

Selective anion effects in chiral complexes of iridium *via* diffusion and HOESY data: relevance to catalysis†

Daniela Drago,^a Paul S. Pregosin^{*a} and Andreas Pfaltz^b

^a Laboratory of Inorganic Chemistry, ETH HCI, Hönggerberg CH-8093, Zürich, Switzerland.

E-mail: PREGOSIN@INORG.CHEM.ETHZ.CH

^b Laboratory of Organic Chemistry, University of Basel, CH-4056 Basel, Switzerland

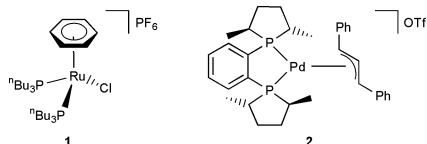
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¹H and ¹⁹F Pulsed Gradient Spin Echo (PGSE) diffusion data, together with ¹H, ¹⁹F-HOESY results are shown to distinguish between different types of anion/cation interactions in chiral dihydrido-P,N-complexes of Ir(III); in CD₂Cl₂ the diffusion coefficients, *D*, for the BArF and the Ir-cation suggest ion-pairing whereas the *D*-values for PF₆⁻ reveal independent motion; the PF₆⁻ approaches the cation *via* a specific pathway; the combined PGSE/HOESY approach offers a unique opportunity for exploring anion effects in organometallic/catalytic chemistry.

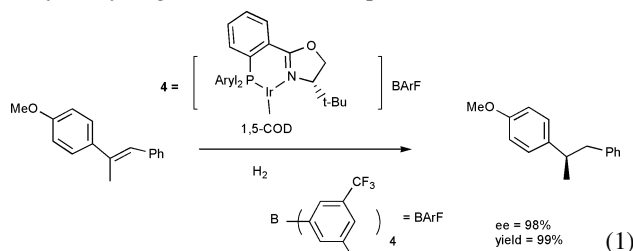
It is not unusual to find that both the structure and reactivity of a transition metal cationic salt depend upon the anion, since anions may be either weakly or strongly co-ordinating. In several homogeneously catalysed reactions^{1,2} one finds that the anion plays a significant role, *e.g.* reaction rates may be excellent or only modest.

We have recently suggested³ that Pulsed Gradient Spin Echo (PGSE^{4,5}) diffusion data can be useful in determining molecular volume. If the complex possesses a fluorine containing salt (BF₄⁻ or PF₆⁻ *etc.*) one can use PGSE data from both ¹H (for the cation) and ¹⁹F (for the anion) to obtain a measure of the ion-pairing,^{6,7} *e.g.* for **1** and **2** the ¹⁹F diffusion data reveal that these



anions move at *ca.* the same rate as their respective larger cations in CDCl₃ solution.⁵ Consequently, these salts exist as ion-pairs.

Recently, a dependence of the reactivity on the anion in Ir-catalysed hydrogenation, shown in eqn. (1), has been observed.⁷

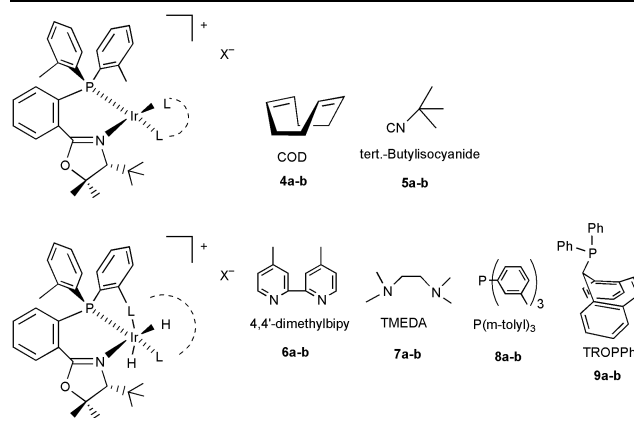


Using the P,N 'PHOX' ligand, **3**,⁷ shown complexed to Ir, Aryl = *o*-tolyl, the rate of hydrogenation is faster with the anion BArF than with PF₆⁻. We show here that ¹H and ¹⁹F PGSE and HOESY measurements on the model compounds **4–9**, anion = PF₆⁻ or BArF, reveal marked differences in how these two anions interact with the corresponding cations.

