilution (V_H^0), the cationic (N^+) and anionic (N^-) aggregation numbers were evaluated (Table 1).[38] To appreciate the meaning of N^+ and N^-, it is important to consider that, if only free ions were present in solution, N^+ and N^- should be ca. 0.9 and 0.1. Complete ion pairing and "ion quadrupoling" would lead to $N^+ = N^- = 1$ and $N^+ = N^- = 2$, respectively. While if only "$\mathbf{Ru}_2X^+$" ion triples and free "X^-" were present in solution, N^+ and N^- should be ca. 1.9 and 1.0.

A comparison of the aggregation tendency of different complexes was carried out in CD_2Cl_2 (Table 1, entries 1−2, 3−6, 7−12, 13, 14). The aggregation tendency follows the order: **2**BF_4 > **3**PF_6 ≈ **4**PF_6 ≈ **5**PF_6. Excluding **2**BF_4, other complexes showed almost the same aggregation tendency in CD_2Cl_2 similar also to that of other half-sandwich ruthenium(II) complexes bearing diamine,[35] acylpyridine,[30] and diimine ligands.[16] Ion pairing is the main aggregative process, and only at concentration higher than ca. 10 mM do other associative processes become active. It has to be noted that also complex **5**PF_6 that has a terminal OH moiety did not show a particularly high aggregation tendency, probably because the OH functionality is engaged in an intramolecular HB as observed in the solid-state structure of **5**BPh_4 and, consequently, cannot establish intercationic HBs. In strict contrast, complex **2**BF_4 containing the Ru−O−C(Py)$_2$−OH functionality was little soluble in CD_2Cl_2 but showed a remarkable tendency to aggregate. As shown in Table 1 (entry 1), already at 0.5 mM V_H^+ is almost twice that expected for the ion pair ($N^+ = 1.9$), while V_H^- is ca. equal to V_H^0 ($N^- = 1.1$). This clearly indicates that **2**BF_4 is prevalently present as ion triples $\mathbf{2}_2BF_4^+$ and BF_4^- in CD_2Cl_2. It is reasonable to believe that $\mathbf{2}_2BF_4^+$ has a structure similar to that observed in the solid state with the two OH···O HBs that are responsible for the high stability of the ion triples. The formation of the latter may also be facilitated by the establishment of the intercationic π−π-stacking interaction between two pyridyl moieties evidenced in the solid state. A similar intercationic π−π-stacking interaction has been observed for [Ru(p-cymene)(κ^2-2-bzpy)Cl]PF_6 (bzpy = 2-benzoylpyridine) whose cation is isosteric with that of **2**BF_4.[30] As a consequence of the stacking interaction, [Ru(p-cymene)(κ^2-2-bzpy)Cl]PF_6 showed a slightly higher tendency to form ion triples than analogous compounds not having the possibility to undergo it.[30] By the way, contrasting the observed V_H^+ and V_H^- with V_H^0 instead of V_{vdW}, as was previously done,[30] it is found that ion triples form but N values are not indicative of their exclusive presence. In the actual case, the establishment of intercationic HBs makes it possible to have

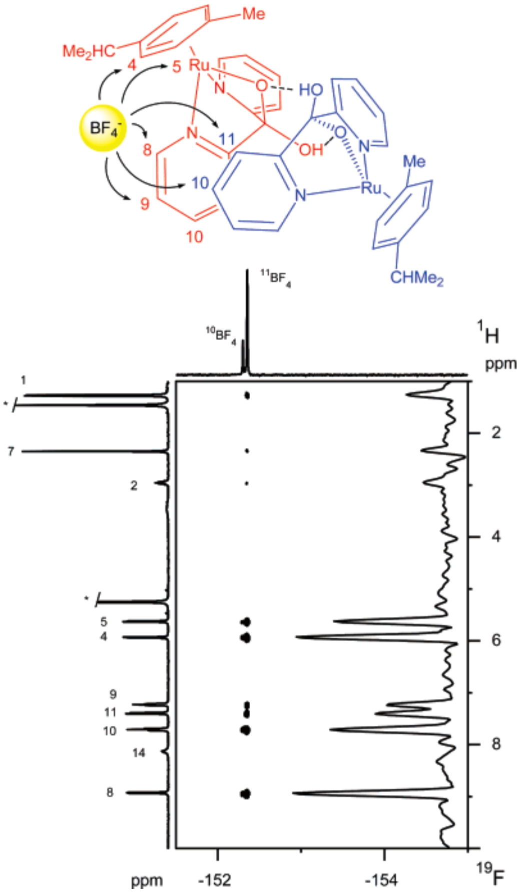

Figure 4. $^{19}F,^1H$-HOESY NMR spectrum (400.13 MHz, 296 K) of complex **2**BF_4 in CD_2Cl_2 at 1.7 mM. * denotes the residues of non-deuterated solvent and water.

