DALTON
FULL PAPER

Applications of pulsed field gradient spin-echo measurements for the determination of molecular volumes of organometallic ionic complexes†

Massimiliano Valentini, Paul S. Pregosin* and Heinz Rüegger*

Laboratory of Inorganic Chemistry, ETH Zentrum, CH-8092 Zurich, Switzerland

Received 18th September 2000, Accepted 30th October 2000
First published as an Advance Article on the web 1st December 2000

^{1}H and ^{19}F Pulsed Field Gradient Spin-Echo (PGSE) measurements on a selection of ruthenium(II) organometallic arene complexes have been made. ^{19}F provides a useful complement to the classical ^{1}H measurements and is especially valuable in the absence of suitable protons and/or overlap of signals from different compounds with similar size. This methodology for estimating molecular size of ionic complexes represents an alternative to classical methods in organometallic chemistry. One complex is shown to have a molecular volume which corresponds to a tight ion pair.

The determination of relative molecular size in solution remains a subject of interest to the inorganic chemistry community. Apart from classical methods such as mass spectroscopy[1] and those based on colligative properties,[2] we have recently recommended Pulsed Field Gradient Spin-Echo (FT-PGSE) measurements.[3] Although this is a relatively old methodology,[4] with few exceptions[5] it has found little application in organometallic chemistry. PGSE measurements make use of the translational properties of molecules and thus are responsive to molecular size and shape. Since one can measure several components of the mixture simultaneously PGSE methods are especially valuable where the material in question is not readily isolable and/or where a mixture is of especial interest.

In our earlier studies we concentrated on the applications of proton PGSE results for neutral complexes.[3] In addition to new applications we show here that (a) the ^{19}F spin is a viable alternative to ^{1}H and (b) studies on organometallic salts, as well as neutral species, can be informative.

Results and discussion

We have described the pulse sequences earlier[3c] and eqn. (1)

$$\ln\left(\frac{I}{I_0}\right) = -\gamma_X^2\delta^2G^2\left(\Delta-\frac{\delta}{3}\right)D \qquad (1)$$

relates the observed intensity changes, $\ln(I/I_0)$, as a function of the variables used, where γ_X = gyromagnetic ratio of the nucleus X, δ = length of the gradient pulse, G = gradient strength, Δ = delay between the midpoints of the gradients and D = diffusion coefficient. As the molecules diffuse the intensity of the spin-echo decreases. The diffusion coefficient, D, is obtained from the slope, m, of the regression line $\ln(I/I_0)$ *vs.* G^2 according to eqn. (1). This slope, expressed in T^{-2} m^2, will be smaller for larger molecules and in the discussion below we will use this parameter m, reported in this study for values of δ and Δ equal to 5 ms and 100 ms respectively.

There are a relatively large number of cationic ruthenium compounds currently in use in homogeneous catalysis and/or organic synthesis.[6] Frequently, these complexes possess fluorine containing anions such as triflate ($CF_3SO_3^-$, TfO^-) or $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ BArF. For these, and other complexes, ^{19}F represents an alternative to ^{1}H PGSE methods. Scheme 1 shows a series of ruthenium(II) complexes which we have considered and Table 1 gives slopes for the regression lines and diffusion coefficients which stem from the analysis of their PGSE diffusion data.

Table 1 $-m$ and D values for compounds **1**–**8**

Compound	Solvent	Nucleus	$-m^a$/T^{-2} m^2	10^{10} D^b/m^2 s^{-1}
1	$CDCl_3$	^{1}H	107 (1)^c	6.15 (6)^c
		^{19}F	106^d (1)	6.03 (6)
	CD_2Cl_2	^{1}H	140 (1)	8.01 (6)
3	$CDCl_3$	^{1}H	97 (1)	5.58 (6)
		^{19}F	93^d (1)	5.35 (6)
4	$CDCl_3$	^{1}H	117 (1)	6.71 (6)
5	$CDCl_3$	^{1}H	139 (1)	7.95 (6)
6	$CDCl_3$	^{1}H	106 (1)	6.01 (6)
7	$CDCl_3$	^{1}H	102 (1)	5.88 (6)
8	CD_2Cl_2	^{1}H	115 (1)	6.61 (6)
		^{19}F	116^d (1)	6.67 (6)

[a] Measured using δ = 5 ms and Δ = 100 ms. [b] Estimated using the diffusion coefficient of HDO in D_2O as reference.[3c] [c] Standard deviation. [d] Corrected for γ_F.

