

PGSE NMR Diffusion Overhauser Studies on $[\text{Ru}(\text{Cp}^*)(\eta^6\text{-arene})][\text{PF}_6]$, Plus a Variety of Transition-Metal, Inorganic, and Organic Salts: An Overview of Ion Pairing in Dichloromethane

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Abstract: PGSE diffusion, ^{19}F , ^1H HOESY and ^{13}C NMR studies for a series of $[\text{Ru}(\text{Cp}^*)(\eta^6\text{-arene})][\text{PF}_6]$ (**1**) salts are presented. The solid-state structure of $[\text{Ru}(\text{Cp}^*)(\eta^6\text{-fluorobenzene})][\text{PF}_6]$ (**1c**) is reported. The extent of the ion pairing and the relative positions of the ions are shown to depend on the arene. For the solvent dichloromethane, new and literature PGSE data for PF_6^- salts of transition-

metal, inorganic, and organic salts are compared. Taken together, these new results show that the charge distribution and the ability of the anion to approach the positively charged positions (steric effects due to molecular shape)

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are the determining factors in deciding the amount of ion pairing. DFT calculations of the charges in four salts of type **1**, as well as in a variety of other salts, using a natural population analysis (NPA), support this view. This represents the first attempt, using experimental data, to understand, correlate, and partially explain the various degrees of ion pairing in a widely different collection of salts.

Introduction

Transition-metal salts are synthesized or generated in an increasing variety of reactions. Frequently, the nature of the anion is ignored or the anion is considered to be relatively

“innocent”. However, a number of reports in the recent literature suggest that the choice of the anion can be important, both in terms of the structure of the salt and its reactivity.^[1–13] Relevant examples include an anion dependence in 1) Diels–Alder catalysis,^[1] 2) polymerization chemistry,^[2] 3) catalytic hydrogenation,^[3] 4) asymmetric ring opening reactions of oxabicyclic alkenes,^[4] 5) asymmetric cyclopropanation,^[5] and 6) C,H-activation reactions,^[6] amongst others. The anions may or may not coordinate to the metal center.^[7] Normally, one does not find an explanation for the effect of the anion; however, occasionally, ion pairing is mentioned as a possible contributor.^[11,17]

It is not always evident how one should measure and recognize this ion pairing; however, recent NMR studies, which combine both pulsed gradient spin-echo (PGSE) diffusion and Overhauser NMR spectroscopy,^[14,15] have begun to shed light on how selected anions interact with their respective cations in solution. Usually, the literature studies involving NMR diffusion measurements emphasize the use of this methodology in connection with recognizing changes in molecular volumes.^[16–30] Nevertheless, one finds an increasing number of reports involving NMR data and ion pairing.^[15,17,31–33] Assuming that the two ions can be measured separately, inspection of the magnitudes of the NMR diffusion constants provides a direct estimate of the extent of the

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Supporting information for this article is available on the WWW under <http://www.chemeurj.org> or from the author. It contains .cif files for the structure of **1c**, plus Tables S1 and S2, with the NPA charge distributions and optimized coordinates. In addition Figures S1 and S2 show optimized geometries of the ion pairs and a representation of the molecular electrostatic potential for the cations.

ion pairing. For 100% ion pairing (and in the absence of, e.g., hydrogen-bonding, or encapsulation effects), the diffusion constants (D values) for the anion and cation will be identical within the experimental error.^[14,15] Despite the recent progress, the relevant reports focus primarily on one related set of salts and thus are rather specific. We know of no study attempting to understand and correlate ion pairing in very different materials.

In the first section of this contribution we present NMR, X-ray and DFT studies for a series of $[\text{Ru}(\text{Cp}^*)(\eta^6\text{-arene})][\text{PF}_6]$ salts. After briefly describing the ion pairing and structures of these salts we move to the second, more significant part in which we extend the discussion, using analogous data from PF_6^- salts of various transition-metals, inorganic, and organic salts, to form a more general picture of this phenomenon. This represents the first attempt to understand, correlate, and partially explain the differing degrees of ion pairing in a very varied collection of salts by using experimental NMR data.

Results and Discussion

$[\text{Ru}(\text{Cp}^*)(\eta^6\text{-arene})][\text{PF}_6]$ salts (1): The ruthenium salts were prepared by addition of a suitable excess of the arene to a solution of $[\text{Ru}(\text{Cp}^*)(\text{CH}_3\text{CN})_3][\text{PF}_6]$ in accordance with the literature.^[34–36] The solid-state structures of a number of Ru–arene complexes are known^[37] and this literature includes examples involving Cp^* .^[38] In some cases, the complexation of the arene to the $\{\text{Ru}(\text{Cp}^*)\}$ fragment is preferred even when other good donor atoms are present, for example, in the reaction of $[\text{Ru}(\text{Cp}^*)(\text{CH}_3\text{CN})_3][\text{PF}_6]$ with

$\text{P}(o\text{-tolyl})_3$ one of the $o\text{-tolyl}$ substituents coordinates to afford $[\text{Ru}(\text{Cp}^*)(\eta^6\text{-}o\text{-tolyl})\text{P}(o\text{-tolyl})_2][\text{PF}_6]$.^[39]

^{13}C NMR spectroscopy: In connection with understanding the positive charge distribution in our complexes we have measured and assigned the ^{13}C spectra of our salts and show these data in Table 1. Figure 1 shows how some of these assignments were made with the help of ^{13}C , ^1H correlations.

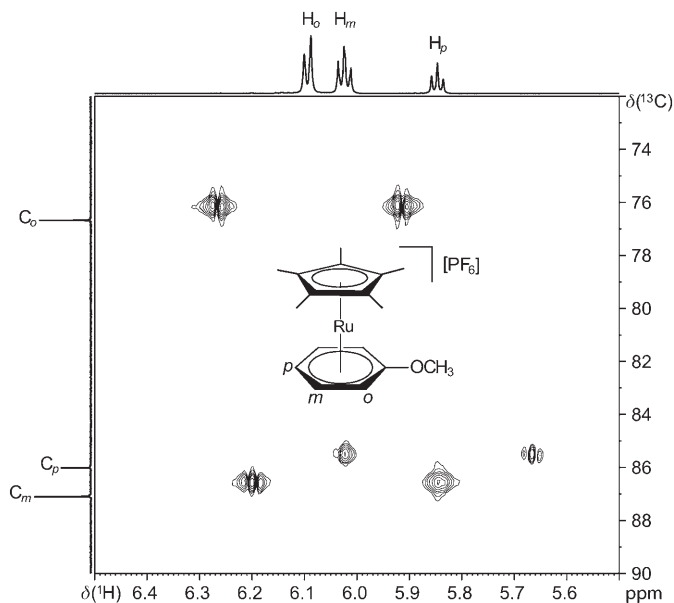
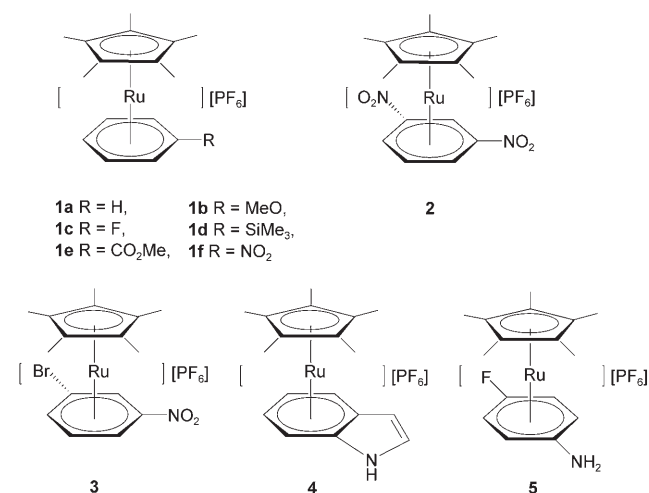


Figure 1. Section of the ^{13}C , ^1H correlation spectrum of **1b** in $[\text{D}_6]$ acetone showing the cross-peaks from the complexed arene due to $^1\text{J}(^{13}\text{C}, ^1\text{H})$. The proton assignment from left to right: *ortho*, *meta*, *para*.

