

Applications of 2-dimensional NMR in organometallic chemistry

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Abstract - Two dimensional X,H Correlations, COSY and NOESY measurements are shown to be valuable aids in assigning spectra and determining structure. Specifically the NOESY pulse sequence is shown to be useful in the determination of a) 3-dimensional structure of cyclic π -allyl complexes, b) subtle geometric distortions of the syn and anti protons in the methylene part of a π -allyl ligand, i.e., $\text{Pd}(\eta^3\text{-CH}_{\text{syn}}\text{H}_{\text{anti}}\text{C}(\text{CH}_3)\text{CHR})$ and c) detecting simultaneous ligand exchange reactions in the complexes $\text{Pt}(\text{SnCl}_3)(\eta^3\text{-CH}_2\text{C}(\text{CH}_3)\text{CH}_2)(\text{PhCH}=\text{CH}_2)$.

INTRODUCTION

Despite the acceptance of two-dimensional methodologies into organic and biochemistry (ref. 1) organometallic and coordination chemists have been slow to incorporate these techniques. This is partially because several of these 2-D pulse sequences have as their goal solely spectral assignment. Specifically, a $^{13}\text{C},\text{H}$ correlation allows connection of these two nuclei via $^1\text{J}(^{13}\text{C},\text{H})$ thereby facilitating the assignment of these spectra and/or discovering hidden resonances. ^1H 2-D homonuclear correlation spectroscopy, COSY, demonstrates J-coupling connectivity between proton spins and is superior to single frequency decoupling in that all the coupling information is available from one experiment. These methods are appealing for the elucidation of organic structures; however, often this is only of secondary importance, e.g., the ^1H spin system has been deliberately chosen to be simple and/or the emphasis is on the metal. One can broaden the scope of the heteronuclear X,H correlation to include a suitable metal resonance and consequently adjust the emphasis of the measurement. Using the $^1\text{H},\text{X}$ coupling constant to help find the metal signal may lead to new structure and bonding data, as the metal chemical shift is recognized to be quite sensitive to the nature of the ligands in the coordination sphere (ref. 2). However, the 2-D NOESY sequence, which, for ^1H , affords both Overhauser and chemical exchange information (ref. 1) is more attractive. The Overhauser effect involves $^1\text{H}-^1\text{H}$ dipole-dipole relaxation and consequently distance data, whereas magnetization transfer between chemically exchanging sites has mechanistic implications.

Our recent interest in π -allyl chemistry (ref. 3) prompted us to consider the following questions:

- i) how might one determine which face of a somewhat complicated π -allyl ligand is coordinated
- ii) would it be possible to generalize the observations for $\text{Ni}(\eta^3\text{-C}_3\text{H}_5)_2$, made via neutron diffraction, that the syn proton is distorted toward the nickel (ref. 4) and

iii) how might one best cope with the simultaneous, relatively complicated exchange phenomena often associated with such molecules.

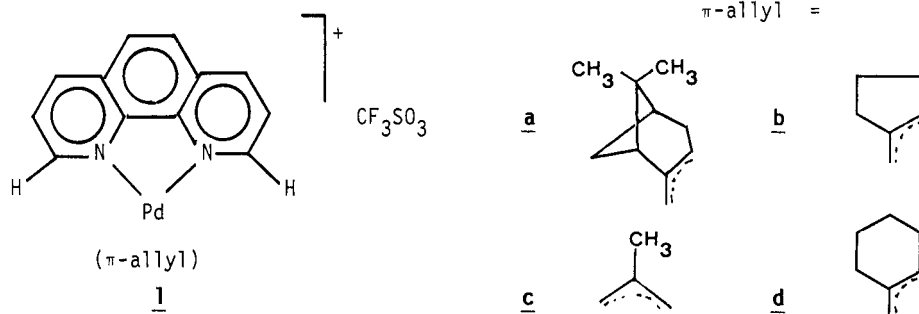
To approach the problem we chose Pd(II) as metal center and considered the molecules, **1**, with the following in mind: NOE effects concerned with the π -allyl face will require an independent "reporter" ligand with suitable protons. Since NOE effects involve T_1 relaxation, the reporter should be relatively rigid both with respect to movement within itself and relative to the π -allyl. The overall molecular motion of the complex should be relatively slow, i.e., τ_c should be fairly long (see eq.) to permit efficient ^1H dipole-dipole re-

$$1/T_1^{\text{dipole-dipole}} \propto \tau_c (1/\sigma^6) \quad (1)$$

laxation between the reporter and the π -allyl. Moreover, the reporter proton inducing relaxation, should be reasonably close to the π -allyl fragment. Since o-phenanthroline seemed likely to fulfill these boundary conditions we prepared several π -allyl complexes using this ligand.