Fig. 1 shows ^{19}F PGSE data for both OTf moieties of cationic compound **1**. The two lines are so closely overlapped that these are not visibly readily resolved (slopes $m = -106$ and -105, corrected for γ_F so that the value of m can directly be compared with that measured using ^{1}H). Moreover these slopes are in excellent agreement with that found from the ^{1}H PGSE study using the protons of the cation ($m = -107$, see below) thus supporting the use of ^{19}F PGSE studies as an alternative and/or complement to the classical ^{1}H variation. These diffusion data suggest that both triflates in **1** are moving at the same rate. Although one could imagine tight ion pairing as an explanation for the observed identical slopes, we note that the reported solid-state structure for **1**[7] suggests a hydrogen bond from the $P(OH)Ph_2$ fragment to the anionic (and not to the complexed) triflate. Consequently, the anionic triflate (which might also be involved in an ion pair) is most likely associated with the cation *via* the OH group.

A similar situation exists for the recently reported[8] novel complex of the Ph_2POBF_2OH bidentate ligand, **2**. Proton and

---

† Electronic supplementary information (ESI) available: plots of $\ln(I/I_0)$ *vs.* the square of the gradient strength for compound **1** at different concentrations, **5**–**7** in $CDCl_3$ solution and **1** and **8** in CD_2Cl_2 solution. See http://www.rsc.org/suppdata/dt/b0/b007530m/

DOI: 10.1039/b007530m

fluorine PGSE measurements reveal the same diffusion constant for both the complex (*via* the various ^{1}H spins) and the hydrogen-bonded HBF_4 (*via* the ^{19}F of the H-bound BF_4^- unit).

Fig. 2 shows ^{1}H diffusion results for the two Duphos compounds **3** and **4**. The two slopes, −97 and −117 T^{-2} m^2, for **3** and **4**, respectively, are quite different despite identical cations. The ratio of the slopes, *ca.* 1.21 : 1, is consistent with **3** having *ca.* twice the volume of **4**. For two spherical molecules, in which one has twice the volume of the other, one expects the ratio of the slopes to be $(2)^{1/3} \approx 1.26:1$. Furthermore, calculations assuming that the mononuclear complex is of spherical shape and the dinuclear species has an elongated shape, the longer axis being twice that of the smaller, give a ratio of *ca.* 1.18 : 1.[9] In the case of **3** one can rationalise the *ca.* 21%

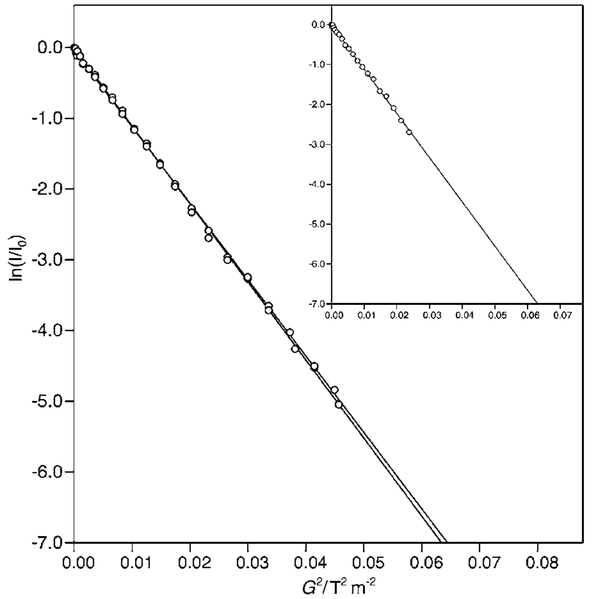


Fig. 1 Plot of $\ln(I/I_0)$ *vs.* the square of the gradient strength for compound **1** in $CDCl_3$ using the ^{19}F resonances and, in the smaller box, ^{1}H signals (see below). The slope measured using ^{19}F, corrected for γ_F, is equal (within experimental error) to that estimated *via* ^{1}H, supporting the use of ^{19}F PGSE as an alternative and/or complement to the ^{1}H variation.