Table 1. ^{13}C Chemical shifts of the complexed arenes in **1–5** in $[\text{D}_6]$ acetone.

Salt	C1	C2	C3	C4	C7	C8	C9	C10		
1a X = H	87.4				96.7	9.8				
1b X = OMe	97.6	90.4	88.6	88.6	97.3	11.1	57.2			
1c X = F	133.6	87.1	76.7	86.0	96.9	10.7				
1d X = SiMe ₃	135.6	79.0	87.1	87.2	98.2	10.0				
1e X = CO ₂ Me	89.5	87.3	88.2	89.0	98.0	9.3	164.8	53.0		
1f X = NO ₂	111.2	84.4	89.2	91.2	100.3	9.9				
	C1	C2	C3	C4	C5	C6	C7	C8		
2 X = NO ₂	110.9	79.1	110.9	86.5	88.6	86.5	102.6	8.7		
3 X = Br	110.7	87.2	91.0	94.6	89.4	84.8	101.4	9.4		
	C2	C3	C3'	C4	C5	C6	C7	C7'	C8	C9
4	135.4	100.3	96.7	79.3	83.5	83.6	73.8	109.0	92.9	9.7
	C1	C2	C3	C4	C7	C8				
5	130.6	76.7	71.5	121.4	96.6	10.4				

As expected,^[38] arene complexation results in much lower frequency ¹³C chemical shifts for all of the arene ligands. Specifically, the coordination chemical shifts, $\Delta\delta$, for the *para*-carbon atoms, fall in the range -35 to -44 ppm. Compared to the changes in the *para*-carbon atoms within the free arene compounds,^[40] the changes in the *para*-carbon atoms in **1a–1f**, ± 3 – 4 ppm, are modest. The difference in



the *para*-carbon ¹³C chemical shift between free nitrobenzene and anisole is about 13.8 ppm, whereas for salts **1b** and **1f**, this value is reduced to 2.6 ppm. For the F-substituted *ipso*-carbon (*para* to the amino group) in the *p*-F-aniline salt **5**, the change is about 3 ppm, relative to that for **1c**. The donor effect of an amino group on the *para* position should be much larger. This suggests that resonance effects due to the substituent R in salts **1** are not as pronounced as in the free organic arene compounds.

PGSE diffusion data: Diffusion constants for the cations and the PF₆⁻ ions were obtained by using PGSE methods as described earlier.^[14a,15] Table 2 shows a compilation of these results for 2 mM solutions of the salts in dichloromethane and acetone. In addition to the experimental *D* values, hydrodynamic radii (*r*_H) derived from the Stokes-Einstein equation [Eq. (1)] are given.

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

This equation is useful as it allows one to calculate a hydrodynamic radius from the viscosity (η) correction, and thus compare the diffusion results from different solvents. However, this relation has been criticized^[14] in that it is now recognized that the value “6” is not correct for small-to-medium sized molecules. An empirical correction has been suggested^[14a] and the values in the table arise from using both the value 6 and a semi-empirical correction. One can compare these radii with those obtained from X-ray data and we show such values in the footnotes to the tables.

In acetone, the measured *D* values for the cation and anion are very different. The *D* values and calculated radii for the anions are in good agreement with previous reports in which little (but not zero) ion pairing was suggested.^[14a,15a] The corrected *r*_H values of approximately 4.3–4.4 Å seem a little large for just the solvated anion; however, similar values for PF₆⁻ have been obtained in methanol and it is not a simple matter to estimate the size of the solvent shell. Although acetone efficiently separates the ions, there is still a range of *D* values: 24.93(6)–27.78(6) ($\times 10^{-10}$ m²s⁻¹). The *D* values for the cations range from 14.62(6) to 16.80(6) with the smallest values associated with the larger cations, and the largest with the smaller cations. The corrected *r*_H values fall in the range 5.2–5.7 Å and we will assume that these values represent a reasonable estimate of the hydrodynamic radius for the solvated cations in acetone.^[41]

In dichloromethane, the *D* values for the anions and cations are much closer. Indeed, for the dinitro and indole salts **2** and **4**, respectively, the values for these two are almost (but not quite) identical, suggesting, for **2**, close to complete

Table 2. *D* [10^{-10} m²s⁻¹] and *r*_H [Å] values^[a] for the salts in CD₂Cl₂ and [D₆]acetone.

Compound	Fragment	<i>D</i>	CD ₂ Cl ₂			[D ₆]acetone			
			<i>D</i> _c / <i>D</i> _a	<i>r</i> _H	<i>r</i> _H ^{corr}	<i>D</i>	<i>D</i> _c / <i>D</i> _a	<i>r</i> _H	<i>r</i> _H ^{corr}
1a	cation	12.50	0.94	4.2	5.1	16.43	0.64	4.4	5.3
	anion	13.33		4.0	4.9	25.87		2.8	4.4
1b ^[b]	cation	12.42	0.95	4.3	5.2	16.35	0.66	4.4	5.3
	anion	13.02		4.1	5.0	24.93		2.9	4.4
1c ^[c]	cation	12.39	0.96	4.3	5.2	16.80	0.64	4.3	5.2
	anion	12.95		4.1	5.0	26.14		2.7	4.4
1d ^[d]	cation	11.67	0.92	4.5	5.4	15.61	0.59	4.6	5.4
	anion	12.65		4.2	5.1	26.31		2.7	4.3
1e	cation	12.10	0.92	4.4	5.2	15.54	0.58	4.6	5.5
	anion	13.14		4.0	5.0	27.00		2.7	4.3
1f	cation	11.75	0.96	4.5	5.3	15.64	0.60	4.6	5.4
	anion	12.28		4.3	5.2	26.07		2.8	4.4
2	cation	11.30	0.98	4.7	5.5	14.62	0.58	4.9	5.7
	anion	11.57		4.6	5.4	25.10		2.9	4.4
3	cation	11.43	0.95	4.6	5.4	15.00	0.55	4.8	5.6
	anion	12.02		4.4	5.3	27.23		2.6	4.3
4 ^[e]	cation	12.07	0.98	4.4	5.2	15.88	0.57	4.5	5.4
	anion	12.28		4.3	5.2	27.78		2.6	4.3
5	cation	12.23	0.97	4.3	5.2	15.88	0.61	4.5	5.4
	anion	12.55		4.2	5.1	25.95		2.8	4.3

