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INTRAMOLECULAR MOBILITY OF η^3-ALLYLPALLADIUM CHLORIDE COMPLEXES OF DIFFERENT PHOSPHINES STUDIED BY TWO DIMENSIONAL NMR SPECTROSCOPY

H. MEYER and A. ZSCHUNKE*
Sektion Chemie, Martin-Luther-Universität Halle-Wittenberg (DDR)

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Summary

The diastereomerization of η^3-allylpalladium chloride complexes (I–III) of the phosphines 4,4-dimethyl-*t*-6-methyl-*t*-2,*r*-3-diphenyl-1,3-oxaphosphorinane (**1**), *o*-bromobenzylphenylmethylphosphine (**2**) 1-phosphabicyclo[3.2.1]octane (**3**) has been studied by two-dimensional ^{1}H NMR spectroscopy. Two processes are distinguished: a faster process, $\eta^3 \rightleftharpoons \eta^1$-conversion combined with a preferred C–C-rotation (α-mechanism), and a slower process, $\eta^3 \rightleftharpoons \eta^1$-conversion combined with C–C-rotation and C–Pd-rotation (γ-mechanism). In complexes containing bulky phosphines both processes are retarded.

Introduction

The diastereomers of the η^3-allylpalladium chloride complexes I–III, I′–III′ of the phosphines **1–3** (see Scheme 1) have been studied in solutions of weakly polar solvents (CD_2Cl_2, $CDCl_3$). These compounds are relative stable under the conditions used [1]. Exchange of the phosphine ligands can take place only when an excess of free phosphine is present [2]. However, the phosphine ligand could exercise a *trans*-effect [3] on one of the terminal C-atoms of the allylic group determining the orientation of an intramolecular $\eta^3 \rightarrow \eta^1$-conversion. Our picture of this intramolecular process is that the $\eta^3 \rightarrow \eta^1$-conversion of the allylic group is assisted by the occupation of the fifth coordination site at the palladium [4]. The coordinating molecules (donors) can be solvent molecules or the chloride ligands of similar molecules via chlorine bridges.

Sterically bulky phosphines should make pentacoordination more difficult and retard the $\eta^3 \rightarrow \eta^1$-conversion. The approximative Tolman cone angles φ [5] (see Scheme 1) are measures of the steric bulk of the phosphine ligands in complexes. A smaller angle φ is connected with an easier pentacoordination and consequently with a faster $\eta^3 \rightleftharpoons \eta^1$-conversion. The $\eta^3 \rightarrow \eta^1$-conversion initiates the detected diastereomerization. The two dimensional (2D) exchange NMR spectra [6,7] of the allylic protons qualitatively confirm this assumption, as will be shown below.

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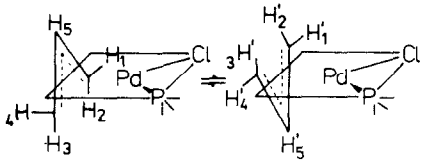
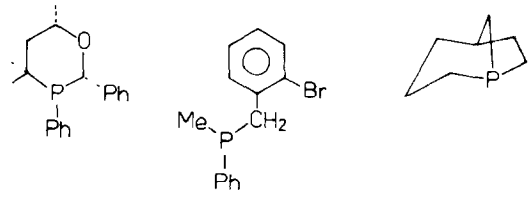


complex		phosphin
I	I'	1
II	II'	2
III	III'	3



1	2	3
φ >150	< 140	< 120

φ = Tolmans cone angles [5]

SCHEME 1

Discussion

α-Mechanism

The contour plots of the ^{1}H-2D-exchange NMR spectra (see Fig. 1–6) display two types of cross-peak networks: One network at room temperature (complex I, I′) or short mixing times (complexes II,II′ and III,III′) is associated with the α-mechanism. Another typical network at higher temperatures (complex I,I′) or at longer mixing times (complexes II,II′ and III,III′) is associated with the γ-mechanism.

In the ^{1}H NMR spectra of I,I′ * at 298 K all the allylic signals of both diastereomers I and I′ are well separated. In the contour plots of the 2D-exchange NMR spectra of I,I′ (see Fig. 1) the cross peaks (connected by a line 135° against the horizontal [8]) at 298 K and a mixing time of t_m 0.5 s reveal the exchanging protons of the allylic group:

$H^1 \rightleftharpoons H^{1'}$

$H^2 \rightleftharpoons H^{2'}$

$H^3 \rightleftharpoons H^{4'}$

$H^{3'} \rightleftharpoons H^4$

$H^5 \rightleftharpoons H^{5'}$

* We always used mixtures of the inseparable diastereomeric pairs I,I′, II,II′ and III,III′ (see Scheme 1).