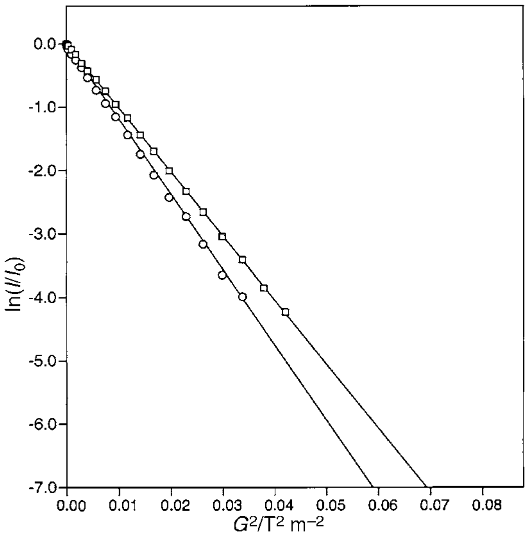
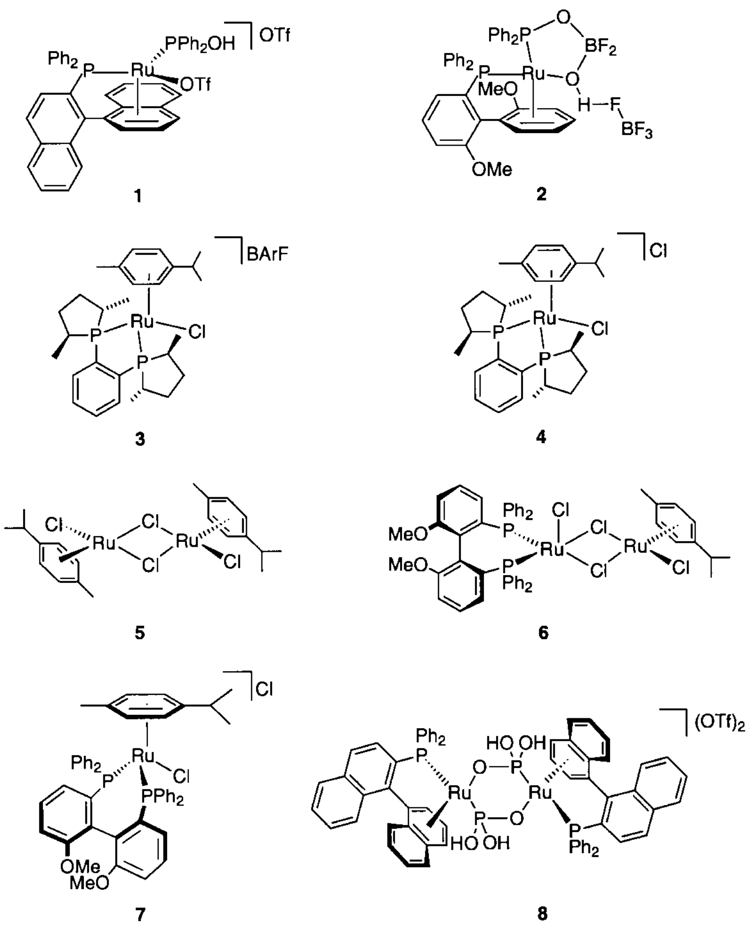


Fig. 2 ^{1}H diffusion results for compounds **3** (squares) and **4** (circles) in $CDCl_3$. The slopes are quite different despite identical positive fragments. This is due to the existence of **3** as a tight ion pair and to the presence of the large counter ion BArF, which almost doubles the molecular volume of **3**.



Scheme 1

Table 2 $-m$ for compound **1** in $CDCl_3$ at different concentrations

Concentration/mg g^{-1}	$-m^a$/T^{-2}m^2
0.8	107 (1)^b
6.6	101 (1)
13.2	98 (1)

^{a} Measured using δ = 5 ms and Δ = 100 ms. ^{b} Standard deviation.

