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^{1}H and ^{19}F PGSE Diffusion Studies on Iridium PHOX Complexes: Counterion and Solvent Dependences

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^{1}H and ^{19}F pulsed gradient spin–echo (PGSE) diffusion studies on cationic mono- and trinuclear iridium complexes containing the PHOX chiral P,N-auxiliary (*S*)-4-*tert*-butyl-2-[2-(di-*o*-tolylphosphino)phenyl]-4,5-dihydrooxazole with the anions BF_4^-, PF_6^-, OTf^-, $B(C_6F_5)_4^-$, and $BArF^-$ in methanol, chloroform, methylene chloride, and 1,2-dichloroethane are reported. In chloroform, the anion and cation within each salt afford almost the same, relatively small, diffusion constant (*D*-value) suggesting strong ion-pairing. In methanol, the *D*-value for the cation is the same in the five mononuclear salts, suggesting that the cation is moving independently of the anion (no ion-pairing). In methylene chloride and 1,2-dichloroethane the diffusion data suggest a mixed picture for the five anions. While the smaller BF_4^-, PF_6^-, and OTf^- anions do not affect the translation of the cations, the larger boron-based anions $B(C_6F_5)_4^-$ and $BArF^-$ clearly slow the motions of the cations. However, it would seem that for all five anions there is some—but not complete—ion pairing in these two solvents.

Introduction

Salts of transition metals play an important role in homogeneous catalysis. They find applications in hydrogenation,[1] Diels–Alder,[2] and allylic alkylation[3] chemistry, among others. Within the metal coordination sphere, it is recognized that the nature of the anion can play an important role.[4] Recently, there have been a number of reports noting that the negative counterion, e.g., PF_6^- or BF_4^- relative to $BArF^-$, exercises a surprisingly large effect in terms of reaction rates.[5,6] The source of these effects is often completely unknown.

Classical NMR diffusion studies are frequently associated with qualitative determinations of molecular volumes.[7–12] However, on the basis of the recent literature, it is becoming clear that pulsed gradient spin–echo (PGSE) diffusion studies offer a unique approach with respect to how cations and anions interact.[13,14] This stems, partially, from the ability to use a multinuclear diffusion approach, e.g., ^{1}H and ^{19}F for the cation and anion, respectively, combined with

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(1) Genêt, J. P. *Agros Organics Acta* **1995**, *1*, 4–9. Wiles, J.; Bergens, S. H. *J. Am. Chem. Soc.* **1997**, *119*, 2940–2941. Bianchini, C.; Barbaro, P.; Scapacci, G.; Zanobini, F. *Organometallics* **2000**, *19*, 2450–2461. Broger, E. A.; Burkart, W.; Hennig, M.; Scalone, M.; Schmid, R. *Tetrahedron: Asymmetry* **1998**, *9*, 4043–4054. Faller, J. W.; Lavoie, A. R. *Organometallics* **2001**, *20*, 5245–5247. Ohkuma, T.; Ishii, D.; Takeno, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 6510–6511.

(2) Kündig, E. P.; Saudan, C. M.; Bernardinelli, G. *Angew. Chem.* **1999**, *111*, 1298–1301. Davenport, A. J.; Davies, D. L.; Fawcett, J.; Garratt, S. A.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **2000**, 4432–4441. Faller, J. W.; Lavoie, A. R.; Grimmond, B. J. *Organometallics* **2002**, *21*, 1662–1666.

(3) Trost, B. M.; van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395. Reiser, O. *Angew. Chem.* **1993**, *105*, 576. Pregosin, P. S.; Salzmann, R. *Coord. Chem. Rev.* **1996**, *155*, 35–68. Evans, D. A.; Campos, K. R.; Tedrow, J. S.; Michael, F. E.; Gange, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 7905–7920.

(4) Fagnou, K.; Lautens, M. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 27–47.

(5) Kündig, E. P.; Saudan, C. M.; Bernardinelli, G. *Angew. Chem.* **1999**, *111*, 1298. Kündig, E. P.; Saudan, C. M.; Viton, F. *Adv. Synth. Catal.* **2001**, *343*, 51.

(6) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Travaglia, M.; Zuccaccia, C.; Milani, B.; Corso, G.; Zangrando, E.; Mestroni, G.; Carfagna, C.; Formica, M. *Organometallics* **1999**, *18*, 3061–3069. Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1998**, *120*, 70.

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

(8) Olenyuk, B.; Lovin, M. D.; Whiteford, J. A.; Stang, P. J. J. *J. Am. Chem. Soc.* **1999**, *121*, 10434–10435.

(9) Gorman, C. B.; Smith, J. C.; Hager, M. W.; Parkhurst, B. L.; Sierzputowska-Gracz, H.; Haney, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 9958–9966.

(10) Stoop, R. M.; Bachmann, S.; Valentini, M.; Mezzetti, A. *Organometallics* **2000**, *19*, 4117–4126.

