^{31}P and ^{35}Cl PGSE Diffusion Studies on Phosphine Ligands and Selected Organometallic Complexes. Solvent Dependence of Ion Pairing

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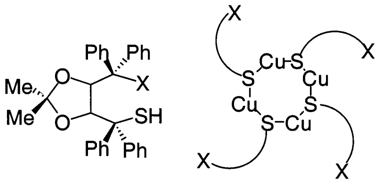
^{31}P and ^{35}Cl PGSE (pulsed gradient spin−echo) diffusion measurements on phosphine ligands and transition-metal complexes show that these nuclei can provide a useful complement to the existing ^{1}H and ^{19}F NMR forms of this experiment. The observed solvent dependence of the diffusion values in several palladium salts suggests that ion pairing is a major contributor in chloroform, important in methylene chloride, but small in acetone and methanol. A concentration dependence of the diffusion values is observed.

Introduction

There are an increasing number of applications of PGSE diffusion measurements[1,2] in inorganic and organometallic chemistry.[3−15] The diffusion coefficient, *D*, can be used to recognize higher molecular weight species, as in the Cu_4 cluster **1**,[3] the iron thiolate dendrimer **2**,[4] and the dinuclear ruthenium compound, **3**.[5] The larger the molecule, the slower it translates, thus giving a smaller *D* value.



Thiotaddol tetra-nuclear Cu-complexes, X = OH, OMe, NMe$_2$

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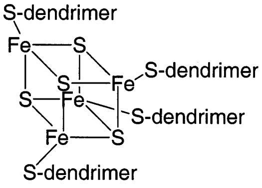

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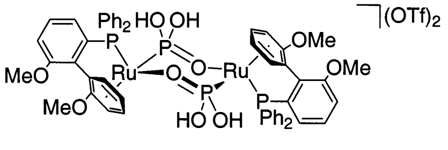

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Recent PGSE diffusion studies have emphasized the potential for recognizing ion pairing.[16−20] Where the anion contains a fluorine atom, e.g., the commonly used BF_4^-, PF_6^-, or triflate (OTf^-) anions, diffusion data from both ^{1}H and ^{19}F measurements allow a separate analysis of the translational properties of the cation and anion, thereby affording insight into whether these species move independently or as a single unit.[20] If the two ions are large enough—and tightly ion-paired—the resulting increase in the molecular volume will be reflected in the observed *D* values.

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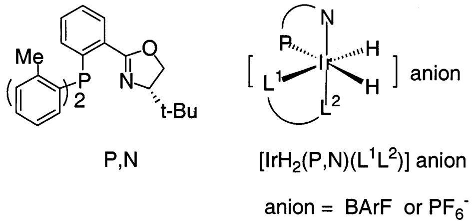
For complexes related to **4**, Drago et al.[6] have suggested that ion pairing involving BArF$^-$ can hinder the aggregation of catalytically active iridium complexes in methylene chloride, on the basis of the observed *D* values. Since the formation of a catalytically inactive trinuclear complex can be avoided, the catalyst lifetime is prolonged. In related studies, Macchioni and coworkers have suggested ion pairing for the tetraphenylborate in the Ru complex **5**[7] and the iridium compound **6**.[8]



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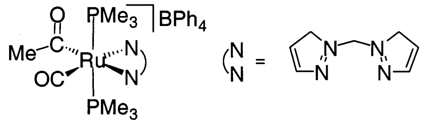

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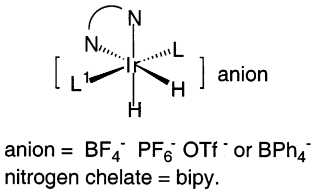

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Despite this progress in applying diffusion techniques, there is still much room for improvement in terms of the methodology. How should one approach related problems in which either there is no suitable proton or fluorine resonance, or would it be preferable to measure in a routine protonated solvent, which might obscure important ^{1}H resonances? Moreover, there has been little reported[17–19] on the solvent dependence of *D* values from cationic transition-metal complexes, and such data are important for the proper interpretation of results derived from charged compounds.

