Letter

Direct observation of an equilibrium between two anion-cation orientations in olefin Pt(II) complex ion pairs by HOESY NMR spectroscopy†

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Received (in New Haven, CT, USA) 5th December 2002, Accepted 9th December 2002
First published as an Advance Article on the web 22nd January 2003

The solution structure of the two intimate ion pairs present in solution for [PtMe(η^2-olefin)(α-diimine)]BF_4 compounds, their relative abundance and the consequent thermodynamic equilibrium parameters have been determined by a quantitative detection of H···F interionic dipolar interactions in the $^{19}F,^1H$-HOESY NMR spectra.

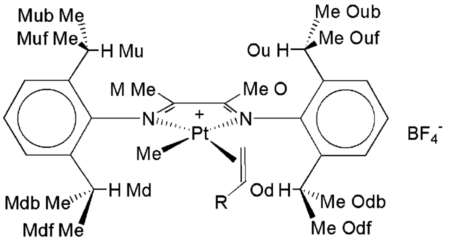
Non-covalent interactions[1] profoundly affect the structure and reactivity of ionic transition metal complexes.[2]

With the ultimate aim of interpreting the changes in reactivity induced by anion-cation interactions based on the interionic structure (anion-cation relative orientation), we have been developing investigative methodologies since 1996[3] for studying transition metal complex ion pairs in the environment where they "work", that is, in solution. The methodologies are based on the detection of homo- and hetero-nuclear interactions in the NOESY and HOESY NMR spectra.[4] We have found that detailed structural information can be obtained and that very often a single anion-cation orientation is dominant in solution.[4,5] After examining many model and catalytically active compounds we were able to rationalize why a particular anion-cation orientation was observed in solution and, in some cases, to correlate the observed interionic structure with the catalytic performances of the complexes.[5] Many square planar complexes were taken into account[6] and it was found that the anion is usually located far away from the expected apical positions due to electronic or a mix of electronic and steric effects exerted by the ligands coordinated to the metal center. Nevertheless, apart from this shift toward peripheral "anchorage" points, the anion was never found to prefer one of the two positions above or below the square planar coordination plane.

Here we report the first case in which the anion preferentially populates one of these positions and, to the best of our knowledge, the first example, in general, in which an equilibrium between two transition metal complex intimate ion pairs has been directly observed in solution.

[PtMe(η^2-olefin)(α-diimine)]BF_4 are the compounds considered in this work (Scheme 1)[7] as they are analogous to nickel and palladium compounds that have been established to be the catalytic resting state of olefin polymerization and for which ion pairing phenomenon has been found to affect their catalytic activity.[2b,8] By applying $^{19}F,^1H$-HOESY NMR spectroscopy to complexes **1**–**3** in chloroform-d, the abundance in solution and the structure of the two ion pairs has been determined, the equilibrium constants and, consequently, $\Delta G°$ for the process that converts the two ion pairs has been obtained, and the average H···F interionic distances have been estimated. The factors governing the preferential formation of one intimate ion pair has been investigated by means of DFT (Density Functional Theory) calculations.

The $^{19}F,^1H$-HOESY spectra[9] of compounds **1**–**3** (*ca.* 4×10^{-2} M in chloroform-d at 277 K) showed that the counterion strongly interacts with Me(M) and Me(O) [Scheme 1; intramolecular characterization is reported in the Electronic Supplementary Information (ESI)], while the almost complete absence of interionic contacts with the olefin protons (with the *important exception* of a contact between the anion and the *ortho* protons of the styrene moiety) and with the methyl directly bonded to the platinum indicates that BF_4^- approaches the organometallic fragment from the side of the N,N-ligand in agreement with a previous study.[10] Furthermore, resolution-enhanced $^{19}F,^1H$-HOESY spectra[9] in the aliphatic regions (Fig. 1) showed that (1) the two CH(d) (Scheme 1) interact more strongly with the counterion than the others and (2) among the four methyl groups that point backward, Me(Mdb) and Me(Odb) strongly interact with BF_4^- while Me(Mub) and Me(Oub) give only weak interactions. Me(Mdf)



R = C_6H_5 (**1**), 4-$(CH_3)C_6H_4$ (**2**), 4-$(CF_3)C_6H_4$ (**3**)

Scheme 1 "M" and "O" indicate groups that stay in the *cis* position with respect to methyl and olefin groups, respectively. "u" and "d" discriminate the up and down methyl orientations with respect to the olefin R group. Finally, "b" and "f" stand for backward and forward with respect to the plane containing the two phenyl groups (assumed to be co-planar).

