PGSE Diffusion Studies on Chelating Phosphine Complexes of Ruthenium(II). Solvent Dependence and Ion Pairing

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Received March 3, 2003

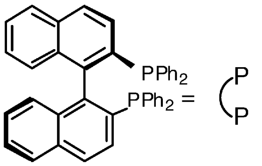
PGSE ^1H and ^{19}F diffusion data, *D* values, and $^1H,^{19}F$ HOESY NMR spectra for a series of [RuCl(*p*-cymene)(BINAP)]X salts, **2a**−**f**, have been recorded in CD_2Cl_2 (X = BF_4^- (**2a**), $CF_3SO_3^-$ (**2b**), $BArF^-$ (**2c**), PF_6^- (**2d**), SbF_6^- (**2e**), Cl^- (**2f**)). The solvent dependence of the *D* values for **2a**−**c** in methanol, chloroform, dichloromethane, and acetone and the resulting ion-pairing effects are discussed. On the basis of HOESY data, it is suggested that small anions in chloroform solution approach the ruthenium atom from the side of the molecule remote from the chloride and slightly below the complexed arene. PGSE diffusion data for the Ru−aqua complexes $[Ru(H_2O)_3(CO)(dppe)]X_2$ (X = BF_4^- (**3a**), $CF_3SO_3^-$ (**3b**), SbF_6^- (**3c**), $N(O_2SCF_3)_2^-$ (**3d**)) are reported. The observed *D* values for **3a**−**d** partially reflect hydrogen bonding from complexed water to the anions.

Introduction

Transition-metal salts and especially cationic complexes are finding increasing applications as reagents in organic synthesis.[1] Slowly but surely, the preparative community, and especially those using soluble salts as catalysts, have centered on a few, presumably “innocent”, anions to accompany the reactive cations, e.g., BF_4^-, PF_6^-, SbF_6^-, $CF_3SO_3^-$, and, increasingly, $BArF^-$ (tetrakis(3,5-bis(trifluoromethyl)phenyl)borate). Occasionally, there are indications that these anions are not “innocent”; i.e., they may coordinate or react.[2] Further, the nature of the cation/anion interaction is often poorly understood.

Recently, we have begun a program on pulsed gradient spin−echo (PGSE) diffusion studies.[3] Diffusion constants are useful, as they can provide an indication of molecular volume,[4−9] hydrogen bonding (i.e., increased volume via association), and how the individual charged species translate in solution. This latter point stems, partially, from the ability to use a multinuclear NMR diffusion approach, e.g.,^1H (and sometimes ^{31}P[10a]) for the cation and ^{19}F for the anion, combined with $^1H,^{19}F$ HOESY data,[11] to follow how the anions and cations interact. Nevertheless, applications of the PGSE method remain sparse[12] and there have been few systematic studies for metal complexes in different solvents.[10]

BINAP (**1**) complexes of Ru(II) have generated considerable interest.[13−18] With a view to further sharpening our NMR analytical capabilities, we have undertaken a PGSE study for the simple model complexes [RuCl(*p*-cymene)(**1**)]X (**2a**−**f**; X = BF_4^-, $CF_3SO_3^-$, $BArF^-$,



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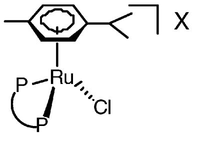

2a-f

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10.1021/om030145p CCC: $25.00
Publication on Web 06/12/2003

PF_6^-, SbF_6^-, Cl^-) in several different solvents. The complexed chloride is important, in that it reduces the possibility of a bonding interaction between the anion and the Ru(II) cation. In this report, we interpret our new diffusion results for these BINAP compounds in terms of ion-pairing effects and then extend these studies to some bidentate phosphine aqua complexes of ruthenium.