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(38) Pochapsky, S. S.; Mo, H.; Pochapsky, T. *J. Chem. Soc., Chem. Commun.* **1995**, 2513. Mo, H.; Pochapsky, T. *J. Phys. Chem. B* **1997**, *101*, 4485. Zuccaccia, C.; Bellachioma, G.; Cardaci, G.; Macchioni, A. *Organometallics* **2000**, *19*, 4663.

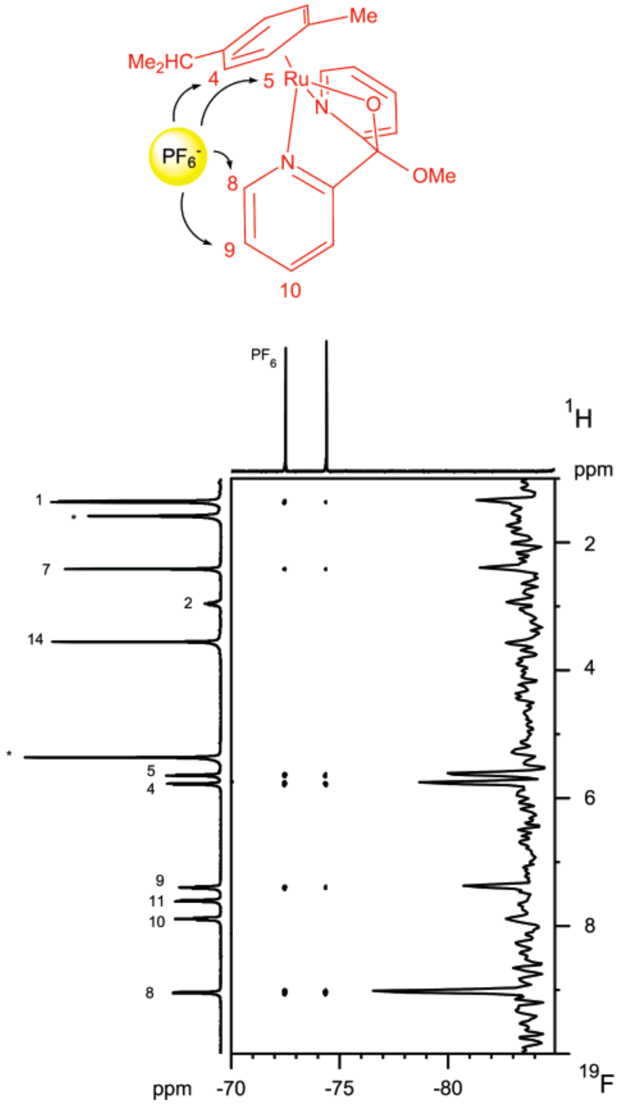

Figure 5. ^{19}F,^{1}H-HOESY NMR spectrum (400.13 MHz, 296 K) of complex **3**PF$_6$ in CD$_2$Cl$_2$ at 3.0 mM. * denotes the residues of non-deuterated solvent and water.

a concentration where ion triples are almost exclusively present (Table 1, entry 1). Increasing the concentration, the aggregation level of **2**BF$_4$ increases, and at the saturated concentration also ion quadruples (**2**BF$_4$)$_2$ become significant (Table 1, entry 2).

(b) NOE Measurements. The relative anion−cation orientations in solution for complexes with fluorinated counterions were investigated by ^{19}F,^{1}H-HOESY NMR spectroscopy. The observed NOEs remarkably depended on the nature of the OR-tail.

For complex **2**BF$_4$, strong NOE contacts were observed between F-atoms of the counterion and 8, 9, 10, and 11 pyridyl resonances (Figure 4); weak NOEs were detected with 1, 2, and 7 cymene resonances. The intensity trend of NOEs with pyridyl protons followed the rather peculiar order: $8 > 10 > 9 \approx 11$. This is completely consistent with the main presence in solution of the ion triple **2**$_2$BF$_4^+$, held together by two intercationic OH···H HBs, having the same structure as that observed in the solid state with the anion located in the orientation A or B. From this position, the anion can interact with both pyridyl rings that undergo the π−π-stacking interaction as illustrated in Figure 4. No interaction was observed between the counterion and the proton of the OH-tail probably because the OH moiety is already engaged in intermolecular HBs. In principle, OH could be a good anchor point for fluorinated counterions. For instance, it has been previously found that a peripheral NH moiety strongly favors ion pairing in the [PtMe(dpa)(Me$_2$SO)]PF$_6$ [dpa = bis(2-pyridyl)amine] complex, allowing the establishment of interionic HBs.[39]

Differently from what was observed for complex **2**BF$_4$, in complexes **3**−**5**PF$_6$ the counterion showed strong interionic NOEs with 8 and 9 pyridyl resonances and 4 and 5 cymene protons (Figure 5). Weak NOEs were also detected with 1, 2, and 7 cymene resonances. No interaction was observed between the counterion and 10 and 11 pyridyl protons and the protons of the OR-tail, even for complex **5**PF$_6$ that contains the OH functionality. All of these observations indicate that PF$_6^-$ is located close to the nitrogen of N,N,O ligand. From the PGSE measurement, we have shown that the ion pair is prevalently present in solution, so the counterion can interact only with the pyridyl rings of the nearest ruthenium center.