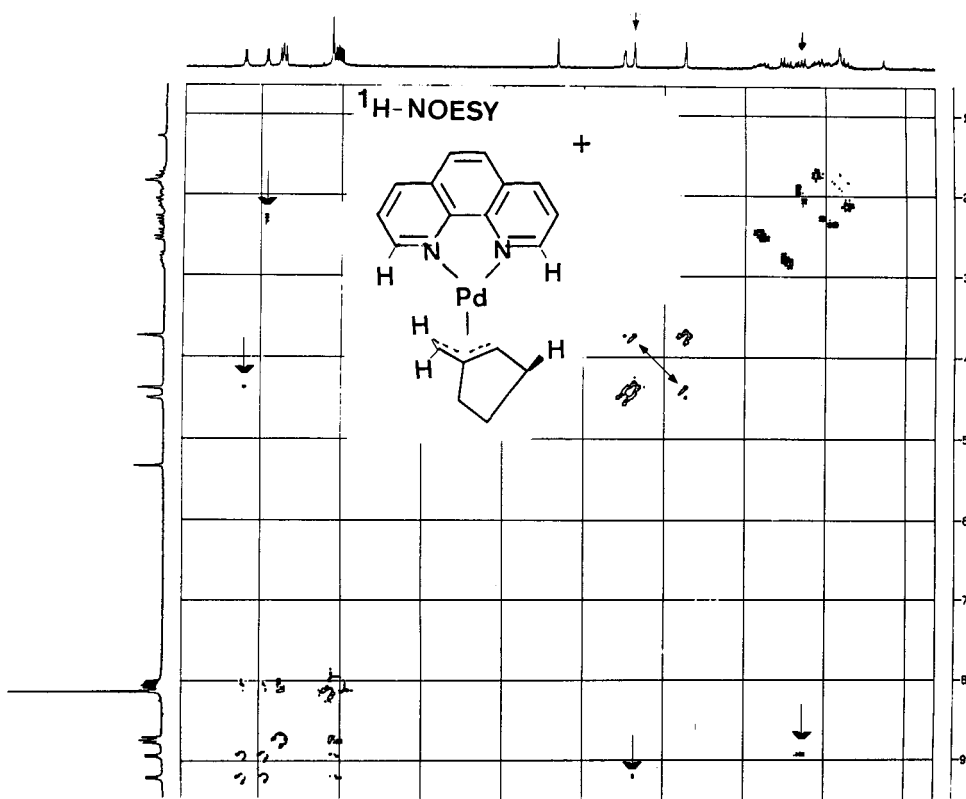
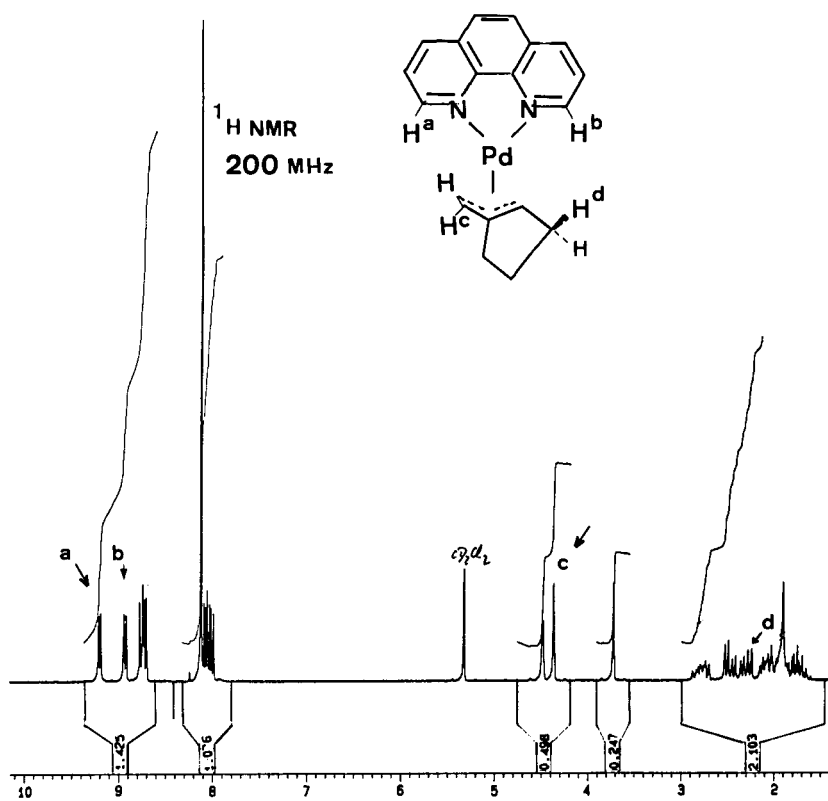
RESULTS AND DISCUSSION