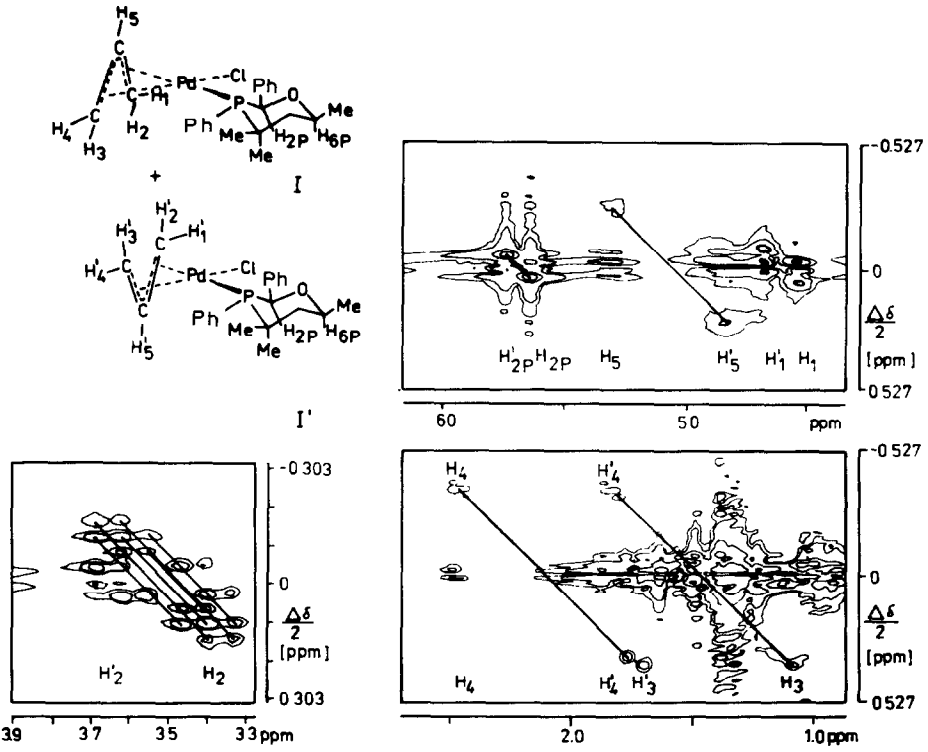


Fig. 1. Sections of the contour plot of the ^{1}H-2D-exchange NMR spectrum of I,I′ in CD_2Cl_2, Temp. 298 K. The contour of the ^{1}H-1D NMR spectrum is placed at the horizontal, mixing time t_m 0.5 s. The signals of a proton which is involved in a chemical exchange have cross peaks on the parallel to the vertical axis, a line 135° to the horizontal connects the cross peaks of the exchanging protons.

The process, which is consistent with this exchange pattern, can be described as a diastereomerization (see Scheme 1). The underlying mechanism we designate an α-mechanism [9].

The α-mechanism can be considered as the combination of the following molecular movements [10]:

$\eta^3 \rightarrow \eta^1$-conversion (formation of a σ-bond between palladium and the C_α-atom bearing the hydrogen atoms H^3 and H^4).

Rotation of the C–C σ-bond axis of the allylic group by ca. 120° and a smaller rotation around the C–Pd σ-bond axis (ca. 60°). The terminal C-atom of the allylic group remains in the vicinity of the palladium atom.

$\eta^1 \rightarrow \eta^3$-conversion (formation of the π-complex, in which the C_α-atom is again in the *cis*-position relative to the phosphine ligand).