(11) Harris, R. K.; Kinnear, K. A.; Morris, G. A.; Stchedroff, M. J.; Samadi-Maybadi, A. *Chem. Commun.* **2001**, 2422–2423.

(12) Pichota, A.; Pregosin, P. S.; Valentini, M.; Wörle, M.; Seebach, D. *Angew. Chem.* **2000**, *112*, 157–160. Valentini, M.; Pregosin, P. S.; Ruegger, H. *Chem. Soc., Dalton Trans.* **2000**, 4507. Chen, Y.; Valentini, M.; Pregosin, P. S.; Albinati, A. *Inorg. Chim. Acta* **2002**, *327*, 4–14. Geldbach, T.; Pregosin, P. S.; Albinati, A.; Rominger, F. *Organometallics* **2001**, *20*, 1932–1938.

(13) Valentini, M.; Ruegger, H.; Pregosin, P. S. *Helv. Chim. Acta* **2001**, *84*, 2833–2853.

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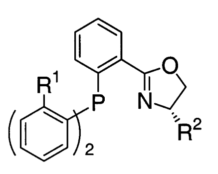
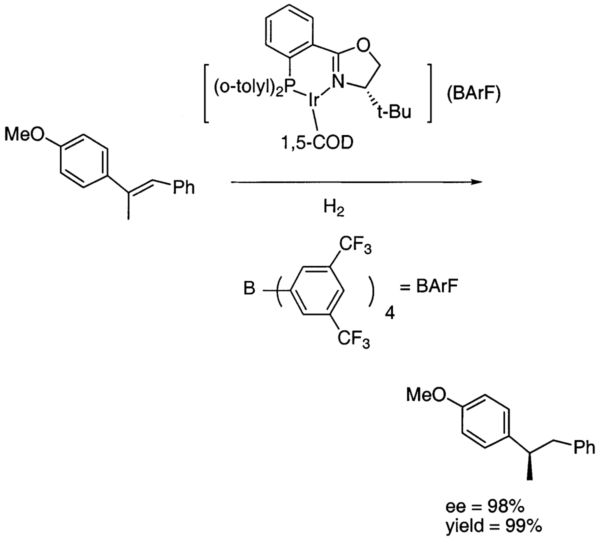
HOESY data, to follow how and where the anions and cations interact. We have recently shown that it is possible to use ^{31}P and, to a lesser extent, even ^{35}Cl, along with the more sensitive nuclei ^{1}H and ^{19}F, as NMR diffusion probes.[15] Nevertheless, the applications of the PGSE method remain sparse and there are no systematic studies for metal complexes in different solvents.

Chiral oxazoline complexes of the late transition metals are recognized as successful enantioselective catalysts in an increasing number of organic transformations.[16-20] Specifically, the Ir(I) catalyst precursor Ir(1,5-COD)(**1**)](BArF) has been shown to hydrogenate trisubstituted olefins in methylene chloride with excellent enantioselectivity (see eq 1).[21] There are relatively few homogeneous catalysts capable of efficiently reducing tri-and tetrasubstituted olefins.[22] However, the lifetime and the activity of the catalyst in eq 1 have been shown to depend on the nature of the anion, with PF_6^- having a rather shorter lifetime than the analogous $BArF^-$ derivative.[23]



1

$R^1 = CH_3$, R^2 = t-butyl

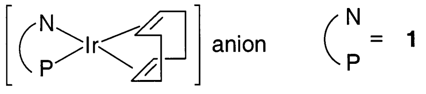


(1)

We have begun to investigate the source of this anion effect via ^{1}H and ^{19}F PGSE NMR diffusion results. For the solvent employed in the hydrogenation runs, methylene chloride, these data suggest that the anion may ion-pair to differing extents, thus differently affecting the mobility of the cation. We report here on detailed diffusion studies with different anions and solvents for mono- and trinuclear Ir compounds of **1** and suggest that methylene chloride is certainly a solvent in which ion-pairing can occur.

Results and Discussion

Diffusion Studies for [Ir(1,5-COD)(1)](anion), 2. Given its relative simplicity, it is convenient to start the diffusion section with data from the 1,5-COD compounds, **2**.



2

Results from the ^{1}H and ^{19}F PGSE measurements on five different salts of [Ir(1,5-COD)(**1**)](anion), **2a**−**e**, with the anions BF_4^-, **2a**, PF_6^-, **2b**, triflate (OTf^-), **2c**, 2,2′,3,3′,4-pentafluorotetraphenylborate, $B(C_6F_5)_4^-$, **2d**, and $BArF^-$, **2e**, in methanol, chloroform, dichloromethane, and 1,2-dichloroethane are given in Table 1.

