Elucidation of the Solution Structures of Transition Metal Complex Ion Pairs by NOE NMR Experiments

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Our results from structural investigations of transition metal complex ion pairs in solution by homonuclear and heteronuclear 1D- and 2D-NOE NMR spectroscopy are reviewed. Both model (**A**) and catalytically active (**B**) complexes have been taken into account; their general formulas are: *trans*-$[ML_2(N,X)(Y)(Z)]^+A^-$ (**A**) {M = Fe^{II}, Ru^{II} and Os^{II}, L = PMe_3, Y = CO, Z = COMe, A^- = BPh_3R^-, $CF_3SO_3^-$, BF_4^-, PF_6^- and $B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$; M = Ir^{III}, L = PR_3, Y = Z = H and A^- = BPh_4^-, $CF_3SO_3^-$, BF_4^-, PF_6^-} and $[M'(N,X)(R,\text{olefin})]^+A^-$ (**B**) {M′ = Pt, R = Me, olefin = ethene, propene and CH_2=CHCOOMe, A^- = BF_4^-; M′ = Pd, (R,olefin) = η^1,η^2-5-methoxycyclooctenyl, A^- = BPh_4^-, $CF_3SO_3^-$, BF_4^-, PF_6^-, SbF_6^- and $B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$}, where N,X = bis(pyrazolyl)methane, bipyridine, α-diimines, α-diamines or α-oxo imines. The detection of dipolar interionic interactions in ^{1}H-NOESY and ^{19}F,^{1}H-HOESY NMR spectra allowed relative anion-cation orientations to be determined, these being well defined in most cases, with one orientation predominating in solution. We often found that the anion approaches the complexes from the side of the N,X-ligands, due to an accumulation of positive charge at the junction of the moieties containing the N- and X-donor atoms. In square-planar complexes **B**, the apparently favoured apical positions were often protected either by electronic factors [N,X = bis(2-pyridyl)amine or bis(pyrazolyl)methane] or by a combination of electronic and steric factors (N,X = α-diimines). For M′ complexes, bearing Ar–N=C(Me)–C(Me)=N–Ar ligands, the position of the counter-anion is finely modulated by the steric hindrance of the *ortho*-aryl substituents. The accessibility of the metal centre, which is directly associated with the catalytic performances of the complexes, was determined by using the counter-anion as a probe. Finally, average interionic distances were estimated for model complexes **A**, bearing unsymmetrical BPh_3R^- counter-anions, based on the quantification of interionic NOEs.

1 Introduction

Several stoichiometric and catalytic reactions mediated by cationic transition metal complexes are strongly affected by the phenomenon of ion-pairing. In most cases the counter-anion effect is carried out through competition with the substrate for coordination to the metal ion; consequently, in terms of reaction rate and yield, better results are obtained when less strongly coordinating anions are used.[1] As an example, Evans et al.[2] showed in 1995 that the degree and rate of conversion of the Diels−Alder reaction between methacrolein and cyclopentadiene, catalysed by dicationic Cu^{II} compounds bearing bis(oxazoline) ligands, was significantly affected by the nature of the counter-anion, and that higher performances were obtained with use

Alceo Macchioni was born in Città della Pieve, Italy, in 1963. He obtained his "Laurea" in Chemistry from the University of Perugia in 1988. He received his Ph.D. degree in Chemistry in 1992 from the same university under the supervision of Giuseppe Cardaci. After a postdoctoral stay (November 1992 until February 1995) with Paul S. Pregosin and Luigi M. Venanzi, Zürich, Switzerland, he returned to Italy as a Researcher at the University of Perugia. In April 2001 he obtained the "Idoneità" to be Associate Professor in General and Inorganic Chemistry. He has recently received the "Raffaello Nasini" prize from the Inorganic Division of the Italian Chemical Society. His main research interests are the synthesis and characterization of ruthenium and palladium complexes and their application in homogeneous catalysis, with particular attention to the role of noncovalent interactions in their structure and reactivity in solution.

MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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of the least strongly coordinating anion (SbF_6^-) of those tested. Kündig et al. found a similar counter-anion influence[3] in the same reaction with catalysis by monocationic Ru^{II} compounds.

Consequently, new types of anions have been engineered in order to diminish their coordinating power. The strategy of introducing large and highly fluorinated moieties, or electron-withdrawing substituents in general, into the counter-anions has often been used to achieve this goal.[4,5]

In some cases the anion plays a direct role in the stoichiometric and catalytic processes.[6−8] RajanBabu et al.,[9] for instance, showed the synergistic effect of hemilabile coordination and the counter-anion effect in hydrovinylation catalysed by cationic Ni^{II} compounds. Faita et al.[10] found that the enantioselectivity of a reaction could be inverted by use of a suitable counter-anion, while Marks and Chen[11] suggested that ion-pairing affects the stereochemistry of propylene chain formation during single-site olefin polymerization. Finally, Arndtsen et al.[12] showed that the use of chiral counter-anions[13] may provide a novel method for inducing enantioselectivity.

It seems clear from the examples reported above that the ion-pairing phenomenon has an established relevance in transition metal chemistry. Until seven years ago, however, there had been no detailed investigations into the structures of transition metal complex ion pairs in solution; that is, the environment in which they "work". Very little was known about the relative anion-cation orientation and, consequently, of the possibility of having one or more favoured points of anchorage for the two ionic moieties. A few structural studies in solution, concerning organolithium[14,15] and organoammonium[16] ion pairs, appeared in the literature after the mid 1980s. They were based on Nuclear Overhauser Effect (NOE) NMR spectroscopy; that is, on the detection of inter-ionic dipolar interactions[17] between the atoms of the cations (lithium or hydrogen) and those of the anions (hydrogen or fluorine).

Our laboratory decided to investigate transition metal complex ion pairs by application of 1D- and 2D-NOE NMR spectroscopy (both homonuclear and heteronuclear). We began by developing appropriate methodologies on "model" systems. We then considered transition metal complexes with structures or reactivities that were affected by the nature of the counter-anion, in the hope of obtaining a better understanding of the role of anion-cation interactions and, possibly, of correlating them with the reactivity of the complexes. During the course of our studies we realized that the detection of anion-cation interactions can afford precious information about the electron density distribution around the metal ion. In particular, the accessibility of the metal centre in square-planar complexes for a generic nucleophile can be accurately determined by assuming that the anion is a good probe.