The *cis*-2,3-diphenyl-1,3-oxaphosphorinane-η^3-allylpalladium chloride shows at 304 K in $CDCl_3$-solution (mixing time t_m 0.3 s) a similar behaviour [9]. In the ^{1}H-NMR spectra of II,II′ and III,III′ the two diastereomers can not be distinguished because the chemical shifts are are too close together, but the signals of the protons 3 and 4 are broadened even at 296 K (see Fig. 2 and 5). The α-mechanism is apparently faster than in I,I′. We must thus use a shorter mixing time t_m to get a pattern of cross-peaks similar to that for I,I′. At t_m 0.05 s, in agreement with the α-mechanism,

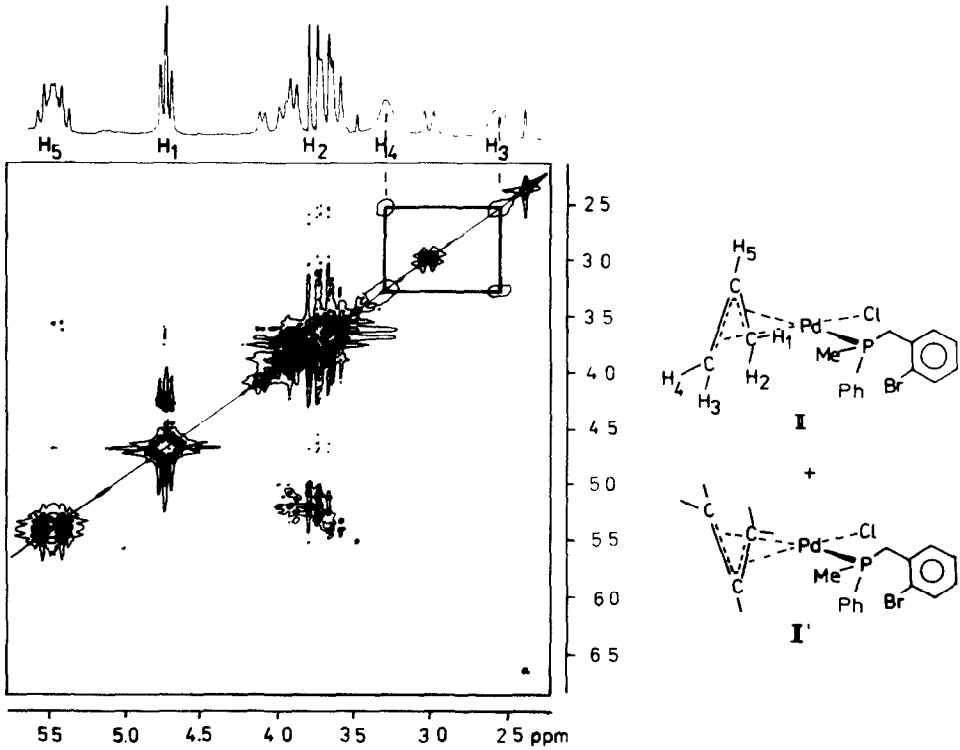


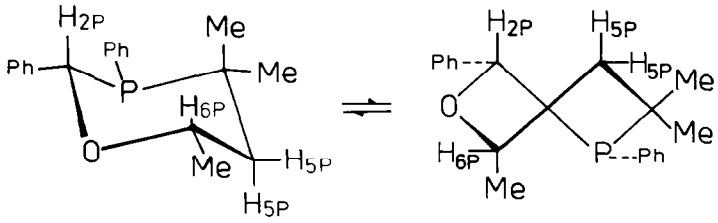
Fig. 2. Upper part: ^{1}H NMR spectrum of II,II′ in CD_2Cl_2, Temp. 296 K. Lower part: contour plot of the ^{1}H-2D-exchange NMR spectrum of II,II′ in CD_2Cl_2, t_m 0.05 s. The ^{1}H-1D-contour NMR spectrum is placed on the diagonal, the associated cross peaks of the exchanging protones are the crossing points of the parallels to both axes. The proton signals of the two diastereomers are superimposed and carried to be distinguished.

only exchange between the protons 3 and 4 is detected. (In Fig. 2–6 the cross peaks are the crossing points of the parallels to the both frequency axes). We can explain the fact that the α-mechanism is faster in terms of the easier attack of a donor on the palladium atom in II,II′ and III,III′ (compared with I,I′) arising from the smaller shielding power of the phosphine.

γ-Mechanism

In the ^{1}H-2D-exchange NMR spectrum of I,I′ at 330 K (t_m 0.3 s) the presence of several additional cross peaks indicates the operation of an additional process (see Fig. 3). With exception of $1 \rightleftharpoons 2$, $1 \rightleftharpoons 2'$, $1' \rightleftharpoons 2$, all the possible exchanges between the allylic protons in both diastereomers take place. Additional cross peaks between the proton signals $H_{2p} \rightleftharpoons H_{6p}$, $H_{2p} \rightleftharpoons H_{5p}$ and $H_{6p} \rightleftharpoons H_{5p}$ are due to the dipolar interaction (NOE) of these protons in the preferred conformers of the ligand **1** (see Scheme 2).