The model complexes IrH₂(chelate)(3), **6–9**, were prepared by standard procedures.⁸ Table 1 gives PGSE data from 48 different measurements,⁹ including those for the four-coor-

dinate Ir(I) models [Ir(1,5-COD)(3)](anion), **4** and [Ir(CN^t-Bu)(3)](anion), **5**. The diffusion results confirm that the cations move slower with increasing molecular size, but that the PF₆⁻ anion moves much faster and thus independently of the cation (see Fig. 1). In a direct comparison, *e.g.* [Ir(CN^t-Bu)(3)]PF₆, **5a** vs. [Ir(CN^t-Bu)(3)]BArF, **5b** or the P(*m*-tolyl)₃ compounds **8a** vs. **8b**, the two cations show almost identical diffusion constants, but the two anions move at very different rates. The data for the BArF anion in **6b** and **9b** suggest ion-pairs;¹⁰ however, in **4b**, **5b**, **7b** and **8b** it is likely that the BArF anion is moving independently.¹⁰ In the two four-co-ordinate BArF complexes, **4b** and **5b**, we observe HOESY contacts from the BArF to the cation. Therefore, even though **4b** and **5b** are not ion-paired, the BArF is close-by. There are no close contacts

Table 1 Diffusion data for **4–9**



| Compound | Nucleus | Fragment | 10 ⁻¹⁰ <i>D</i> /m ² s ⁻¹ |
|--|-----------------|------------------------------|--|
| Ir(COD)(3)PF ₆ 4a | ¹ H | Cation | 9.92(6) |
| | ¹⁹ F | PF ₆ ⁻ | 13.78(6) |
| Ir(COD)(3)BArF 4b | ¹ H | Cation | 9.73(6) |
| | ¹ H | BArF | 8.90(6) |
| Ir(CN ^t -Bu)(3)PF ₆ 5a | ¹ H | Cation | 9.14(6) |
| | ¹⁹ F | PF ₆ ⁻ | 13.84(6) |
| Ir(CN ^t -Bu)(3)BArF 5b | ¹ H | Cation | 9.09 (6) |
| | ¹ H | BArF | 8.92(6) |
| IrH ₂ (Mebipy)(3)PF ₆ 6a | ¹ H | Cation | 9.05 (6) |
| | ¹⁹ F | PF ₆ ⁻ | 13.65(6) |
| IrH ₂ (Mebipy)(3)BArF 6b | ¹ H | Cation | 8.09(6) |
| | ¹ H | BArF | 7.93(6) |
| IrH ₂ (TMEDA)(3)PF ₆ 7a | ¹ H | cation | 9.67(6) |
| | ¹⁹ F | PF ₆ ⁻ | 13.18(6) |
| IrH ₂ (TMEDA)(3)BArF 7b | ¹ H | cation | 9.43(6) |
| | ¹ H | BArF | 8.55(6) |
| IrH ₂ (PAr ₃) ₂ (3)PF ₆ 8a | ¹ H | cation | 7.70(6) |
| | ¹⁹ F | PF ₆ ⁻ | 13.43(6) |
| IrH ₂ (PAr ₃) ₂ (3)BArF 8b | ¹ H | Cation | 7.87(6) |
| | ¹ H | BArF | 8.13(6) |
| IrH ₂ (TROPPh ₂)(3)PF ₆ 9a | ¹ H | cation | 8.54(6) |
| | ¹⁹ F | PF ₆ ⁻ | 14.27(6) |
| IrH ₂ (TROPPh ₂)(3)BArF 9b | ¹ H | cation | 7.96(6) |
| | ¹ H | BArF | 8.24(6) |

† Electronic supplementary information (ESI) available: spectroscopic data for **6b**. See <http://www.rsc.org/suppdata/cc/b1/b110066c/>

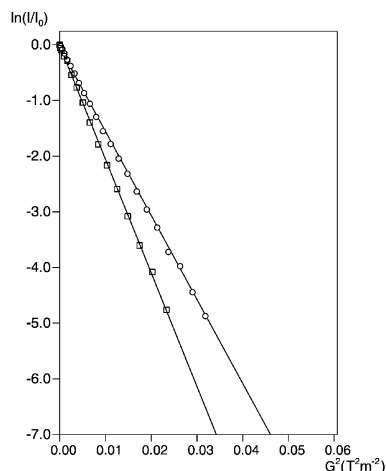
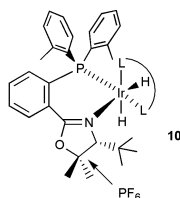


Fig. 1 PGSE diffusion data for **6a** showing that the PF_6^- anion (\square) moves much faster than the slower Ir-cation (\circ).

between the BARf and the dihydro Ir(III)-cations in any of these complexes. The ^1H , ^{19}F -HOESY data, e.g. in Fig. 2, for the PF_6^- anion indicate a specific interaction with the cation, i.e. in



4a–7a the PF_6^- anion does not make a random approach (see **10**) but rather moves toward the cation *via* the oxazoline ring.¹¹ For **8** and **9** the large phosphine ligands¹² block this PF_6^- approach completely. This regiospecific approach is interesting but need not be of catalytic relevance.