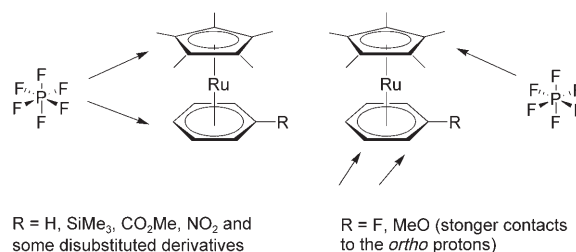
[a] All at 2 mM. For the calculation of *r*_H, the viscosity of the nondeuterated solvent at 299 K was used. $\eta(\text{CD}_2\text{Cl}_2) = 0.41 \times 10^{-3} \text{ kg s}^{-1} \text{ m}^{-1}$; $\eta(\text{[D}_6\text{]acetone}) = 0.31 \times 10^{-3} \text{ kg s}^{-1} \text{ m}^{-1}$. *r*_H was calculated using the Stokes-Einstein equation, while *r*_H^{corr} was calculated using a semiempirical estimation of *c*.^[14a] The measurements were carried out using the ¹H NMR resonance of Cp* for the cation and the ¹⁹F NMR resonance of PF₆⁻ for the anion. [b] For [Ru(Cp*)(η⁶-anisole)][OTf], *r*_H^{cryst} = 4.9 Å.^[38c] [c] *r*_H^{cryst} = 4.7 Å. [d] For [Ru(Cp*)(η⁶-phenyltrimethylsilane)][OTf], *r*_H^{cryst} = 5.1 Å.^[38b] [e] For [Ru(Cp*)(η⁶-indole)][OTf], *r*_H^{cryst} = 4.9 Å.^[38c]

ion pairing. For the indole and aniline salts, **4** and **5**,^[36b] respectively, hydrogen bonding between the N–H moieties and the anion is likely to be a major contributor to the observed *D* values. It is interesting that, despite the substantial increase in ion pairing, relative to the acetone data, the corrected r_H values suggest that the cation is not larger than in acetone.

¹⁹F, ¹H HOESY results: Although Branda et al.^[42] have recently summarized the combined use of diffusion and Overhauser methods, Macchioni and co-workers in a series of papers^[14,24,31] have made specific use of ¹⁹F, ¹H HOESY measurements on transition-metal salts, and have shown that this is a viable method for placing the fluorine-containing anions relative to their cations, in three-dimensional space.

The HOESY results for **1** in dichloromethane (for which we suspect significant ion pairing) can be summarized as follows: 1) one always finds a significant interaction of the anion with the Cp* methyl groups as well as several contacts to the complexed arene protons; 2) in all cases the PF₆[−] ions appear to be sitting close to the two planes of the ligands near to the meta and para protons of the arene; and 3) in two cases, **1b**, R=MeO and **1c**, R=F, the HOESY contacts to the *ortho*-arene protons are somewhat stronger. This last point is illustrated in Figure 2, which shows results for **1b** and **1f** and is summarized in Scheme 1. For the indole and

aniline salts, **4** and **5**, respectively, the observed selective HOESY contacts to the arene protons are consistent with the presence of N–H⋯F–PF₅ hydrogen bonds, thereby bringing the anion close to the =CH protons proximate to the N atoms.



Scheme 1. Selected HOESY results.

An approach of the anion which brings it close to the *meta*- and *para*-protons of the complexed arene might be expected based on steric grounds. However, it is not evident why the PF₆[−] ion would be attracted towards the region of the electronegative O or F atoms, since this approach is sterically less favorable.

We will return to the solution *D* values and HOESY results for the salts **1** in connection with the second section.

Solid-state structure of 1c: The structure of **1c** was determined by X-ray diffraction methods and Figure 3 gives an ORTEP view of the cation, a space-filling model of the salt, and selected interionic distances as well as selected bond lengths and bond angles in the cation. The various Ru–C separations are all normal and in keeping with the literature for such salts.^[37,38] The presence of the F-substituent on the arene does not seem to have induced any marked deviations due to steric effects, as the six Ru–C(arene) bond lengths are not significantly different.

From the space filling model (Figure 3, middle) it is clear that the anion approaches both the Cp* and the coordinated arene and that the observed closest contacts are under 3 Å for both rings. These relatively short contacts are consistent with the postulated strong ion pairing from the diffusion data. The location of the PF₆[−] ion close to the *meta*-proton of the arene is also in agreement with the specificity observed in the HOESY spectrum, in that the *ortho*-proton is relatively close.

Calculations: To help in understanding the diffusion and Overhauser data, we have calculated the charge distribution in **1a***–**1c***, R=H, MeO, F and **1f***, R=NO₂, using a natural population analysis (NPA)^[43] performed on geometries optimized by means of DFT calculations.^[44] The results are summarized in Table 3 and in Tables S1 and S2 in the Supporting Information (the asterisk indicates that Cp rather than Cp* was used in the calculations). The Ru atom carries only a modest positive charge, about 0.20, in all four cases. A more positive anisole in **1b*** (0.51), with respect to nitroben-

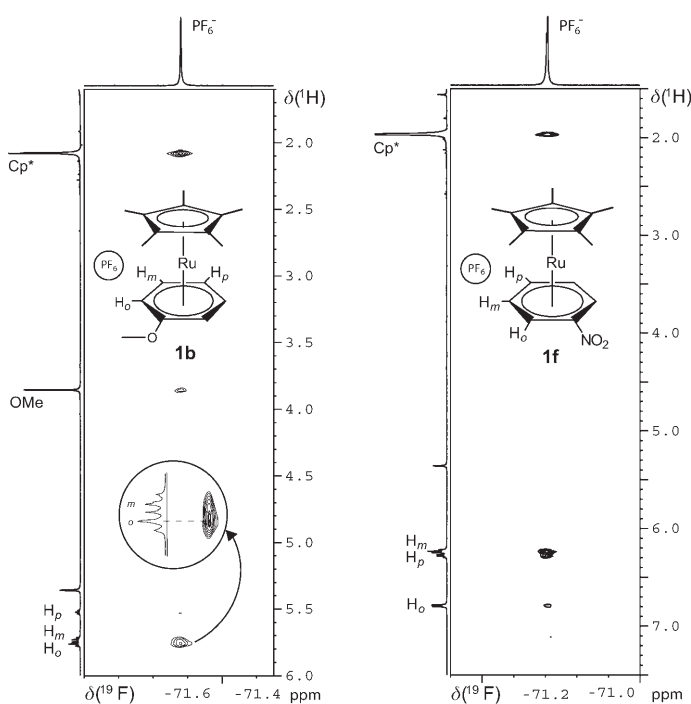


Figure 2. The ¹⁹F, ¹H HOESY NMR spectra of the salts **1b** and **1f** at ambient temperature showing the selective interactions. In the methoxy-substituted-salt **1b**, there are substantial contacts to both the *ortho* and *meta* protons, whereas in the nitro-substituted salt **1f**, the contact to the *ortho* protons is weak, but contacts to the *meta* and *para* protons stronger (CD₂Cl₂/C₆D₆ 5:1, for **1b** and CD₂Cl₂ for **1f**, 400 MHz, 10 mm).

