Self-Diffusion Coefficients of Transition-Metal Complex Ions, Ion Pairs, and Higher Aggregates by Pulsed Field Gradient Spin−Echo NMR Measurements

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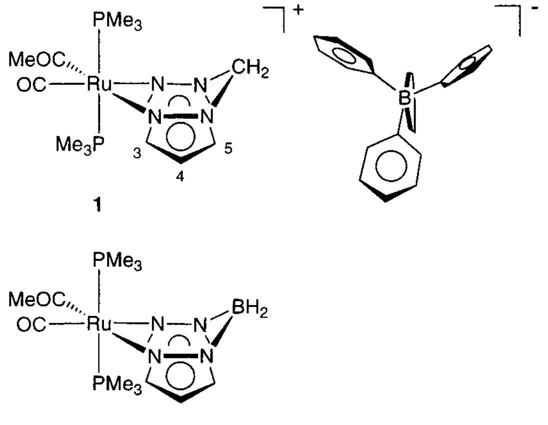
Summary: The molecular self-diffusion coefficients of the complexes trans-[Ru(PMe$_3$)$_2$(CO)(COMe)(pz$_2$-CH$_2$)]BPh$_4$ and trans-[Ru(PMe$_3$)$_2$(CO)(COMe)(pz$_2$-BH$_2$)] have been measured by pulsed field gradient spin−echo NMR measurements in nitromethane, chloroform, and methylene chloride as a function of concentration. By using the neutral complex as reference with the assumption that it does not undergo associative processes, clear indications of the presence of ions (in nitromethane), ion pairs (in chloroform at low concentration), and ion quadruples (in chloroform at high concentration) have been obtained.

We are currently involved in the investigation of the solution structure of charged organometallic complexes.[1] One of the main goals of our research is to determine the relative anion−cation positions (interionic structure), especially for compounds that are active homogeneous catalysts and where the catalytic activity is affected by the nature of the counterion.[2] The approach used to determine the interionic structure in solution of organometallic complexes is based on Overhauser NMR spectroscopy.[3]

Another valuable methodology for investigating the aggregation of molecular species in solution is based on the determination of molecular self-diffusion coefficients by pulsed field gradient spin−echo (PGSE) measurements.[4] While this methodology is longstanding,[5] its application to organometallic ion pairs has been very limited. To our knowledge there have only been a few papers dealing with charged compounds[6] in general, and even less with organometallic compounds.[7]

The information gained from the PGSE measurements can be complementary to that derived from the Overhauser NMR investigations. The latter gives a detailed picture of the reciprocal anion−cation position inside the ion pair. The PGSE measurements can be used to determine whether ions, ion pairs, or higher aggregates are mainly present in solution.

Chart 1



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We decided to perform PGSE measurements on the cationic complex *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(pz$_2$-CH$_2$)]-BPh$_4$ (**1**, where pz = pyrazolyl ring; Chart 1) because (a) its interionic structure in solution was previously investigated[8] and (b) the neutral analogue *trans*-[Ru-(PMe$_3$)$_2$(CO)(COMe)(pz$_2$-BH$_2$)] (**2**) has been synthesized[9] and can be used as an internal reference, assuming that it does not undergo associative processes in solution. The PGSE NMR measurements[10] were performed by using the standard stimulated echo pulse sequence[4] shown in Figure 1 in three different solvents (nitromethane, chloroform, and methylene chloride) at room temperature with various concentrations of complexes **1** and **2**.

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[10] All the measurements were performed 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 5 ms, and their strength (G) was varied during the experiments (at least 15 times for each experiment). All the spectra were acquired using 32K points, 32−128 scans depending on the concentration, a spectral width of 4800 Hz, and a total recycle time of 15 s and processed with a line broadening of 1 Hz. The semilogarithmic plots of $\ln(I/I_0)$ vs G^2 were fitted using a standard linear regression algorithm with an R factor always better than 0.99.

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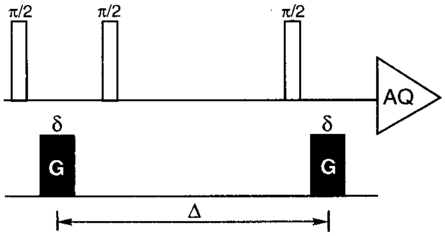

Figure 1. Stimulated echo pulse sequence[4] used for the PGSE NMR experiments.

