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Application of ^{1}H-NOESY NMR Spectroscopy to the Investigation of Ion Pair Solution Structures of Organometallic Complexes by the Detection of Interionic Contacts

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Summary: The interionic solution structures of trans-[Ru(PMe$_3$)$_2$(CO)(COMe)(pz$_2$-CH$_2$)]BPh$_4$ and trans-[Ru(PMe$_3$)$_2$(CO)(COMe)(η^2-pz$_3$-CH)]BPh$_4$ have been "directly" investigated by the detection of interionic contacts in ^{1}H-NOESY NMR spectra between the protons of the organometallic fragments and those of the counterion BPh$_4^-$. A comparison with the solid-state structures obtained by single-crystal X-ray studies has been made.

The detection of intermolecular contacts by nuclear Overhauser effects (NOEs)[1] represents a unique tool for investigating the aggregation and specific localization of the interacting fragments in solution.[2] In spite of this, only a few studies have been done, principally on biological molecules[3] or organic salts which catalyze phase-transfer reactions.[4]

The importance of charged organometallic complexes in homogeneous catalytic processes is well-documented.[5] The reactions are very often carried out in organic solvents having low dielectric constants, where compounds are mainly present as ion pairs.[6] It is known that the counterion plays a fundamental role in activating or preventing these catalytic processes, but it is difficult to get "direct" information on the relative position of the counterion with respect to the organometallic fragments and, consequently, on the specific interactions of the two moieties. Several years ago, Schleyer published a few papers showing that the 3-D structure of organolithium ion pairs can be investigated precisely and directly by NOEs *via* interionic contacts.[7] In any event, there have been no reports on the application of this methodology to the investigation of the interionic structure of organometallic compounds containing transition metals which are those usually used in homogeneous catalysis.

Here we describe an application of ^{1}H-NOESY NMR spectroscopy to determine the interionic structure in solution of two test complexes: *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(pz$_2$-CH$_2$)]BPh$_4$ (**1**) and *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(η^2-pz$_3$-CH)]BPh$_4$ (**2**; pz = pyrazlolyl ring) in CD$_2$Cl$_2$. The principal goals are (a) to understand whether **1** and **2** are present as ion pairs, (b) to identify the type of ion pair,[8] and (c) to localize the BPh$_4^-$ counterion with respect to the cationic fragment.

Complexes **1** and **2** were synthesized by reaction of the previously prepared[9] *trans,cis*-Ru(PMe$_3$)$_2$(CO)$_2$(Me)I with pz$_2$-CH$_2$ and pz$_3$-CH, respectively. Single-crystal X-ray structures were determined and will be reported elsewhere, together with a full account of the synthesis procedure.

As can be seen from Figure 1, there are several protons that can be used as "reporters" [10] to localize the position of the BPh$_4^-$ counterion using NOEs, if we consider that those interactions between protons that are closer than 3.5−4 Å to each other are detectable. If the distances observed in the solid state are maintained in solution, we should observe interionic contacts between PMe$_3$, CH$_2$, and 5-pz protons and BPh$_4^-$ protons for **1**, while for **2** there should be interionic contacts only between one of the PMe$_3$ groups, −CH, and one of the two 5-pz protons of coordinated rings and BPh$_4^-$ protons.

The ^{1}H-NOESY NMR spectrum[11] of **1**, apart from obvious peaks due to the atoms that are close together in the same molecular fragment, also shows all of the

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[11] The NMR sample was prepared by dissolving about 20 mg of compound in 0.5 mL of CD$_2$Cl$_2$ and bubbling for 5 min with dried nitrogen. The phase-sensitive ^{1}H-NOESY experiments were obtained at 298 K on a Varian UNITY 400WB instrument using a mixing time period of 0.5 s.

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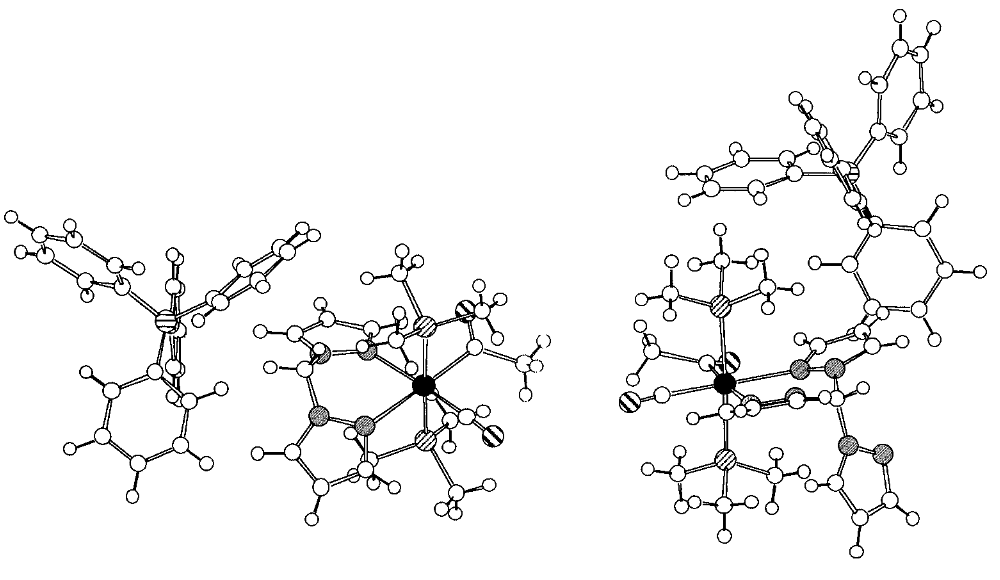

1 **2**

Figure 1. Views of complexes **1** and **2** showing the different localizations of BPh_4^- with respect to the organometallic fragment. Shadings indicate the following atoms: solid, Ru; ascending stripes, P; gray, N; descending stripes, O; horizontal stripes, B; no shading, C and H.