A similar network of the cross peaks of the allylic proton signals is shown in the ^{1}H-2D-exchange NMR spectra of II,II′ at 296 K and t_m 0.3 s (Fig. 4) and III,III′ at 294 K and t_m 0.4 s (Fig. 6). Unfortunately distinction between the two diastereomers is only possible for I,I′. A corresponding feature of the exchange pattern is the



SCHEME 2

absence of the exchange between the protons 1 and 2.

From the ^{1}H-2D-exchange NMR spectrum of I,I′ at 330 K we conclude that both diastereomerization and topomerization take place (see Fig. 3).

The γ-mechanism can be considered in terms of the following steps:
$\eta^3 \rightarrow \eta^1$-Conversion (formation of a σ-bond between the palladium and the C_α-atom bearing the H-atoms H^3 and H^4; fixation of the positions H^1 and H^2 relatively to H^5).
Rotation around the Pd–C-bond axis turning the terminal C-atoms of the allylic group from the *trans* position relatively to the phosphine ligand into the *cis* position.

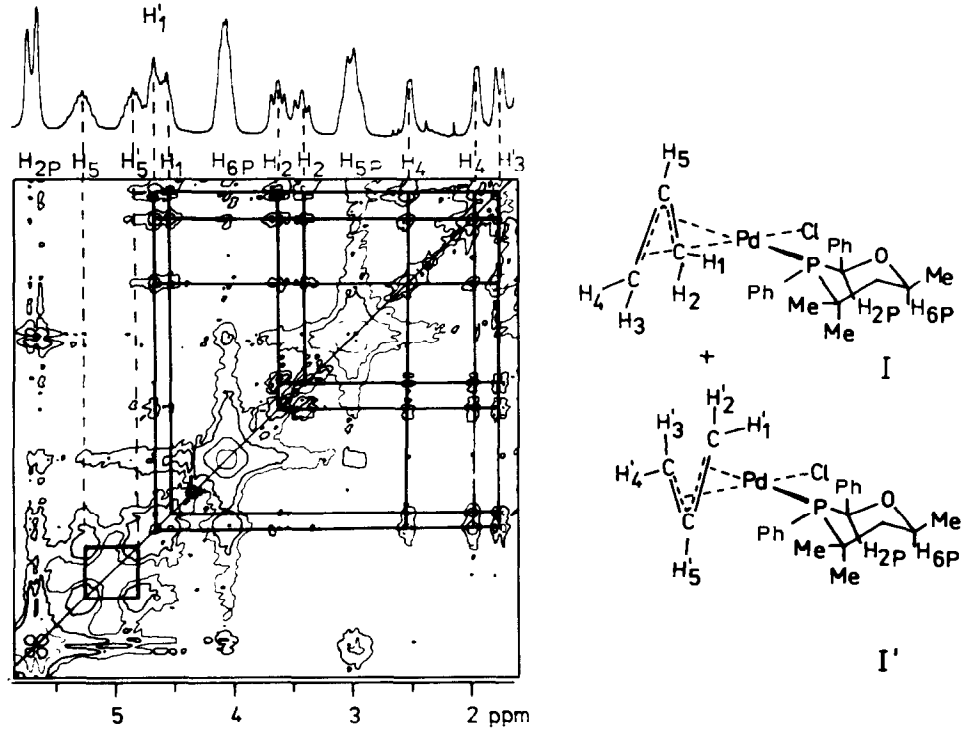


Fig. 3. Upper part: ^{1}H NMR spectrum of I,I′ in CD_2Cl_2, Temp. 330 K. Lower part: contour plot of the ^{1}H-2D-exchange NMR spectrum of I,I′ in CD_2Cl_2, t_m 0.3 s. The ^{1}H-1D-contour NMR spectrum is placed on the diagonal, the attached cross peaks of the exchanging protons are the crossing points of the parallels to both axes.