Results and Discussion

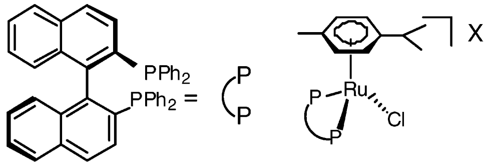
Diffusion Data for 2. PGSE diffusion results from the ^1H and ^{19}F PGSE measurements on the salts [RuCl(*p*-cymene)(**1**)]X (**2a**−**f**), in several solvents, are given in Table 1. In methanol, the most strongly solvating and most polar of the three solvents, the observed diffusion values, *D*, for the cation with several anions are all found to be ca. 6.0×10^{-10} m^2 s^{-1}, indicating independent movement of the cation in this solvent. The hydrodynamic radii, *r*, can be estimated from the Stokes−Einstein relation (eq 1), where *k* is the Boltzmann constant and η is the viscosity.

$$r_H = \frac{kT}{6\pi\eta D} \quad (1)$$

$$D = \text{diffusion constant; } \eta = \text{viscosity}$$

The calculated *r* values assume spherical shapes (clearly a crude approximation) and do not consider that the solvent, e.g., methanol, may hydrogen bond (especially to the anion). Nevertheless, the calculated *r* value permits a direct comparison between diffusion measurements in different solvents, as it corrects for the different viscosities. Since the hydrodynamic radius of the Ru−BINAP cation is found in all three cases to be constant at ca. 7.0 Å,we suggest that, for **2a**−**c** in methanol solution, the cation and anion are well separated.

Table 1. Diffusion Constants[a,b] and Radii[c] and for 2a−f in Several Solvents



	CD$_3$OD			CDCl$_3$	
	D	*r* (Å)		*D*	*r* (Å)
		2a (X = BF$_4$)			
cation	5.98	7.0	cation	5.89	7.0
anion	15.73	2.6	anion	5.99	6.9
		2b (X = CF$_3$SO$_3$)			
cation	5.96	7.0	cation	5.93	7.0
anion	12.28	3.4	anion	6.05	6.9
		2c (X = BArF)			
cation	5.98	7.0	cation	4.78	8.6
anion	6.42	6.5	anion	4.88	8.5
		NaBArF			
salt	6.53	6.3			

	CD$_2$Cl$_2$			(CD$_3$)$_2$CO	
	D	*r* (Å)		*D*	*r* (Å)
		2a (X = BF$_4$)			
cation	7.89	6.8	cation	10.07	7.2
anion	10.95	4.9	anion	26.85	2.7
		2b (X = CF$_3$SO$_3$)			
cation	7.73	6.9	cation	9.95	7.3
anion	10.46	5.1	anion	23.39	3.1
		2c (X = BArF)			
cation	7.71	6.9	cation	9.91	7.3
anion	8.05	6.6	anion	10.83	6.7
		2d (X = PF$_6$)			
cation	7.87	6.8			
anion	10.99	4.9			
		2e (X = SbF$_6$)			
cation	7.81	6.8			
		2f (X = Cl)			
cation	7.83	6.8			

[a] All measurements are for 2 mM solutions. Anions were measured using ^{19}F and cations via ^1H. [b] *D* values are in units of 10^{-10} m^2 s^{-1}. [c] The values for the radii are given to only one significant figure after the period. Consequently, different *D* values can lead to the same *r* value. The viscosities used in the calculations (300 K) are those of the pure solvents: CH$_2$Cl$_2$, 0.405; CHCl$_3$, 0.529 (0.542); CH$_3$OH, 0.526 (0.547); (CH$_3$)$_2$CO, 0.303; H$_2$O, 1.002.

