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PGSE and NOE NMR Evidence for Higher Order Aggregation in Some Cationic Ruthenium Complexes in Both Protic and Aprotic Solvents

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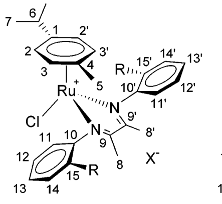
PGSE and NOE NMR measurements were carried out for complexes [Ru(η^6-cymene)((2-R-C_6H_4)N=C(Me)−C(Me)=N(2-R-C_6H_4))Cl]X (X = BF_4 or BPh_4) in both protic and aprotic solvents with a relative permettivity (ϵ_r) ranging from 2.27 (benzene-d_6) to 46.45 (dimethyl sulfoxide-d_6). PGSE and NOE results indicate that complexes have a tendency to aggregate even in medium-polarity solvents such as ethanol (ϵ_r = 24.55) and methanol (ϵ_r = 32.66). In addition, the aggregation process is favored by a decrease of ϵ_r and, unexpectedly, by protic solvents. NOE measurement investigations, interpreted with the help of theoretical calculations and confirmed by X-ray single crystal studies, suggest different aggregation processes for the two counteranions: two cationic moieties approach each other when X = BF_4 while the anion bridges two cationic moieties when X = BPh_4.

Anion−cation interactions increasingly affect the structure and reactivity of ionic organometallics.[1] This is nowadays proved for low-polarity solvents where organometallics may form intimate ion pairs, ion quadruples, and even higher aggregates. On the other hand, it is usually thought that solvated organometallic ions are mainly present in medium- and high-polarity solvents, and consequently, anion−cation interactions do not play a relevant role in such solvents. Here we report the results of a combined PGSE (pulsed field gradient spin−echo)[2] and NOE (nuclear Overhauser effect)[3] NMR investigation on the solvent role on the aggregation of [Ru(η^6-cymene)((2-R-C_6H_4)N=C(Me)−C(Me)=N(2-R-C_6H_4))Cl]X (R = H, **1**; Me, **2**; Et, **3**; *i*-Pr, **4**; X = BF_4 or BPh_4). They afforded (1) evidence for tendency to aggregate that, with constant relative permittivity, is unexpectedly higher in protic solvents and (2) a direct, and unprecedented, proof of the presence of ion pairs in protic solvents, such as 2-propanol-d_8, ethanol-d_6, and methanol-d_4.



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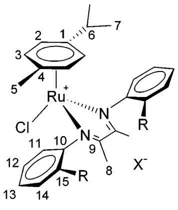

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^1H and ^{19}F PGSE NMR experiments[4] were carried out for **3**BF_4 *anti* and **3**BPh_4 *anti* in different solvents, with a relative permittivity (ϵ_r) ranging from 2.27 (benzene-d_6) to 46.45 (dimethyl sulfoxide-d_6), using tetrakis(trimethylsilyl)silane (TMSS) as internal standard. They allowed the determination of the translational self-diffusion coefficients (D_t) for both cationic (D_t^+) and anionic (D_t^-) moieties (Table 1). According to the Stokes−Einstein equation ($D_t = kT/c\pi\eta r_H$), D_t is inversely proportional to the hydrodynamic radius (r_H) of the diffusing particles, but it also depends on the solution