Conclusions

The aggregation tendency of [Ru(arene)(κ^3-dpk-OR)]X complexes strongly depends on the nature of the OR-tail. When R = H, the complex has the possibility of establishing a [1 × 1] network of HBs that stabilize the dication. As a consequence, a rare example of formation of Ru$_2$X$^+$ ion triples driven by intercationic HB is evidenced in CD$_2$Cl$_2$ by PGSE NMR experiments. ^{19}F,^{1}H-HOESY NMR experiments further support the formation of ion triples and allow one to locate the counterion in ion triples. The anion position in solution is consistent with that observed in the solid state through X-ray single-crystal studies.

Complexes bearing R = alkyl group, not having the possibility to undergo intercationic HB, do not afford aggregation higher than ion pairs in CD$_2$Cl$_2$. The same is observed also for complex with R = CH$_2$CH$_2$OH that in principle could undergo intercationic HB. X-ray and NMR studies allow understanding that the tail is folded back toward the metal center and the terminal OH is engaged in an intracationic HB with the oxygen atom coordinated to the ruthenium.

Experimental Section

RuCl$_3$·3H$_2$O and dpk were purchased from Sigma. [Ru(η^6-arene)-Cl$_2$]$_2$ dimers were prepared according to Benneth and Smith.[40] Compounds **1**−**7** were prepared under nitrogen using standard Schlenk techniques. Solvents were freshly distilled (hexane with Na, Et$_2$O with Na/benzophenone, MeOH and CH$_2$Cl$_2$ with CaH$_2$) and degassed, by many gas−pump−nitrogen cycles, before use.

One- and two-dimensional ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra were measured on Bruker DPX 200 and DRX 400 spectrometers. Referencing is relative to TMS (^{1}H and ^{13}C), CCl$_3$F (^{19}F), and 85% H$_3$PO$_4$ (^{31}P). NMR samples were prepared by dissolving the suitable amount of compound in 0.5 mL of solvent.

Synthesis of Complex 1BF$_4$. [Ru(η^6-cymene)Cl$_2$]$_2$ (0.100 g, 0.163 mmol) was added to a solution of dpk (0.066 g, 0.358 mmol) in CH$_2$Cl$_2$ (5 mL). To the resulting red-brown solution was added AgBF$_4$ (0.064 g, 0.326 mmol). AgCl 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: 80%.^{1}H NMR (acetone-d_6, 298 K, J in Hz): δ 1.27 (d, $^3J_{1-2} = 6.90$, 1), 1.96 (s, 7), 2.81 (sept, $^3J_{H2-H1} = 6.9$, 2), 5.74 (d, $^3J_{5-4} = 5.7$, 5), 5.95 (d,

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[39] Romeo, R.; Nastasi, N.; Monsù Scolaro, L.; Plutino, M. R.; Albinati, A.; Macchioni, A. *Inorg. Chem.* **1998**, *37*, 5460.

[40] Benneth, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans* **1974**, 233.

$^3J_{4-5} = 5.7$, 4), 7.96 (dd, $^3J_{9,10} = 7.6$, $^3J_{9,8} = 5.2$, 9), 8.27 (d, $^3J_{11,10} = 7.6$, 11), 8.38 (dd, $^3J_{10,11} = {}^3J_{10,9} = 7.6$, 10), 9.24 (d, $^3J_{8,9} = 5.2$, 8). ^{13}C{^{1}H} NMR (acetone-d_6, 298 K): δ 17.46 (s, 7), 21.93 (s, 1), 31.01 (s, 2), 86.33 (s, 3), 86.86 (s, 6), 101.71 (s, 3), 109.05 (s, 5), 127.36 (s, 11), 129.93 (s, 9), 141.11 (s, 10), 153.91 (s, 12), 158.02 (s, 8), 185.46 (s, 13). ^{19}F NMR (acetone-d_6, 298 K): δ −152.32 (br,^{10}BF$_4$), −152.37 (br, ^{11}BF$_4$). Anal. Calcd for $C_{21}H_{22}BClF_4N_2ORu$: C, 46.56; H, 4.09; N, 5.17. Found: C, 46.51; H, 4.06; N, 5.13.

