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Specificity of Interionic Contacts and Estimation of Average Interionic Distances by NOE NMR Measurements in Solution of Cationic Ru(II) Organometallic Complexes Bearing Unsymmetrical Counterions

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Summary: The interionic structure in methylene chloride of trans-[Ru(PMe$_3$)$_2$(CO)(COMe)(CH$_2$-pz$_2$)]BPh$_3$R (where pz = pyrazolyl ring; R = Me, n-Bu, n-Hex, and Ph) complexes has been investigated by the detection of interionic contacts in ^{1}H NOESY NMR spectra. We observed an unexpected specificity of interionic contacts that allowed, for the first time, the estimation of reasonable average interionic distances by measuring the kinetic of ^{1}H NOE buildup.

Although most of the important processes in homogeneous catalysis are mediated by charged organometallics and a crucial role is attributed to the phenomenon of ion-pairing,[1] direct structural information on ion-pairs in solution is difficult to obtain, and they are usually studied indirectly assuming that the solid state and solution structures are the same.[1b,d]

We have recently proposed[2] a direct method for investigating organometallic ion-pairs in solution based on the detection of interionic contacts in the ^{1}H NOESY and ^{19}F{^{1}H} HOESY NMR spectra. We observed specific interactions between the counteranion and particular groups of the organometallic moiety when intimate ion-pairs are predominant. These allow the localization of the counterion position with respect to the organometallic cation. In our complexes,[3] the counterion, regardless of its nature, is specifically localized close to the more organic fragment of the molecule. Quantomechanical and mechanical calculations[4] showed that this is principally due to a nonsymmetrical charge distribution on cationic complexes.

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(1) (a) Chen, Y.-X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 2582. (b) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842. (c) Chen, Y.-X.; Stern, C. L.; Yang, X.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451. (d) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015. (e) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267. (f) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663. (g) Milani, B.; Vicentini, L.; Sommazzi, A.; Garbassi, F.; Chiarparin, E.; Zangrando, E.; Mestroni, G. *J. Chem Soc., Dalton Trans.* **1996**, 3139. (h) Evans, D. A.; Murry, J. A.; von Matt, P.; Norcross, R. D.; Miller, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 798. (i) Carmona, D.; Cativiela, C.; Garcia-Correas, R.; Lahoz, F. J.; Lamata, M. P.; Lopez, J. A.; Lopez-Ram de Viu, M. P.; Oro, L. A.; San José, E.; Viguri, F. *J. Chem. Soc., Chem. Commun.* **1996**, 1247.

(2) (a) Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G.; Terenzi, S. *Organometallics* **1996**, *15*, 4349. (b) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Gramlich, V.; Rüegger, H.; Terenzi, S.; Venanzi, L. M. *Organometallics* **1997**, *16*, 2139.

(3) [M(PMe$_3$)$_x$(CO)$_y$Z(pz$_{4-x}$CH$_x$)]BY$_4$ (where M = Fe and Ru, Z = COMe or Me, Y = Ph or F, pz = pyrazolyl ring, x and y = 1 or 2) and *trans*-[M(PMe$_3$)$_2$(CO)(COMe)(N,O)]BPh$_4$ (where M = Fe and Ru, N,O = 2-acetylpyridine, 2-benzoylpyridine, and 2, 2′-dipyridylketone).

(4) Macchioni, A.; Bellachioma, G.; Cardaci, G.; Cruciani, G.; Foresti, E.; Sabatino, P.; Zuccaccia, C. *Organometallics*, in press.

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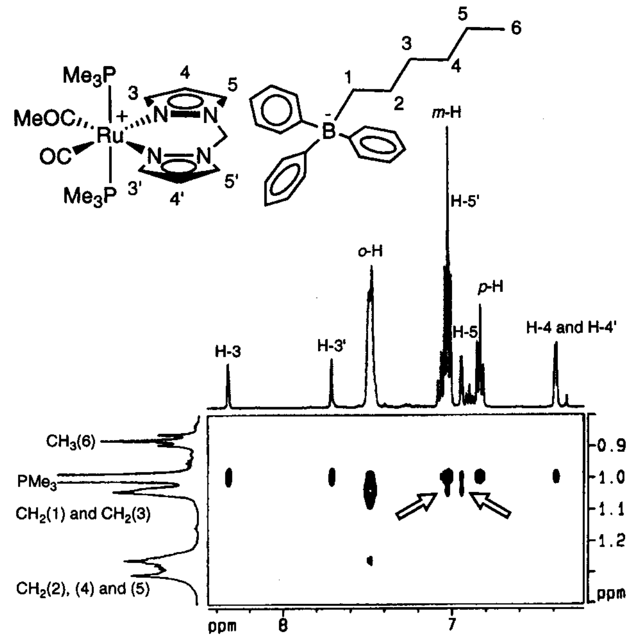
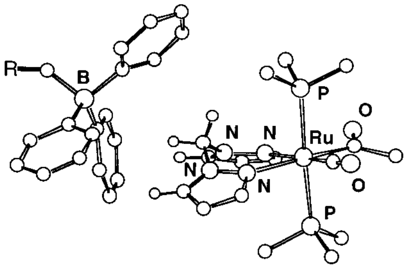