We report here the first ^{31}P and ^{35}Cl diffusion studies on transition-metal complexes (using their phosphine ligands and perchlorate anions) and suggest that these nuclei provide a useful addition to either ^{1}H or ^{19}F PGSE probes. ^{31}P PGSE diffusion studies have been previously used to study phosphorus-containing metabolites in vivo,[21] emulsions,[22] and the mass transport of phosphoric acid in water.[23]

We also consider aspects of ion pairing via the solvent and concentration dependences of the observed diffusion coefficients and briefly discuss technical problems encountered in optimizing our results.

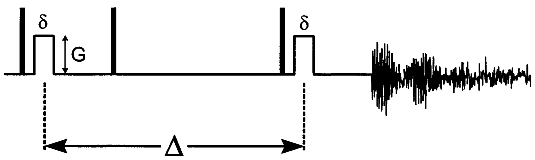

Figure 1. Pulse sequence for the PGSE measurements. The dark vertical bars represent the three 90° pulses, and the broader open bars represent the gradient pulses.

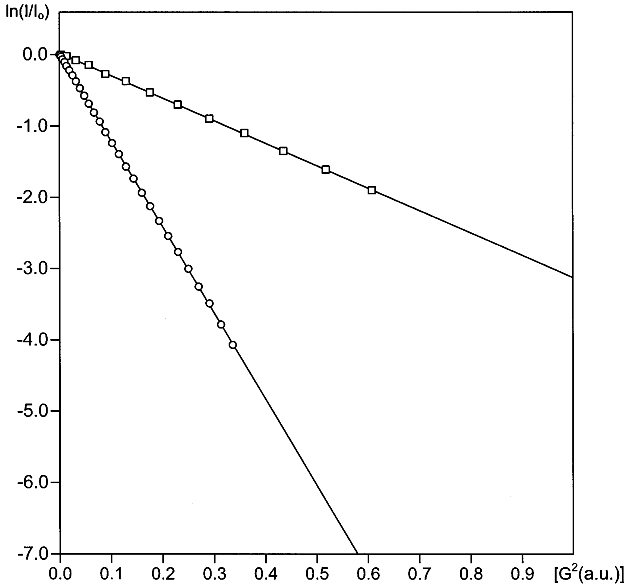

Figure 2. Plot of ln(I/I_o) vs arbitrary units proportional to the square of the gradient amplitude, for two diffusion measurements on a 10 mM CD_2Cl_2 solution of **10**, using ^{31}P (squares) and ^{1}H (circles) as probes. The slopes of the lines are related through eq 3 and correspond to the same value of the diffusion coefficient. For the ^{31}P measurement $\Delta = 250$ ms. Data were acquired using a 5 mm broadband probe in a 300 MHz spectrometer.

Results and Discussion

New Diffusion NMR Probes. PGSE measurements make use of Hahn or stimulated echo sequences with incorporated pulsed field gradients, as shown in Figure 1.[1,2] Moving molecules cause attenuated signal intensities, since they diffuse from their original environment via Brownian motion and thus no longer experience the same field strength when the second refocusing gradient is applied. We have discussed the details of this technique previously.[19] Equation 1 relates the observed intensity changes, ln(I/I_o), as a function of the variables used.[24]

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

Initial ^{31}P studies were carried out on an unrealistically concentrated (but quickly measurable) 0.5 M CD_2

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[24] γ = gyromagnetic ratio of the observed nucleus, δ = length of the gradient pulse, G = gradient strength, Δ (diffusion delay) = delay between the midpoints of the gradients, and D = diffusion coefficient. D is obtained from the slope of the regression line ln(I/I_o) vs G^2.