In methanol, the strongest solvating and most polar of the three solvents, the observed diffusion values, D, for the cation $[Ir(1,5\text{-}COD)(\mathbf{1})]^+$, with all five anions, are found to be the same within experimental error, indicating independent movement of the cation in this solvent. The hydrodynamic radius, r_H, can be obtained from the Stokes−Einstein relation; see eq 2, where k is the Boltzmann constant and η is the viscosity.[24] This calculated r-value permits a direct comparison between diffusion measurements in different solvents, as it corrects for the different viscosities.[25] For **2a**−**e** in

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(14) Zuccaccia, C.; Bellachioma, G.; Cardaci, G.; Macchioni, A. *Organometallics* **2000**, *19*, 4663−4665. Macchioni, A.; Zuccaccia, C.; Clot, E.; Gruet, K.; Crabtree, R. H. *Organometallics* **2001**, *20*, 2367−2373. Bellachioma, G.; Cardaci, G.; D'Onofrio, F.; Macchioni, A.; Sabatini, S.; Zuccaccia, C. *Eur. J. Inorg. Chem.* **2001**, 1605−1611. Binotti, B.; Bellachioma, G.; Cardaci, G.; Macchioni, A.; Zuccaccia, C.; Foresti, E.; Sabatino, P. *Organometallics* **2002**, *21*, 346−354. Bellachioma, G.; Binotti, B.; Cardaci, G.; Carfagna, C.; Macchioni, A.; Sabatini, S.; Zuccaccia, C. *Inorg. Chim. Acta* **2002**, *330*, 44−51.

(15) Martinez-Viviente, E.; Rüegger, H., Pregosin, P. S. and López-Serrano, J. *Organometallics*, in press.

(16) Helmchen, G.; Pfaltz, A. *Acc. Chem. Res.* **2000**, *33*, 336−345. Tye, H. *J. Chem. Soc., Perkin Trans. 1* **2000**, 275−298. Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1−45. All these references offer useful overviews.

(17) Helmchen, G. *J. Organomet. Chem.* **1999**, *576*, 203−214.

(18) Nishibayashi, Y.; Takei, I.; Uemura, S.; Hidai, M. *Organometallics* **1999**, *18*, 2291−2293.

(19) Langer, T.; Helmchen, G. *Tetrahedron Lett.* **1996**, *37*, 1381−1384. Nishibayashi, Y.; Takei, I.; Uemura, S.; Hidai, M. *Organometallics* **1998**, *17*, 3420−3422. Nishibayashi, Y.; Segawa, K.; Takada, H.; Ohe, K.; Uemura, S. *Chem. Commun.* **1996**, 847−848. Nishibayashi, Y.; Segawa, K.; Ohe, K.; Uemura, S. *Organometallics* **1995**, *14*, 5486−5487.

(20) Ghosh, A. K.; Mathivanan, P.; Cappiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1−45. Ogasawara, M.; Yoshida, K.; Kamei, H.; Kato, K.; Uozumi, Y.; Hayashi, T. *Tetrahedron: Asymmetry* **1998**, *9*, 1779−1787. Braunstein, P.; Naud, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 680−699. Pfaltz, A. *Acta Chim. Scand.* **1996**, *50*, 189−194.

(21) Lightfoot, A.; Schnider, P.; Pfaltz, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2897−2899. Cozzi, P. G.; Zimmermann, N.; Hilgraf, R.; Schaffner, S.; Pfaltz, A. *Adv. Synth. Catal.* **2001**, *343*, 450−454. Blankenstein, J.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4445−4447. Menges, F.; Pfaltz, A. *Adv. Synth. Catal.* **2002**, *344*, 40−44. Blankenstein, J.; Hilgraf, R.; Hörmann, E.; McIntyre, S.; Menges, F.; Pfaltz, A.; Schönleber, M.; Smidt, S. P.; Wüstenberg, B.; Zimmermann, N. *Adv. Synth. Catal.*, in press.

(22) Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331−338.

(23) Blackmond, D. G.; Lightfoot, A.; Pfaltz, A.; Rosner, T.; Schnider, P.; Zimmermann, N. *Chirality* **2000**, *12*, 442−449.

(24) It has been suggested that the factor 6 in eq 2 is not valid for small species whose van der Waals radii are <5 Å (Edward, J. T. *J. Chem. Educ.* **1970**, *47*, 261. Ue, M. *J. Electrochem. Soc.* **1994**, *141*, 3336). To be consistent and facilitate comparisons, we have used eq 2 as shown.