Synthesis of Complex 2BF$_4$. [Ru(η^6-cymene)Cl$_2$]$_2$ (0.100 g, 0.163 mmol) was added to a solution of dpk (0.066 g, 0.358 mmol), NaOH (0.013 g, 0.358 mmol), and NaBF$_4$ (0.040 g, 0.358 mmol) in H$_2$O (5 mL). The resulting red-orange suspension was stirred for 1 h at rt until it transformed into a yellow suspension. The solution was filtered, and the yellow solid was washed with cold H$_2$O and *n*-hexane. Yield = 70%. ^{1}H NMR (acetone-d_6, 298 K, J in Hz): δ 1.36 (d, $^3J_{1-2} = 6.90$, 1), 2.42 (s, 7), 3.13 (sept, $^3J_{\mathrm{H2-H1}} = 6.9$, 2), 5.91 (d, $^3J_{5-4} = 5.7$, 5), 6.17 (d, $^3J_{4-5} = 5.7$, 4), 7.16 (s, 14), 7.47 (ddd, $^3J_{9,10} = 7.7$, $^3J_{9,8} = 6.0$, $^4J_{9,11} = 1.3$, 9), 7.76 (dd, $^3J_{11,10} = 7.6$, $^4J_{11,9} = 1.3$, 11), 8.03 (dd, $^3J_{10,11} = {}^3J_{10,9} = 7.7$, $^4J_{10,8} = 1.3$, 10), 9.36 (d, $^3J_{8,9} = 6.0$, 8). ^{13}C{^{1}H} NMR (acetone-d_6, 298 K): δ 17.51 (s, 7), 22.47 (s, 1), 31.26 (s, 2), 81.92 (s, 5), 83.87 (s, 4), 100.68 (s, 6), 103.70 (s, 13), 106.03 (s, 13), 121.24 (s, 11), 124.57 (s, 9), 140.34 (s, 10), 153.46 (s, 8), 163.80 (s, 12). ^{19}F NMR (acetone-d_6, 298 K): δ −152.32 (br,^{10}BF$_4$), −152.37 (br, ^{11}BF$_4$). Anal. Calcd for $C_{21}H_{23}BClF_4N_2O_2Ru$: C, 48.20; H, 4.43; N, 5.35. Found: C, 48.25; H, 4.46; N, 5.33.

Synthesis of Complex 3BPh$_4$. [Ru(η^6-cymene)Cl$_2$]$_2$ (0.100 g, 0.163 mmol) was added to a solution of dpk (0.066 g, 0.358 mmol) in MeOH (5 mL). The resulting red-orange suspension was stirred for 3 h at rt until it changed into a yellow solution; a large excess of NaBPh$_4$ (10 equiv) dissolved in 0.5 mL of MeOH was added, and a precipitate formed. The solution was filtered, and the yellow solid was washed with cold MeOH and *n*-hexane. Yield = 85%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K, J in Hz): δ 1.30 (d, $^3J_{1,2} = 6.9$, 1), 2.24 (s, 7), 2.81 (sept, $^3J_{2,1} = 6.9$, 2), 3.55 (s, 14), 5.29 (d, $^3J_{5,4} = 6.2$, 5), 5.47 (d, $^3J_{4,5} = 6.2$, 4), 6.91 (t, $^3J_{\mathrm{p,m}} = 7.2$, p), 7.03 (dd, $^3J_{\mathrm{m,p}} = {}^3J_{\mathrm{m,o}} = 7.8$, m), 7.19 (ddd, $^3J_{9,10} = 7.7$, $^3J_{9,8} = 5.38$, $^4J_{9,11} = 1.4$, 9), 7.40 (br, o), 7.57 (d, $^3J_{11,10} = 7.4$, 11), 7.79 (ddd, $^3J_{10,11} = {}^3J_{10,9} = 7.68$, $^4J_{10,8} = 1.3$, 10), 8.71 (d, $^3J_{8,9} = 5.38$, 8). Anal. Calcd for $C_{46}H_{45}BN_2O_2Ru$: C, 71.78; H, 5.89; N, 3.64. Found: C, 71.71; H, 5.84; N, 3.68.