Using ^{19}F PGSE methods for the anions (except for the SbF_6^- case **2e**, whose ^{19}F spectrum is not readily obtained), we find that the volumes increase (as expected) in the order $BF_4^- < CF_3SO_3^- <$ BArF$^-$ (see Figure 1). However, these anions are likely to be solvated, and, for quite small anions such as BF_4^-, the number “6” in the denominator of eq 1 may may be too large.[19] Specifically, the crystallographically determined value for the BF_4^- bond length is ca. 1.35 Å,[20] so that the calculated *r* value of 2.6 Å clearly reflects some degree of solvation. Interestingly, in methanol, the *r* value for the anion in Na(BArF) is only slightly smaller than that found for the BArF anion in the ruthenium salt (see Table 1). As expected, the *r* values for the

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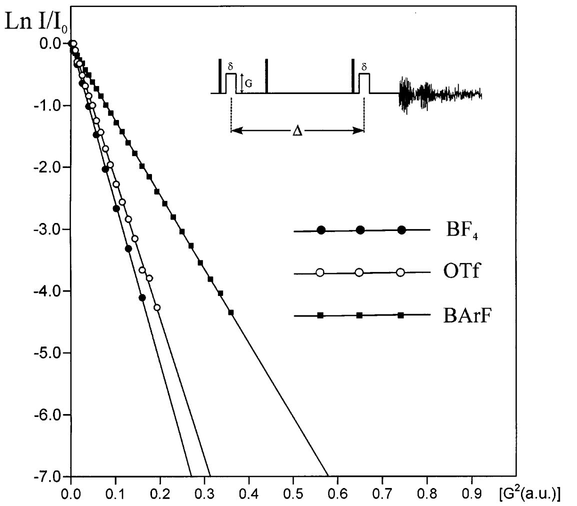

Figure 1. PGSE diffusion data for the different anions of **2a**−**c** in acetone-d_6. As expected, the volumes increase in the order $BF_4^- < CF_3SO_3^- <$ BArF$^-$. The pulse sequence for the PGSE NMR is shown in the inset.

BINAP-based cations are found to be larger than those for the BF_4^-, PF_6^-, and $CF_3SO_3^-$ anions.

Several PGSE measurements were made in acetone-d_6. These diffusion data, for the BF_4^- and $CF_3SO_3^-$ anions, suggest that this solvent successfully separates these anions from their respective cations; however, as there is some water in the acetone, this reagent may well play a role. We will refer to these acetone data in connection with the ruthenium aqua complexes to be discussed below.

In chloroform solution, we observe almost identical *D* and *r* values for both the cation and anion, thus indicating that fairly tight ion pairs make a major contribution in this solvent. This conclusion is based primarily on the apparent increase in radius: e.g., $r =$ 6.9 Å for the BF_4^- anion. For the BArF analogue in this solvent, the calculated radii for the cation and anion are (a) much larger than in, for example, methanol and (b) almost identical, since the two moieties are moving together. We have observed this type of diffusion behavior in chloroform previously, in Pd(II) and Ir(I) complex salts.[10,21] Unexpectedly, for the cation with BF_4^- and $CF_3SO_3^-$ as anions, there seems to be no change in effective volume. We will return to this point following the dichloromethane discussion.

The most comprehensive data set stems from the measurements in CD_2Cl_2. For all six anions the radius of the cation is approximately constant and falls in the range 6.8−7.0 Å. However, the radii for the anions change significantly relative to the methanol measurements. For the BF_4^- anion the calculated radius is now 4.9 Å instead of 2.6 Å, and for the $CF_3SO_3^-$ anion the value is 5.1 Å instead of 3.4 Å. For the BArF$^-$ salt, the value is 6.6 Å instead of 6.5 Å. From previous measurements in methanol we find an *r* value of 2.6 Å for the PF_6^- anion, so that the change to 4.9 Å is similar to that observed for the BF_4^- anion.

We believe that these increased *r* values for the anions in dichloromethane solution arise due to partial ion-pairing effects; i.e., equilibrium is established between solvent-separated and intimate ion pairs. In terms of percentage change, the small BF_4^- and PF_6^- anions will be most effected since, when ion-paired, their *D* values will sink drastically and thus their averaged *r* values will increase accordingly. The relatively large BArF$^-$ anion will be least effected. On average, a small amount of ion pairing will not significantly change the effective volume of the relatively large Ru cation, and therefore, these values do not reflect the ion pairing. It is interesting that there is some ion pairing in CD_2Cl_2, a solvent often used in organometallic reactions.