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Table 1. $10^{10}D_t$ ($m^2\ s^{-1}$ at 296 K), r_H (Å), and *N* Values for Compounds **3**BF$_4$ *anti* and **3**BPh$_4$ *anti* 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*
		3BF$_4$ *anti*						
1	benzene-d_6 (2.27)	5.53	5.54	6.1	6.0	1.9	1.8	34.1
2	chloroform-*d* (4.81[a])	6.73	7.15	6.0	5.7	1.8	1.6	34.0
3	CD_2Cl_2 (8.93)	9.54	10.70	5.3	4.9	1.3	1.0	34.1
4	2-propanol-d_8 (19.92)	1.85	2.05	5.5	5.1	1.4	1.1	39.6[b]
5	2-propanol-d_8 (19.92)	2.12	2.37	5.0	4.5	1.1	0.8	19.8
6	2-propanol-d_8 (19.92)	2.15	2.59	4.9	4.3	1.0	0.7	3.2
7	2-propanol-d_8 (19.92)	2.23	2.93	4.8	3.9	0.9	0.5	0.2
8	acetone-d_6 (20.56)	15.39	25.46	4.9	3.4	1.0	0.3	34.1
9	ethanol-d_6 (24.55)	4.12	4.98	4.9	4.3	1.0	0.7	34.1
10	methanol-d_4 (32.66)	7.62	13.54	5.4	3.5	1.3	0.4	34.0
11	CD_3NO_2 (35.94)	7.23	16.61	4.8	2.7	0.9	0.2	34.0
		3BPh$_4$ *anti*						
12	benzene-d_6 (2.27)	5.56	5.69	6.8	6.7	1.9	1.8	0.4[b]
13	chloroform-*d* (4.81[a])	5.25	5.20	7.7	7.6	2.7	2.7	32.4
14	CD_2Cl_2 (8.93)	8.43	8.65	5.7	5.6	1.1	1.1	43.0
15	acetone-d_6 (20.56)	11.6	13.6	5.3	4.6	0.9	0.6	31.8
16	CD_3NO_2 (35.94)	6.86	7.91	5.1	4.5	0.8	0.5	31.9
17	DMSO-d_6 (46.45)	1.95	2.46	5.3	4.5	0.9	0.5	31.7

[a] ϵ_r at 20 °C. [b] Saturated solution.

viscosity and the numerical factor *c*.[5] The latter tends to 6 for diffusing species having $r_H > 5$ Å, but it falls rapidly to 4 for a smaller molecule. The factor *c* can be predicted by using a semiempirical improvement (expression reported in a following equation)[6] of the formula deriving from the microfriction theory proposed by Wirtz and co-workers,[7] in which *c* is expressed as a function of the solute-to-solvent ratio of radii.

$$c = \frac{6}{\left[1 + 0.695\left(\frac{r_{\mathrm{solv}}}{r_H}\right)^{2.234}\right]}$$

By introducing such an expression in the Stokes–Einstein equation, r_H values of the solute were derived (Table 1) from the measured D_t values using the van der Waals radii for the solvent[8] and the solution viscosity corrected with the help of TMSS self-diffusion coefficients (Supporting Information, SI). The volumes of the diffusing particles, assumed to be spherical, were then estimated and compared with the van der Waals volumes of ion pairs known from the solid state[9] or from calculations. The ratios between the apparent volume of the cationic or anionic moieties and that of the ion pairs, N^+ and N^-, respectively, are reported in Table 1 and represent a sort of aggregation number. Of course, a distribution of ionic species is present in solution; consequently, N^+ and N^- indicate which is the apparent average aggregation number of the ionic moieties. For example, if they are both equal to 1 or 2, this means that ion pairs and ion quadruples, i.e., "$(Ru^+X^-)_2$", are the predominant species in solution, respectively. Solid state and theoretical structural data (SI) indicate that free ions for **3**BF$_4$ *anti* correspond to N^+ and N^- equal to 0.92 and 0.09, respectively, and, for **3**BPh$_4$ *anti*, to 0.60 and 0.40, respectively.[10] If $N^+ > 0.92$ and 0.60, for **3**BF$_4$ or **3**BPh$_4$ *anti*, respectively, and/or $N^- > 0.09$ and 0.40, then ion pairing and/or aggregation occurs.

Table 2. Relative NOE Intensities Determined by Arbitrary Fixing at 1 the Intensity of the NOE(s) between the Anion Resonances (*o*-H in the Case of BPh_4^-) and the Imine Methyls.

	8/8′	C*H*$_2$CH$_3$	CH$_2$C*H*$_3$	11′	2/3	7/7′	5
3BF$_4$ *anti*[a]	1	1.23	0.46	1.78	0.17	0.10	0.25
3BF$_4$ *anti*[b]	1	1.50	0.75	3.12[c]	0.65	0.17	0.40
3BF$_4$ *anti*[d]	1	1.50	0.76	1.68	0.51	0.16	0.58
3BF$_4$ *syn*[a]	1	1.42	0.61		0.28	0.13	0.24
3BPh$_4$ *anti*[e]	1	0.85	0.54	*f*	1.47	0.38	0.70
3BPh$_4$ *syn*[e]	1	1.33	0.72		1.60	0.40	1.11

[a] In methylene chloride-d_2 at 286 K. [b] In 2-propanol-d_8 at 296 K. [c] Overestimated due to the superimposition of 12′ and 13′. [d] In benzene-d_6 at 296 K. [e] In chloroform-*d* at 296 K. [f] Difficult to quantitatively evaluate due to the overlapping between 12′ and *o*-H resonances.