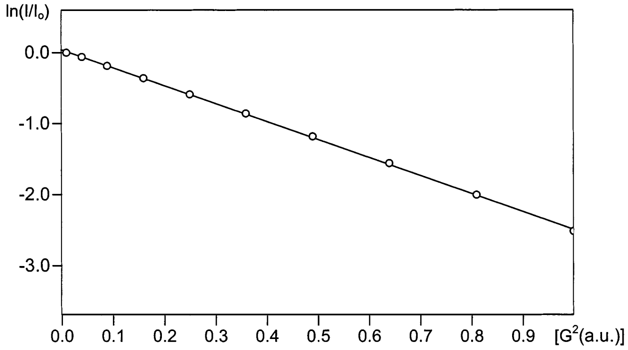
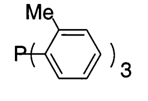


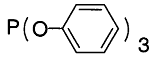
Figure 3. Plot of ln(I/I_o) vs arbitrary units proportional to the square of the gradient amplitude, for a ^{35}Cl-PGSE diffusion measurement on a 9 mM solution of **18** in acetone-d_6. Data were acquired using an 8 mm broadband probe in a 500 MHz spectrometer.

Cl_2 solution of the model compound tri-*o*-tolylphosphine.



The ^{1}H diffusion coefficient could readily be measured by monitoring the methyl resonance. Comparison with the D value obtained via $^{31}P\{^1H\}$-PGSE experiments was excellent when inverse gated ^{1}H decoupling was employed. The D value for this sample was [10.50(6)] × 10^{-10} m^2 s^{-1} from the ^{1}H data and [10.53(6)] × 10^{-10} m^2 s^{-1} from the average of six ^{31}P measurements with different diffusion delays (Δ) and decoupling power. Clearly, the agreement is excellent. For the remaining discussion the units will be omitted.

A similar set of test experiments was carried out for a 1 M CD_2Cl_2 solution of triphenyl phosphite (**7**).



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The D value for this sample was 9.12(6) from the ^{1}H data and 9.16(6) from the average of six ^{31}P measurements with different Δ and decoupler parameters. The agreement between the ^{1}H and ^{31}P data is again excellent. For 25 and 10 mM solutions of phosphite **7** the D values are 13.91(6) and 13.79(6) (from the ^{31}P experiments) and 14.04(6) and 13.75(6) (from the ^{1}H experiments), respectively. Clearly, there is a significant increase in D for the less concentrated samples; however, the D values obtained from the two diluted solutions are the same within experimental error.

Table 1 gives D values and hydrodynamic radii, r_H, for several tertiary phosphorus ligands and related organometallic complexes, **7**–**14**, at modest concentrations. Figure 2 shows a typical experiment for **10**. The radii are calculated via the Stokes–Einstein equation:[26]

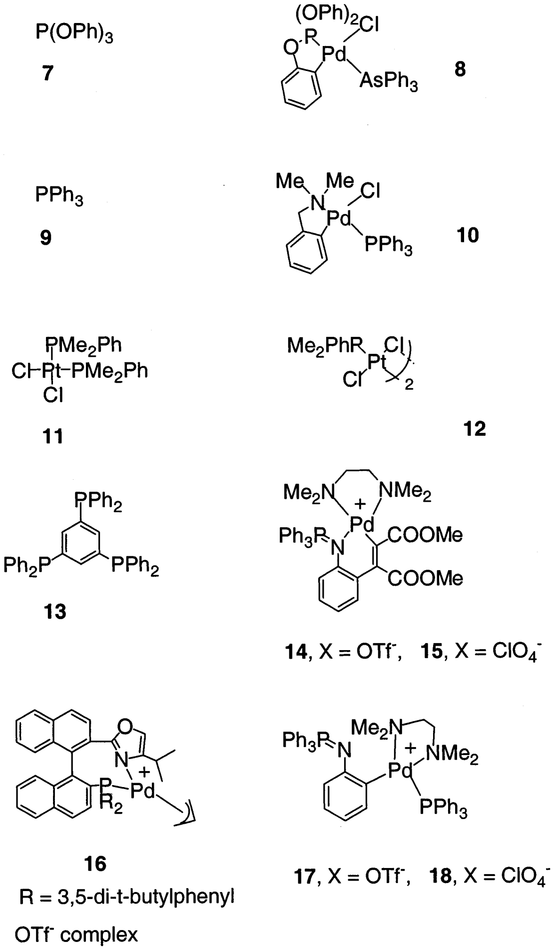
$$r_H = \frac{kT}{6\pi\eta D}$$

Table 1. ^{1}H and ^{31}P Diffusion Coefficients ($\times 10^{-10}$ m^2 s^{-1})^a in CD_2Cl_2