Table 1. Diffusion Values,[a] Hydrodynamic Radii, and Volumes for **2a−e**

	CD$_3$OD				CDCl$_3$			
	compd	D	r_H (Å)	10^2V (Å^3)	compd	D	r_H (Å)	10^2V (Å^3)
cation (^{1}H)	**2a,** BF$_4$	7.58(6)	5.5(1)	7.0	**2a,** BF$_4$	7.23(6)	5.7(1)	7.7
anion (^{19}F)		16.62(6)	2.5(1)	0.6		7.43(6)	5.6(1)	7.4
cation (^{1}H)	**2b,** PF$_6$	7.57(6)	5.5(1)	7.0	**2b,** PF$_6$	7.13(6)	5.8(1)	8.2
anion (^{19}F)		15.82(6)	2.6(1)	0.7		7.21(6)	5.8(1)	8.2
cation (^{1}H)	**2c,** OTf	7.65(6)	5.5(1)	7.0	**2c,** OTf	7.04(6)	5.9(1)	8.6
anion (^{19}F)		12.95(6)	3.2(1)	1.4		7.05(6)	5.9(1)	8.6
cation (^{1}H)	**2d,** B(C$_6$F$_5$)$_4$	7.62(6)	5.5(1)	7.0	**2d,** B(C$_6$F$_5$)$_4$	6.06(6)	6.9(1)	14
anion (^{19}F)		7.69(6)	5.4(1)	6.6		5.91(6)	7.0(1)	14
cation (^{1}H)	**2e,** BArF	7.55(6)	5.5(1)	7.0	**2e,** BArF	5.70(6)	7.3(1)	16
anion (^{1}H)		6.77(6)	6.2(1)	10		5.63(6)	7.4(1)	17
anion (^{19}F)		6.67(6)	6.2(1)	10		5.59(6)	7.4(1)	17

	CD$_2$Cl$_2$				ClCH$_2$CH$_2$Cl			
	compd	D	r_H (Å)	10^2V (Å^3)	compd	D	r_H (Å)	10^2V (Å^3)
cation (^{1}H)	**2a,** BF$_4$	9.72(6)	5.5(1)	7.0	**2a,** BF$_4$	5.44(6)	5.4(1)	6.6
anion (^{19}F)		13.79(6)	3.9(1)	2.5		8.52(6)	3.4(1)	1.6
cation (^{1}H)	**2b,** PF$_6$	9.72(6)	5.5(1)	7.0	**2b,** PF$_6$	5.37(6)	5.4(1)	6.6
anion (^{19}F)		13.27(6)	4.0(1)	2.7		8.00(6)	3.6(1)	1.9
cation (^{1}H)	**2c,** OTf	9.71(6)	5.5(1)	7.0	**2c,** OTf	5.36(6)	5.4(1)	6.6
anion (^{19}F)		12.52(6)	4.3(1)	3.3		7.67(6)	3.8(1)	2.3
cation (^{1}H)	**2d,** B(C$_6$F$_5$)$_4$	9.24(6)	5.8(1)	8.2	**2d,** B(C$_6$F$_5$)$_4$	5.17(6)	5.7(1)	7.7
anion (^{19}F)		9.12(6)	5.9(1)	8.6		5.08(6)	5.8(1)	8.2
cation (^{1}H)	**2e,** BArF	9.20(6)	5.8(1)	8.2	**2e,** BarF	5.09(6)	5.7(1)	7.7
anion (^{1}H)		8.40(6)	6.4(1)	11				
anion (^{19}F)		8.43(6)	6.4(1)	11		4.71(6)	6.2(1)	10

[a] Measured at 400 MHz, 2 mM; D values, 10^{-10} m^2 s^{-1}.

methanol the cationic radii are found to be ca. 5.5 Å. On the basis of the observed solution r-values, one can estimate the corresponding cationic and anionic volumes. For the anions, the volumes vary in size, increasing (as expected) in the order $BF_4^- < PF_6^- < OTf^- < B(C_6F_5)_4^- < BArF^-$; however, as these anions are likely to be solvated, we take these radii and volumes as an upper limit.[26]

$$r_H = \frac{kT}{6\pi\eta D} \tag{2}$$

In chloroform, we note that the anion and cation afford almost the same observed D-value within each salt and, thus, the same hydrodynamic radius. The calculated volumes (assuming molecular spheres) correspond roughly to the sum of the cationic and anionic volumes in methanol. For the $B(C_6F_5)_4^-$ anion (ca. 17 × 10^2 Å^3) and for the BArF$^-$ anion (ca. 14 × 10^2 Å^3), the volumes are now ca. 70−100% greater than those found for either the cation or anion in methanol. Clearly, strong ion-pairing exists in chloroform for **2a−e**, and the cation and anion are moving together. We have noted this type of ion-pairing in chloroform previously.[13,15]

In methylene chloride, the solvent often used in hydrogenation chemistry, the diffusion data suggest a mixed picture for the five anions (see Figure 1). The results for the cations of the BF_4^-, PF_6^-, and OTf$^-$ salts reveal radii and molecular volumes (5.5 Å and 7 × 10^2 Å^3, respectively) which are essentially identical to those observed in methanol. Clearly, these anions seem unimportant for the translation of the cation in this solvent, giving the impression of little or no ion-pairing. However, relative to the methanol data, the BF_4^-, PF_6^-, and OTf$^-$ anions have larger radii. Possibly, there may be a small amount ion-pairing.[27]