Synthesis of Complex 3PF$_6$. [Ru(η^6-cymene)Cl$_2$]$_2$ (0.100 g, 0.163 mmol) was added to a solution of dpk (0.066 g, 0.358 mmol) in MeOH (5 mL). The resulting red-orange suspension was stirred for 3 h at rt until it changed into a yellow solution; a large excess of NH$_4$PF$_6$ (10 equiv) dissolved in 0.5 mL of MeOH was added, and a precipitate formed. The solution was filtered, and the yellow solid was washed with cold MeOH and *n*-hexane. Yield = 65%. Alternatively, 0.118 g (0.154 mmol) of **3**BPh$_4$ was dissolved in 5 mL of acetone. 0.056 g of TlPF$_6$ (0.161 mmol) was added under nitrogen atmosphere, and TlBPh$_4$ precipitated from the solution. The solution was filtered and dried under vacuum, giving a yellow solid. Yield = 98%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K, J in Hz): δ 1.35 (d, $^3J_{1,2} = 6.9$, 1), 2.37 (s, 7), 2.95 (sept, $^3J_{2,1} = 6.9$, 2), 3.55 (s, 14), 5.64 (d, $^3J_{5,4} = 6.2$, 5), 5.77 (d, $^3J_{4,5} = 6.2$, 4), 7.40 (ddd, $^3J_{9,10} = 7.7$, $^3J_{9,8} = 5.38$, $^4J_{9,11} = 1.4$, 9), 7.60 (d, $^3J_{11,10} = 7.4$, 11), 8.87 (ddd, $^3J_{10,11} = {}^3J_{10,9} = 7.68$, $^4J_{10,8} = 1.3$, 10), 9.05 (d, $^3J_{8,9} = 5.38$, 8). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K, J in Hz): δ 18.1 (s, 7), 22.7 (s, 1), 31.7 (s, 2), 50.5 (s, 14), 82.6 (s, 5), 83.1 (s, 4), 99.8 (s, 6), 106.1 (s, 3), 106.6 (s, 13), 121.6 (s, 11), 124.7 (s, 9), 140.0 (s, 10), 153.1 (s, 8), 161.8 (s, 12). ^{19}F NMR (CD$_2$Cl$_2$, 298 K): δ −71.6 (d, $^1J_{\mathrm{FP}} = 711.0$). ^{31}P{^{1}H} NMR (CD$_2Cl_2$, 298 K): δ −141.0 (sept, $^1J_{\mathrm{PF}} = 711.0$). Anal. Calcd for $C_{22}H_{25}F_6N_2O_2PRu$: C, 44.37; H, 4.23; N, 4.70. Found: C, 44.31; H, 4.24; N, 4.72.

Synthesis of Complex 4PF$_6$. [Ru(η^6-hexamethylbenzene)Cl$_2$]$_2$ (0.100 g, 0.149 mmol) was added to a solution of dpk (0.061 g, 0.330 mmol) in MeOH (5 mL). The resulting red-orange suspension was stirred for 3 h at rt until it changed into a yellow solution; a large excess of NH$_4$PF$_6$ (10 equiv) dissolved in 0.5 mL of MeOH was added, and a precipitate formed. The solution was filtered, and the yellow solid was washed with cold MeOH and *n*-hexane. Yield = 62%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K, J in Hz): δ 2.25 (s, HMB), 3.55 (s, 14), 7.40 (ddd, $^3J_{9,10} = 7.7$, $^3J_{9,8} = 5.38$, $^4J_{9,11} = 1.4$, 9), 7.55 (d, $^3J_{11,10} = 7.4$, 11), 7.85 (ddd, $^3J_{10,11} = {}^3J_{10,9} = 7.68$, $^4J_{10,8} = 1.3$, 10), 8.75 (d, $^3J_{8,9} = 5.38$, 8). ^{19}F NMR (CD$_2$Cl$_2$, 298 K): δ −71.6 (d, $^1J_{\mathrm{FP}} = 711.0$). ^{31}P{^{1}H} NMR (CD$_2Cl_2$, 298 K): δ −141.0 (sept, $^1J_{\mathrm{PF}} = 711.0$). Anal. Calcd for $C_{24}H_{29}F_6N_2O_2PRu$: C, 46.23; H, 4.69; N, 4.49. Found: C, 46.29; H, 4.66; N, 4.46.

Synthesis of Complex 5BPh$_4$. [Ru(η^6-cymene)Cl$_2$]$_2$ (0.100 g, 0.163 mmol) was added to a solution of dpk (0.066 g, 0.358 mmol) in HOCH$_2$CH$_2$OH (5 mL). The resulting red-orange suspension was stirred for 3 h at rt until it changed into a yellow solution; a large excess of NaBPh$_4$ (10 equiv) dissolved in 0.5 mL of HOCH$_2$CH$_2$OH was added, and a precipitate formed. The solution was filtered, and the yellow solid was washed with cold HOCH$_2$CH$_2$OH and *n*-hexane. Yield = 85%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K, J in Hz): δ 1.29 (d, $^3J_{1,2} = 7.0$, 1), 2.22 (s, 7), 2.80 (sept, $^3J_{2,1} = 6.9$, 2), 3.73 (m, 15), 4.03 (m, 14), 4.93 (d, $^3J_{16,15} = 5.1$, 5), 5.28 (d, $^3J_{5,4} = 6.2$, 5), 5.49 (d, $^3J_{4,5} = 6.2$, 4), 6.91 (t, $^3J_{\mathrm{p,m}} = 7.2$, p), 7.03 (dd, $^3J_{\mathrm{m,p}} = {}^3J_{\mathrm{m,o}} = 7.8$, m), 7.22 (ddd, $^3J_{9,10} = 7.8$, $^3J_{9,8} = 5.4$, $^4J_{9,11} = 1.3$, 9), 7.37 (br, o), 7.62 (dd, $^3J_{11,10} = 7.2$, $^4J_{11,9} = 0.5$, 11), 7.82 (ddd, $^3J_{10,11} = {}^3J_{10,9} = 7.7$, $^4J_{10,8} = 1.3$, 10), 8.72 (d, $^3J_{8,9} = 5.45$, 8). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ 19.0 (s, 7), 22.8 (s, 1), 31.5 (s, 2), 62.6 (s, 15), 68.4 (s, 14), 81.8 (s, 5), 83.9 (s, 4), 100.5 (s, 6), 105.5 (s, 3), 106.0 (s, 13), 121.9 (s, 11), 122.3 (s, p), 125.0 (s, 9), 126.1 (s, m), 136.4 (s, o), 140.4 (s, 10), 152.7 (s, 8), 160.1 (s, 12), 164.4 (q, $^1J_{\mathrm{C}^{11}\mathrm{B}} = 49.5$, C$_{\mathrm{ipso}}$). Anal. Calcd for $C_{47}H_{47}BN_2O_3Ru$: C, 70.58; H, 5.92; N, 3.50. Found: C, 70.50; H, 5.95; N, 3.52.