Figure 1. Section of the ^{1}H NOESY spectrum of the compound where R = *n*-Hex, recorded at 400.13 MHz in CD_2Cl_2, showing the interionic contacts between α-CH_2 protons and H-5 and H-5′ (indicated with arrows) and the absence of interionic contacts between CH_3 and protons belonging to the cation.

Scheme 1



The above results on the specificity of NMR interionic interactions prompted research in two directions: (a) the utilization of unsymmetrical counterions and (b) the quantification of the NOE in order to estimate the average interionic distances. To the best of our knowledge there are no previous reports on the latter. The investigations were carried out on the complexes *trans*-[Ru(PMe$_3$)$_2$(CO)(COMe)(CH$_2$-pz$_2$)]BPh$_3$R (where pz = pyrazolyl ring; R = Me, *n*-Bu, *n*-Hex, and Ph)[5] in CD$_2$Cl$_2$ solution where the complexes are mainly present as intimate ion-pairs.[6]

The ^{1}H NOESY NMR spectra[7] of complexes bearing unsymmetrical counterions indicate that the specificity of interionic interactions is more marked than we expected. There are interionic interactions only between the aromatic and α-aliphatic protons of the counterions and CH$_2$, H-5, and PMe$_3$ protons of the cation. Interestingly, there are no interionic contacts between the CH$_3$ groups of the counterions and the protons belonging to the cation when R = Bu and *n*-Hex (see Figure 1). The average interionic structure that can be inferred from the above observations is reported in Scheme 1 where (a) the counterion is localized in front of the face defined by PMe$_3$ and by the two arms of the N,N-bidentate ligand, (b) two phenyl groups of the counterion strongly interact with the pyrazolyl rings, and (c) the aliphatic tail points away from the organometallic cation, but the α-CH$_2$ protons are still close enough to interact with the CH$_2$ protons.

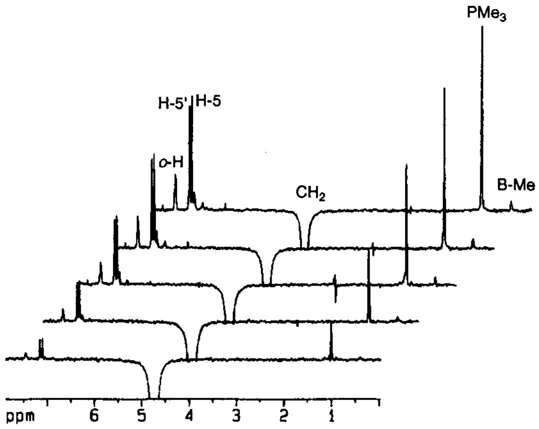


Figure 2. ^{1}H NOE spectra of the compound where R = Me, recorded at 400.13 MHz in CD_2Cl_2 with the Selno sequence,[8b] showing the inversion of CH$_2$ and the buildup of the enhancements on H-5, H-5′, and PMe$_3$ (intramolecular NOEs) and *o*-H and B-Me (interionic NOEs).

Table 1: Average Intramolecular and Interionic (in Bold) Distances and Cross Relaxation Rates for the Compound Where R = Me Determined by the Kinetics of NOE Buildup in CD$_2$Cl$_2$[a]

		σ_{XY} (10^3 s^{-1})	r_{XY} (Å)
X = CH$_2$	Y = *o*-H	**2.1 ± 0.2**	**3.3 ± 0.1**
	H-5	22.0 ± 0.5	2.24 ± 0.02
	PMe$_3$	2.4 ± 0.1	2.4 ± 0.1
	B-Me	**0.9 ± 0.2**	**3.8 ± 0.2**
X = *o*-H	Y = B-Me	7.0 ± 0.2	2.72 ± 0.03
	m-H	7.3 ± 0.3	2.45[b]
	CH$_2$	**2.1 ± 0.1**	**3.32 ± 0.05**
X = PMe$_3$	Y = *m*-H	**0.18 ± 0.01**	**5.0 ± 0.1**
	CH$_2$	2.5 ± 0.1	3.22 ± 0.04
	COMe	1.9 ± 0.1	3.40 ± 0.05
	H-3	2.05 ± 0.06	3.33 ± 0.04
	H-3′	1.72 ± 0.06	3.43 ± 0.04
X = B-Me	Y = *o*-H	7.1 ± 0.2	2.71 ± 0.03
	H-5	**2.6 ± 0.1**	**3.20 ± 0.04**

[a] X and Y represent the groups whose resonances have been inverted and enhanced by NOE, respectively. The errors in distances and cross relaxation rates take into consideration only the standard deviation on the slope of the linear fittings and are underestimated. [b] Reference distance.