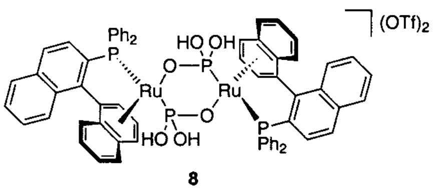
difference reported above by assuming that the BArF, in $CDCl_3$, is present as a relatively tight ion pair, thus effectively doubling the molecular volume. This conclusion is supported by the ^{19}F PGSE experiment, which gives a slope for the BArF almost equal to that of the cation.

We have recently prepared the dinuclear halide-bridged MeO-Biphep species, **6**, from the cymene complex **5** (despite the addition of two equivalents of phosphine per Ru atom). While this chemistry is not completely unexpected,[10] the protons and carbons of the cymene are sufficiently far from those of the MeO-Biphep so that the NMR spectra do not differ very much from the starting materials. However the slopes of the two lines (see ESI Fig. S1 and the Contents entry) for these compounds, −139 for **5** and −106 T^{-2} m^2 for **6**, clearly indicate the very different molecular volumes. Interestingly, **5** and **6** both show larger slopes than that found for **7**, −102 T^{-2} m^2, the desired product of the reaction (the line for this material is also given in ESI Fig. S1). It is not immediately clear why the slope for **6** should be somewhat larger than that for **7**, *i.e.* why **7** seems to have a larger volume, given that its molecular weight is smaller than that for **6**. However, assuming that a cationic complex can organise the solvent to a larger extent than for a neutral species, it is likely that the observed slopes reflect the differing abilities of neutral and charged species to interact with their surroundings. This raises the obvious *caveat*: diffusion results for neutral and charged species will not be directly comparable. Solvent polarity (and, as already noted,[3c] solvent viscosity) will markedly affect the results.

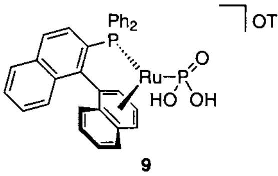
An additional subtlety in diffusion studies involves concentration. Table 2 contains the ^{1}H diffusion results for compound **1** at three different concentrations (see also ESI Fig. S2). The measured slopes change by *ca.* 9% as a function of the concentrations[11] employed and show the expected smaller effective volumes at lower concentrations. Such variation is due to a change of the viscosity of the solvent according to the equations[11] for the viscosity of dilute electrolyte solutions. This concentration effect on m is relatively large and must be taken into account in order to avoid ambiguous results.

We conclude with a rather exotic, but informative application of diffusion measurements involving the distinction between the possible structures **8** and **9**. ^{1}H PGSE diffusion data for a CD_2Cl_2 solution of this substance relative to the model cationic Ru–P(OH)Ph_2 complex **1** are given in Table 1 (see ESI Fig. S3 for the corresponding plot). The two slopes, −115 for the unknown and −140 T^{-2} m^2 for **1**, indicate that **8** is the correct structure since their ratio (=*ca.* 1.22 : 1) suggests that the unknown has *ca.* twice the molecular volume of the model. Given the shape of **8** one might have expected a ratio closer to *ca.* 1.18 : 1; however since the triflates of the unknown complex are hydrogen bonded to the P(OH) groups (^{19}F PGSE data) they have the same diffusion coefficient as the cation, thereby making the molecule more spherical in shape. Although we are convinced that the diffusion data indicate the correct structure, the fact that we are comparing a model monocation complex with an unknown dication should not be overlooked. In contrast to our previous measurements in CD_2Cl_2 on neutral organometallic compounds,[3c] for both **1** and **8** only molecular translation due to diffusion was observed.[12]

Concluding, we suggest that both ^{19}F and ^{1}H PGSE methods will find applications in organometallic chemistry. The extension to charged salts with complicated structural features is not necessarily trivial and care will be required in interpretation of the data.