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† Electronic supplementary information (ESI) available: details of the experimental measurements and calculations, along with the NMR intramolecular characterization of complexes **1**–**3**. See http://www.rsc.org/suppdata/nj/b2/b212088g/

DOI: 10.1039/b212088g

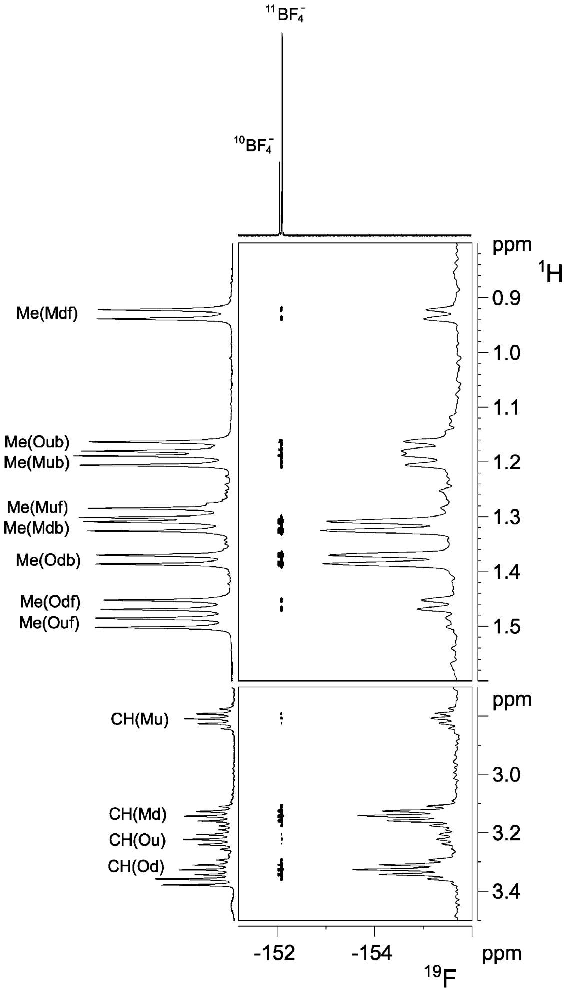
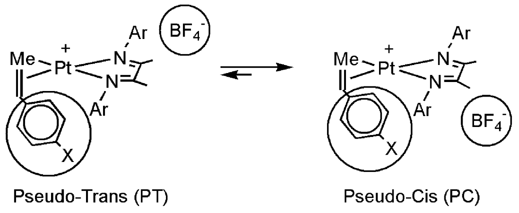


Fig. 1 Two sections of the $^{19}F,^1H$-HOESY NMR spectrum (376.65 MHz, 302 K, chloroform-d) of complex **3** showing the preferential interionic interactions of BF_4^- with groups pointing backward [Me(Mdb), Me(Odb), CH(Md) and CH(Od)]. The F1 trace (indirect dimension) relative to the $^{11}BF_4^-$ resonance is reported on the right.

and Me(Odf) also interact weakly with the anion while Me(Muf) and Me(Ouf) do not show any interaction. These observations indicate that (1) in contrast to all previous investigated square planar complexes,[6] in this case PC and PT anion-cation orientations, defined in Scheme 2, are not equally abundant in solution and that (2) the counterion prefers to locate on the intuitively unexpected, more hindered side where the olefin substituent lies (PC position). The possibility that the two anion-cation orientations could be explained by a further aggregation in solution of ion pairs was explored. In fact, a $^{19}F,^1H$-HOESY spectrum was recorded for compound **3** at a lower concentration (*ca.* 2×10^{-3} M) in methylene-d_2 chloride at 277 K and the same preference for the PC ion pair was observed. Furthermore, PGSE (pulsed field gradient spin-echo) measurements[11] for the same complex, under the same conditions as the HOESY measurements, indicated that the anion and the cation diffuse at the same rate (see ESI).



Scheme 2 The equilibrium between the two types of intimate ion pairs with the BF_4^- above (PT) and below (PC) the square planar coordination plane.