The main results of our studies to date are reviewed here. After an examination of some basic aspects of NOE theory essential for facilitating the reading of this paper, the results of qualitative NOE NMR investigations and the consequent interionic structures are reported for compounds grouped according to the geometry of the metal centre. When the analysed complexes are active catalysts, the connections between the interionic interactions and the catalytic performances are outlined. The last paragraph illustrates the results of quantitative NOE measurements, which have allowed average interionic distances to be estimated.

2 NOE and Suitable Systems for Investigation

In an ideal two-spin ($I = 1/2$) system, the NOE, defined as the fractional change in the intensity of one nucleus (I) on perturbation of the nucleus (S), dipolar coupled to it, is related to the cross-relaxation rate constant (σ_{IS}) and the dipolar longitudinal relaxation rate constant (ρ_{IS}) according to Equation (1),[18] where I^0 is the equilibrium intensity of I, and γ_S and γ_I are the giromagnetic ratios;[19] σ_{IS} can be related to the molecular tumbling rate by Equation (2), where μ_0 is the permeability constant in a vacuum, $\hbar$ is Planck's constant divided by 2π, τ_c is the rotational correlation time, and ω_I and ω_S are the resonance frequencies of the I and S nuclei, respectively.

$$\mathrm{NOE} = f_I\{S\} = \frac{(I - I^0)}{I^0} = \frac{\gamma_S}{\gamma_I}\frac{\sigma_{IS}}{\rho_{IS}} \tag{1}$$

$$\sigma_{IS} = \frac{1}{10}\left[\left(\frac{\mu_0}{4\pi}\right)\hbar\gamma_I\gamma_S r_{IS}^{-3}\right]^2 \tau_c\left[\frac{6}{1+(\omega_I+\omega_S)^2\tau_c^2} - \frac{1}{1+(\omega_I-\omega_S)^2\tau_c^2}\right] \tag{2}$$

When small molecules in nonviscous solvents are considered (as in all our cases) the *extreme narrowing limit* approximation is reached. In such a situation $\omega_{I(\text{or } S)}\tau_c << 1$ and, consequently, σ_{IS} simply depends on τ_c and r_{IS} according to Equation (3).

$$\sigma_{IS} \propto \tau_c r_{IS}^{-6} \tag{3}$$

Because σ_{IS} is related to the internuclear distance (r_{IS}), the NOE is often *qualitatively* used to obtain information about the proximity of the I and S nuclei.

By considering Equation (4) (where I_z is the macroscopic longitudinal magnetization due to I, and τ_m is the mixing time[20]), σ_{IS} can be *quantitatively* derived (a) by limiting attention to the linear build-up of the I enhancement for short mixing times ($\tau_m \rightarrow 0$), or (b) by measuring the complete kinetics of NOE build-up and fitting the experimental data with the theoretical Equations derived from integration of Equation (4), in which the proportionality constant between $dI_z/d\tau_m$ and σ_{IS} depends on the type of NOE NMR experiment.[21]

$$\left.\frac{dI_z}{d\tau_m}\right|_{\tau_m=0} \propto \sigma_{IS} \tag{4}$$

By comparison of σ_{IS} with that relative to two nuclei (A and B) of known internuclear distance (r_{AB} = calibration or reference distance), an estimation of r_{IS} can be obtained by Equation (5), if it is assumed that the proportionality constant between σ and r^{-6} is the same for the two couples of nuclei (IS and AB); this condition is satisfied when the rotational correlation times (τ_c), the other variable on which σ depends, of the I-S and A-B vectors are the same.

$$\frac{\sigma_{IS}}{\sigma_{AB}} = \left(\frac{r_{IS}}{r_{AB}}\right)^{-6} \qquad (5)$$

The essential features of NOE illustrated above should be sufficient for understanding of which systems can be successfully investigated and what precautions must be taken. Some obvious requirements for the systems are: (1) the presence of NMR-active nuclei with high receptivity (H or F) in both ionic moieties, and (2) the presence of magnetically nonequivalent nuclei, spatially dispersed around the ionic moieties, that will make it possible to discriminate different anion-cation orientations. Protons or fluorine atoms are frequently present in cationic moieties bearing the transition metal ion and in its usual counter-anions, and condition (1) is respected. Requirement (2) is often satisfied by the transition metal cation but rarely by its counter-anion.

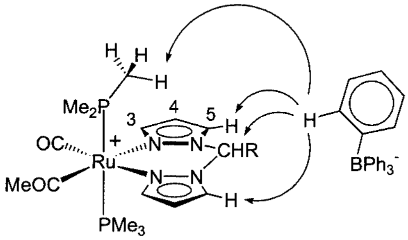
NOEs strongly decrease with increasing r_{IS}. As a consequence, NOEs can be observed only if the internuclear distances are shorter than ca. 5 Å, thereby introducing the apparent limitation that only intimate ion pairs can be structurally investigated. However, this is only an apparent limitation, because, if we are interested in studying systems in which ion-pairing affects the reactivity, an acceptable percentage of intimate ion pairs have to be present. A real limitation, however, is that when a quantitative analysis is carried out, the correlation times of the reference and distances of interest must be the same. In fact, the reference distance must refer to a pair of nuclei belonging to the cation or the anion (intramolecular distance), while the distances that we want to estimate are between the nuclei of the cation and those of the anion (interionic distances). Their correlation times are not necessarily the same and have to be determined in order to verify that the interionic distances are reasonably accurate. These last are inevitably average distances, because of the presence of several motions in ionic compounds: (1) overall rotation of ion pairs and/or ions constituting them, (2) ion pair dissociation and formation, and (3) internal motions (Me group rotations around single bonds and chair-boat inversion of the six-member cycles etc.). Although these motions could affect both τ_c and r_{IS}, it has been found[22] that the distances calculated from the observed σ by assuming rigid isotropic motion are not often in error by more than about 10%.