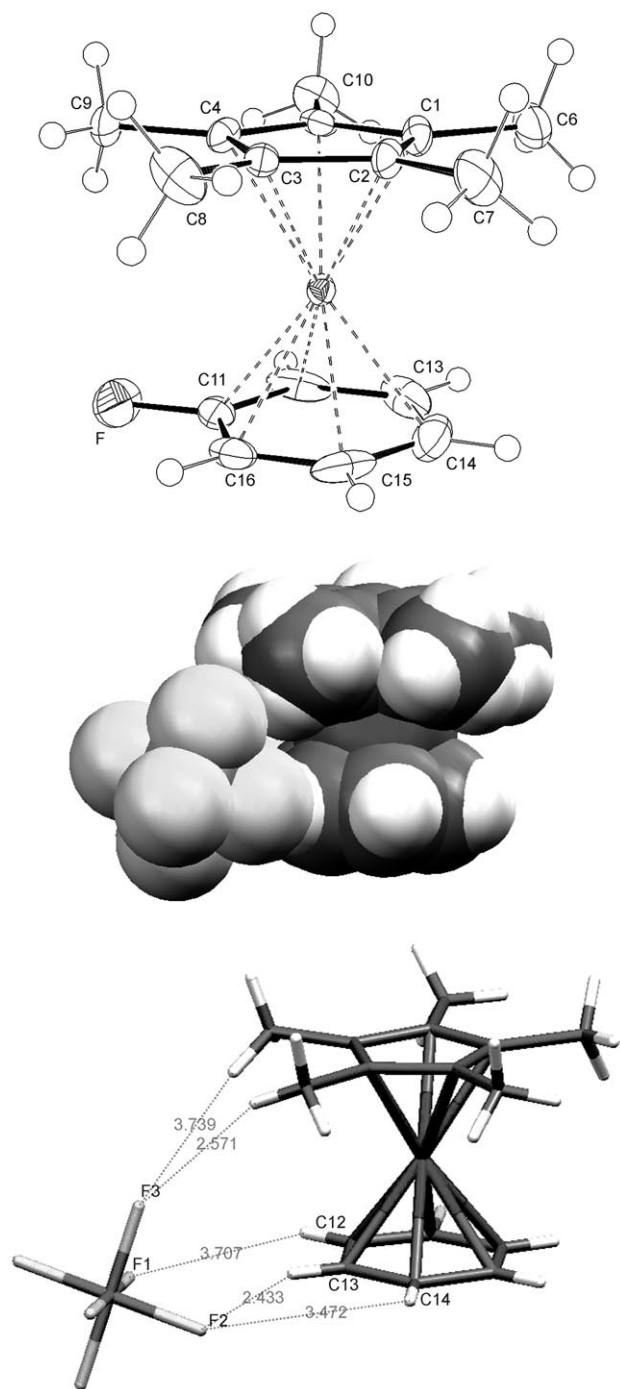


Figure 3. On the structure of salt **1c**. Top: Selected bond lengths [Å] and bond angles [°] in the cation: Ru–C1 2.180(6), Ru–C2 2.197(6), Ru–C3 2.187(6), Ru–C4 2.183(6), Ru–C5 2.169(6), Ru–C11 2.208(6), Ru–C12 2.207(7), Ru–C13 2.198(7), Ru–C14 2.213(8), Ru–C15 2.214(7), Ru–C16 2.227(7), C11–F 1.342(8), F–C11–C12 119.2(7), F–C11–C16 118.2(7). Center: Space filling model of the salt, showing the placement of the anion relative to one cation, in the unit cell. Bottom: Ball and stick model indicating the calculated packing distances (only the first decimal figure is significant).

zene in **1f*** (0.41), reflects the better donor character of this arene. In the nitro analogue (**1f***) the weaker electron donation from the arene to the metal is balanced by the Cp

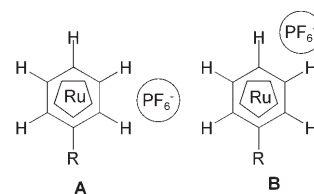
Table 3. Selected positive charges from the NPA analysis of the cations.

		Ru	Cp	Arene
1a*	R=H	0.21	0.32	0.47
1b*	R=MeO	0.20	0.29	0.51
1c*	R=F	0.19	0.34	0.47
1f*	R=NO ₂	0.21	0.38	0.41

ligand (0.38), which becomes more positive than in **1b*** (0.29). This balance results in essentially the same metal charge for the two complexes.

Continuing, the polarization of the C–H bonds is such that the carbon atoms are negative by approximately -0.2 to -0.3 units and the hydrogen atoms positive by about the same amount. However, two points are especially relevant: 1) the substituted *ipso*-carbon atoms of the arene in **1b***, **1c***, and **1f*** are positive for all three complexes, but with considerably different charges, $+0.37$, $+0.46$, and $+0.05$, respectively; and 2) the charge on the *para*-carbon atoms of the arene ligands are all essentially the same (ca. -0.23 to -0.24). The second point supports the conclusions from the ¹³C data with respect to the lack of strong resonance effects, while the first suggests that, combined with the C–H bond polarization, the PF₆[−] ion will be attracted somewhat more towards the *ortho* positions of the F- and MeO-substituted arene (in agreement with the observed HOESY data), despite the negative charges on the F and O atoms.

Additional DFT calculations were performed in order to obtain the optimized geometry of the ion pairs formed by a PF₆[−] ion and each of the three model cation complexes, **1b***(MeO), **1c***(F) and **1f***(NO₂). For each ion pair, two different structures were found, depending on the starting geometry: **A** in which the cation and the PF₆[−] ion are situat-



ed in a “side-by-side” arrangement, or **B** in which the PF₆[−] is placed in a remote position relative to the R substituent in the arene. For cations in **1b*** and **1c***, the two arrangements are clearly distinct. The ion pair resulting from geometry **A** has the PF₆[−] ion placed in between the *ortho*- and *meta*-H atoms of the arene ligand, while the ion pair resulting from geometry **B** has the anion approaching the *meta*- and *para*-H atoms of that same ligand. In the case of cation in **1f***, the two geometries obtained are essentially equivalent with the anion remote from the *ortho*-H atom and approaching the *meta*- and *para*-H atoms of the arene. In all cases the PF₆[−] ion is placed in between the planes of the Cp and arene π ligands. The structures calculated for the ion pairs are presented in the Supporting Information (Figure S1).

The two ion-pair geometries (**A** and **B**) are practically iso-energetic for the F and NO₂ arene cations in **1c*** and **1f*** (within 0.3 kcal mol⁻¹), but in the case of the methoxy-arene cation in **1b*** geometry **A** is clearly preferred by 5.7 kcal mol⁻¹. The position of the PF₆⁻ ion relative to the arene *ortho*- and *meta*-H atoms (in geometry **A**) can be evaluated through the hydrogen–phosphorus (H–P) separations in each calculated ion pair. The results obtained (see Supporting Information) indicate that the PF₆⁻ approaches the *ortho*-H atom of the arene in the case of cation in **1b*** (H_{*ortho*}–P = 2.83 Å, H_{*meta*}–P = 3.95 Å), while it moves closer to the *meta*-H atom in the case of complex cation in **1f*** (H_{*ortho*}–P = 4.97 Å, H_{*meta*}–P = 2.86 Å). For **1c*** an intermediate situation occurs. This result agrees with the observed HOESY data and with the conclusions drawn above, based on the analysis of the calculated atomic NPA charges, thereby validating this approach. The results above are further confirmed by the calculated electrostatic potential for cations in **1b*** and **1f*** (see Figure S2 in the Supporting Information).

PF₆⁻ ion pairing in dichloromethane for a wide variety of salts: For **1** in dichloromethane, a common solvent in organometallic chemistry, the data in Table 2 suggest a rather large extent of ion pairing. It is not clear if this is a special property of this anion and to what extent this observation

might be extrapolated to other cations. Table 4 shows a selection of literature PGSE diffusion data in dichloromethane for a variety of monocationic transition-metal salts with the PF₆⁻ ion. These include other ruthenium salts as well as iridium, rhodium, and palladium examples, all in the concentration range of about 1–2 mM.