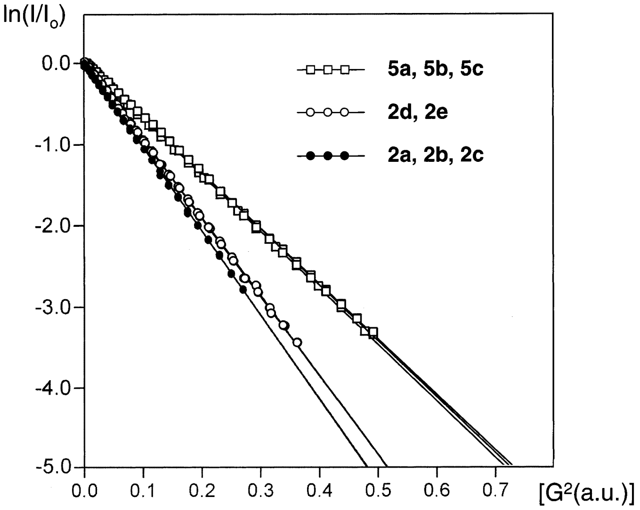

Figure 1. Plot of ln(I/I_o) vs arbitrary units proportional to the square of the gradient amplitude, for ^{1}H-PGSE diffusion measurements on 2 mM CD$_2$Cl$_2$ solutions of **2a−c** (black circles), **2d,e** (white circles), and **5a−c** (squares), showing the different intensity decays obtained for the cationic fragments in these three groups of compounds.

On the other hand, the radii and volumes for the salts possessing the larger boron-based anions $B(C_6F_5)_4^-$ and

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(25) The viscosities have been taken from the on line version of the following: *Chemical Properties Handbook*; McGraw-Hill: New York, 1999 (http://www.knovel.com). The values at 300 K are the following (kg s^{-1} m^{-1}): for methylene chloride, 0.410; for chloroform, 0.529; for 1,2-dichloroethane, 0.751; for methanol, 0.526.

(26) In a given solvent, a direct comparison of D-values is useful. For solvents of different viscosity, the radii or volumes are more indicative, as they contain a viscosity correction; however, these calculated radii and volumes make no allowance for solvation and/or electrostatic effects. Consequently, the value suggested in Table 1 for the triflate anion in methanol is probably larger than that which might be estimated from X-ray crystallography on a suitable triflate salt, due to H-bonding to the solvent.

(27) A minor ion-pairing component will strongly affect the averaged D-value for the relatively small anion but scarcely affect the relatively large cation. Further, adventitious water might bring two anions together via a hydrogen bond. See also note 24.

Table 2. Diffusion Data[a] for the Trinuclear Hydride Compound **3a**

	CD$_3$OD				CDCl$_3$			
	compd	D	r_H (Å)	$10^2 V$ (Å^3)	compd	D	r_H (Å)	$10^2 V$ (Å^3)
cation (^{1}H)	**5a**, (PF$_6$)(OTf)[b]	5.09(6)	8.2(1)	23	**5a**, (PF$_6$)(OTf)[b]	4.64(6)	8.9(1)	29
PF$_6$ (^{19}F)		15.16(6)	2.7(1)	0.8		4.70(6)	8.8(1)	29
OTf (^{19}F)		12.34(6)	3.4(1)	1.6		4.71(6)	8.8(1)	29
cation (^{1}H)	**5b**, (PF$_6$)$_2$[b]	5.06(6)	8.2(1)	23	**5b**, (PF$_6$)$_2$	4.94(6)	8.4(1)	25
PF$_6$ (^{19}F)		15.51(6)	2.7(1)	0.8		5.12(6)	8.1(1)	22
cation (^{1}H)	**5c**, (OTf)$_2$	5.10(6)	8.2(1)	23	**5c**, (OTf)$_2$	4.33(6)	9.6(1)	37
OTf (^{19}F)		12.12(6)	3.4(1)	1.6		4.43(6)	9.4(1)	35

	CD$_2$Cl$_2$				ClCH$_2$CH$_2$Cl			
	compd	D	r_H (Å)	$10^2 V$ (Å^3)	compd	D	r_H (Å)	$10^2 V$ (Å^3)
cation (^{1}H)	**5a**, (PF$_6$)(OTf)	6.43(6)	8.3(1)	24	**5a**, (PF$_6$)(OTf)	3.50(6)	8.3(1)	24
PF$_6$ (^{19}F)		9.65(6)	5.5(1)	7.0		6.04(6)	4.8(1)	4.6
OTf (^{19}F)		9.82(6)	5.5(1)	7.0		6.19(6)	4.7(1)	4.3
cation (^{1}H)	**5b**, (PF$_6$)$_2$	6.53(6)	8.2(1)	23	**5b**, (PF$_6$)$_2$	3.57(6)	8.2(1)	23
PF$_6$ (^{19}F)		9.57(6)	5.6(1)	7.3		6.21(6)	4.7(1)	4.3
cation (^{1}H)	**5c**, (OTf)$_2$	6.47(6)	8.3(1)	24	**5c**, (OTf)$_2$	3.52(6)	8.3(1)	24
OTf (^{19}F)		9.84(6)	5.4(1)	6.6		5.83(6)	5.0(1)	5.2