3 Qualitative NMR Investigations

The results illustrated in this section derive from NOESY and HOESY NMR studies carried out in deuterated solvents with low dielectric constants ([D$_2$]dichloromethane: ε = 8.93 at 298 K; [D]chloroform: ε = 4.81 at 293 K) for $10^{-2}-10^{-1}$ M solutions. Under such conditions, compounds are mainly present in solution as intimate ion pairs.[23] The interionic NOEs observed in the spectra were classified as strong, medium and weak. Consequently, the relative anion-cation orientation is qualitatively, or perhaps better semiquantitatively, deduced by means of simple triangulations. Most of the complexes considered in this paper were synthesized in our laboratory. Nevertheless, the synthetic procedures are not illustrated here, but can be found in the quoted references.

3.1 Octahedral Iron(II), Ruthenium(II), Osmium(II) and Iridium(III) Complex Ion Pairs

The interionic structure of *trans*-[Ru(COMe){(pz$_2$)CHR}(CO)(PMe$_3$)$_2$]BPh$_4$ (R = H or pz; pz = pyrazol-1-yl ring) in [D$_2$]dichloromethane was investigated first.[24,25] The interionic contacts, between the *ortho*-protons of the anion and the 5- and CHR protons (medium) of the cation and the phosphane protons (weak) observed in the ^{1}H-NOESY NMR spectra, and the absence of interactions with the COMe protons, allowed us to conclude that the anion is specifically located close to the bis(pyrazolyl) ligand (Scheme 1).



Scheme 1

The same relative anion-cation orientation was found (a) by ^{19}F,^{1}H-HOESY NMR studies with fluorinated counterions (BF$_4^-$, PF$_6^-$ and CF$_3$SO$_3^-$) (Figure 1), (b) for isoelectronic and isostructural iron(II) and osmium(II)[26] complexes, and (c) for similar ruthenium(II) complexes containing neutral N,O-ligands.[27] An explanation of the observed specific localization of the anion with respect to the cation was found with the help of quantum mechanical and mechanical docking calculations.[28] There is, in fact, an accumulation of positive charge at the −CHR carbon atom, while the negative charge is concentrated on the oxygen atom of the COMe group. The ion pair with the counteranion on the side of the pyrazolyl rings is consequently dictated by a gain in the electrostatic interaction energy. When BPh$_4^-$ is taken into account, the observed relative anion-cation position is further stabilized by the favourable lipophilic interactions between the phenyl groups of the anion and the pyrazolyl rings. Very interesting studies carried out by Schneider and co-workers on organic ion pairs in water[29,30] show that π-stacking interactions give the ion pairs additional stabilization of about 2 kJ/mol for every phenyl moiety. In our complexes, we found that two phenyl groups of BPh_4^- are oriented in such a way that they are almost parallel to the two pyrazolyl rings, as illustrated in Scheme 2 for *cis*-[Ru(COMe){$(pz_2)CH_2$}$(CO)_2(PMe_3)$]BPh_4.[28]

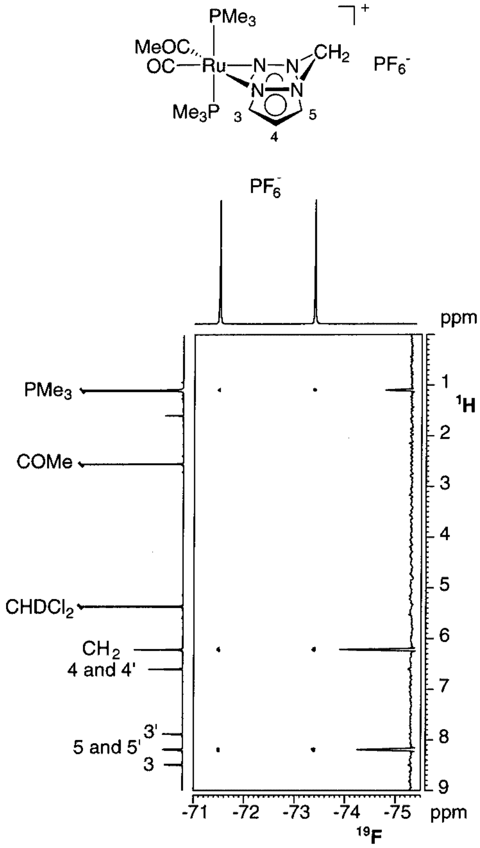
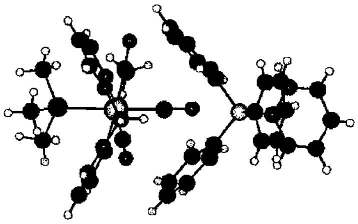


Figure 1. ^{19}F, ^{1}H-HOESY NMR spectrum of the *trans*-[Ru(COMe){$(pz_2)CH_2$}$(CO)(PMe_3)_2$]PF_6 complex, showing the heteronuclear interionic contacts of PF_6^- with CH_2, H5/H5′ and PMe_3 protons; the F1 trace (indirect dimension) relative to one component of the fluorine doublet is reported on the right (376.65 MHz, 298 K, [D_2]dichloromethane, $\tau_m = 0.8$ s); reproduced from ref.[37] with the permission of the American Chemical Society



Scheme 2. Reproduced from ref.[28] with the permission of the American Chemical Society

According to Schneider this should give rise to a consequent energy gain of about 4 kJ/mol, which could compensate for the reduction of favourable Coulomb interaction due to an increase in the average anion-cation distance on going from BF_4^- or PF_6^- to BPh_4^-. Studies in more polar solvents (acetone, methanol and nitromethane) indicated that the same interionic structure is maintained but the anion-cation dipolar interactions are more difficult to detect because the increased solvent polarity decreases the percentage of intimate ion pairs. The effect of increasing the polarity of the solvent is also mimed by the reduction of the coordinating property of the counter-anion when, for instance, the poorly coordinating $B[3,5\text{-}(CF_3)_2(C_6H_3)]_4^-$ counter-ion is used. Very weak interionic contacts were observed for *trans*-[Ru(COMe){$(pz_2)CH_2$}$(CO)(PMe_3)_2$]B[3,5-$(CF_3)_2C_6H_3]_4$ complex in [D_2]dichloromethane, while interionic interactions of acceptable intensity between the fluorine atoms of the counter-anion and the "usual" protons of the cation in [D]chloroform were visible in the ^{19}F,^{1}H-HOESY NMR spectra.