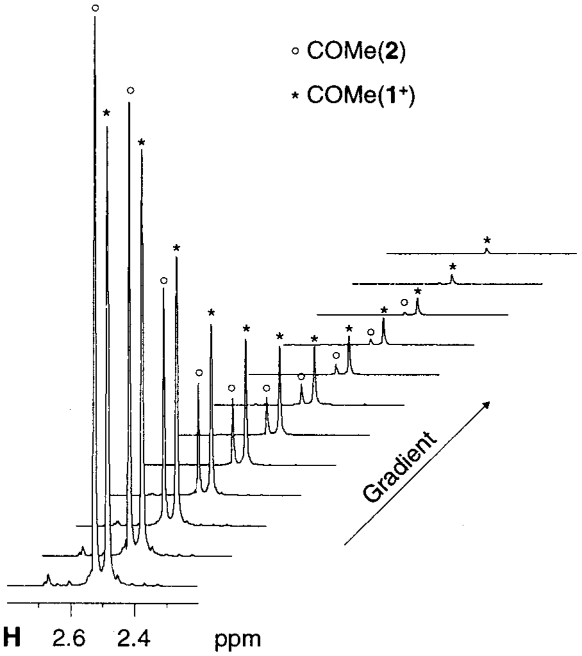

Figure 2. Section of the ^{1}H NMR spectrum recorded at 400.13 MHz in chloroform-*d* (solution saturated in **1**) of a mixture of complexes **1** and **2** showing the effect of the gradient strength on the COMe resonances. It clearly shows that the intensity of the resonance due to the neutral complex **2** (which has a higher self-diffusion coefficient) diminishes more quickly by increasing the gradient strength.

An example of an ^{1}H NMR spectrum section as a function of the gradient strength is reported in Figure 2. The dependence of the resonance intensity (I) on a constant waiting time and on a varied gradient strength (G) is described by the equation

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

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

The diffusion coefficient D is directly proportional to the slope of the regression line ($-m$) divided by $\Delta - \delta/3$; it was estimated using the known diffusion coefficient of HDO in D_2O.[7b] The data for the PGSE measurements are reported in Table 1. All the samples were prepared by dissolving equimolecular quantities of complexes **1** and **2**. For each solvent, different measurements were performed by changing the Δ values in order to establish the validity of the diffusion values.[7b] From the ratio between the diffusion coefficients of **2** and the cation ($\mathbf{1}^+$) or anion ($\mathbf{1}^-$) moieties of **1**, it is immediately clear that the diffusion coefficients strongly depend on the choice of the solvent and concentration.

Table 1. Data of the PGSE Measurements

solvent (concn, M)	species	Δ (ms)	$-m/(\Delta - \delta/3)$	$10^{10}D^a$ (m²/s)	D_2/D_1	N
CD_3NO_2 (4×10^{-3} M)	$\mathbf{1}^+$	30	0.403	8.01	1.11	1.4
		90	0.398	7.91	1.12	1.4
	$\mathbf{1}^-$	30	0.415	8.25	1.08	1.3
		90	0.413	8.21	1.08	1.3
	2	30	0.439	8.74		
		90	0.438	8.72		
$CDCl_3$ (8.4×10^{-2} M)	$\mathbf{1}^+$	30	0.253	5.03	1.60	4.1
		90	0.259	5.15	1.58	3.9
	$\mathbf{1}^-$	30	0.254	5.05	1.59	4.0
		90	0.260	5.17	1.57	3.9
	2	30	0.404	8.03		
		90	0.409	8.13		
$CDCl_3$ (4.0×10^{-2} M)	$\mathbf{1}^+$	30	0.319	6.32	1.48	3.2
		90	0.309	6.14	1.50	3.4
	$\mathbf{1}^-$	30	0.318	6.32	1.49	3.3
		90	0.309	6.14	1.50	3.4
	2	30	0.473	9.40		
		90	0.463	9.20		
$CDCl_3$ (7.2×10^{-3} M)	$\mathbf{1}^+$	30	0.332	6.59	1.44	3.0
	$\mathbf{1}^-$	30	0.335	6.65	1.43	2.9
	2	30	0.479	9.51		
$CDCl_3$ (3.6×10^{-3} M)	$\mathbf{1}^+$	90	0.361	7.17	1.35	2.5
	$\mathbf{1}^-$	90	0.362	7.19	1.35	2.5
	2	90	0.488	9.69		
$CDCl_3$ (4.7×10^{-4} M)	$\mathbf{1}^+$	30	0.391	7.77	1.27	2.1
	2	30	0.495	9.80		
CD_2Cl_2 (2×10^{-1} M)	$\mathbf{1}^+$	30	0.332	6.60	1.46	3.1
		90	0.329	6.54	1.47	3.2
		120	0.332	6.60	1.46	3.1
	$\mathbf{1}^-$	30	0.341	6.78	1.43	2.9
		90	0.341	6.78	1.42	2.9
		120	0.342	6.80	1.41	2.8
	2	30	0.486	9.66		
		90	0.484	9.62		