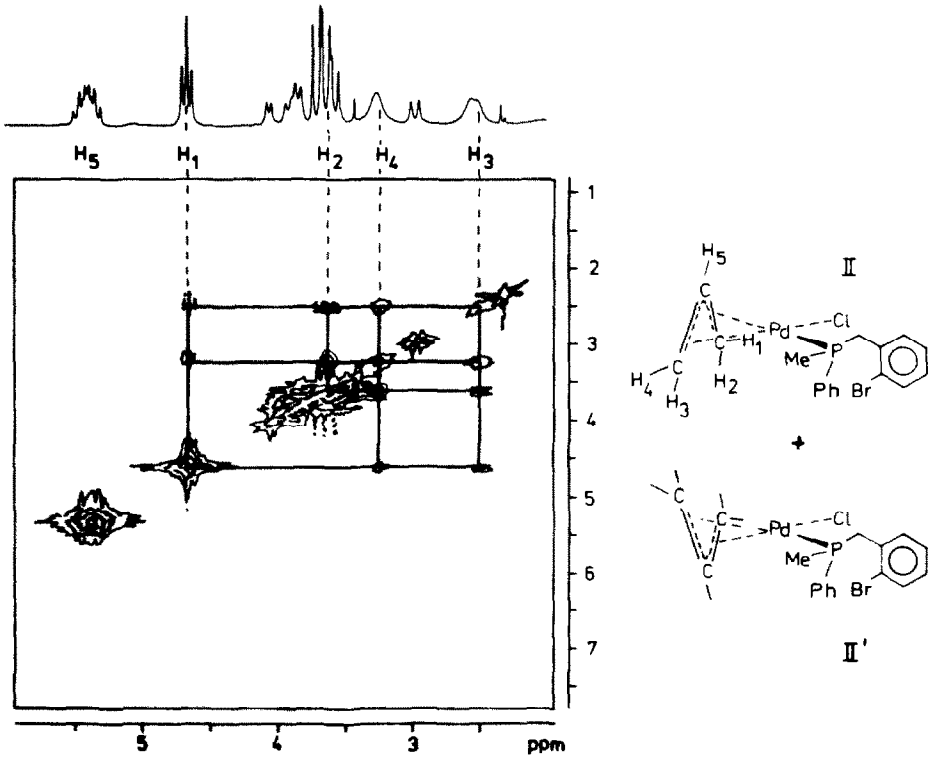


Fig. 4. Upper part: ^{1}H-NMR spectrum of II,II' in CD_2Cl_2, Temp. 296 K. Lower part: contour plot of the ^{1}H-2D-exchange NMR spectrum of II,II' in CD_2Cl_2, t_m 0.3 s (explanations of the cross peaks see Fig. 2).

This movement is superimposed upon the easier rotations of the α-mechanism which cause a diastereomerization or a topomerization.

$^1\eta \rightarrow {}^3\eta$-conversion (formation of the π-complex, in which the C_α-atom is now in a *trans* position relatively to the phosphine ligand.

All other mechanism mechanism mentioned in ref. 9 can be excluded. The examples show, that bulky phosphines in the η^3-allylpalladium chloride complexes retard both processes (α- and γ-mechanism).

Experimental

The 2D-exchange-^{1}H NMR spectra were measured on solutions containing 4 mg of the complex in 0.5 ml of solvent. The FT NMR 2D-program version 810115.4 was adopted using a Bruker WP 200 spectrometer equipped with an Aspect 2000 Computer (Fig. 1–5) and a VARIAN XL 200 spectrometer (Fig. 6) under the conditions indicated in the legends to the figures. The Bruker program uses a 16 phase rotation cycle to eliminate the axial and positive type peaks and also ghost peaks in the quadrature detection mode in both frequency dimensions, but it is therefore not so effective in the ghost peak suppression as the preferred 32 phase cycle [11]. The *J*-cross-peaks from the coherent magnetization transfer between the coupled nuclei are suppressed by a random variation of max. $\Delta t_m \leqslant 10$ ms of the