Interestingly, results from NOE and Pulsed-Field Gradient Spin-Echo (PGSE)[31−34] NMR experiments in [D]chloroform for analogous complexes bearing the more coordinating BPh_4^- anion indicated that the same anion-cation orientation is present, but that aggregates higher than ion pairs form at elevated concentrations in solution.[35]

With the aim of obtaining even more detailed information about anion-cation orientation in solution, *trans*-[Ru(COMe){$(pz_2)CH_2$}$(CO)(PMe_3)_2$]BPh_3R (R = Me, *n*Bu and *n*Hex) compounds, with unsymmetrical counter-anions, were synthesized and investigated.[36,37] The results obtained corresponded to our expectations: the counter-anion is located in the same position, but it orients the aliphatic chain far from the cationic organometallic moiety. By assuming this orientation, the anion maximizes the favourable lipophilic interactions allowing two π-stackings with the energetic gain mentioned above.

The possibility that the high specificity in the anion-cation interactions could be confined to the presence of N-aromatic ligands was excluded by synthesis and investigation of analogous ruthenium(II) compounds bearing α-diimines or substituted ethylenediamines.[38] A section of the ^{1}H-NOESY NMR spectra, relating to the simplest compound taken into account, is reported in Figure 2, and shows interionic interactions between the anion and the protons of the ethylenediamine, the intensity decreasing on moving from NH_2^d to NH_2^a. In the absence of conjugation, the anion is not only still located close to the N,N-ligand, but it even prefers the N-arm *trans* to the COMe group, where the electron density is less, due to the high *trans* influence of COMe. The introduction of steric hindrance in the N,N-ligand (by use of $NRHCH_2CH_2NR'H$ ligands) affords a fine modulation of the anion position that shifts toward less crowded "places". For example, when R = R′ = $CH_2C_6H_5$ (bz), two stereoisomers are present, depending on the orientation of the bz groups with respect to the phosphanes. In the stereoisomer with the two bz groups oriented toward the same phosphane, the anion stays close to the N,N-ligand but preferentially interacts with the protons of the other phosphane group.

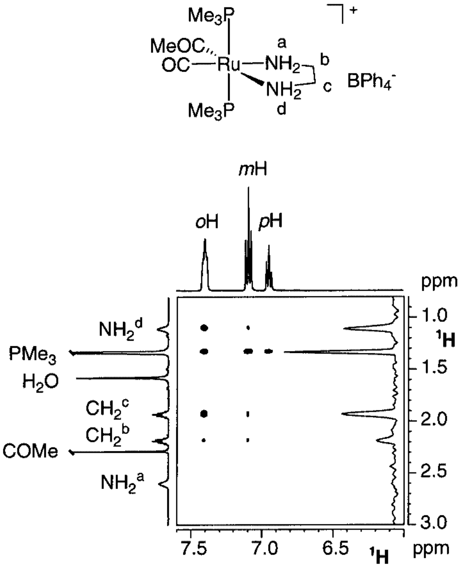
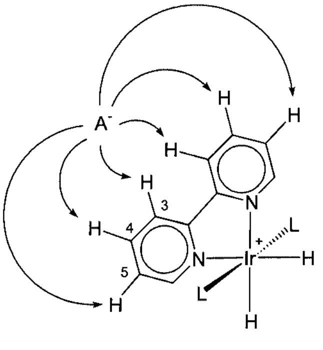


Figure 2. A section of the ^{1}H-NOESY NMR spectrum of the illustrated complex, showing the gradual decrease of the interionic contact intensity on passing from positions d to a; the 1D trace relative to the *ortho*-proton column is reported on the right (400.13 MHz, 298 K, [D$_2$]dichloromethane, τ_m = 0.8 s)

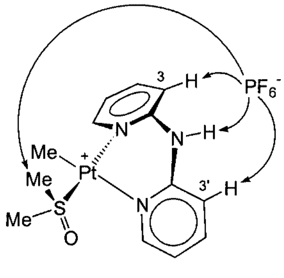
Inspection of *cis,trans*-[Ir(bipy)H$_2$(PRPh$_2$)$_2$]A complex ion pairs (A$^-$ = PF$_6^-$, BF$_4^-$, CF$_3$SO$_3^-$ and BPh$_4^-$; R = Me and Ph) afforded other hints about the tendency of the anion to stay close to N,N-ligands.[39] In such complexes, the anion would have the apparently favourable possibility to bind near the MH$_2$ group, which would give the closest M−anion distance and allow hydrogen bonding.[40] Instead, the anion is specifically located near to the bipy ligand interacting with the 3- (strong), 4- (medium), 5- (weak) and phosphane protons (Scheme 3); the interaction specificity falls off with increasing anion size. Calculations identify the predominant location of the positive charge at the bipyridyl ring carbon atoms that take part in the inter-ring C−C bond. The electrostatic potential calculated for the cation confirms the location of the preferred binding site. Pregosin et al.[41] recently reported specific anion-cation interactions in similar dihydridoiridium(II) complexes.



Scheme 3

3.2 Square-Planar Platinum(II) and Palladium(II) Complex Ion Pairs

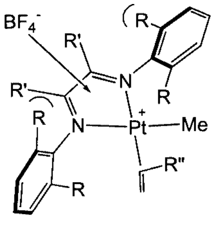
In the case of ionic square-planar complexes, the determination of the relative anion-cation position might appear to be trivial because of the apparently favoured option for the anion to approach the organometallic moiety from the apical positions. In our studies we soon realized that the apical positions are usually protected both by electronic and by steric properties of the coordinated ligands. The first square-planar complex that we investigated[42] was [PtMe(dpa)(Me$_2$SO)]PF$_6$ [where dpa = bis(2-pyridyl)amine], and we found that the anion is located in the periphery of the N,N-ligand, close to the amine NH-proton. The ^{19}F,^{1}H-HOESY NMR spectra showed only selective interionic interactions between the fluorine nuclei and the bridging NH (strong), 3- and 3′- (strong) and DMSO (very weak) protons (Scheme 4).