A quantitative comparison between compound **3** and the previously investigated[10] compound in which R = Me (**4**) was carried out by recording two $^{19}F,^1H$-HOESY NMR spectra under exactly the same conditions. In compound **4**, the PC and PT ion pairs have the same abundance. By assuming that the anion, in the PT ion pair of complex **3**, is located in the same position as in **4**, the percentage of such ion pairs was estimated by a comparative and quantitative integration of the interionic NOEs for analogous resonances in the two compounds. In particular, the intensity decrease of the interionic NOEs between BF_4^- and Me(Mub), Me(Oub), CH(Mu) and CH(Ou) going from **4** to **3** allowed us to conclude that, for **3**, only 20% of the total ion pairs present in solution have the PT structure (Table 1, last column). Three pieces of experimental evidence shed light on the PC and PT ion pair structures: (1) there is a decrease in the anion Me(O) and Me(M) NOE intensities upon going from **4** to **3**; (2) a weak contact between the *ortho* protons of the styrene ring and BF_4^- is observed in the PC ion pair of **3**; (3) the ^1H-NOESY spectra show that the interactions between Me(O) or Me(M) and "d" resonances are more intense than the analogous ones with "u" resonances; furthermore, those cis to olefin are slightly stronger than "M". All these observations indicate that the stryrene is oriented almost perpendicular to both the coordination plane and the phenyls of the *N,N*-ligand; furthermore, the latter phenyl moieties are inclined in such a way so as to orient the "d" resonances closer to Me(O) and Me(M), with the inclination of that cis to Me(O) being slightly higher. Interestingly, the rotation around the N–C(sp^2) bond, responsible for such an inclination, seems to drag the anion so as to increase its distance only from Me(O) and Me(M), while not significantly changing the distances between the anion and the methyl and CH groups. In fact, by assuming that such distances are the same in the two ion pairs, the percentages of the latter ion pairs can be estimated and do not differ, within experimental error, from those obtained as discussed above: PC = 81% and PT = 19% (Table 1, third column). The estimation was done by considering that the observed interionic NOEs, for analogous resonances in the PC and PT ion pairs [for example CH(Mu)–BF_4^- in PT and CH(Md)–BF_4^- in PC], differ only because of their abundance, which was varied until a minimization of the square difference between the two weighted NOEs was obtained. By applying this methodology to complexes **1** (277 K) and **2** (302 K) the relative abundances of the two ion pairs were determined: 72% (**2**), 71% (**1**) in the PC orientation and 28% (**2**), 29% (**1**) in the PT orientation (Table 1).

In order to determine possible reasons for the different populations of the PC and PT ion pairs, we performed density

Table 1 PC and PT abundance, equilibrium constants and $\Delta G°$ (kJ mol^{-1}) in chloroform-d estimated by the quantification of interionic heteronuclear NOE

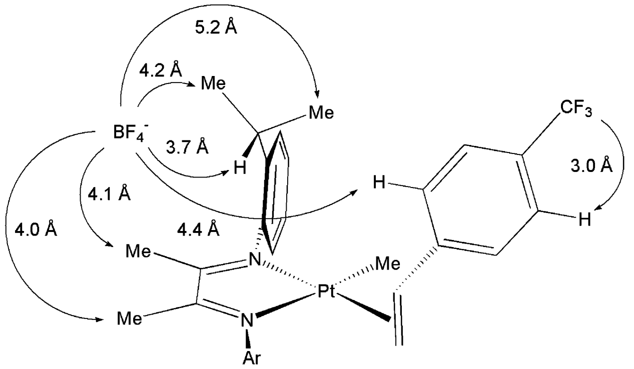
	1[a] 277 K	**2**[a] 302 K	**3**[a] 277 K	**3**[a] 204 K	**3**[b] 277 K
PC ion pair/%	71 ± 4	72 ± 4	81 ± 4	66 ± 4	80 ± 4
PT ion pair/%	29 ± 4	28 ± 4	19 ± 4	34 ± 4	20 ± 4
K	2.4 ± 0.5	2.6 ± 0.5	4.3 ± 1.1	2.0 ± 0.4	4.0 ± 1.0
$\Delta G°$	−2.0 ± 0.4	−2.4 ± 0.5	−3.4 ± 0.9	−1.2 ± 0.2	−3.2 ± 0.8

[a] Determined by assuming that analogous interionic distances in the two ion pairs are the same within experimental error. [b] Determined by a quantitative comparison between the interionic NOEs of analogous resonances of the PT ion pair in **3** and those of the PC or PT ion pairs in **4**. The error in the abundance, *K* and $\Delta G°$ values comes from the integration of the NOEs and was estimated by integrating δ ranges containing only noise.