From this table, one finds that the *D* values for the cations are considerably smaller than those for the anions and that the anion values fall in the range 9.87–14.70. Consequently one can conclude that complete—or almost complete—ion pairing is not the general case. The smaller *D* (and larger *r_H*) values for the anion are not what might be expected for a “free” solvated anion (in methanol or acetone), so that one can consider these data as representing examples of varying intermediate ion pairing. To avoid the assumptions associated with the Stokes–Einstein equation, and its modifications, only the experimental *D* values will be used in the discussion that follows. Tables 2 and 4 show the ratios *D_c/D_a* (subscripts: c = cation, a = anion) immediately to the right of the concentration values. We will assume that this ratio qualitatively reflects differences in the amount of ion pairing.^[45]

The largest ratio in Table 4 is found for the [RuCl(tmeda)(η⁶-cymene)] (TMEDA = tetramethylethylenediamine) cation^[31d] (0.93) and the smallest value (0.57) for the [Ir^{III}H₂{P(*m*-tol)₃}₂(phox)] cation.^[46] There are several fac-

Table 4. *D* [× 10⁻¹⁰ m² s⁻¹] and *r_H* [Å] values in CD₂Cl₂ for PF₆⁻salts.^[a]

	6		7		8a ^[31d]		8b ^[31g]		9		10			
	<i>D</i>	<i>r_H</i>	<i>D</i>	<i>r_H</i>	<i>D</i>	<i>r_H</i>	<i>D</i>	<i>r_H</i>	<i>D</i>	<i>r_H</i>	<i>D</i>	<i>r_H</i>		
cation	8.49	6.6	7.87	7.3	10.9	4.9	11.6	4.5	8.18	7.0	9.72	6.0	9.92	5.9
PF ₆ ⁻	9.87	5.8	10.99	5.5	11.7	4.7	12.5	4.3	11.8	5.2	13.27	4.7	13.78	4.6
	11		12		13a ^[b]		13b ^[b]		14 ^[c]		15a ^[d]		15b ^[51]	
	<i>D</i>	<i>r_H</i>	<i>D</i>	<i>r_H</i>	<i>D</i>	<i>r_H</i>	<i>D</i>	<i>r_H</i>	<i>D</i>	<i>r_H</i>	<i>D</i>	<i>r_H</i>	<i>D</i>	<i>r_H</i>
cation	9.67	6.0	7.70	7.4	9.33	6.2	8.67	6.6	8.61	6.7	9.36	6.2	6.67	8.4
PF ₆ ⁻	13.18	4.7	13.43	4.7	14.70	4.3	14.02	4.5	12.13	5.0	13.38	4.7	9.93	5.9

[a] Values in parenthesis after the concentration represent the quotient *D_c/D_a*, while *r_H* was calculated by using a semiempirical estimation of *c*.^[14a]
 [b] See reference [50]. [c] See reference [32c]. [d] See reference [67].

tors that are likely to contribute to the observed differences in this parameter. Molecular weight (more properly molecular volume) will play a role, but this cannot be the only component, since the ratio (0.86) for the Ru–bis(phosphine) **6**^[47] (cation weight = 618) is similar to that (0.80) for the ammonium salt **17**^[48] (cation weight = 366). Formal oxidation state does not seem critical as indicated by a comparison of the Ir^I/Ir^{III}–phox salts **10**^[46] and **11**, respectively, both of which have essentially identical D_c/D_a ratios. Moreover, the Ru^{IV}–allyl salt, [Ru(Cp*)(κ^2 -OAc)(η^3 -CH₂-CH=CH{CH=CH₂})][PF₆] (not shown in Table 4), has a D_c/D_a ratio of 0.90 (D (cation) = 12.20 and D (anion) = 13.51), not very far from the values for **1** in Table 2, again suggesting no major effect of oxidation state.

We suggest that the positive charge distribution, together with the ability of the anion to approach the positively charged positions (steric effects due to molecular shape), represent the determining factors. The structure of the TMEDA salt **8a** (D_c/D_a ratio = 0.93), with its two partially positively charged ammonium-like N atoms concentrates the positive charge near the metal, and the relatively small chelating TMEDA ligand will allow the anion to approach. The bis-phosphine **6**^[47] (D_c/D_a ratio = 0.86), with its longer chains and modestly bulky *Pn*Bu₃ ligands will keep the anion a little further away from the positive P atoms. Indeed the HOESY spectrum for **6**, see Figure 4 (left), reveals only a weak contact to the PCH₂ group, but shows strong contacts to the remaining three aliphatic resonances. This is in contrast to what one observes in the corresponding spectrum

for [N(*n*Bu)₄][PF₆], see Figure 4 (right), for which there are strong HOESY contacts to all of the aliphatic resonances.

Extending this view, the binap salt **7** (binap = 2,2'-bis(di-phenylphosphino)-1,1'-binaphthyl),^[49] with almost the same donor set as in **6**, shows a smaller D_c/D_a ratio (0.72), because the anion has to find its way past the bulky binaphthyl moiety in order to approach the P atoms. Salt **9**,^[29] with its relatively large phosphoramidite ligand, has the same problem. Experience has shown that despite the relatively small size of the chloride ligand, the anion will not approach formally negatively charged donors.^[14,15] The Ir–tris(phosphine)–oxazoline complex (**12**),^[32e] reveals the smallest ratio (the least ion pairing), because 1) the positive charges are likely to be distributed across four centers (three P atoms and one N atom) and 2) the approach of the anion is hindered by the nine substituted aromatic moieties.

The dinuclear, hydroxide-bridged, binap–palladium salt **15b**^[51] is informative in that it shows a relative small ratio of 0.67. One might have expected a larger value in that this contains a dication (larger electrostatic interactions), plus there is the possibility of a hydrogen bond between an F atom of the anion and the OH donor(s). However, as noted,^[14,15] the anion prefers to avoid the negatively charged areas, and thus is forced to approach the positively charged P atoms and consequently encounters significant steric interactions from the various binap organic moieties. These steric effects will be even more pronounced for the second anion, if and when the first anion associates with the dication.

Continuing, NPA calculations have also been carried out for the iridium(I)–1,5-cyclooctadiene (COD) complex **10*** (with methyl instead of *tert*-butyl and phenyl instead of *o*-tolyl), and the rhodium(I)–carbene salt **13a***^[50] (with methyl

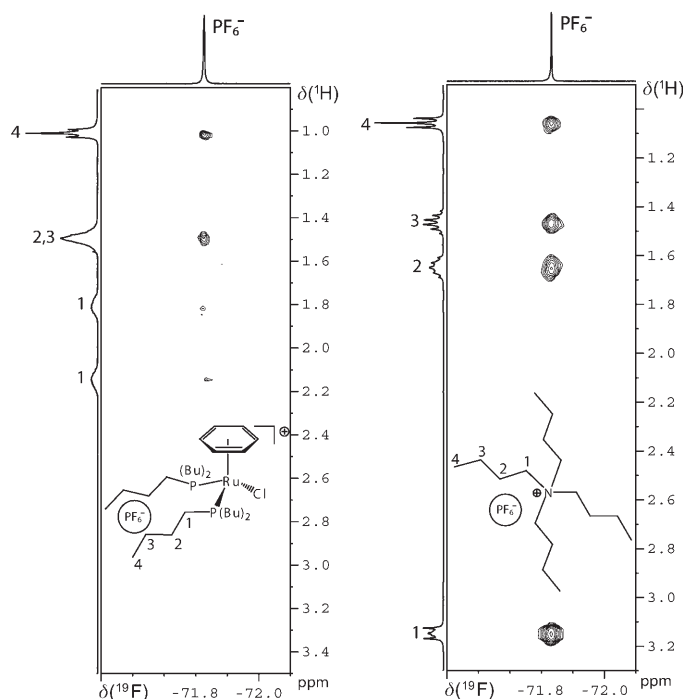
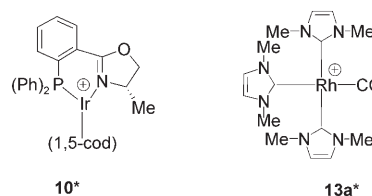


Figure 4. Comparison of the ¹⁹F, ¹H HOESY spectra for **6** and [N(*n*Bu)₄][PF₆]. Note that in **6** the contacts to the PCH₂ group are very weak (CD₂Cl₂ 400 MHz, 10 mM).



instead of cyclohexyl). Both of these salts show relatively small D_c/D_a ratios. For **10***, the positive charges are located primarily on the P atom (1.19), a second-row element, and on the oxazoline ring carbon C10 (0.68), a close neighbor of both the imine N and O atoms. The positive charge on the Ir atom (0.24) is modest and similar to what was found in the [Ru(Cp)(arene)] series. The four coordinated olefinic carbon atoms of the 1,5-COD carry modest negative charges (−0.25 to −0.30). Relatively large calculated positive charges for the complexed P atoms of tertiary phosphines have been reported earlier.^[51] Assuming that the anion will be attracted towards C10 and the P atom, it is clear that steric effects will make a close approach of the anion more difficult.