compd (concn (mM))	$D(^1H)$	$D(^{31}P)$	r_H (Å)
7 (10)	13.75(6)	13.79(6)	3.8(1)
7 (25)	14.04(6)	13.91(6)	3.8(1)
8 (10)	9.24(6)	9.29(6)	5.7(1)
9 (10)	14.60(6)		3.6(1)
9 (25)	14.42(6)	14.51(6)	
10 (10)	10.37(6)	10.29(6)^b 10.47(6)	5.1(1)
11 (20)	11.79(6)	11.97(6)	4.4(1)
12 (10)	10.62(6)		5.0(1)
12 (20)		10.52(6)^b 10.58(6)	
13 (10)	9.13(6)	9.08(6)	5.9(1)
14 (9)	8.42(6)	8.41(6)^c	6.4(1)

^{a} ^{31}P measurements used a Δ delay of ca. 968 ms. The r_H value represents the calculated hydrodynamic radius. ^{b} Δ = ca. 268 ms. ^{c} Δ = ca. 468 ms.

Chart 1. Ligands and Complexes for Diffusion Studies



These compounds are shown in Chart 1. There are several points of interest.

1. The observed diffusion coefficients, for both neutral (**7**–**13**) and charged compounds (**14**), via the ^{31}P measurements are in very good agreement with those from the analogous ^{1}H data. Consequently, the ^{31}P spin can be used whenever protons happen to be unsuitable.

2. Not surprisingly, the tris(phosphine) ligand **13** moves relatively slowly; e.g., its calculated radius is larger than that for phosphite **7** and phosphine **9** and comparable to that of complex **8**.

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(25) In the Stokes–Einstein equation, k is the Boltzmann constant and η is the viscosity.

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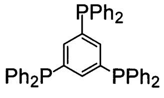

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3. The relatively small changes in concentration for **9** and **12** do not seem to produce significant variations in *D*.

Relative to the cyclometalated complexes **8** and **10**, the estimated volumes for the ligands **7** and **9** seem to be smaller than what might be expected. However, this is most probably an artifact, as the factor of 6 in the Stokes–Einstein equation is too large for small molecules. [26–28]

Not all anions contain a suitable proton, phosphorus, or fluorine atom for PGSE diffusion studies. For instance, the perchlorate anion, ClO_4^-, is commonly used in both inorganic and organometallic chemistry and we note one report on ^{35}Cl-PGSE measurements on this anion, in concentrated aqueous solutions of simple electrolytes.[29] Consequently, we have extended our studies to the organometallic complexes **15** and **18** in dilute chloroform and acetone solutions. Table 2 shows their ^{1}H and ^{35}Cl diffusion data, as well as the result for $NaClO_4$ in acetone. Figure 3 shows the ^{35}Cl PGSE results for **18**. A 2 M solution of $NaClO_4$ in methanol was also measured for a rapid check of the method (see Experimental Section).

We encountered some technical problems with these measurements. These were partially due to the poor receptivity and broad lines (ca. 6–8 Hz) associated with the ^{35}Cl isotope, both of which contributed to a poor signal-to-noise ratio. The short T_1 values in $CDCl_3$ required the reduction of the diffusion delay and produced a further decrease in the signal intensities. The best results required the use of 8 mm tubes to improve the sensitivity without increasing the concentration (see Experimental Section for further details).

A comparison of the acetone results for the three samples **15**, **18**, and $NaClO_4$ shows that the ClO_4^- ion is moving independently of the cation, and as expected, the cation in **18** is larger than in **15** due to the complexed PPh_3. The chloroform data for **15** and **18** suggest a different picture, and this brings us to ion pairing.