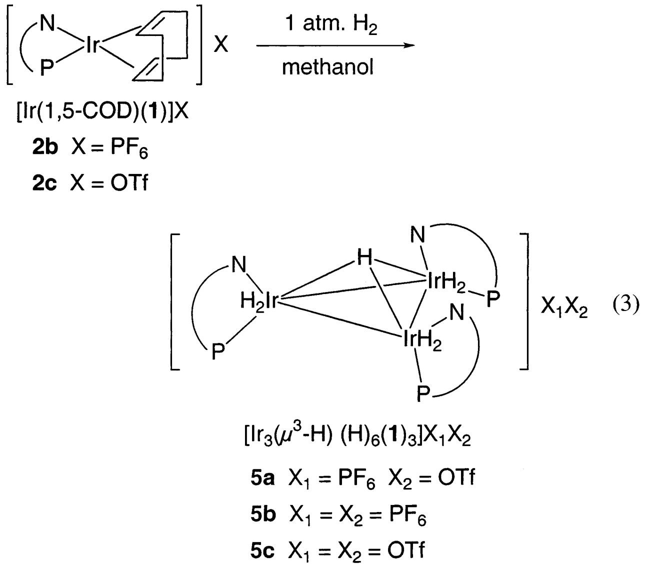
[a] 400 MHz, 2mM; D values, 10^{-10} m^2 s^{-1}. [b] Saturated solution (less than 2 mM).

BArF$^-$ increase modestly for *both* cation and anion, relative to the methanol data. These differences indicate some—but not complete—ion-pairing. The volume increases for the cations in **2d**,**e** on going from methanol (ca. 7×10^2 Å^3) to methylene chloride (ca, 8×10^2 Å^3) are of the order of ca. 10–15%.

In 1,2-dichloroethane, we find similar results to those reported for methylene chloride; i.e., the boron-based anions B(C$_6$F$_5$)$_4^-$ and BArF$^-$ reveal increases in radii and volumes for *both* cation and anion. For the smaller anions there seems to be little of no effect on the diffusion of the cation. We presume that these data also reflect partial ion-pairing in this solvent.

Diffusion Studies on Trinuclear Ir–Hydride Complexes, 5. It is known that mononuclear iridium complexes, e.g., [Ir(1,5-COD)(P,N ligand types)](anion), react under hydrogen in solution to afford trinuclear hydrido-cluster complexes. Crabtree and co-workers[28] and Pignolet and co-workers[29] have reported preparative, NMR, and X-ray diffraction studies for the cationic species [Ir$_3$(μ-H)H$_6$(PCy$_3$)$_3$(pyridine)$_3$](PF$_6$)$_2$, **3**, and [Ir$_3$(μ-H)H$_6$(PN)$_3$](BF$_4$)$_2$, **4**, PN = 1-(2-pyridyl)-2-(diphenylphosphino)ethane, respectively. These trinuclear bridging hydride complexes contain three "IrH$_2$(PCy$_3$)(pyridine)" and three "IrH$_2$(PN)" units, respectively, held together by Ir–Ir metal bonds and the bridging hydride. These clusters are thought not to be catalytically active in hydrogenation chemistry.

We have recently prepared several trinuclear clusters, **5**, from the 1,5-COD complexes, **2**, as shown in eq 3.[29] The mixed salt [Ir$_3$(μ-H)H$_6$(**1**)$_3$](PF$_6$)(OTf), **5a**, was prepared from **2c** in the presence of excess KPF$_6$. Both the solid- and solution-state structures for **5a** were determined via X-ray diffraction and NOESY methods, respectively.[30] The anions come quite close to the cationic species in the solid state. In **5a**, a close contact of ca. 2.46 Å is found between an F atom of the PF$_6^-$ anion and the aromatic –H *para* to the oxazoline moiety, and another contact of ca. 2.85 Å between an O atom of the triflate to the same H atom of another aryl ring is also found.



[Ir(1,5-COD)(**1**)]X
2b X = PF$_6$
2c X = OTf

[Ir$_3$(μ^3-H) (H)$_6$(**1**)$_3$]X$_1$X$_2$ (3)
5a X$_1$ = PF$_6$ X$_2$ = OTf
5b X$_1$ = X$_2$ = PF$_6$
5c X$_1$ = X$_2$ = OTf

The diffusion results for **5a**–**c** in the same four solvents are given in Table 2. As expected, these data confirm that the cation possesses a considerably larger volume relative to **2a**–**e** (see Figure 1). In methanol, the cations of **5a**–**c** all afford the same volume, $V = 23 \times 10^2$ Å^3, more than three times the volume of the cation in **2a**–**e**. On the other hand, the calculated volumes for the PF$_6^-$ and OTf$^-$ anions in this solvent are very similar to those found in **2b,c**.