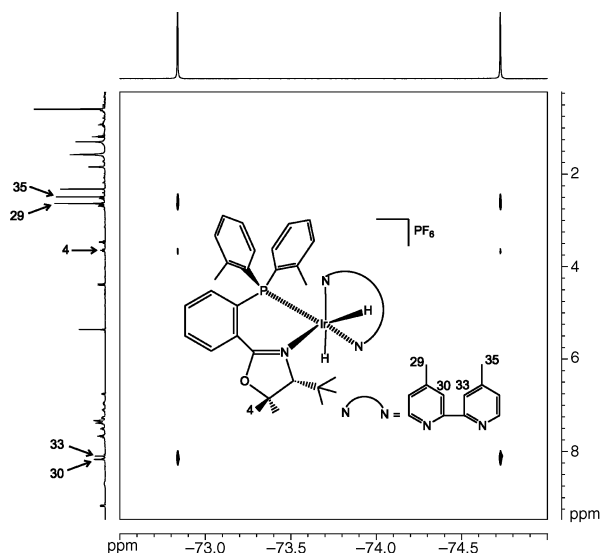


Fig. 2 HOESY spectrum of **6a**. There are three types of contacts, one weak and two strong, to: (a) oxazoline methine H-4, *trans* to the ^tBu group; (b) the bipyridyl methyls H-29 and H-35 and (c) the $=\text{CH}$ H-30 and H-33 from the bipyridyl moiety. The PF_6^- has no contacts to the hydride ligands (400 MHz, CD_2Cl_2).

We assume that the catalytically active Ir-species are deactivated *via* trimerization to bridging hydrides.¹³ For the cation/ PF_6^- combination, the cation is more available for intermolecular reaction in that the anion is often further away from the metal. For the cation/BARf pair, ion-pairing is possible, although it may be sufficient for the large BARf to be

close enough to slow the intermolecular attack leading to the bridging hydride. We believe this combined diffusion/HOESY approach to anion effects in catalysis to be unique. The results do not directly explain the observed differences in catalytic activity since we employed model compounds; however, the data from this approach offer a new and more direct way of studying this type of problem.

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- Synthesis of 6b**: To $[\text{Ir}(1,5\text{-COD})(3)](\text{BARf})$ (30 mg, 0.0190 mmol) in distilled acetone (0.8 ml) was added 4,4'-dimethyl-2,2'-bipyridine (3.5 mg, 0.0190 mmol). Hydrogen gas was then bubbled gently through the solution at RT for 3.5 h. The solvent was removed *in vacuo* and the yellow residue washed with pentane. Recrystallization from ether/pentane gave an analytically pure product. Yield: 25 mg (79%).
- The anion (^{19}F for PF_6^- , ^1H for BARf) and the cation (^1H) are measured separately, twice, with 100 ms and 150 ms delays. The diffusion constant given represents an average of the two runs. The D -values stem from 22–25 points per measurement to characterize the line and our R -values are always >98%. The complexes were dissolved in distilled CD_2Cl_2 and measured without spinning. The shape of the gradient was rectangular, its length was 5 ms, and the strength was varied in the course of the experiment. The diffusion coefficients reported in Table 1 were estimated using the diffusion coefficient of HDO in D_2O as a reference. Measuring the HDO and the complex under the same conditions allows one to use the following simple relationship shown to obtain the D -value of the complex.

$$\left(\frac{m_{\text{HDO}}}{m_{\text{compl}}}\right) = \left[\frac{m_{\text{HDO}}/(\Delta - \delta/3)}{m_{\text{compl}}/(\Delta - \delta/3)}\right] = \frac{D_{\text{HDO}}}{D_{\text{compl}}}$$
- We suggest ion-pairing when the BARf anion diffusion constant is close to that of the cation and simultaneously when the diffusion constant for the cation decreases on going from the PF_6^- to the BARf anion.
- During the preparation of this communication a report on the use of HOESY in connection with ion-pairing in $[\text{IrH}_2(\text{bipy})(\text{PPh}_3)_2](\text{anion})$ appeared: A. Macchioni, C. Zuccaccia, E. Clot, K. Gruet and R. H. Crabtree, *Organometallics*, 2001, **20**, 2367. This paper emphasizes the placement of the anion near the bipy and away from the hydrides. There are no contacts between the hydrides and either PF_6^- or BARf in **6–9** so that the anion is remote from the hydride ligands.
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