Only the anionic moiety of **3**BF$_4$ *anti* approaches the situation of free ions in nitromethane-d_3. In other solvents, a degree of aggregation is observed that increases not only by decreasing ϵ_r, as usual, but also when protic solvents, with ϵ_r comparable with that of aprotic solvents, are considered (entries 4 and 8, or 10 and 11). In addition, N^+ is always larger than N^-. The difference between the latter decreases when ϵ_r decreases and when the sample concentration increases (entries 4–7). Compound **3**BPh$_4$ *anti* is not soluble in protic solvents and was, consequently, investigated only in aprotic solvents. In all solvents, a certain degree of aggregation is present that increases with decreasing ϵ_r, if solutions with comparable concentrations are compared, and again, N^+ is always larger than N^-, with the exception of entries 13 and 14 where they are equal.

The interionic structure of the complexes was investigated in solution by means of ^{1}H NOESY (X = BPh$_4$) and the ^{19}F,^{1}H HOESY (X = BF$_4$) NMR experiments,[11] using a mixing time of 0.1 s and a relaxation delay of 7 s (initial rate approximation).[3] A selected list of the detected interionic interactions are reported in Table 2. For **3**BF$_4$ *anti*, interionic interactions were observed in all solvents, even in methanol-d_4, with the exception of nitromethane-d_3 (Figure 1). In all cases, the anion does not interact with protons belonging to the R group that points toward the chlorine atom and it shows the strongest contact with the 11′ proton. The observed

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(5) We thank a reviewer for having suggested us to take into account the importance of the parameter *c*.

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(9) Crystal data of **3**BPh$_4$ *anti*: $RuC_{54}H_{58}BClN_2 \cdot 0.5CH_2Cl_2$, $M = 907.09$ g mol^{-1}, orthorombic space group $P2_1/b2/c2_1/n$ (No. 60), $a = 19.726(5)$ Å, $b = 16.920(5)$ Å, $c = 28.889(5)$ Å, $V = 9642$ (4) Å^3, $T = 293$ (2) K, $Z = 8$, $D_c = 1.274$ g cm^{-3}, $\mu = 0.473$ mm^{-1}, $F(000) = 3864$, crystal size = 0.25 × 0.15 × 0.15 mm^3. Crystal data of **2**BF$_4$ *syn*: $RuC_{28}H_{34}ClN_2BF_4$, $M = 621.90$ g mol^{-1}, monoclinic space group $P2_1/c$ (No. 14), $a = 17.250(5)$ Å, $b = 11.526(5)$ Å, and $c = 17.310(5)$ Å, $\beta = 113.19(5)$°, and $V = 3163.6(19)$ Å^3. $T = 293$ (2) K, $Z = 4$, $D_c = 1.306$ g cm^{-3}, $\mu = 0.621$ mm^{-1}, $F(000) = 1272$, crystal size = 0.20 × 0.15 × 0.15 mm^3.

(10) Theoretical volumes were calculated from X-ray data and/or theoretical calculations and the van der Waals atomic radii: $V(\mathbf{3}^+) = 423$ Å^3, $V(BF_4^-) = 49$ Å^3, $V(BPh_4^-) = 284$ Å^3, $V(\mathrm{TMSS}) = 263$ Å^3, $V(\mathbf{3}BF_4\ anti) = 496$ Å^3, $V(\mathbf{3}BPh_4\ anti) = 704$ Å^3.

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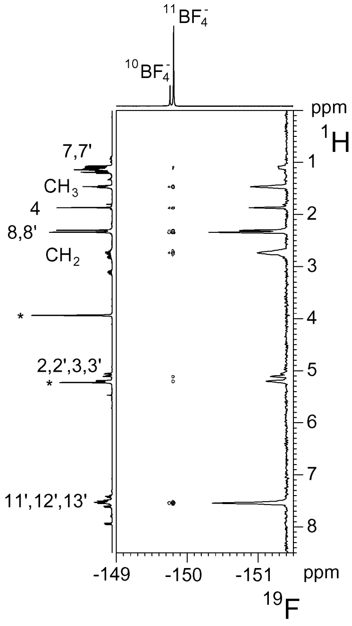