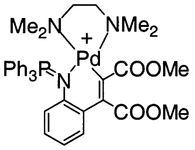
Ion Pairing. Several groups[9,16–20] have recently used diffusion measurements in connection with recognizing ion pairing. The approach involves separate measurements for the cation and anion. For **15** and **18** in $CDCl_3$, the ClO_4^- moves much slower than in acetone and its *D* value approaches that of the cation. At this point it is useful to consider the *D* value solvent dependence shown for the palladium aryl complexes in Table 3. This table contains data for both **15** and **18** and their analogous OTf^- complexes. In acetone, the results do not suggest significant ion pairing for either anion. The cation seems to move independently and much slower than the anion, and at about the same rate within each pair of complexes. The two anions are moving quite rapidly, and the larger triflate is slightly slower than the perchlorate. However, in chloroform solution, the situation is different. For the triflates **14** and **17**, the *D* values for cation and anion can be considered to be identical (complete ion pairing). For the perchlorates **15** and **18**, the ion pairing does not seem to be quite so strong, especially for **18**.

Given the solvent dependence of the ion pairing noted above, we extended our measurements on the ions in **14** to dichloromethane and methanol. The results for the four solvents are shown together in Table 4. The hydrodynamic radii (r_H values) contain the correction for the different viscosities,[30] so that a comparison of these values is informative. The *r* values are similar in chloroform, due to the strong ion pairing, and very different in acetone, where the cation and anion move separately. In methanol, there seems to be little or no

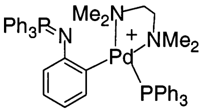
Table 2. *D* Values for ClO_4 Salts ($\times 10^{-10}$ m^2 s^{-1})

salt (concn (mM))	solvent		*D*	r_H (Å)
15 (9)	$CDCl_3$	cation (^{1}H)	5.79(6)	7.3(1)
		anion (^{35}Cl)	6.51(6)	6.5(1)
	acetone-d_6	cation (^{1}H)	11.18(6)	6.6(1)
		anion (^{35}Cl)	24.16(6)	3.0(1)
18 (9)	$CDCl_3$	cation (^{1}H)	5.69(6)	7.1(1)
		anion (^{35}Cl)	7.19(6)	5.6(1)
	acetone-d_6	cation (^{1}H)	10.30(6)	7.1(1)
		anion (^{35}Cl)	25.49(6)	2.9(1)
$NaClO_4$ (9)	acetone-d_6	anion (^{35}Cl)	24.73(6)	3.0(1)

Table 3. *D* Values ($\times 10^{-10}$ m^2 s^{-1}) for the Arylpalladium Complexes (9.0 mM)



14 as OTf$^-$
15 as ClO_4^-



17 as OTf$^-$
18 as ClO_4^-

	14	**15**	**17**	**18**
	Acetone Diffusion Data			
cation	11.06(6) (^{1}H)	11.18(6) (^{1}H)	10.72(6) (^{1}H)	10.30(6) (^{1}H)
anion	23.08(6) (^{19}F)	24.16(6) (^{35}Cl)	23.81(6) (^{19}F)	25.49(6) (^{35}Cl)
	Chloroform Diffusion Data			
cation	6.27(6) (^{1}H)	5.79(6) (^{1}H)	5.98(6) (^{1}H)	5.69(6) (^{1}H)
anion	6.17(6) (^{19}F)	6.51(6) (^{35}Cl)	6.11(6) (^{19}F)	7.19(6) (^{35}Cl)

Table 4. *D* Values ($\times 10^{-10}$ m^2 s^{-1}) for the Triflate Complex 14 (9.0 mM)

	solvent	*D*	r_H (Å)
cation (^{1}H)	$CDCl_3$	6.27(6)	6.6(1)
anion (^{19}F)		6.17(6)	6.7(1)
cation (^{1}H)	CD_2Cl_2	8.42(6)	6.3(1)
cation (^{31}P)		8.41(6)[a]	6.3(1)
anion (^{19}F)		10.81(6)	4.9(1)
cation (^{1}H)	acetone-d_6	11.06(6)	6.5(1)
anion (^{19}F)		23.07(6)	3.1(1)
cation (^{1}H)	CD_3OD	6.64(6)	6.2(1)
anion (^{19}F)		12.35(6)	3.4(1)

[a] Δ = ca. 468 ms.