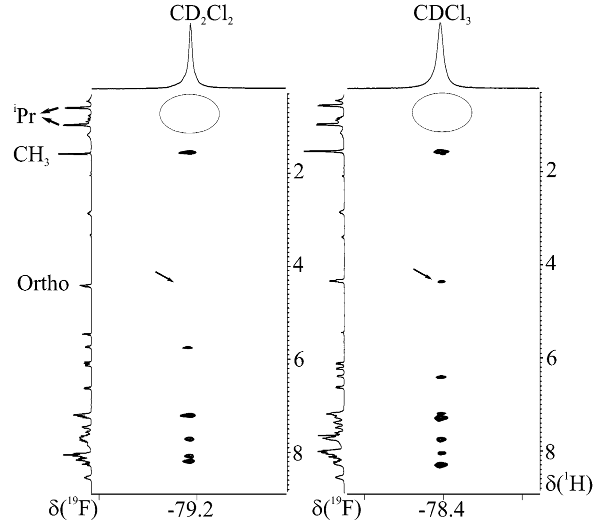

Figure 2. $^1H,^{19}F$ HOESY spectra of **2b** ($X = CF_3SO_3^-$) in chloroform-*d* and dichloromethane-d_2. The oval emphasizes that there are no contacts to the isopropyl group of the *p*-cymene. However, the anion is closer to the methyl group of the *p*-cymene in both solvents. The arrows indicate the absence and presence of a weak contact to the protons ortho to the *p*-cymene methyl group. There are *five selective* contacts to the aromatic protons of the BINAP in $CDCl_3$, but only four in CD_2Cl_2 solvent.

Having established ion pairing in several solvents, we considered that the smaller anions, e.g., triflate, might take up a specific position[22] in chloroform and thus not significantly increase the effective volume of the cation. To test this idea, we have measured $^1H,^1H$ NOESY and $^1H,^{19}F$ HOESY spectra for the BF_4^- and $CF_3SO_3^-$ salts. The NOESY results help to assign the ^1H NMR spectra of the complexed η^6-arene[23] and thus determine that the *p*-cymene methyl group faces toward the BINAP and the isopropyl group toward the chloride.

The $^1H,^{19}F$ HOESY spectra, in both chloroform and dichloromethane (see Figure 2), were similar and show *no* ^{19}F contacts to the *p*-cymene isopropyl group, a modest contact to the *p*-cymene methyl group, a weak contact to the protons ortho to the *p*-cymene methyl group and *four to five selective strong* contacts to the aromatic protons of the BINAP. For the triflate case there were fewer contacts in methylene chloride, consistent with weaker ion pairing. Consequently, in both solvents, and for both BF_4^- and $CF_3SO_3^-$, the anions approach the ruthenium atom from the side of the

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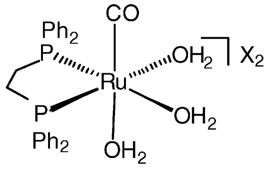
[23] The η^6-arene protons are readily assigned via NOEs, e.g., from the alkyl side chains, together with vicinal $^3J(H,H)$) COSY interactions.

Table 2. Diffusion Constants[a,b] and Radii[c] for 3a−d in Several Solvents

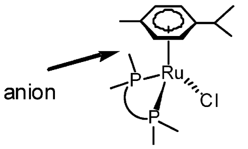


3a-d

	X	solvent		D	r (Å)
3a	BF_4^-	acetone	cation	9.36	7.7
			anion	19.88	3.6
		D_2O	cation	3.44	6.2
			anion	15.29	1.4
3b	$CF_3SO_3^-$	acetone	cation	9.24	7.8
			anion	15.58	4.6
		D_2O	cation	3.47	6.1
			anion	9.25	2.3
3c	SbF_6^-	acetone	cation	9.95	7.3
		D_2O	cation	3.30	6.5
		CD_2Cl_2	cation	6.76	7.9
3d	$N(O_2SCF_3)_2^-$	acetone	cation	9.31	7.7
			anion	17.59	4.1
		D_2O	cation	3.43	6.2
			anion	6.74	3.2
4		acetone	cation	9.31	7.7
			anion	17.70	4.1