Figure 1. ^{19}F, ^1H HOESY NMR spectrum (376.65 MHz, 302 K, 2-propanol-d_8) of complex **3**BF_4 *anti*. The F1 trace (indirect dimension) relative to the $^{11}BF_4^-$ resonance is reported on the right. Asterisks denote the residual nondeuterated resonances of 2-propanol-d_8.

interionic interactions were interpreted with the help of DFT calculations (SI) by a single anion−cation orientation in which the anion lies on the plane containing C8, C9, C8′, and C9′ and is shifted toward the less hindered N-arm having the R-group pointing toward the chlorine atom. From this position, BF_4^- can still weakly interact with cymene protons. ^{19}F,^1H HOESY NMR spectra in different solvents and at different concentrations always show the same interactions with comparable relative intensities. Also, for **3**BPh_4 *anti* the anion does not interact with protons belonging to R group that points toward the chlorine atom, but an increased intensity of *ortho*-anion/cymene protons interactions was observed (Table 2). The result is that the two orientations, one with the anion close to the N,N-ligand and the other with the anion in the proximity of cymene, are almost equally probable.

The general picture that can be deduced from these results is that both **3**BF_4 *anti* and **3**BPh_4 *anti* have the tendency to aggregate forming quadrupoles (entry 1) and even higher aggregates (entry 13). In addition, comparison between entries 2 and 13 indicates that **3**BPh_4 *anti* has a higher tendency to aggregate than **3**BF_4 *anti* in low-polarity solvents that can be reasonably explained considering that the ion pair dipole moment in **3**BPh_4 *anti* is larger than that in **3**BF_4 *anti*. The observation that N^+ is always larger than N^- can be easily justified considering the smaller volume of the anions compared to that of the cation. Consequently, the anion dissociation does not afford a significant change of N^+, especially for BF_4^-. Furthermore, there is the possibility that some solvent molecules tightly bond to the resulting cation. On the other hand, solvation cannot be the only responsible process for the increased apparent average volume due to the observation of NOE anion−cation interactions. The surprising finding that aggregation processes are favored by protic solvents could be explained by the minimization of solvent structure-breaking.[12] Results in 2-propanol-d_8 deserve a special comment because 2-propanol is very frequently used as solvent and, at the same time, as proton donor in the transfer hydrogenation of ketones.[13] From entries 4−7 (Table 1), it appears that ion pairs are the most abundant species in solution at high concentration values.

NOE investigations shed some light on the structure of the aggregates. In particular, the independence of the interionic interactions on the concentration observed for **3**BF_4 *anti* in 2-propanol-d_8 and on changing solvent suggests that two cationic moieties have to approach each other, from the side of cymene and Cl ligands, in the formation of the aggregates. For instance, quadrupoles "$BF_4^-Ru^+Ru^+BF_4^-$" are likely to be predominant in benzene-d_6. As for **3**BPh_4 *anti*, the two anion−cation orientations observed suggest that in aggregates the anion bridges two cationic moieties. Consequently, quadruple ions should be "$Ru^+BPh_4^-Ru^+$-BPh_4^-". Both the structures hypothesized for multiple ions higher than ion pairs in solution find confirmation in the solid state. The solid state structures of **3**BPh_4 *anti* and **2**BF_4 *syn* were determined by X-ray single crystal diffraction. It was found that the two cation−anion orientations described for **3**BPh_4 *anti* are present and pairs of cations really approach each other from the side of Cl and cymene ligands for **2**BF_4 *syn* (see SI). The latter finding agrees with the very recent results of Brunner and co-workers that show how similar arene ruthenium compounds may undergo a sort of tight-inverted piano stool molecular recognition.[14]

In conclusion, we have shown, for the first time, that the aggregation of some ionic organoruthenium compounds is high and "counterintuitively" favored by protic solvents. This broadens the field in which anion−cation interactions may be relevant for the structure and reactivity of organometallics. Indeed, the compounds investigated are active catalysts for the transfer hydrogenation of ketones in 2-propanol[15] where we found the significant presence of ion pairs even at concentrations comparable with those used in catalysis.

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Supporting Information Available: Details of complex synthesis and characteriation, ONIOM calculations, X-ray data, PGSE and NOE NMR measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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