In chloroform, the volumes of the dications increase due to ion-pairing, and the anion is now strongly associated with the cation and translating at about the same rate.[31]

In methylene chloride and 1,2-dichloroethane, the dication of **5a**–**c** affords a hydrodynamic radius similar or identical to the one observed in methanol. However, the effective

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(28) Chodosh, D. F.; Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1978**, *161*, C67–C70.

(29) Wang, H.; Casalnuovo, A. L.; Johnson, B. J.; Mueting, A. M.; Pignolet, L. H. *Inorg. Chem.* **1988**, *27*, 325–331. Wang, H. H.; Pignolet, L. H. *Inorg. Chem.* **1980**, *19*, 1470.

(30) Smidt, S. P.; Pfaltz, A.; Martínez-Viviente, E.; Pregosin, P. S.; Albinati, A. *Organometallics*, in press.

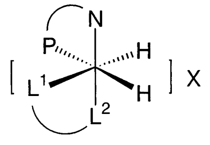
Table 3. Selected Diffusion Data[a] for the Dihydride Compounds **6a,b** in CD_2Cl_2

	6a, PF_6			**6b,** BArF		
	D	r_H (Å)	10^2V (Å^3)	D	r_H (Å)	10^2V (Å^3)
cation (^{1}H)	9.09(6)	5.9(1)	8.6	8.09(6)	6.6(1)	12
anion (^{19}F)	13.65(6)	3.9(1)	2.5	7.93(6)	6.8(1)	13

[a] 400 MHz, approximately 2 mM; *D* values, 10^{-10} m^2 s^{-1}.

volume of the anion has changed by more than a factor of 7 due to some ion-pairing in this solvent.[27]

In our earlier PGSE study on a model complex,[32] $[IrH_2(4,4'\text{-dimethylbipyridine})(\mathbf{1})](PF_6$ or BArF), **6a** or **6b**, there was also evidence for anion effects on the mobility of the cation in CD_2Cl_2 (see Table 3).



X = PF_6 **6a**
X = BArF **6b**
L^1L^2 = 4,4'-dimethyl bipyridiyl

The data in Tables 1−3 represent the most comprehensive anion/solvent dependence of diffusion data yet reported.

HOESY Results. To further explore the observed solvent dependence of the ion-pairing, we measured ^{1}H, ^{19}F HOESY spectra for $[Ir_3(\mu\text{-}H)H_6(\mathbf{1})_3](OTf)_2$, **5c**, in chloroform, methylene chloride, and methanol. If indeed there is more ion-pairing in chloroform, we expect this difference to be reflected via the various possible Overhauser contacts between the cation and anion.[33] Figure 2 compares the HOESY spectra in $CDCl_3$ and CD_2Cl_2 for equal concentrations, number of scans, and plotting cutoff levels. It can be readily seen that the cross-peaks in $CDCl_3$ are significantly more intense than in CD_2Cl_2. Specifically, the interactions from the two *o*-tolyl methyl groups are much stronger in chloroform, and for the diastereotopic OCH_2 protons, one observes modest interactions in chloroform but nothing at all in methylene chloride. This is consistent with closer contacts in $CDCl_3$ due to increased ion-pairing. The spectrum in methanol afforded no observable cross-peaks, as expected for a strongly solvating solvent. Interestingly, even in $CDCl_3$ we find no cross-peaks from the three nonequivalent hydride ligands to the triflate trifluoromethyl group. The most intense contacts arise from the interactions with the aryl groups, so that we assume that the anion approaches the cation via the 1,2-disubstituted aryl backbone moiety.

Conclusions. It is now clear that, for the five anions under consideration, there is a strong tendency to form ion-pairs in chloroform solution. In methylene chloride and 1,2-dichloroethane there exists significant, but not complete, ion-pairing. While the smaller BF_4^-, PF_6^-, and OTf^- anions in the 1,5-COD compounds **2a−c** do not affect the translation of the cation in methylene chloride, the larger $BArF^-$ and $B(C_6F_5)_4^-$ anions in **2d**,**e** slow the motions of the cations. A similar effect is observed for the small iridium cluster compounds **5a−c**. It would seem that in all cases there is some ion-pairing in methylene chloride.

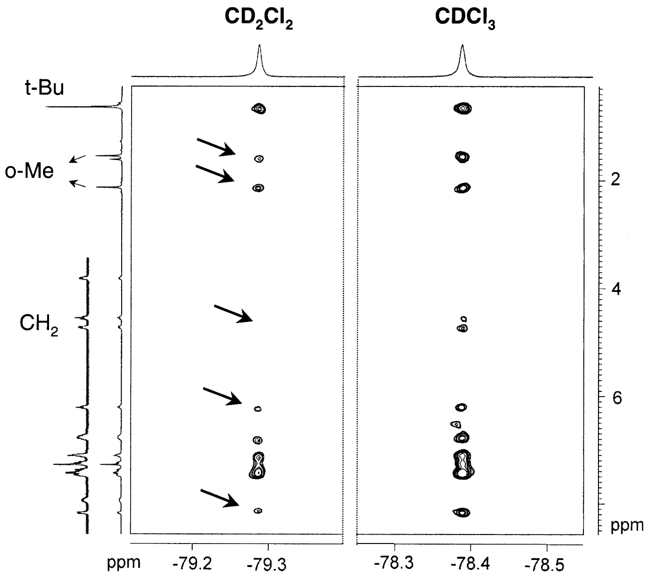


Figure 2. ^{1}H−^{19}F HOESYspectra of **5c** in CD_2Cl_2 and $CDCl_3$, showing the different Overhauser contacts (in number and intensity) between cation and anion.