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(28) Beck, S.; Geyer, A.; Brintzinger, H.-H. *Chem. Commun.* **1999**, 2477–2478.

(29) Heil, S. R.; Holz, M.; Kastner, T. M.; Weingärtner, H. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1877–1880.

(30) The viscosities have been taken from the online version of: *Chemical Properties Handbook*; McGraw-Hill: New York, 1999 (http://www.knovel.com). The corresponding value of the temperature for each of the spectrometers (299, 300, or 301 K) has been used in the calculation of r_H. The values at 300 K (in kg s^{-1} m^{-1}) are as follows: for methylene chloride, 0.410; for chloroform, 0.529; for acetone 0.303; for methanol, 0.526.

Table 5. D Values ($\times 10^{-10}$ m^2 s^{-1}) for Triflates 14 and 16

compd (concn (mM))		solvent	D	r_H (Å)
14 (3.5)	cation (^{1}H)	$CDCl_3$	6.35(6)	6.4(1)
	anion (^{19}F)		6.37(6)	6.4(1)
	cation (^{1}H)	CD_2Cl_2	8.69(6)	6.1(1)
	anion (^{19}F)		11.11(6)	4.8(1)
	cation (^{1}H)	acetone-d_6	11.36(6)	6.3(1)
	anion (^{19}F)		24.52(6)	3.0(1)
	cation (^{1}H)	CD_3OD	7.07(6)	5.8(1)
	anion (^{19}F)		12.86(6)	3.2(1)
16 (2.9)	cation (^{1}H)	$CDCl_3$	5.80(6)	7.1(1)
	anion (^{19}F)		6.22(6)	6.6(1)
	cation (^{1}H)	CD_2Cl_2	8.03(6)	6.6(1)
	anion (^{19}F)		12.97(6)	4.1(1)
	cation (^{1}H)	acetone-d_6	10.51(6)	6.8(1)
	anion (^{19}F)		25.11(6)	2.9(1)
	cation (^{1}H)	CD_3OD	6.22(6)	6.6(1)
	anion (^{19}F)		12.94(6)	3.2(1)

ion pairing, whereas in methylene chloride the r values suggest that the ion pairing is significant but not complete. Clearly, both the solvent and anion are important in the question of ion pairing.

Table 5 gives diffusion data from more dilute solutions (ca. 3 mM instead of 9 mM) of **14** and the relatively large chiral allyl complex **16** (both with a triflate anion), in the same four deuterated solvents. The conclusions from the paragraph above remain: the chloroform data suggest strong (but for **16** not as complete) ion pairing, the methanol and acetone results support little or no ion pairing, and the methylene chloride D values suggest an intermediate situation, where the ion pairing is significant but not as important as in chloroform. The D values for the triflate anions in **14** and **16** are significantly different in methylene chloride, pointing to a considerable difference in the degree of ion pairing for both complexes in this solvent. In $CDCl_3$, where the ion pairing is strong for both, the D values for the triflates do not differ significantly, as the cationic fragments are both voluminous.

For **14** the D values at 3 mM are generally slightly larger than at 9 mM, suggesting some intermolecular association at the higher concentration. However, the ratio of the D values for cation and anion in each of the solvents has not changed significantly. Consequently, qualitative conclusions about ion pairing can be drawn from the studies at ca. 9 mM, which concentration is more suitable when ^{31}P is to be used as a probe.

To support these diffusion results, we have measured the conductivity of solutions of **14** in chloroform, methylene chloride, methanol, and acetone, obtaining values of ca. 0.35, 33, 65, and 95 Ω^{-1} cm^2 mol^{-1}, respectively. Due to their low permittivity, chloroform and methylene chloride are problematic solvents for conductivity measurements.[31-33] However, these results are also consistent with strong ion pairing in chloroform[34] and a 1:1 electrolyte in methanol and acetone,[31] while the value in methylene chloride is intermediate, supporting the existence of an equilibrium in which there is some, but not complete, ion pairing. We suggest that the PGSE methodology is advantageous with respect to conductivity data[35-37] in that it allows the separate observation of cation and anion, instead of the resulting global conductivity. Moreover, it bases the determination of ion pairing on a positive result, i.e., measured D coefficients, which lead to the calculation of higher hydrodynamic radii, rather than on a negative effect, i.e. a somewhat reduced conductivity.