8



9

Experimental

All the measurements were performed on a Bruker AVANCE 400 spectrometer equipped with a microprocessor controlled gradient unit and a multinuclear probe with an actively shielded Z-gradient coil. *ca.* 1 mg of the complexes was dissolved in 0.7 mL of the deuteriated solvents and the samples measured at 298 K without spinning. The sequence used was the "three pulses Stimulated-Echo". The shape of the gradients was rectangular, their length 5 ms and the strength varied automatically in the course of the experiment. The time between the midpoints of the gradients (Δ) was chosen as 100 ms for the complexes measured in $CDCl_3$ while for those in CD_2Cl_2 the experiments were repeated three times using three different Δ values (100, 120 and 150 ms) while leaving all the remaining parameters unchanged. Complexes **1**–**8** have been synthesized in this laboratory and details will be reported separately. **1**[7] and **2**[8] were prepared according to the literature and **5** was bought from Aldrich and used without further purification.

Acknowledgements

We thank C. den Reijer for the synthesis of compounds **1**, **2**, **6** and **7**, T. J. Geldbach for **8** and Dr Y. Chen for **3** and **4**. P. S. P. thanks the Swiss National Science Foundation and the ETH Zurich for financial support. We also thank Johnson Matthey for the loan of metal salts, and F. Hoffmann-La Roche for a gift of chemicals.

References

1 R. Colton, A. D'Agostino and J. C. Traeger, *Mass Spectrom. Rev.*, 1995, **14**, 79.

2 G. L. Beyer, in *Physical Methods of Chemistry*, eds. A. Weissberger and B. W. Rossiter, Wiley-Interscience, New York, 1971, vol. 1, ch. 3, p. 126.

3 (*a*) Q. Jiang, H. Rüegger and L. M. Venanzi, *Inorg. Chim. Acta*, 1999, **290**, 64; (*b*) A. Pichota, P. S. Pregosin, M. Valentini, M. Wörle and D. Seebach, *Angew. Chem.*, 2000, **112**, 157; A. Pichota, P. S. Pregosin, M. Valentini, M. Wörle and D. Seebach, *Angew. Chem., Int. Ed.*, 2000, **39**, 153; (*c*) M. Valentini, P. S. Pregosin and H. Rüegger, *Organometallics*, 2000, **19**, 2551.

4 B. D. Boss, E. O. Stejskal and J. D. Ferry, *J. Phys. Chem.*, 1967, **71**, 1501; for a review of applications see P. Stilbs, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1987, **19**, 1.

5 A. Mayzel and Y. Cohen, *J. Chem. Soc., Chem. Commun.*, 1994, 1901; R. E. Hoffmann, E. Shabtai, M. Rabinovitz, V. S. Iyer, K. Müllen, A. K. Rai, E. Bayrd and L. T. Scott, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1659; S. Beck, A. Geyer and H. H. Brintzinger, *Chem. Commun.*, 1999, **24**, 2477; C. Zuccaccia, G. Bellachioma, G. Cardaci and A. Macchioni, *Organometallics*, 2000, **19**, 4663.

6 R. Noyori, in *Asymmetric Catalysis in Organic Synthesis*, ed. R. Noyori, John Wiley & Sons, New York, 1994; T. Naota, H. Takaya and S. Murahashi, *Chem. Rev.*, 1998, **98**, 2599.

7 C. J. den Reijer, M. Wörle and P. S. Pregosin, *Organometallics*, 2000, **19**, 309.

8 C. J. den Reijer, H. Rüegger and P. S. Pregosin, *Organometallics*, 1998, **17**, 5213.

9 P. Schurtenberger and M. E. Newman, in *Environmental Particles*, eds. J. Buffle and H. P. van Leeuwen, Lewis, Boca Raton, FL, 1993, vol. 2, p. 37.

10 A. Fürstner, A. F. Hill, M. Liebl and J. D. E. T. Wilton-Ely, *Chem. Commun.*, 1999, 601.

11 A. Chandra and B. Bagchi, *J. Chem. Phys.*, 2000, **113**, 3226, and references therein.

12 For compounds **1** and **8** repeating the PGSE measurements using different diffusion times (Δ) and keeping all the other parameters constant gave identical $m/[\Delta - (\delta/3)]$ results (within experimental error).