[a] All measurements are for 2 mM solutions. Anions were measured using ^{19}F and cations via ^1H. [b] D values are in units of 10^{-10} m^2 s^{-1}. [c] The values for the radii are given to only one number after the period. The viscosities used in the calculations (300 K) are as follows: CH_2Cl_2, 0.405; $(CH_3)_2CO$, 0.303. Legend: **4**, $[Ru(H_2O)(pyridine)_2(CO)(dppe)](CF_3SO_3)_2H_2O$, 1.002.

molecule remote from the chloride and slightly below the complexed arene: i.e., electronic rather than steric control (see fragment A).



fragment A

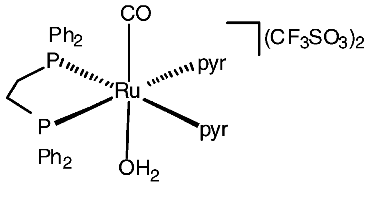
Given the strong ion pairing in chloroform, and the individual HOESY contacts, it seems reasonable to suggest that these small anions are resting in a position between the arene and the BINAP ligand, which does not result in any marked increase in the overall volume of the salt.

Diffusion Data for 3a−d. Table 2 shows PGSE diffusion data for the Ru−aqua complexes $[Ru(H_2O)_3(CO)(dppe)]X_2$ (X = BF_4^- (**3a**), $CF_3SO_3^-$ (**3b**), SbF_6^- (**3c**), $N(O_2SCF_3)_2^-$ (**3d**)) in water, acetone, and in one case, for the SbF_6^- anion, dichloromethane solutions.[24]

These dicationic dppe complexes are only modestly stable in acetone and CD_2Cl_2 solutions, and then only in the presence of excess water (see Experimental Section). The dichloromethane data for the SbF_6^- anion (**3c**) allow a comparison with [RuCl(*p*-cymene)(**1**)]SbF_6 (**2e**). Interestingly, our diffusion data suggest that this dppe complex is larger than complex **2e**; i.e., *r* = 7.9 Å, as opposed to *r* = 6.8 Å. This seems strange; however, two points require further consideration: (i) the naphthyl groups of the BINAP complex may be tucked inside the shell created by the four P-phenyl groups and (ii) the complexed water ligands in **3c** may hydrogen bond to anions and/or solvent.

Comparing the *D* and *r* values for **3a−d** in both water and acetone solutions suggests that the aqueous solutions afford well-separated ions; i.e., on the basis of the ^{19}F *D* and subsequent *r* values, the BF_4^-, CF_3 SO_3^-, and $N(O_2SCF_3)_2^-$ ions are all much smaller in water than in acetone solutions. Indeed, for these same three salts, the cations in water reveal reduced radii by ca. 1.5−1.6 Å. Since strong water solvation of the anions does not reduce their actual volume, the relatively large *r* values for the cations and anions in acetone are likely to result from hydrogen-bonding effects. The three complexed water molecules interact with the anions, thereby significantly increasing their relative averaged volumes, while simultaneously increasing the average size of the cations to a lesser extent. This hydrogen bonding is also reflected in several solid-state structures of these dications.[25]

The monoaquo dicationic complex $[Ru(H_2O)(CO)(pyridine)_2(dppe)](CF_3SO_3)_2$ (**4**)[25] was measured as a model for **3b**. The two complexed pyridine rings of **4** are expected to add to the observed cationic volume; however, on the basis of a comparison of their *D* and *r* values in acetone, this is not observed. Indeed, the two are almost identical in size. Moreover, the triflate anion in **4**, *r* = 4.1 Å, is slightly smaller than for **3b**, *r* = 4.6 Å. We believe that these observed differences arise due to the more efficient hydrogen bonding of the triflate anion to the triaqua cation of **3**, relative to that of the monoaqua complex **4**.