Scheme 4

The most reasonable explanation of this observation is the formation of NH···FPF$_5^-$ hydrogen bonds, providing electronic protection of the metal centre.

Access to the metal centre can also be denied by a synergistic effect between electrostatic attraction and the introduction of suitable steric hindrance in the apical positions. This was made evident in an investigation of the interionic structures of [PtMe(η^2-olefin)(α-diimines)]BF$_4$ complexes[43] {where α-diimines = [2,6-(R)$_2$-C$_6$H$_3$]N=C(R′)-C(R′)=N[2,6-(R)$_2$-C$_6$H$_3$], R = H, Me, Et and *i*Pr, R′ = H and Me, olefin = CH$_2$=CHR″ with R″ = H, Me and COOMe}. In these complex ion pairs, the anion is located on the side of the diimine ligands, but accessibility of the metal centre for it is finely modulated by the steric hindrance of the R and R″ groups (Scheme 5) which protect the apical positions.[44]



Scheme 5

When R'' = Me and R ≥ Et, the anion is completely trapped between the R and R' substituents and does not interact with any olefin or Me protons. For R'' = Me and R = H and Me, weak interionic NOEs between fluorine nuclei of the anion and olefin and Me protons are visible in the $^{19}F,^{1}H$-HOESY NMR spectra (Figure 3). Interestingly, in agreement with our findings for these platinum(II) complexes and our calculations on octahedral complexes, Tilset et al. showed[45] by DFT calculations that the association of solvent molecules such as H_2O or TFE (trifluoroethanol) to the cationic square-planar σ-complex $[(\alpha\text{-diimine})PtMe(CH_4)]^+$ occurs at the C−C diimine bond where the positive charge accumulates.

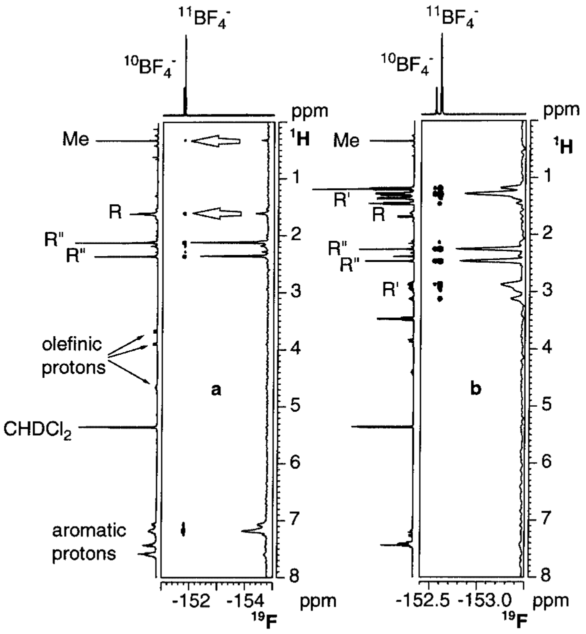


Figure 3. The two ^{19}F, ^{1}H-HOESY NMR spectra (376.65 MHz, 298 K, [D$_2$]dichloromethane, τ_m = 0.8 s) show the disappearance of interionic interactions between BF_4^- and Me−Pt and R'' (indicated with arrows) on going from R = H (a) to R = *i*Pr (b); the F1 trace (indirect dimension) relative to one component of the fluorine doublet is reported on the right of every spectrum

The complexes illustrated in Scheme 5 were studied because they are analogous to nickel(II) and palladium(II) compounds that have been established to be the catalytic resting state of olefin polymerization[46,47] and for which R substituents have been found to affect their catalytic activity.[48,49] Bulky substituents block the axial coordination sites and consequently slow the chain-transfer rate relative to propagation, resulting in the formation of polymers with higher molecular weights. Our results confirm the protection of the axial coordination sites exerted by R groups but they also allow the steric hindrance necessary to afford complete protection to be directly evaluated, if it is assumed that BF_4^- is a good nucleophilic probe.

In the absence of specific F···H interactions and/or steric protection, the two axial positions are preferred and equally populated by the counter-anion. As an example, in $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(bipy)]A$ complexes {where bipy = 2,2'-bipyridine and A^- = BPh_4^-, $CF_3SO_3^-$, BF_4^-, PF_6^-, SbF_6^- and $B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$} the anion occupies the axial positions even if it slightly prefers to locate close to the bipy ligand and, in particular, close to the N-arm *trans* to the Pd−C σ-bond (Figure 4).[50] This anion-cation relative orientation is always observed independently of the nature of the counter-anions; instead the intensity of the interionic NOEs decreases with decreasing coordinating tendency of the anion: $CF_3SO_3^- > BF_4^- > PF_6^- > B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$.

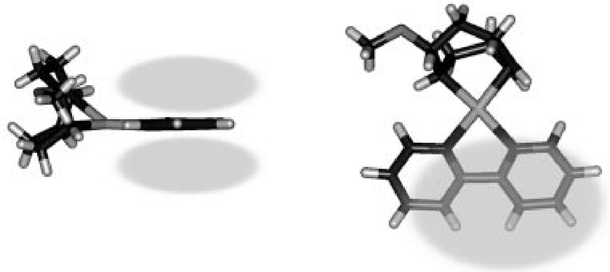


Figure 4. Two views of the solution interionic structure of $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(bipy)]A$ complexes, in which the gray clouds represent the action space of the A^- counter-anion; the two positions above and below the coordination plane are equally populated, and the anion is shifted on the side of bipy ligand with a slight preference for the ring *trans* to the Pd−C σ-bond

It is known that complexes $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(bipy)]A$ are good catalysts for alternating CO/styrene co-polymerization carried out under mild conditions[51] and that the A^- counter-anion strongly affects the catalytic performances.[50] Higher catalytic efficiency is obtained by use of less strongly coordinating anions: that is, those showing weaker interionic interactions. The persistence of the same anion-cation orientation on changing the anion features (size and electron density distribution) and the correlation between the catalytic performances of the complexes with the noncoordinating power of the anion, clearly indicate that the anion competes with the substrates for coordination to the metal ion. Interestingly, the interionic solid-state structure is different from that observed in solution. In fact, due to the stack between two cation moieties, in the solid state the counter-anions are located sideways surrounding the coordination plane (Figure 5).