Synthesis of Complex 5PF$_6$. [Ru(η^6-cymene)Cl$_2$]$_2$ (0.100 g, 0.163 mmol) was added to a solution of dpk (0.066 g, 0.358 mmol) in HOCH$_2$CH$_2$OH (5 mL). The resulting red-orange suspension was stirred for 3 h at rt until it changed into a yellow solution; a large excess of NH$_4$PF$_6$ (10 equiv) dissolved in 0.5 mL of HOCH$_2$CH$_2$OH was added, and a precipitate formed. The solution was filtered, and the yellow solid was washed with cold MeOH and *n*-hexane. Yield = 63%. Alternatively, 0.123 g (0.154 mmol) of **3**BPh$_4$ was dissolved in 5 mL of acetone. 0.056 g of TlPF$_6$ (0.161 mmol) was added under nitrogen atmosphere, and TlBPh$_4$ precipitated from the solution. The solution was filtered and dried under vacuum, giving a yellow solid. Yield = 98%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K, J in Hz): δ δ 1.34 (d, $^3J_{1,2} = 6.9$, 1), 2.38 (s, 7), 2.93 (sept, $^3J_{2,1} = 6.9$, 2), 3.74 (m, 14), 4.04 (m, 15), 4.52 (7, $^3J_{16,15} = 5.1$, 16), 5.65 (d, $^3J_{5,4} = 6.2$, 5), 5.84 (d, $^3J_{4,5} = 6.2$, 4), 7.43 (ddd, $^3J_{9,10} = 7.7$, $^3J_{9,8} = 5.38$, $^4J_{9,11} = 1.4$, 9), 7.66 (d, $^3J_{11,10} = 7.4$, 11), 7.91 (ddd, $^3J_{10,11} = {}^3J_{10,9} = 7.68$, $^4J_{10,8} = 1.3$, 10), 9.08 (d, $^3J_{8,9} = 5.38$, 8). ^{19}F NMR (CD$_2$Cl$_2$, 298 K): δ −71.6 (d, $^1J_{\mathrm{FP}} = 711.0$). ^{31}P{^{1}H} NMR (CD$_2Cl_2$, 298 K): δ −141.0 (sept, $^1J_{\mathrm{PF}} = 711.0$). Anal. Calcd for $C_{23}H_{26}F_6N_2O_3PRu$: C, 44.23; H, 4.20; N, 4.49. Found: C, 44.29; H, 4.23; N, 4.49.

Synthesis of Complex 6BPh$_4$. [Ru(η^6-cymene)Cl$_2$]$_2$ (0.100 g, 0.163 mmol) was added to a solution of dpk (0.066 g, 0.358 mmol) in ethanol (5 mL). The resulting red-orange suspension was stirred for 3 h at rt until it changed into a yellow solution; a large excess of NaBPh$_4$ (10 equiv) dissolved in 0.5 mL of ethanol was added, and a precipitate formed. The solution was filtered, and the yellow solid was washed with cold ethanol and *n*-hexane. Yield = 75%. ^{1}H NMR (CD$_2$Cl$_2$, 298 K, J in Hz): δ 1.30 (d, $^3J_{1,2} = 7.0$, 1), 1.41 (d, $^3J_{15,14} = 7.1$, 15), 2.25 (s, 7), 2.82 (sept, $^3J_{2,1} = 6.9$, 2), 3.81 (q, $^3J_{14,15} = 7.1$, 14), 5.31 (d, $^3J_{5,4} = 6.2$, 5), 5.49 (d, $^3J_{4,5} = 6.2$, 4), 6.90 (t, $^3J_{\mathrm{p,m}} = 7.2$, p), 7.03 (dd, $^3J_{\mathrm{m,p}} = {}^3J_{\mathrm{m,o}} = 7.8$, m), 7.20 (ddd, $^3J_{9,10} = 7.8$, $^3J_{9,8} = 5.4$, $^4J_{9,11} = 1.3$, 9), 7.36 (br, o), 7.59 (d, $^3J_{11,10} = 7.2$, 11), 7.80 (ddd, $^3J_{10,11} = {}^3J_{10,9} = 7.7$, $^4J_{10,8} = 1.3$, 10), 8.73 (d, $^3J_{8,9} = 5.45$, 8). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ 15.9