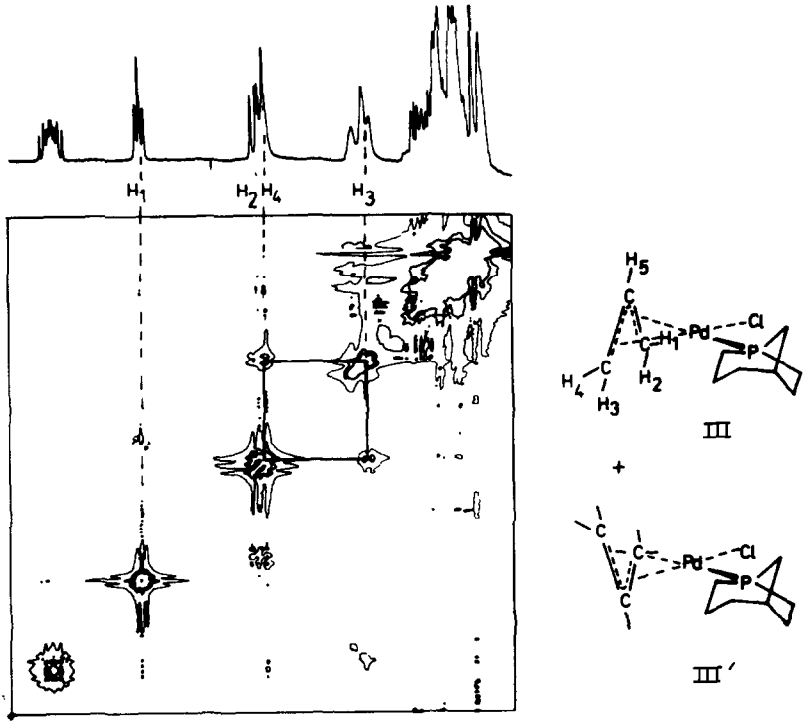


Fig. 5. Upper part: ^{1}H NMR spectrum of III,III′ in $CDCl_3$, Temp. 297 K. Lower part: contour plot of the ^{1}H-2D-exchange NMR spectrum of III,III′ in $CDCl_3$, t_m 0.05 s (explanation of the cross peaks see Fig. 2).

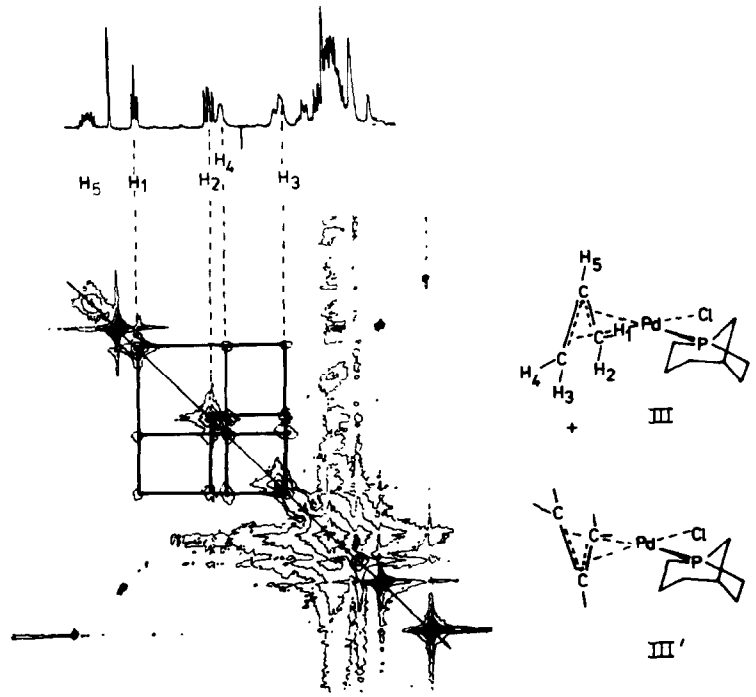


Fig. 6. Upper part: ^{1}H NMR spectrum of III,III′ in CD_2Cl_2, Temp. 294 K. Lower part: contour plot of the ^{1}H-2D-exchange NMR spectrum of III,III′ in CD_2cl_2, t_m 0.4 s, P-type selection [12] (explanation of the cross peaks see Fig. 2).

mixing-time t_m [11]. The 2D-exchange spectrum of Fig. 1 is measured with a ($90°$-t_1|$90°$-($t_m \pm \Delta t_m$)|$90°$-t_1-acquisition) pulse sequence to yield a SECSY-like representation of the 2D-spectrum [12] in order to save storage capacity. The other spectra are taken with a ($90°$-t_1|$90°$-($t_m \pm \Delta t_m$)|$90°$-acquisition) pulse sequence with N-type selection (Fig. 2–5) or P-type selection (Fig. 6) in a 256×1024 (Fig. 1) respectively, 512×1024 point data matrix which results in a 3.9 Hz/Pt digital resolution of the spectra. The FID is multiplied by a $\pi/3$-shifted sine bell window function to prevent cut off of the FID's taken with acquisition time t_{acq} 0.128 s in the presence of longer T_2^* (sharp lines). All 2D NMR spectra are shown in the absolute value mode.

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