The substitution of bipy with the nonplanar $(pz_2)CH_2$ ligand results in a very specific localization of the counter-anion (PF_6^-), far from the apical positions and close to the CH_2 moiety of the N,N-ligand.[52] Because of the small axial steric hindrance introduced by the $(pz_2)CH_2$ ligand, the reason for such an unexpected specificity has to be sought in the formation of $^-F_5P{-}F{\cdots}H_2C(pz_2)$ weak interactions. As a confirmation, analogous five-coordinated palladium complexes $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(pz_3)CH)]PF_6$ showed a remarkable specificity of interaction between the counter-ion and the $(pz_3)CH$ and 5'/5'''-protons (Figure 6) in solution; in the solid state, H-bonding between the highly polarized $(pz_3)CH$ proton and fluorine lone pairs (3.16−3.20 Å) gives rise to a sort of anion-cation recognition.[52]

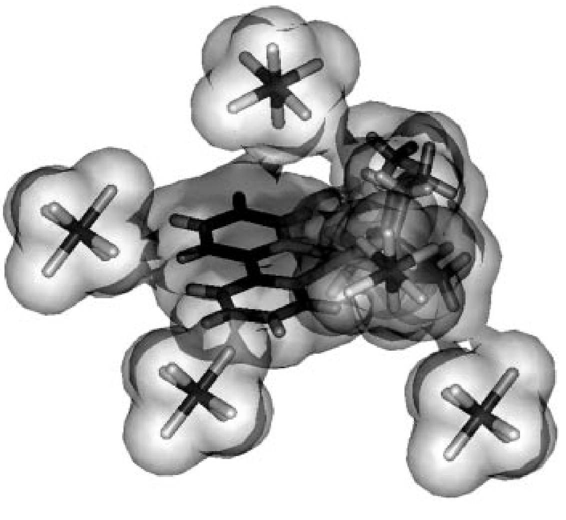


Figure 5. Solid-state structure of $[Pd(\eta^1,\eta^2-C_8H_{12}OMe)(bipy)]PF_6$, showing one cationic moiety surrounded by five counter-anions lying in the periphery of the coordination plane leaving the apical positions free; the van der Waals surface is also shown

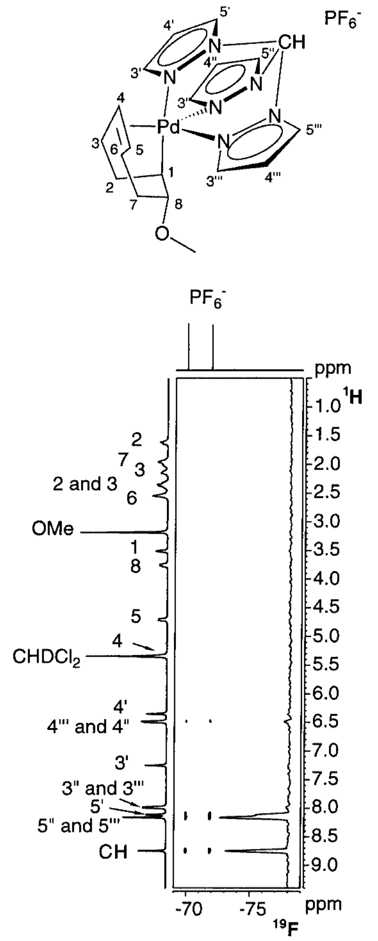


Figure 6. ^{19}F, ^1H-HOESY NMR spectrum (376.65 MHz, 188 K, [D_2]dichloromethane, τ_m = 0.8 s) of $[Pd(\eta^1,\eta^2-C_8H_{12}OMe)\{(pz_3)CH\}]PF_6$ recorded showing the remarkable specificity of interaction between PF_6^- and the 5′-5′′′ and 4′-4′′′ (very weak) protons of the cation; the 1D-trace relative to the PF_6^- column is reported on the right; reproduced from ref.[52] with the permission of the American Chemical Society

The introduction of more hindered substituents, such as α-diimines $\{[2,6-(R)_2-C_6H_3]N=C(R')-C(R')=N[2,6-(R)_2-C_6H_3]$ where R = H, Me, Et and *i*Pr, R'_2 = Me_2 and An}, the steric contribution of which in the axial positions is easily tuned, afforded results similar to those found for the platinum complexes discussed above.[53] Two new pieces of information were produced: a) for R'_2 = Me_2, complete steric protection of the metal centre already occurs with R = Me, and b) for R'_2 = An (9-Anthryl) and R′ = *i*Pr, nonspecific interionic structure was observed. The first point indicates that the steric hindrance in the axial positions was additive over all the ligands coordinated to the metal ion. Consequently, when there is a methoxycyclooctenyl moiety as well as the α-diimine ligand, it is sufficient that R = Me to protect the metal centre completely. As a confirmation, in the case of platinum complexes shown in Scheme 5, complete protection occurs for R′′ = Me and R = Et but not for R′′ = H and R = Et. Point b) allows even more interesting deductions. In fact, the substitution of the two R′ methyl groups with the An moiety[54] has the effect of dispersing the positive charge on the side of the N,N-ligand or of making it difficult to approach. Consequently, the anion no longer has its "anchorage" point and it interacts with several protons, including those belonging to the methoxycyclooctenyl moiety. One implication is that steric protection alone does not guarantee a specific interionic structure, but that, if for electronic reasons, the latter is present, modulation of the introduced steric hindrance finely determines the relative anion-cation position. This point may have interesting connections with the catalytic performances of $[PdMe(\eta^2$-olefin)(α-diimines)]A complexes toward olefin polymerization. From the literature, it is known that the molecular weights of the obtained polymers increase in the following order: R′ = Me > An > H.[47] It seems reasonable that, when R′ = H, the reduced steric protection deriving from the less restricted rotation around the N−C(*ipso*) bond favours the chain-transfer process, with polymers of lower molecular weight consequently being obtained. The reason why higher polymers are obtained with R′ = Me relative to R′ = An, however, is not obvious. Our results indicate that, in complexes in which R groups are the same, there is a greater dispersion of the positive charge for R′ = An than for R′ = Me. It could be that, in the latter case, the association of olefin is slowed by its favourable interaction with the C−C diimine carbon atoms, affording a sort of added electronic protection of the axial coordination sites and reducing the chain-transfer process rate.