The largest positive charge in the Rh–carbene salt **13a*** is located on the carbon of the CO ligand (0.58), reflecting a

neighboring electronegative O atom and, also electron donation from the C atom to the metal. The three carbene-carbon donors are all positive (ca. 0.2). Somewhat surprisingly, the rhodium atom is slightly negative (−0.16), perhaps in keeping with the known good σ -donor capability of such heterocyclic carbene ligands. Assuming that the C atom of the CO ligand cannot readily be approached due to the O atom (which is strongly negative, −0.45 units), then the anion will seek a path that will require it to pass the cyclohexyl groups. Consequently, steric hindrance will play a role. The reported^[50] HOESY spectrum for **13a** shows only significant contacts to the ring =CH protons in keeping with this idea.

Returning to the Cp*–arene complexes **1**, all of which show D_j/D_a ratios greater than 0.90, it seems clear that, due to the modest size of the cation, the PF₆[−] ion can readily approach, so that there are no major steric problems which might prevent tight ion pairing and this is also in accordance with the solid-state results.

It is worth remembering that the values of the charges obtained from the NPA calculations in, for example, **1a***–**c***, **1f***, **10*** and **13a***, show a strong dependence on the electronegativity differences between adjacent atoms and, also, on the size of the atoms.^[52a]

Our increased understanding of the ion pairing in transition-metal salts prompted us to prepare and measure D values for several new PF₆[−] salts of both inorganic and organic cations and these results are shown in Table 5. The D values for all three P-based cations are similar, suggesting almost the same amount of ion pairing. Perhaps the amount of ion pairing is slightly less for the larger tetraphenyl phosphonium salt. Figure 5 shows the HOESY spectrum for the [PMePh₃][PF₆] analog and it is clear that the anion approaches the cation from the more accessible methyl group. Using this pathway the PF₆[−] will come close to the *ortho*-phenyl protons, but remain remote from the *meta*- and *para*-protons.

For the six nitrogen salts, [N(*n*Bu)₄][PF₆] and **16–19**, the D_j/D_a ratios vary from 0.66 to 0.97 and the two extremes, **18a** and **19**, are the most interesting. For **18a**, the positive charge is localized and the anion has no problem approaching from the side remote from the aromatic moiety. The

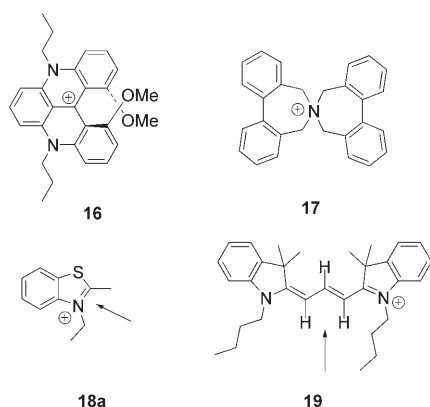


Table 5. PGSE diffusion measurements for organic and inorganic salts in CD₂Cl₂: D [$\times 10^{-10}$ m² s^{−1}] and r_H [Å].^[a]

Compound	conc. [mM]	fragment	D	D_j/D_a	r_H	r_H^{corr}
in CH ₂ Cl ₂						
[N(<i>n</i> Bu) ₄][PF ₆] ^[b]	2	cation	11.66	0.88	4.5	5.3
		anion	13.22		4.0	5.0
16 ^[c]	1	cation	10.0	0.68	5.3	6.0
		anion	14.8		3.6	4.7
17	1	cation	10.7	0.79	4.9	5.7
		anion	13.5		3.9	4.9
18a ^[d]	2	cation	14.12	0.97	3.7	4.8
		anion	14.57		3.6	4.7
18b	2	cation	11.17	0.92	4.7	5.5
		anion	12.14		4.4	5.2
19	2	cation	9.80	0.66	5.4	6.0
		anion	14.90		3.6	4.7
[PCH ₃ Ph ₃][PF ₆] ^[e]	2	cation	11.72	0.81	4.5	5.3
		anion	14.48		3.7	4.7
[P(<i>n</i> Bu)Ph ₃][PF ₆] ^[f]	2	cation	11.76	0.84	4.5	5.3
		anion	13.94		3.8	4.8
[PPh ₄][PF ₆] ^[g]	2	cation	11.73	0.79	4.6	5.3
		anion	14.82		3.6	4.7
in CDCl ₃						
18a	2	cation	9.63	0.99	4.2	5.2
		anion	9.71		4.2	5.2
1d	2	cation	8.46	0.99	4.8	5.7
		anion	8.50		4.8	5.7

[a] For the calculation of r_H , the viscosity of the nondeuterated solvent at 299 K was used. $\eta(\text{CD}_2\text{Cl}_2) = 0.41 \times 10^{-3}$ kg s^{−1} m^{−1}. r_H was calculated using the Stokes–Einstein equation, while r_H^{corr} was calculated using a semiempirical estimation of c . [b] $r^{cryst} = 4.94$ Å.^[68] [c] For [BPh₄] salt, $r^{cryst} = 6.2$ Å.^[69] [d] For [BF₄] salt, $r^{cryst} = 4.2$ Å.^[70] [e] For [BF₄] salt, $r^{cryst} = 4.8$ Å.^[71] [f] For Br salt, $r^{cryst} = 4.8$ Å.^[72] [g] $r^{cryst} = 5.0$ Å.^[73]

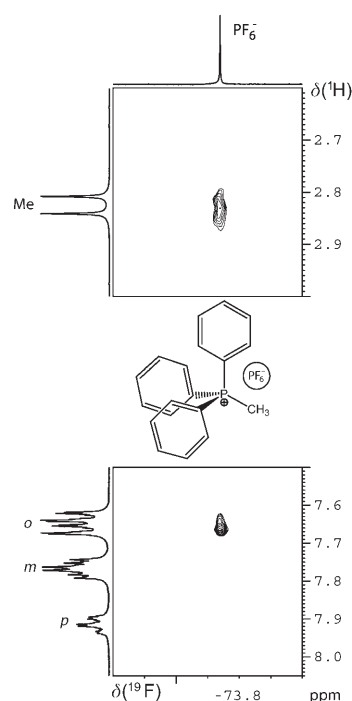


Figure 5. The ¹⁹F, ¹H HOESY spectrum for [PMePh₃][PF₆]. The strongest contact is to the methyl group and a weaker contact is observed to the *ortho* ring protons (CD₂Cl₂ 400 MHz, 10 mm).