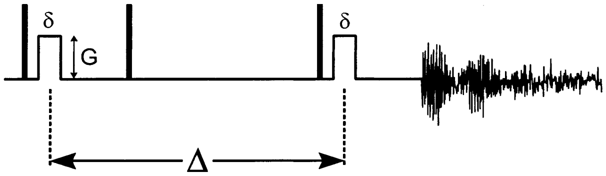


Figure 3. Pulse sequence for the PGSE measurements. The dark vertical bars represent the three 90° pulses, and the broader open bars represent the gradient pulses.

Clearly, we cannot directly extrapolate our diffusion data to catalytic solutions. However, if the mechanism of the formation of an inactive Ir_3 cluster requires that two fairly large species associate and subsequently add yet another large moiety, then, in methylene chloride, these processes are likely to be faster for a complex containing a relatively small rapidly moving anion, such as PF_6^-, than for a larger, partially ion-paired complex with $BArF^-$.

Experimental Section

All the diffusion measurements were performed 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, and its strength varied automatically in the course of the experiments. These were carried out without spinning and with the airflow disconnected.

The Hahn or stimulated echo sequence (Figure 3) was used.[34,35] Moving molecules cause attenuated signal intensities since they

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(31) As expected, the total volume for the triflate salt is larger than that for the hexafluorophosphate salt.

(32) Drago, D.; Pregosin, P. S.; Pfaltz, A. *Chem. Commun.* **2002**, 286−287.

(33) Zuccaccia, C.; Ballachioma, G.; Cardaci, G.; Macchioni, A.; Price, W. S. *J. Am. Chem. Soc.* **2001**, *123*, 11020.

(34) Price, W. S. *Ann. Rep. NMR Spectrosc.* **1996**, *32*, 51−142.

(35) Stilbs, P. *Prog. NMR Spectrosc.* **1987**, *19*, 1.

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.[13] Equation 4 relates the observed intensity changes, $\ln(I/I_o)$, as a function of the variables used.[36] D is obtained from the slope of the regression line $\ln(I/I_o)$ vs G^2. All of the data leading to the reported D-values afforded lines whose correlation coefficients were above 0.999.

$$\ln\left(\frac{I}{I_o}\right) = -(\gamma\delta)^2\left(\Delta - \frac{\delta}{3}\right)DG^2 \qquad (4)$$

The calibration of the spectrometer was carried out via a diffusion measurement of HDO in D_2O, which afforded a slope of 2.022×10^{-4}. The D of each sample was then calculated according to eq 5, where $D_{HDO} = 1.9 \times 10^{-9}$ m^2 s^{-1}.[37] The correction factor for the ^{19}F-PGSE measurements is $(\gamma(^1H)/\gamma(^{19}F))^2 = 1.129$.

$$D = \left(\frac{\gamma(^1H)}{\gamma(\text{obs})}\right)^2 \frac{m_{obs}D_{HDO}}{m_{HDO}} \qquad (5)$$

For all the measurements on **2** and **5** a diffusion time Δ of 167.75 ms and a gradient length δ of 1.75 ms were used. The gradient strength was incremented in 2 or 3% steps, so that 25−35 points could be used for regression anaysis. For ^{19}F, T_1 was always determined before the measurement and the recovery delay D_1 set to $5T_1$. For ^{1}H, D_1 was always 5 s. The number of scans per increment was usually 16 for ^{1}H and between 12 or 16 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's). We note two exceptions: (a) ^{1}H measurements in nondeuterated 1,2-dichloroethane, where only the region between 2.5 and −0.5 ppm was measured and 40 scans/increment were accumulated; (b) the ^{19}F measurements on the $B(C_6F_5)_4^-$ anion, which were carried out on the triplet signal at ca. −164 ppm, with 160−200 scans/increment. Sample concentrations are noted in the tables.

The ^{19}F−^{1}H HOESY measurements were carried on a 400 MHz Bruker AVANCE spectrometer equipped with a doubly tuned (^{1}H, ^{19}F) TXI probe. A mixing time of 600 ms was used. The triflate ^{19}F T_1 was 3 s in chloroform and 5 s in dichloromethane. The concentration of the sample was 5 mM, the number of scans 148, and the number of increments in the F1 dimension 200.

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(36) 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.

(37) Tyrrell, H. J. W.; Harris, K. R. *Diffusion in Liquids*; Butterworths: London, 1984.