All $[Pd(\eta^1,\eta^2-C_8H_{12}OMe)(N,N)]A$ complexes are active catalysts for the CO/*p*-methylstyrene alternating copolymerization, and the counter-anion effect has been discussed above. As far as the N,N-ligand effect is concerned, in contrast to olefin polymerization, increased steric hindrance on the apical positions decreases the catalytic performance. For example, when N,N = $[2,6-(R)_2-C_6H_3]N=C(Me)-C(Me)=N[2,6-(R)_2-C_6H_3]$ for R = H, the compound is a reasonably good catalyst for the CO/styrene copolymerization reaction. In contrast, the complex with R = *i*Pr is completely inactive in the copolymerization, but catalyses the formation of the homopolymer (polystyrene). This is probably due to the need for initial CO coordination at the fifth coordination site[55] in the copolymerization reaction; this is difficult to approach when sterically protected by the substituents in the N,N-ligands. The information derived from investigation of the interionic structure could also be useful for probing accessibility of the metal centre in this case.

Another example of reduced anion-cation interaction specificity was observed during the investigation of $[Pt(Me)(PPh_3)(dmphen)]PF_6$ complexes (where dmphen = 2,9-dimethyl-1,10-phenanthroline).[56] In such tetrahedral distorted square-planar complexes, the anion is located on the side of the phenanthroline but has sufficient mobility to interact with all the protons, with the exception of those of the Me group bonded directly to the platinum centre. The explanation can be found in (a) the difficulty that the anion has in approaching the carbon atoms of the pyridyl ring junctions, where it is reasonable to assume that the positive charge accumulates, and (b) the inclination (42.6°) of the coordination plane with respect to that containing the phenanthroline ligand.

Finally, we have recently synthesized $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe)(N,O)]BF_4$ compounds {where N,O = $[2,6\text{-}(i\text{Pr})_2\text{-}C_6H_3]N{=}C(Ph){-}C(Ph){=}O$, $[2,6\text{-}(i\text{Pr})_2\text{-}C_6H_3]N{=}C(Me){-}C(Ph){=}O$} in which only the N-arm affords steric protection of the axial positions.[57] The counter-anion can choose between the least crowded side, close to the O-arm, or the electronically favoured position close to the −N=C(R) bond. The interionic contacts observed in ^{19}F,^{1}H-HOESY NMR spectra suggest that the two anion-cation orientations are simultaneously present in solution with almost equal probability.

4 Quantitative NMR Investigations

After we had found preferred anion-cation orientations in most of the investigated transition metal complex ion pairs in solution, we then attempted to quantify the NOEs for estimation of average interionic distances. The first systems to be investigated were chosen on the basis of (a) their stabilities, because quantitative NOE measurements are rather time-consuming, especially if the complete kinetics of NOE build-up has to be recorded, and (b) the existence of a well-defined anion-cation "anchorage" point, in that the deduced interionic distances, already averaged by fast internal motions and ion dissociation and re-association, would be difficult to interpret if more than one anion-cation orientation were present in solution. Considering these two points, we decided to start our investigations with *trans*-$[Ru(COMe)\{(pz_2)CH_2\}(CO)(PMe_3)_2]BPh_3R$ (R = Me and Ph) complexes,[37] the semiquantitative interionic structures of which were already known. As anticipated in Section 2, the interionic NOEs can be related to σ_{IS} and consequently to the interionic distances by fitting the experimental NOE data of the complete kinetics of the NOE build-up or the initial linear trends for short mixing times. A reference distance is needed in both cases, and it inevitably refers to two nuclei belonging to the same ionic moiety. The possibility of applying Equation (5) to estimate the average interionic distances is subordinated to inspection of the correlation time of the reference distance (intramolecular) and those of interest (interionic). The *o*-H/*m*-H distance in BPh_3R^- was chosen as the reference distance, because its value in the solid state (2.47 Å) was known from neutron diffraction investigations relating to a cationic platinum(II) dinuclear single hydrido-bridged complex.[58] The complete kinetics of NOE build-up was measured by selective inversion of several target resonances by use of the *selno* (*se*lective *no*esy)[59,60] and *selnogp* (*se*lective *no*esy with field *g*radient *p*ulses)[61,62] NMR pulse sequences. An example is reported in Figure 7, in which the kinetics of NOE build-up for H4, CH_2 and *o*-H upon irradiation of H5 are reported (R = Ph). The determined structure and selected internuclear distances for the complex with the BPh_3Me^- counter-anion are illustrated in Scheme 6.

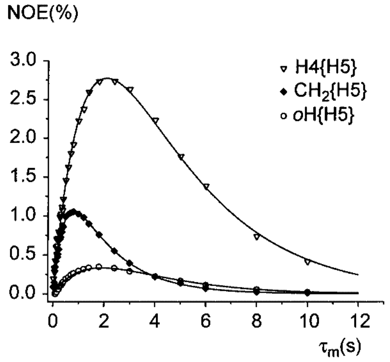
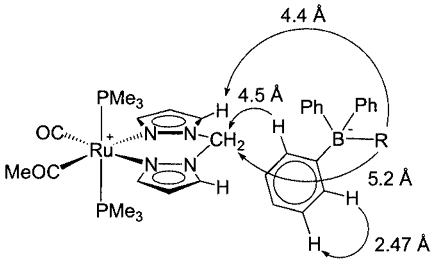


Figure 7. Experimental data relating to % NOE as a function of τ for the irradiation of H5 protons for the complex *trans*-$[Ru(COMe)\{(pz_2)CH_2\}(CO)(PMe_3)_2]BPh_4$ (400.13 MHz, 302 K, $[D_2]$dichloromethane, Gaussian-shaped pulse); reproduced from ref.[37] with the permission of the American Chemical Society



Scheme 6

An interesting point is the difference between <r>(CH_2-*o*H) (= 4.5 Å) and <r>(CH_2−BMe) (= 5.2 Å). In fact,

$\Delta<r> = 0.7$ Å and this agrees perfectly with a situation in which the anion orients the Me group far away from the metal centre.