HOESY spectrum, given in Figure 6, reveals contacts to the =C–Me group, the CH₂ group, and a weak interaction with the CH₃ of the ethyl group. There are no contacts to the aromatic protons. This modest-sized benzothiazonium cation

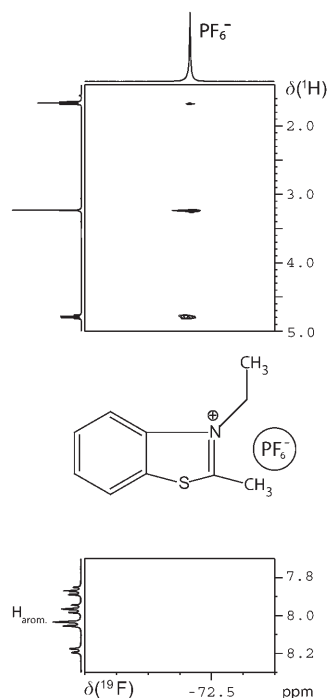


Figure 6. The ¹⁹F, ¹H HOESY spectrum for **18a** revealing the strong contacts to the =C–CH₃ and the NCH₂ groups (CD₂Cl₂ 400 MHz, 10 mm).

tucks the anion in as indicated by the arrow. An NPA analysis places a relatively large amount of positive charge, 0.6 units, on the S atom, a second-row element,^[52a] supporting the idea of localized charges. In an attempt to move the anion towards the S atom,^[52b] **18b** (with a relatively large substituent on the nitrogen atom) was prepared. The diffusion data suggest slightly less ion pairing ($D_c/D_a=0.92$); however, the HOESY contacts (see structure below) indicate that the anion remains close to the N atom and has no strong interest in the S atom.

The cyanine salt, **19**, has the positive charge distributed over two remote N=C fragments and this is also supported by the NPA results. This delocalization weakens the ion pairing and the HOESY spectrum

(see Figure 7) shows that the anion sits almost exactly between the two N atoms such that the two equivalent vinyl protons at about 6.2 ppm show the strongest contacts. There are also weaker contacts to the two NCH₂ methylene protons. The single =CH vinyl proton, H_b, at about 8.5 ppm, does not show any contact to the anion.

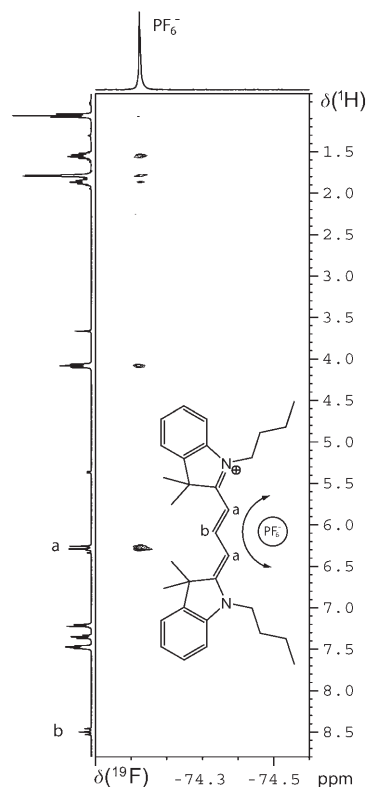
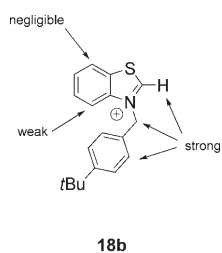


Figure 7. The ¹⁹F, ¹H HOESY spectrum for **19**. One finds the strongest contacts to the vinyl protons, H_a. There are no contacts to either the aromatic protons or the central =CH vinyl proton, H_b (CD₂Cl₂ 400 MHz, 10 mm).

Carbocation **16** is interesting in that the ratio of D values is relatively small. The charges found from the NPA calculations suggest that C3, the carbonium ion carbon, is only modestly positive (0.12), whereas C9 and C42 (directly attached to the electronegative O atoms) carry most of the charge (0.40). Perhaps the observed reduced amount of ion pairing is due to the charge separation (in analogy to **19**) and the reluctance of the anion to approach the O atoms (in analogy to the rhodium carbonyl salt, **13a**). Unfortunately, we have not been able to obtain HOESY data for **16**, despite several attempts.

Before continuing, two control experiments in CDCl₃ (for **1d** and **18a**) are worth mentioning and the results for these are given at the bottom of Table 5. In cases in which small cations are involved, one can ask whether the $D(\text{cation})$ and $D(\text{anion})$ values are coincidentally similar, that is, there is no ion pairing but the two solvated species happen to have about the same size. It is known that one finds almost complete ion pairing in CDCl₃.^[14,15] Consequently, in this solvent, one expects that 1) the ratio D_c/D_a should be close to or equal to one and 2) the r_H values will be larger than in dichloromethane. The CDCl₃ data reveal D_c/D_a ratios of 0.99 for both salts and in both cases the r_H values increase so that our assumptions with respect to ion pairing in dichloromethane are supported.

Conclusion

For all of the various PF_6^- salts in dichloromethane, the PGSE diffusion results help us to understand ion pairing in a more general sense and suggest, logically enough, that the amount of ion pairing will depend on the nature of the salts. Within any one class of salt, for example, the Ru^{II} -arene complexes, there may be extensive or more modest ion pairing. Combining the NMR data with calculations and crystallography, one can now qualitatively rationalize the amount of ion pairing. Further, the HOESY data contribute to our understanding of the solution structure of the salt. Specifically, these measurements help to support the idea that steric effects, due to the presence of large substituents, will hinder the ability of the anion to approach the cation. The predictive value associated with this combined approach is limited in that it is not quantitative; nevertheless, this mixture of NMR, DFT, and X-ray studies represents the first attempt to understand and partially explain the various degrees of ion pairing in such a different collection of salts.

Experimental Section

All reactions and manipulations were performed under a N_2 atmosphere using standard Schlenck techniques. Yields refer to purified compounds. Solvents were dried and distilled under standard procedures and stored under nitrogen. NMR spectra were recorded with Bruker Avance-400 and DPX-500 MHz at ambient temperature. Chemical shifts are given in ppm and coupling constants (J) in Hz. Elemental analyses and mass spectroscopic studies were performed at ETHZ.

We thank Prof J. Lacour (University of Geneva) for salts **16** and **17** and Mr. S. Gruber (ETHZ 2007) for the gift of $[\text{Ru}(\text{Cp}^*)(\kappa^2\text{-OAc})(\eta^3\text{-CH}_2\text{CHCH}(\text{CH}=\text{CH}_2))] [\text{PF}_6]$.

General procedure for the synthesis of $[\text{Ru}(\text{Cp}^*)(\eta^6\text{-arene})] [\text{PF}_6]$ (1**–**4**):** In a typical procedure, acetone (2–3 mL) was added to an oven-dried Schlenk containing $[\text{RuCp}^*(\text{CH}_3\text{CN})_3] [\text{PF}_6]$ (45–80 mg). After addition of the arene (3 equiv) the brown reaction solution was stirred for 4 h at 50 °C. The solution was then slowly concentrated under vacuum and the resulting crude product precipitated with acetone/pentane, affording a brownish powder, which was washed with Et_2O . Variations on this approach, as well as yields (mg/%) and elemental analysis data (%) are shown in Table 6.

General procedure for the synthesis of the organic and inorganic salts: In a typical procedure the halide salt (0.1–0.3 mmol) was dissolved in CH_2Cl_2 (1.5–3 mL) and added to a solution of $\text{Ag}[\text{PF}_6]$ (1 equiv) in CH_3CN (1–2 mL). An immediate precipitate was formed and the reaction solution stirred for 10 h at RT in the dark. After filtration of the suspen-

sion the filtrate was slowly concentrated under vacuum. The resulting crude was washed with Et_2O and dried under vacuum affording a white powder. Microanalytical data (C, H, N) for $[\text{PRPh}_3][\text{PF}_6]$ [$\text{R} = \text{Me}$ (99%), $n\text{Bu}$ (92%), Ph (65%)], **18a** (71%) and **19** (72%) are excellent (yield in brackets).