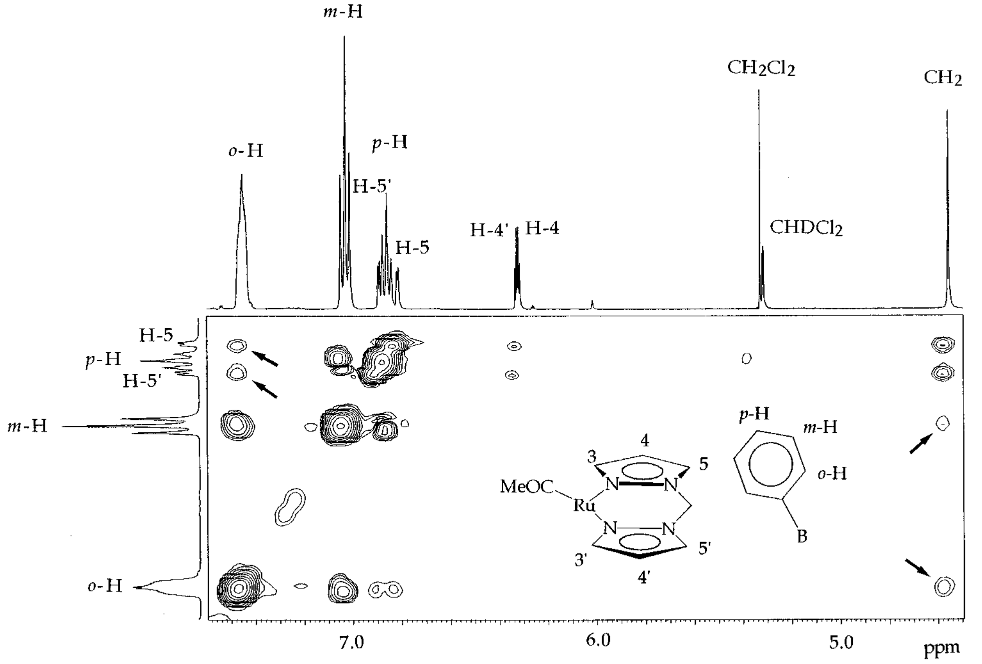

Figure 2. Section of the ^1H-NOESY NMR spectrum of **1** showing the interionic contacts between (a) H-5, H-5′, CH_2, and *o*-H and (b) CH_2 and *p*-H. The distinction between protons belonging to different pz rings was done by 3-H−COMe NOE detection.

predicted cross-peaks relative to interactions between the organometallic moiety and the counterion (Figure 2). In particular, both 5-H and 5′-H show contacts with *o*-H of BPh_4^-. The CH_2 protons show contacts with *o*-H and weak contacts with *m*-H. Finally, the protons of the PMe_3 groups interact with all the protons of BPh_4^-. No contacts are observed between the protons of BPh_4^- and the protons of COMe. Further support for a proximity between the CH_2 protons and the aromatic rings of BPh_4^- comes from the low value of the chemical shift in **1** (4.57 ppm) compared to that of the free ligand (6.30 ppm). This can be explained by considering the shielding effect exerted on CH_2 protons by the aromatic protons.

The ^1H-NOESY NMR spectrum of **2** also indicates that, in solution, BPh_4^- has the same position as in the solid state, and all the contacts predicted have been observed.

The existence of interionic contacts in itself indicates that **1** and **2** in CD_2Cl_2 are principally present as ion pairs. Furthermore, the fact that all the predicted contacts, on the basis of X-ray crystal structures, are observed suggests that an intimate or solvent-shared ion pair[8] has to be considered. Finally, the BPh_4^- counterion is located close to bis(pyrazolyl)methane in **1** and in front of the octahedral face delimited by the pz ring *cis* to COMe, by the upper phosphine, and by COMe in **2**. In both cases BPh_4^- prefers the position that maximizes the lyophilic interaction with the organic part of the organometallic fragment. The van der Waals and electrostatic energies were estimated and compared using the GRID force field program.[12] It indicates that the electrostatic energy is smaller than the van der Waals energy, its value being almost independent of the position of the counterion. On the other hand, the van der Waals interactions are strongly dependent on the localization of BPh_4^- and are responsible for the structure both in solution and in the solid state.

The methodology reported here, based on the detection of interionic NOEs for the determination of the ion pair structure and the localization of the counterion with respect to the organometallic fragment, can be extended to any type of charged organometallic complex preferably under 1000 Da (otherwise, if we still want to distinguish saturation transfer from exchange peaks, techniques such as ROESY[3c,13] or CAMELSPIN[14] must be used[4b]) having active nuclei in NMR in both the cation and the anion fragments. This can afford important indications on the role of the counterion in catalytic homogeneous processes mediated by charged organometallics. Work is in progress concerning the extension to different counterions (detecting, in addition, heteronuclear Overhauser effects) and different compounds, including negative organometallic fragments with positive counterions. Furthermore, we are currying out studies on the effect of temperature, dielectric constant of the solvent, and mixing time on interionic NOEs.

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