The distances involving the protons of the counter-anion, which can undergo dynamic motion (demonstrated by the equivalence of the four phenyl groups) and those of CH_2 and H5 protons (involved in the chair-boat inversion of the six-membered $Ru-N-N-CH_2-N-N$ ring) were increased by 10% in order to correct, at least partially, for overestimation of the short distances.

In order to check the accuracy of the determined average interionic distances, rotational correlation times were estimated by two independent NMR methodologies: ^{13}C relaxation measurements[63−65] and the dependence of ^1H-^1H cross-relaxation on the temperature. The latter methodology is based on nonlinear fitting of the experimental σ_{IS} values against T (see Figure 8), in which the dependence of the rotational correlation time on temperature is introduced by means of Equation (6), where E_R is the activation energy for rotational reorientation, τ_0 is a constant, and k is the Boltzmann constant.[66,67]

$$\tau_c = \tau_0 \cdot e^{\frac{E_R}{kT}} \qquad (6)$$

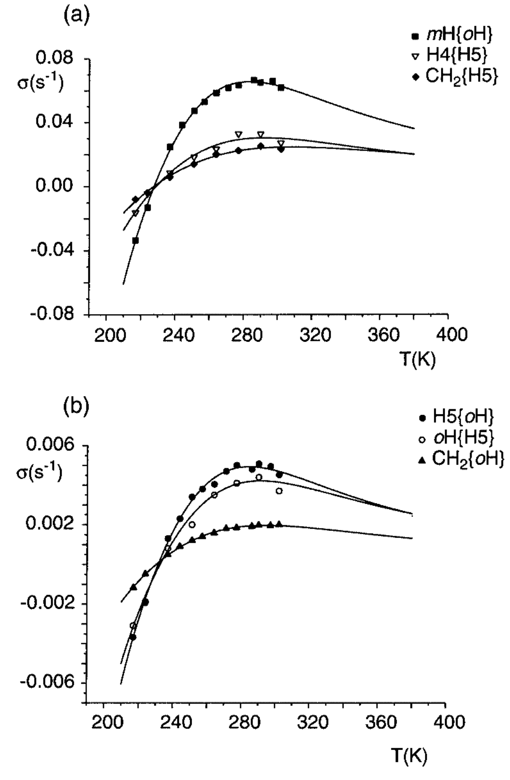


Figure 8. Intramolecular (a) and interionic (b) experimental values of σ_{IS} as a function of temperature and best nonlinear least-squares fits for the complex *trans*-[Ru(COMe) {(pz$_2$)CH$_2$}-(CO)(PMe$_3$)$_2$]BPh$_4$; it can be seen that the temperature values of the σ zero cross and maximum points are the same for both intermolecular and interionic couples of nuclei, indicating the same correlation times (400.13 MHz, 298 K, [D$_2$]dichloromethane); reproduced from ref.[37] with the permission of the American Chemical Society

With both methodologies, it was found that intramolecular and interionic couples of nuclei have rotational correlation times that are the same within experimental error (ca. 100 ps)[37] and are about 3.8 times higher than those relating to pairs of nuclei belonging to *trans*-[Ru(COMe){(pz$_2$)BH$_2$}(CO)(PMe$_3$)$_2$]. The latter compound[68] is isosteric with, and has almost the same mass as, the cationic fragment of the investigated ruthenium(II) ion pairs. Consequently, it was concluded that the overall ion pair rotation contributes mainly to the dipolar relaxation processes and that the determined interionic average distances were accurate. The error on r_{IS} was estimated to be ± 0.2 Å in view both of the goodness of the fittings and of the presence of the exchange processes mentioned above.

The usefulness of the average interionic distances can be seen by considering the complexes containing unsymmetrical BPh_3R^- counter-anions. While the tendency of the anion to orient the R aliphatic chain far away from the metal centre is clearly illustrated when R = *n*Bu and *n*-Hex, by the absence of interionic NOEs in the ^1H-NOESY NMR spectra of the terminal Me, when R = Me, this is not true because, while also orienting the methyl group far away from the metal centre, it remains close enough to interact with CH_2 and H5 cationic protons. Only the $\Delta<r>$ value mentioned above allows us to conclude that B−Me is oriented like the other B−R moieties.

5 Conclusion

The structures of transition metal complex ion pairs in solution can be determined by the use of NOE NMR spectroscopy, which provides valuable information about the interplay between interionic weak interactions and the reactivity of complexes. ^1H-NOESY and ^{19}F,^1H-HOESY investigations of several Fe^{II}, Ru^{II}, Os^{II}, Pd^{II}, Pt^{II} and Ir^{III} complex ion pairs have shown that in most cases there is a predominant relative anion-cation orientation, determined mainly by a gain in electrostatic interaction energy. This in turn is derived from positioning the anion close to the cationic moiety where the positive charge accumulates; we have very often found this to be far away from the metal centre. In complexes bearing N,N-ligands, the positive charge is concentrated in the bridging units of the two moieties containing the N-donor. Steric effects are important in the modulation of the fine anion-cation orientation, and two different cases have been observed, depending on whether or not the "steric protection" acted on the point at which the positive charge was located. In the first case, a general loss of specificity was observed; in the second case a remarkably well-defined interionic structure was observed. Quantitative NOE measurements were carried out on systems belonging to this second case and the average interionic distances were estimated. Despite the precautions that must be taken and the careful checks that must be made, the possibility of determining average interionic distances offers a unique tool for detailed structural investigation of ion pairs in solution.

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