functional (DFT) and mixed quantum mechanics/molecular mechanics (QM/MM) calculations (with DFT as the underlying electronic structure method) for compounds **1**, **3**, and **4**. Two different computational models were used in our calculations (see ESI†). In both models, the two aryl substituents of the *N*,*N*-ligand were included in the MM region, while R (the substituent of the olefin) was either included in the QM or in the MM part for Models A and B, respectively. In Model A, the positioning of the counterion in the PC position is the most thermodynamically stable form for all complexes in agreement with the experimentally observed stability order. The relative thermodynamic stability of the PC orientation, with respect to the PT ion pair, is −8.7, −6.7 and −2.5 kJ mol^{-1} for complexes **3**, **1** and **4**, respectively. In Model B, on the other hand, the PC ion pair is disfavored with respect to the PT form by 1.7, 2.9 and 4.6 kJ mol^{-1} for complexes **3**, **1** and **4**, respectively. In order to further analyze the influence of the electronic features of R on the stability of the two ion pairs, we performed an analysis of the charge distribution[12] on a full QM model of the cationic complexes **1**, **3**, and **4**. A small positive charge of 0.39 e (neglecting CF_3 in **3**) is accumulated on the $CH_2{=}CHR$ moiety, *versus* 0.20 e and 0.05 e in **1** and **4**, respectively. Thus, our results suggest that the differences in the relative thermodynamic stabilities of the PC *versus* the PT ion pairs could originate from an interaction between the anion with the positive charge accumulated on the olefin ligand. In fact, in PC the anion is much closer to the olefin (the average distance between BF_4^- and the *ortho*-proton of the phenyl ring is 4.4 and 4.2 Å for **3** and **1**, respectively, while the distance between BF_4^- and the methyl of the propylene is 6.0 Å) than in the PT position (8.6 and 8.5 Å for **3** and **1**, respectively and 8.8 Å for **4**). This should maximize the electrostatic interaction between the anion and the partial positive charge of R for **3** and **1**. However, due to the calculated differences in the dipole moments (*i.e.*, in the charges of the olefin) this interaction is stronger in complex **3**.

Based on the above-determined percentages of the PC and PT ion pairs (Table 1), the following values for the equilibrium constants were calculated for the equilibrium shown in Scheme 2: $K = 4.3$ (**3**, 277 K), $K = 2.6$ (**2**, 302 K) and $K = 2.4$ (**1**, 277 K). In the case of complex **3**, the ^{19}F,^{1}H-HOESY spectrum at 204 K showed a minor discrimination between the two types of ion pairs: 34% PT and 66% PC. The equilibrium constant at 204 K is 2.0. Consequently, for complex **3**, $\Delta G°(277\ K) = -3.4$ kJ mol^{-1} while $\Delta G°(204\ K) = -1.2$ kJ mol^{-1} (Table 1). Due to the low absolute value of $\Delta G°$ it is difficult to separate the entropic from the enthalpic contribution. In any case, the decrease in the $\Delta G°$ absolute value with decreasing temperature should be mainly due to a greater difficulty in orientating the phenyl and styrene moieties as discussed above, which seems to have a stabilizing effect on the PC ion pairs. This means that the entropic contribution is important but, as a consequence of the new orientation, the anion can interact with the styrene moiety that has an accumulation of positive charge, which affords an enthalpic contribution, as well.

Average interionic H···F distances were estimated for complex **3** by quantifying the NOE by measuring the kinetics of heteronuclear NOE build-up (recording several ^{19}F,^{1}H - HOESY spectra[9] as a function of the mixing time) and a resolution-enhanced single ^{19}F,^{1}H-HOESY experiment with a mixing time of 0.2 s (initial rate approximation).[13] The average intramolecular F–H distance between the CF_3 fluorine nuclei and the *meta* protons was taken as reference (see ESI). The validity of such referencing was checked by measuring the dependence on the temperature of the intramolecular and interionic heteronuclear NOE[14] (323–204 K) for compound **3**, which was found to be very similar (see ESI). In Scheme 3 a representation of the PC ion pair structure with some significant average interionic distances is given;[15] it can be seen that an almost perpendicular disposition of the phenyl ring of the styrene allows the *ortho* proton to interact with the anion [$\langle r \rangle = 4.4(8)$ Å is in remarkable agreement with the value obtained by DFT calculations].



Scheme 3 Representative average interionic distances in the PC ion pair of complex **3** determined from the experimental NOEs, using the average *m*H-CF_3 distance as reference, taking into account the number of equivalent F and H nuclei[16] and the abundance of the ion pair to which the H resonance belongs. All the interionic $\langle r_{IS} \rangle$ values were increased by 10% in order to correct for the over-estimation of the short distances. The error is around 20%.

In conclusion, through HOESY NMR spectroscopy it was possible to: (1) directly observe an equilibrium between two intimate olefin platinum complex ion pairs; (2) determine the thermodynamic parameters of such equilibrium and, at the same time, the anion-cation relative orientations within the two ion pairs; and (3) evaluate the average interionic distances. DFT calculations showed that the favorable interaction of the anion BF_4^- with a small partial positive charge (~0.39 e) accumulated on the olefin moiety seems to be responsible for the unequal populations of the two intimate ion pairs in solution.

Acknowledgements

This work was supported by grants from the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, Rome, Italy), Programma di Rilevante Interesse Nazionale, Cofinanziamento 2002–3.

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