Conclusions

The applications of the PGSE methodology to organometallic complexes can be extended from the high-sensitivity nuclei ^{1}H and ^{19}F to both ^{31}P and the quadrupolar ^{35}Cl (in the perchlorate anion). The diffusion delays and gradient lengths have to be adapted to the magnetic properties of these nuclei, and a certain amount of care must be taken to obtain good signal-to-noise (S/N) ratios. The solvent dependences of the observed D values in the palladium salts clearly point to significant changes in ion pairing between the different solvents. The PGSE diffusion methodology constitutes a unique, sensitive, and flexible tool for the study of this phenomenon. The strong tendency to form ion pairs in chloroform solution suggests that this could well be exploited, chemically, in terms of, for example, designed blocking via an anion, and studies in this direction are in progress. The apparent lower tendency of the perchlorate anion toward ion pairing in chloroform, compared with triflate, could prove useful as well.

Experimental Section

Triphenyl phosphite, triphenylphosphine, and tri-*o*-tolylphosphine were commercially available. The triphosphine **13** was a gift from James.[38] Complexes **8**, **10**−**12**, and **16** were available in our laboratory. Complexes **14**, **15**, **17**, and **18** are derived from unpublished studies by Vicente, Abad, and López-Serrano.[39]

All the measurements were performed on Bruker AVANCE spectrometers (300, 400, and 500 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 strength varied automatically in the course of the experiments. These were carried out without spinning and with the airflow disconnected.

The calibration of the gradients on each spectrometer and probe was carried out via a diffusion measurement of HDO in D_2O. The data obtained were used to calculate the D values of the samples, according to eq 2.

$$D = \frac{m_{\mathrm{obs}} D_{\mathrm{HDO}}}{m_{\mathrm{HDO}}} \tag{2}$$

All of the data leading to the reported D values afforded lines whose correlation coefficients were above 0.99.

According to eq 1, the ratio between the signal attenuation in a ^{1}H diffusion measurement and that with a different nucleus, for the same molecular fragment (same D), is given by eq 3.

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$$\frac{m_{X}}{m_{H}} = \left(\frac{\gamma_{X}}{\gamma_{H}}\right)^{2}\left(\frac{\delta_{X}}{\delta_{H}}\right)^{2}\frac{\left(\Delta - \frac{\delta}{3}\right)_{X}}{\left(\Delta - \frac{\delta}{3}\right)_{H}} \qquad (3)$$

The first factor, which corrects for the different gyromagnetic ratios, is 0.886 for ^{19}F, 0.164 for ^{31}P, and 0.0096 for ^{35}Cl. Consequently, if the same parameters as for ^{1}H are applied and the same value of D is assumed, the attenuation resulting from a ^{19}F diffusion measurement will not be very different from ^{1}H. However, for ^{31}P the attenuation will be around 1/6 and, for ^{35}Cl, 1/100 of that observed with ^{1}H. As a very small intensity decrease does not allow an accurate measurement of D, the diffusion delay (Δ) and/or the gradient length (δ) has to be changed. Generally, the selection of these parameters will depend on the magnetic properties of the observed nucleus, the concentration of the sample, and the diffusion coefficient.

(I) ^{1}H- and ^{19}F-PGSE Diffusion Measurements. Δ = 167.75 ms, and δ = 1.75 ms. For the ^{19}F measurements in acetone-d_6 Δ = 92.75 ms. In all the measurements the gradient strength was incremented in 2 or 3% steps, so that 25−35 points could be used for regression anaysis. For ^{19}F, the T_1 value was always determined before the measurement and the recovery delay D1 set to 5T_1. For ^{1}H, D1 was always 5 s. The number of scans per increment was 16 for ^{1}H and between 4 and 12 for ^{19}F. Typical experimental times were around 1.5 h for ^{1}H and 2−3 h for ^{19}F (due to the longer T_1 values).