(s, 15), 18.2 (s, 7), 22.7 (s, 1), 31.7 (s, 2), 59.1 (s, 14), 82.2 (s, 5), 83.0 (s, 4), 99.9 (s, 6), 105.8 (s, 3), 106.7 (s, 13), 121.7 (s, 11), 122.2 (s, p), 124.6 (s, 9), 126.1 (s, m), 136.5 (s, o), 140.1 (s, 10), 152.6 (s, 8), 162.2 (s, 12), 164.4 (q, $^1J_{C^{11}B} = 49.5$, C_{ipso}). Anal. Calcd for $C_{47}H_{47}BN_2O_2Ru$: C, 72.02; H, 6.04; N, 3.57. Found: C, 72.12; H, 6.06; N, 3.50.

Synthesis of Complex 7BPh$_4$. [Ru(η^6-cymene)Cl_2]$_2$ (0.100 g, 0.163 mmol) was added to a solution of dpk (0.066 g, 0.358 mmol) in isobutanol (5 mL). The resulting red-orange suspension was stirred for 3 h at rt until it changed into a yellow solution; a large excess of $NaBPh_4$ (10 equiv) dissolved in 0.5 mL of isobutanol was added, and a precipitate formed. The solution was filtered, and the yellow solid was washed with cold isobutanol and *n*-hexane. Yield = 71%. ^{1}H NMR (CD_2Cl_2, 298 K, J in Hz): δ 1.09 (d, $^3J_{16,15} = 6.7$, 16), 1.31 (d, $^3J_{1,2} = 6.9$, 1), 2.09 (m, $^3J_{15,14} = 6.5$, $^3J_{15,16} = 6.7$, 15), 2.26 (s, 7), 2.82 (sept, $^3J_{2,1} = 6.9$, 2), 3.54 (d, $^3J_{14,15} = 6.5$, 14), 5.31 (d, $^3J_{5,4} = 5.9$, 5), 5.49 (d, $^3J_{4,5} = 5.9$, 4), 6.90 (t, $^3J_{p,m} = 7.2$, p), 7.03 (dd, $^3J_{m,p} = {}^3J_{m,o} = 7.8$, m), 7.20 (ddd, $^3J_{9,10} = 7.8$, $^3J_{9,8} = 5.4$, $^4J_{9,11} = 1.3$, 9), 7.36 (br, o), 7.59 (d, $^3J_{11,10} = 7.6$, 11), 7.80 (ddd, $^3J_{10,11} = {}^3J_{10,9} = 7.6$, $^4J_{10,8} = 1.0$, 10), 8.73 (d, $^3J_{8,9} = 5.3$, 8). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 17.9 (s, 7), 19.7 (s, 16), 22.8 (s, 1), 29.3 (s,15), 31.7 (s, 2), 69.4 (s, 14), 82.2 (s, 5), 83.1 (s, 4), 99.9 (s, 6), 105.8 (s, 3), 106.7 (s, 13), 121.7 (s, 11), 122.2 (s, p), 124.9 (s, 9), 126.0 (s, m), 136.4 (s, o), 140.1 (s, 10), 152.6 (s, 8), 162.3 (s, 12), 164.3 (q, $^1J_{C^{11}B} = 49.5$, C_{ipso}). Anal. Calcd for $C_{49}H_{51}BN_2O_2Ru$: C, 72.49; H, 6.33; N, 3.45. Found: C, 72.40; H, 6.30; N, 3.48.

NOE Measurements. The ^{1}H-NOESY[41] NMR experiments were acquired by using the standard three-pulse sequence or by the PFG version.[42] Two-dimensional ^{19}F,^{1}H-HOESY NMR experiments were acquired using the standard four-pulse sequence or the modified version.[43] The number of transients and the number of data points were chosen according to the sample concentration and to the desired final digital resolution. Semiquantitative spectra were acquired using a 1 s relaxation delay and 800 ms mixing times.

PGSE Measurements. ^{1}H and ^{19}F PGSE NMR measurements were performed by using the standard stimulated echo pulse sequence[44] 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 dependence of the resonance intensity (I) on a constant waiting time and on a varied gradient strength (G) is described by eq 1:

$$\ln\frac{I}{I_0} = -(\gamma\delta)^2 D_t\left(\Delta - \frac{\delta}{3}\right)G^2 \qquad (1)$$

where I is the intensity of the observed spin echo, I_0 is the intensity of the spin echo without gradients, D_t is the diffusion coefficient, Δ is the delay between the midpoints of the gradients, δ is the length of the gradient pulse, and γ is the magnetogyric ratio.