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Conclusions. The PGSE diffusion data, when combined with a suitable ^1H,^{19}F HOESY spectrum, offer a valuable structural aid. These NMR data allow a qualitative estimate of how and where the anions and cations interact in that the two can be monitored individually (assuming a suitable ^{19}F spin is present). For the complexes [RuCl(*p*-cymene)(**1**)]X (**2a−f**) the relatively strong ion pairing in chloroform leads to specific placement of the anion. The ion pairing in dichloromethane is much less pronounced. For the compounds $[Ru(H_2O)_3(CO)(dppe)]X_2$ the anion can strongly hydrogen bond to the complexed water molecules, thus creating a species with a much larger volume. Both the chloroform ion-pairing and hydrogen-bonding conclusions stem from anion (^{19}F) NMR diffusion data which indicate a volume for the anion that is almost identical with that found for the much larger cation.

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(25) Goicoechea, J. M.; Hargreaves, M. D.; Mahon, M. F.; Whittlesey, M. K. Unpublished results.

Experimental Section

All the measurements were performed on Bruker AVANCE spectrometers (300 and 400 MHz) equipped with a microprocessor-controlled gradient unit and a multinuclear probe (normal or inverse) with an actively shielded Z-gradient coil. The shape of the gradient pulse was rectangular, and its length (1.75 ms) and its strength were varied automatically in the course of the experiment. The time between midpoints of the gradients (Δ) was chosen as 167.75 ms. The measurements were carried out without sample spinning and in the absence of external airflow.

The slopes of the lines, *m*, were obtained by plotting their decrease in signal intensity vs G^2 (see eq 2). The diffusion

$$\ln\left(\frac{I}{I_o}\right) = -(\gamma\delta)^2\left(\Delta - \frac{\delta}{3}\right)DG^2 \qquad (2)$$

coefficients reported were estimated using the diffusion coefficient of HDO in D_2O as a reference. The data obtained were used to calculate the *D* values of the samples, according to eq 3.

$$D = \frac{m_{\mathrm{obsd}}D_{\mathrm{HDO}}}{m_{\mathrm{HDO}}} \qquad (3)$$

All the reported *D* values are derived from lines which have correlation coefficients above 0.99. The recovery delay for ^{1}H diffusion measurements was kept constant (D1 = 5 s). For the ^{19}F measurements, the T1 values (~1−5 s, for complexes **2a**−**f** and **3a**−**d** in different solvents) were calculated using Bruker Xwin-NMR software and the delay, D1, was set to 5(T1) accordingly. The number of scans was 16 for ^{1}H and between 4 and 16 for ^{19}F experiments. The sample was dissolved in 0.6 mL of the deuterated solvent, with the concentration maintained at 2 mM unless otherwise stated. The solutions for complexes of **3** were stabilized by adding 10 μL of distilled water.

The ^{1}H,^{19}F HOESY measurements were carried on a 400 MHz Bruker Avance spectrometer equipped with a doubly tuned (^{1}H, ^{19}F) TXI probe. A mixing time of 600 ms was used. The T1 values for ^{19}F (4 s for **2b** in chloroform and 2.2 s in dichloromethane) were calculated using Bruker Xwin-NMR software, and D1 was set to 5(T1) accordingly. The concentration of the sample was 10 mM; the number of scans was 64 and the number of increments in the F1 dimension 512.

Acknowledgment. Special thanks are due Dr. H. Rüegger for both experimental assistance and timely advice. P.S.P. thanks the Swiss National Science Foundation and the ETH Zürich for financial support and Johnson Matthey for the loan of precious metal salts. M.K.W. thanks the EPSRC and the University of Bath for financial support.

OM030145P