NMR measurements: The PGSE measurements were carried out without spinning and in the absence of external airflow. The sample was dissolved in 0.55 mL of the deuterated solvent, with the concentration maintained at 2 mM unless otherwise stated. The sample temperature was calibrated, before the PGSE measurements, by introducing a thermocouple inside the bore of the magnet.

All the PGSE diffusion measurements were performed using the standard stimulated echo pulse sequence on a 400 MHz Bruker Avance spectrometer equipped with a microprocessor-controlled gradient unit and an inverse multinuclear probe with an actively shielded Z-gradient coil. The shape of the gradient pulse was rectangular, its duration δ was 1.75 ms and its strength varied automatically in the course of the experiments. The calibration of the gradients was carried out by a diffusion measurement of HDO in D_2O , which afforded a slope of 1.976×10^{-3} . The data obtained were used to calculate the D values of the samples, according to the literature.^[14,15,53]

In the ^1H -PGSE experiments, Δ was set to 167.75 ms. The number of scans varied between 8 and 16 per increment with a recovery delay of 15 to 25 s. Typical experimental times were 1–2 h. For ^{19}F , Δ was set to 117.75 or 167.75 ms; 8–16 scans were taken with a recovery delay of 12 to 20 s and with a total experimental time of about 1–2 h.

All the spectra were acquired using 32 K points and a spectral width of 2796.4–4006.4 Hz (^1H) and 1882.5 Hz (^{19}F) and processed with a line broadening of 1 Hz (^1H) and 2 Hz (^{19}F). The slopes of the lines, m , were obtained by plotting their decrease in signal intensity versus G^2 using a standard linear regression algorithm. Normally, 12–20 points were used for regression analysis and all of the data leading to the reported D values afforded lines whose correlation coefficients were >0.999 . The gradient strength was incremented in 3–5% steps from 3–5% to 42–65%.

A measurement of ^1H and ^{19}F T_1 was carried out before each diffusion experiment, and the recovery delay set to five times T_1 . We estimate the experimental error in D values at $\pm 2\%$. The hydrodynamic radii, r_{H} , were estimated using the Stokes–Einstein equation ($c=6$) or by introducing the semiempirical estimation of the c factor that can be derived from the micro friction theory proposed by Wirtz and co-workers,^[54] in which c is expressed as a function of the solute to solvent ratio of radii.

The ^{19}F , ^1H HOESY measurements were acquired using the standard four-pulse sequence on a 400 MHz Bruker Avance spectrometer equipped with a doubly tuned (^1H , ^{19}F) TXI probe. A mixing time of 800 ms was used. The number of scans was 8–16 and the number of increments in the F_1 dimension 512. The delay between the increments was set to 6 s. The concentration of the sample was 10 mM.

Computational details: The calculations were performed using the Gaussian 03 software package,^[55] and the PBE1PBE functional, without symmetry constraints. That functional uses a hybrid generalized gradient approximation (GGA), including 25% mixture of Hartree–Fock^[56] exchange with DFT^[44] exchange-correlation, given by Perdew, Burke, and

Ernzerhof functional (PBE).^[57] The optimized geometries were obtained with the LanL2DZ basis set^[58] augmented with an f-polarization function,^[59] for Ru, and a standard 6-31G-(d,p)^[60] for the remaining elements. A natural population analysis (NPA)^[43] was used to obtain the charge distribution.

Crystallography: Air stable, colorless crystals of **1c**, suitable for X-ray diffraction, were obtained by crystallization from dichloromethane. A crystal was mounted on a Bruker APEX dif-

Table 6. Reaction conditions and elemental analyses for compounds **1**–**4**.

Salt	t [h]	T [°C]	Yield [mg/ %]	calcd/ %			found/ %		
				C	H	N	C	H	N
1a	15	50	40/87	41.83	4.61	–	41.29	4.56	–
1b	3	20	33/68	41.72	4.74	–	41.54	4.65	–
1c	4	20	52/69	40.26	4.22	–	39.98	3.97	–
1d	3	50	38/80	42.93	5.50	–	42.69	5.34	–
1e	3	40	22/36	41.78	4.48	–	41.78	4.49	–
1f	22	60	38/63	38.10	4.00	2.78	38.16	4.14	3.01
2	21	70	62/82	34.98	3.49	5.10	34.77	3.51	5.02
3	21	70	49/71						
4	3	50	23/53	43.38	4.45	2.81	43.55	4.36	2.81

fractometer, equipped with a CCD detector, and cooled, using a cold nitrogen stream, to 120(2) K for the data collection. The space group was determined from the systematic absences, while the cell constants were refined, at the end of the data collection with the data reduction software SAINT.^[61] The experimental conditions for the data collections, crystallographic and other relevant data are listed in Table 7 and in the Supporting Information.

Table 7. Experimental data for the X-ray diffraction study of compound **1c**.

formula	C ₁₆ H ₂₀ F ₇ PRu
<i>M_w</i>	477.36
<i>T</i> [K]	120 (2)
diffractometer	Bruker APEX CCD
crystal system	monoclinic
space group (no.)	<i>P</i> 2 ₁ / <i>n</i> (no.14)
<i>a</i> [Å]	8.533(2)
<i>b</i> [Å]	14.581(3)
<i>c</i> [Å]	14.234(3)
β [°]	93.952(3)
<i>V</i> [Å ³]	1766.6(7)
<i>Z</i>	4
ρ_{calcd} [g cm ⁻³]	1.795
μ [cm ⁻¹]	10.43
radiation	MoK α (graphite monochrom.)
	$\lambda = 0.71073$ Å
θ range [°]	2.00–29.43
data collected	21 026
independent data	4485
observed reflections (<i>n_o</i>)	3633
[$ F_o ^2 > 2.0\sigma(F ^2)$]	
parameters (<i>n_p</i>)	228
<i>R_{int}</i> ^[a]	0.0408
<i>R</i> (obsd reflns) ^[b]	0.0756
<i>wR</i> ² (obsd reflns) ^[c]	0.2485
GOF ^[d]	1.046

[a] $R_{\text{int}} = \frac{\sum |F_o^2 - \langle F_o^2 \rangle|}{\sum F_o^2}$, [b] $R = \frac{\sum (|F_o - (1/k)F_c|)}{\sum |F_o|}$, [c] $wR^2 = \frac{\sum [w(F_o^2 - (1/k)F_c^2)]}{\sum w|F_o|^2}$, [d] $\text{GOF} = \frac{\sum w(F_o^2 - (1/k)F_c^2)^2}{(n_o - n_p)^2}$.

The collected intensities were corrected for Lorentz and polarization factors^[61] and empirically for absorption using the SADABS program.^[62] The structure was solved by direct and Fourier methods and refined by full-matrix least-squares methods,^[63] minimizing the function $[\sum w(F_o^2 - (1/k)F_c^2)^2]$ and by using anisotropic displacement parameters for all atoms, except the hydrogen atoms and those affected by disorder (see below). The difference Fourier maps showed clearly the fluorine atoms in the equatorial plane of one of the PF₆⁻ octahedron, disordered over two positions, that were refined using isotropic displacement parameters. The refinement yielded equal occupancy for both sites (0.52(2) and 0.48(2) respectively). Upon convergence the final Fourier difference map showed no chemically significant peaks.

The contribution of the hydrogen atoms, in their calculated position, was included in the refinement using a riding model ($B(\text{H}) = 1.3 \times B(\text{C}_{\text{bonded}})(\text{\AA}^2)$). The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion were taken from the literature.^[64] The standard deviations on intensities were calculated in term of statistics alone. All calculations were carried out by using the PC version of the programs: WINGX^[65] SHELX-97^[63] and ORTEP^[66] CCDC-668025 (**1c**) contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

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