[a] D values were estimated by measuring the $-m/(\Delta - \delta/3)$ parameter for a sample of HDO (5%) in D_2O (known diffusion coefficient: 1.902×10^{-9} m²/s)[11] under the same conditions as those for complexes **1** and **2**. They were determined for individual NMR signals of complexes **1** and **2**. The mean deviations for the average values reported here are less than 5%.

In nitromethane the D_2/D_1 ratios are equal to 1.11 and 1.08 for $\mathbf{1}^+$ and $\mathbf{1}^-$, respectively. Section a of Figure 3 clearly shows that the slopes of the three straight lines relative to $\mathbf{1}^+$, $\mathbf{1}^-$, and **2** are very similar. The fact that $\mathbf{1}^-$ is almost the same size as **2** indicates that most of complex **1** is present in solution as dissociated ions. The D values for **2** are ca. 10% lower that those of $\mathbf{1}^+$ and $\mathbf{1}^-$ due to the contribute to the diffusion of the solvent molecules that charged species can drag during the translational motion.[6a]

In chloroform the D_2/D_1 ratio of $\mathbf{1}^+$ and $\mathbf{1}^-$ is the same, within experimental error, independent of the concentration and substantially higher than **1** (see section b of Figure 3). This ensures that (a) both $\mathbf{1}^+$ and $\mathbf{1}^-$ fragments belong to the same aggregate and (b) aggregates are present in solution. Furthermore, the D_2/D_1 values range from 1.265 for a concentration of 4.7×10^{-4} M to 1.597 for a saturated solution in **1** (8.4×10^{-2} M) containing an equimolar quantity of **2**. According to the Stokes–Einstein equation,[12] the diffusion coefficients are proportional to $1/r$ (where r represents the hydrodynamic radius of the diffusing particle, which is

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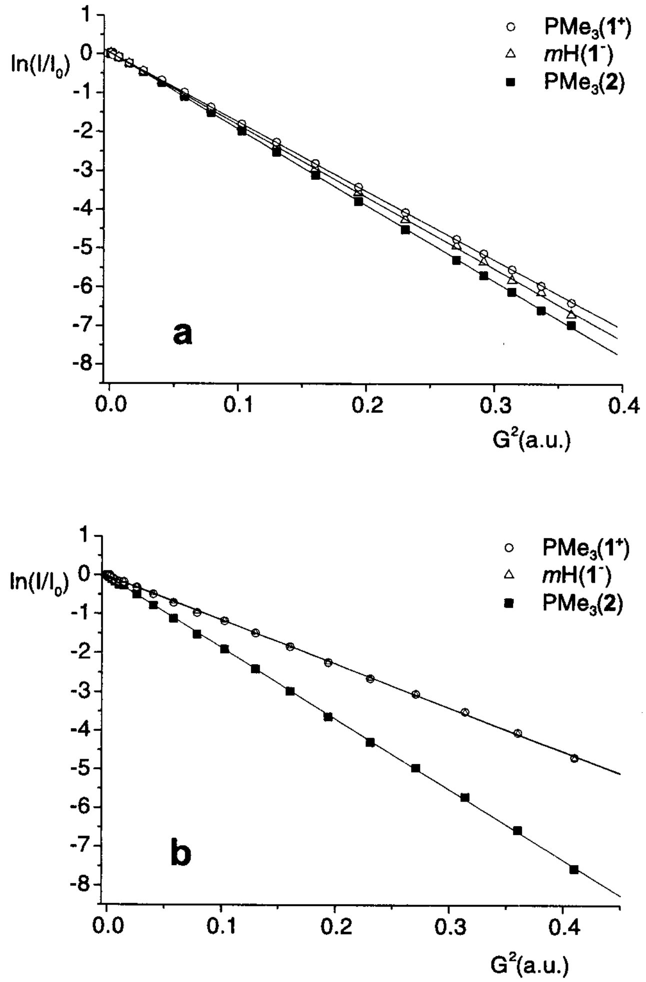