The fact that an average structure is predominant convinced us to try to quantify the NOE and to estimate the interionic average distances. This was done by measuring the kinetics of intramolecular and interionic

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(5) The synthesis of complexes as well as of the unsymmetrical counterions will be reported elsewhere.

(6) Conductometric measurements for similar compounds show that the ion-pair dissociation constants are ca. 10^{-4} mol^{-1} L (Bellachioma, G.; Cardaci, G.; Macchioni, A.; Reichenbach, G. *Gazz. Chim. It.* **1991**, *121*, 101). Furthermore, the resonances in the ^{1}H NMR spectra are not sensitive to an increase in the concentration of the compounds.

(7) The NMR spectra were recorded on a Bruker DRX 400 dissolving ca. 20 mg of compound in 0.6 mL of CD$_2$Cl$_2$. The ^{1}H NOESY spectra were recorded by using the Bruker sequence *noesytp* dedicating 2K and 1K of memory to f2 and f1, respectively. The mixing time was 800 ms.

NOE buildup with both the Selno[8] and the GOESY pulse sequences, recently reported by Keeler et al.[8b,9] We performed several experiments by selectively exciting[10] the *o*-H, CH_2, and PMe_3 protons, and we found good linearity between the percent of NOE and the mixing time *t* in the range 0−400 ms (see Figure 2). As reference distances we used *o*-H/*m*-H, $r = 2.45$ Å. In the case of interionic contacts and intramolecular contacts of protons that undergo dynamic processes, the slopes of the straight lines are proportional to an average cross relaxation rate constant[11] ($\langle\sigma\rangle_{av}$), and consequently we can obtained only average distances ($\langle r\rangle_{av}$) (see Table 1).[12] It is interesting to outline three aspects to check the validity of the measurements: (1) the values of distances obtained from "symmetrical" experiments (saturating X and detecting the NOE in Y and vice versa) are identical within the experimental error; (2) the average distance B-Me/CH_2 is about 0.5 Å longer than the average distance *o*-H/CH_2, in agreement with the qualitative representation reported in Scheme 1, where the aliphatic chain points away from the cationic moiety; (3) the intramolecular distances where there are active dynamic processes are well reproduced.

In conclusion, the investigation of the interionic structure of charged organometallic complexes in solution based on the measurement of interionic NOEs can afford both qualitative (namely localization of the relative cation−anion position) and quantitative (namely average interionic distances) information. The requirements are the presence of NMR-active nuclei in both anion and cation fragments and the predominance of intimate ion-pairs in solution.[13]

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[8] (a) Bauer, C. J.; Freeman, R.; Frenkiel, T.; Keeler, J.; Shaka, A. J. *J. Magn. Reson.* **1984**, *58*, 442. (b) Kessler, H.; Oschinat, H.; Griesinger, C.; Bermel, W. *J. Magn. Reson.* **1986**, *70*, 106.

[9] Stonehouse, J.; Adell, P.; Keeler, J.; Shaka, A. J. *J. Am. Chem. Soc.* **1994**, *116*, 6037.

[10] Important parameters: both the selective 90° and 270° pulses were of 80 ms duration, while the power levels were 75 and 69 dB, respectively, and shaped to a 1% truncated Gaussian. The gradients were regulated as suggested by the Bruker microprograms. Each point of the kinetics consisted of 256 acquisitions with a recycle delay of 12 s.

[11] Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH Publishers: New York, 1989; Chapters 4 and 5.

[12] There are several equations to determine average distances that depend on the time scale of averaging compared to the correlation time τ_c and on the type of dynamic process. They are usually expressed as a function of a minimum distance r_1 and a maximum distance r_2 and a distribution function $f(r)$ (ref 11, pp 170−173). We measured τ_c from the NOE max values and from the longitudinal relaxation time of ^{13}C and tested the various equations. We found the best estimation of interionic distances can be obtained by simply increasing the $\langle r\rangle_{av}$ values by 10% in order to correct for the overestimation of short distances.

[13] In solvents with dielectric constants higher than methylene chloride (acetone, methanol, and nitromethane) or when using less coordinating counterions such as $B(3,5\text{-}(CF_3)_2(C_6H_3))_4^-$, we observed that in some cases the specificity of interionic contacts was lost and in other cases the intensity of contacts was scaled down by the partial dissociation of the intimate ion-pairs.