The shape of the gradients was rectangular, their duration (δ) was 4−5 ms, and their strength (G) was varied during the experiments. All of the spectra were acquired using 32K points, a spectral width of 5000 (^{1}H) and 18 000 (^{19}F) Hz, and processed with a line broadening of 1.0 (^{1}H) and 1.5 (^{19}F) Hz. The semilogarithmic plots of ln(I/I_0) versus G^2 were fitted using a standard linear regression algorithm; the R factor was always higher than 0.99. Different values of Δ, "nt" (number of transients), and number of different gradient strengths (G) were used for different samples.

PGSE data were treated taking into account all of the methodological precautions described in our recent paper.[35]

The uncertainty of the measurements was estimated by determining the standard deviation of the slope of the straight lines, obtained by plotting ln(I/I_0) versus G^2, by performing experiments with different Δ values. The standard propagation of error analysis gave a standard deviation of approximately 3−4% in hydrodynamic radii and 10−15% in hydrodynamic volumes. The van der Waals volumes of **2**BF_4 and **5**BPh_4 ion pairs were determined from their crystal structures; for the other complexes, V_{vdW} was obtained starting from those of **2**BF_4 or **5**BPh_4 by adding or removing the appropriate moieties according to Bondi.[45] The ratios between the experimentally determined V_H^{0+} and V_{vdW}^+ for **4**$^+$ was 1.46. This factor was used to calculate the V_H^{0+} of other cations from V_{vdW}^+. The volumes of ion pairs were evaluated adding V_{vdW}^- to V_H^{0+}.[37]

Crystal Structure Determination of 2BF$_4$ and 5BPh$_4$. Crystal data for **2**: $C_{21}H_{23}BF_4N_2O_2Ru{\cdot}CH_2Cl_2$, $M_w = 608.22$, monoclinic, $P2_1$, $a = 15.781(4)$, $b = 18.160(2)$, $c = 9.047(5)$ Å, $\beta = 103.98(3)°$, $V = 2515.97$ Å^3, $F(000) = 1184$, $\mu = 0.88$ mm^{-1}, $Z = 4$, 7969 independent measured reflections. Crystal data for **5**: $C_{47}H_{50}BN_2O_3Ru{\cdot}{}^1/_2CH_2Cl_2$, $M_w = 1641.96$, $a = 10.240(5)$, $b = 18.724(5)$, $c = 22.536(5)$ Å, $\alpha = 75.79(1)$, $\beta = 77.62(1)$, $\gamma = 80.57(1)°$, triclinic, P-1, $V = 4063(2)$ Å^3, $F(000) = 1706.0$, $\mu = 0.46$ mm^{-1}, $Z = 4$, 29 957 independent measured reflections. Suitable crystals for the X-ray diffraction studies were grown from CH_2Cl_2. Preliminary examination and data collection were carried out at ambient temperature on a Enraf-Nonius CAD-4 diffractometer for **2BF$_4$** and on a BRUKER AXS SMART 2000 CCD diffractometer for **5BPh$_4$**, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data of **5** were collected using 0.3° wide ω scans and a crystal-to-detector distance of 5.0 cm and corrected for absorption empirically using the SADABS routine.[46] Data collection nominally covered a full sphere of reciprocal space with 30 s exposure time per frame. Both structures were solved by direct methods and refined on F^2 by full matrix least-squares calculations using the SHELXTL package.[47] Thermal vibrations were treated anisotropically; H atoms were experimentally located but geometrically positioned [C−H 0.93 and 0.97 Å for aromatic and aliphatic distances; OH 0.82 Å] and refined "riding" on their corresponding carbon or oxygen atom. Refinement converged at a final $R = 0.0488$ for 7532 $F_o > 4\sigma(F_o)$ for 588 parameters, w$R_2 = 0.130$, $S = 1.21$ for **2**; $R = 0.0463$ for 11 304 $F_o > 4\sigma(F_o)$ and 903 parameters, w$R_2 = 0.163$, $S = 1.15$ for **5**. Flack parameter for **2** was 0.085 for the correct absolute structure. The final residual electron density maps showed no remarkable features.

In compound **2**, the asymmetric unit contains two crystallographically independent ion pairs and two solvent (CH_2Cl_2) molecules. The isopropyl moiety of the cymene ring is characterized by large thermal vibrations; however, no satisfactory alternative model for the disordered atoms could be refined despite repeated attempts.

Compound **5** also contains two crystallographic independent ion pairs (BPh_4 as a counterion) in the asymmetric unit and one dichloromethane solvent molecule, treated with half occupancy because it is disordered.

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Supporting Information Available: Crystallographic data for complexes **2** and **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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