Figure 3. (a) Plot of $\ln(I/I_0)$ versus G^2 (a.u. = arbitrary unit) for the PMe_3 resonances of $\mathbf{1}^+$ and **2** and for the *m*-H resonance of $\mathbf{1}^-$ relative to ^1H NMR spectra recorded in nitromethane (4×10^{-3} M). The slopes of the three straight lines are roughly the same, indicating that free ions are present in solution. (b) The same plot in chloroform solution saturated in **1**. In this case the straight lines relative to $\mathbf{1}^+$ and $\mathbf{1}^-$ have exactly the same slope, which is substantially lower than that of the straight line relative to **2**.

assumed to be spherical and larger than the solvent). If we consider valid the approximation that the diffusing particles are spherical, the ratio between the volumes of the neutral and cationic or anionic species amounts to

$$\frac{V_1}{V_2} = \left(\frac{D_2}{D_1}\right)^3 = N = \text{aggregation number}$$

For the most dilute solution ($D_2/D_1 = 1.265$), $V_1/V_2 = 2.05$. Considering that $\mathbf{1}^+$ and $\mathbf{1}^-$ have roughly the same volume, this strongly indicates that intimate ion pairs are mainly present in the solution. Simple calculations show that the ratio of the $\mathbf{1}^+$ and $\mathbf{1}^-$ volumes is equal to 1.15. The volume of the ion pair should be 1.87 times that of $\mathbf{1}^+$ or **2**. The difference in the experimental value (2.05) can be attributed to the presence of a small percentage of higher aggregates and/or to the solvent. In any case, the difference is only ca. 10% in volume, which means a ca. 3% difference in the diffusion coefficients. In the most concentrated solution the D_2/D_1 value (average) is 1.585 and $V_1/V_2 = 3.98$. While it is difficult to believe that in such a solution only ion quadruples are present or are the most predominant species, the theoretical ratio of V_1/V_2 for ion quadruples is 3.74. Again the difference between the experimental and theoretical values is 7% in volume and 2−3% in the diffusion coefficients. For this most highly concentrated solution, an ^1H NOESY spectrum was recorded in order to obtain some information about the interionic structure of the aggregates. The observed interionic contacts are the same as those for the more dilute solutions: the *o*-H and *m*-H protons belonging to the counterion interact with the CH_2, 5, and PMe_3 protons of the cation. This information suggests that it is less probable to have aggregates where one cation stays between two counterions (head to tail) rather than side by side (otherwise the contact of the anion protons with the COMe ones should be observed). This is in agreement with the interaction energy gain of two dipoles.[13]

Methylene chloride is not a good solvent for the PGSE measurements because of its low viscosity. In spite of this, we decided to perform some measurements in methylene chloride because of its widespread use in general and for our specific studies of the interionic structure. The results were acceptable, especially for concentrated solutions (Table 1). Again, the D_2/D_1 values obtained for 2×10^{-1} M solution gave an aggregation number of ca. 3. At this concentration, there are not only ion pairs but also higher aggregates.

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(12) $D = (kT)/(6\pi\mu r_H)$, where μ and r_H are the solution viscosity and the hydrodynamic radius of the diffusing particles, respectively.

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