(II) ^{31}P-PGSE Diffusion Measurements. To obtain a suitable attenuation, the diffusion delay (Δ) was increased. Values of Δ = 267.75, 467.76, and 967.75 ms (δ = 1.75 ms) were used. A measurement of T_1 was carried out before each experiment and the recovery delay D1 set to 5T_1 (this was sometimes up to 1 min). Typically, for the 10−25 mM solutions of **7**−**14** in CD_2Cl_2 increments of 5% in the gradient strength were used, with 64−128 scans per increment, resulting in 10−14 points to define the line. These samples required ca. 9−12 h of measurement time. Concentrations on the order of ca. 3 mM would require a significantly longer time investment. A decoupling power of 26 dB was used (with 17 dB, D values which were too high compared with the result from the ^{1}H measurements were obtained, probably due to a warming of the sample).

D values for the test samples ($\times 10^{-10}$ m^2 s^{-1}), with the Δ value and the decoupler settings in parentheses, are as follows. (a) 0.5 M solution of P(*o*-Tol)$_3$ in CD_2Cl_2: 10.54(6) (167.75 ms, 26 dB), 10.53(6) (467.75 ms, 26 dB), 10.58(6) (967.75 ms, 26 dB), 10.54(6) (167.75 ms, 17 dB), 10.50(6) (467.75 ms, 17 dB), 10.49(6) (967.75 ms, 17 dB). (b) 1 M solution of P(OPh)$_3$ in CD_2Cl_2: 9.17(6) (267.75 ms, no decoupling), 9.14(6) (467.75 ms, no decoupling), 9.17(6) (267.75 ms, 17 dB), 9.19(6) (467.75 ms, 17 dB), 9.15(6) (267.75 ms, 26 dB), 10.49(6) (467.75 ms, 26 dB).

These measurements were carried out with increments of 5 or 6% in the gradient strengths and with only one scan per increment. In these short experiments, the decoupler power had no influence on the result.

(III) ^{35}Cl-PGSE Diffusion Measurements. (a) Measurements were carried out on 9 mM solutions of **15** and **18** in $CDCl_3$. The T_1 values were so short (130 ms for **15** and 114 ms for **18**) that the diffusion delay Δ had to be diminished if any signal was to be detected. The most suitable option available to compensate for the low gyromagnetic ratio of ^{35}Cl involved a considerable increment of the gradient lengths (δ). The values chosen were Δ = 78.1 ms and δ = 18 ms. Ten points were acquired from 7% to 70% gradient strength. NS = 3600 for **15** and 4000 for **18**. The duration of each of the experiments was ca. 22 h.

(b) Measurements were carried out on 9 mM solutions of **15** and **18** in acetone-d_6. T_1 = 1.1 s for **15** and 1.3 s for **18**. Values of Δ = 171 ms and δ = 5 ms were used. Ten points were acquired, from 10% to 100% gradient strength, with 1100 scans each. The duration of each of the experiments was ca. 20 h.

(c) The measurements was carried out on a 9 mM solution of $NaClO_4$ in acetone-d_6. T_1 = 250 ms. Δ = 44.1 ms, and δ = 14 ms. Ten points were acquired, from 7% to 70% gradient strength, with 2000 scans each. The duration of the experiment was ca. 15 h.

(d) A 2 M solution of $NaClO_4$ in methanol was also measured. Three different gradient lengths were used, to check the coincidence of the three results. T_1 = 44 ms. Δ = (40.1 + δ) ms, and δ = 15, 17, and 20 ms. D = 7.83(6), 7.94(6), and 8.00(6) ($\times 10^{-10}$ m^2 s^{-1}), respectively. Ten points were acquired, from 10% to 100% gradient strength, with 800 scans per increment.

Experimental Errors. On the basis of several ^{31}P diffusion measurements on a single complex, we find an error of ±3. However, on the basis of our experience on diffusion over several years, we believe that ±6 (although not specific) is more general. We think that the same error can be extended to the ^{35}Cl measurements, as the lower sensitivity is compensated by a considerably higher number of scans.

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