The four chosen π -allyl ligands are shown below



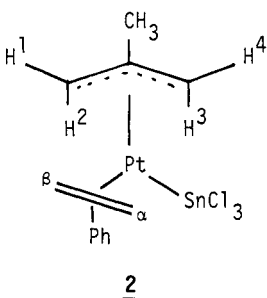
A ^1H spectrum of **1b** is shown in Fig. 1 and a corresponding ^1H 2-D NOESY in Fig. 2. Clearly, the two non-equivalent sides (ortho protons) of the reporter, which appear at lowest field "see" different environments across the metal. In all four cases, one ortho reporter induces NOE selectively at the syn (lower field) allyl CH_2 proton suggesting a similar distortion for these as was found in the neutron work mentioned above. In the three allyl fragments with stereochemistry, the other phenanthroline ortho proton "sees" that proton of an adjacent CH_2 fragment which faces the metal thereby differentiating between the two faces of these ligands. Naturally, these measurements are also useful aids in assigning complicated ^1H spectra. Indeed, one often needs 2-D COSY and heterocorrelation spectra combined with high resolution work to assign the ^1H spectra, in order to make use of this type of NOE data. One should not confuse distance **from the metal** with orientation with respect to the plane defined by the three carbons of the allyl ligand. The anti proton in $\text{Ni}(\eta^3\text{-C}_3\text{H}_5)_2$ is closer to the metal, but the syn proton distorts out of the plane towards the metal and the second π -allyl ligand (ref. 4).

Having considered points i) and ii) we come to iii). If a molecule undergoes slow exchange, e.g., $\text{A} \rightleftharpoons \text{B}$, with an exchange rate comparable to, or somewhat slower than, T_1 for the observed nucleus, the NOESY sequence gives rise to cross peaks arising from the transference of magnetization. For a simple two site problem there is no advantage in 2-D over 1-D methods.

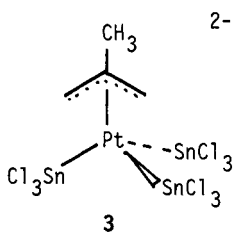


When several exchange processes occur simultaneously, or where a number of sites reflect the same exchange process, the 2-D methodology offers the advantage of allowing observation of all of these processes in one spectrum. Further, signals hidden due to spectral complexity may afford cross peaks which are readily observed thereby identifying exchange processes which might have gone unnoticed. In general, the more complicated the spectrum, the more valuable is the 2-D approach.

Complex 2 exists in two forms (ref. 3) due to the prochiral olefin, PhCH=CH₂. Each isomer has seven individual CH proton signals, plus CH₃ resonances, affording a moderately complex ¹H-spectrum. All of these absorptions can be unambiguously assigned using COSY and ¹⁹⁵Pt, ¹H heterocorrelation methods. The 2-D exchange spectrum (which contains both exchange and NOE information) in the CH₃ region (see Fig. 3) reveals an unexpected result. Not only are the two forms in equilibrium, but both are exchanging with a third as yet unidentified complex. Separate efforts on this molecule allowed its structure to be established as 3.

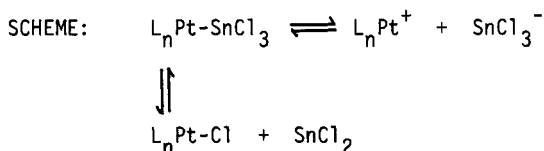


structure to be established as 3. Apart from



the mechanistic implications of detecting 3 in solution, it is worth emphasizing that it might easily have been overlooked employing conventional 1-D magnetization transfer methods, but was made obvious by the relative simplicity and intensity (Note a) of the cross peaks. Having recognized 3, it is clear that as yet undefined cations, perhaps of structure [Pt(styrene)(solvent)(CH₂C(CH₃)CH₂)], must arise in solution. In any case, both SnCl₃⁻ and released styrene are involved in the exchange.

Support for PhCH=CH₂ exchange comes from two related observations. Examination of the spectral region at low field reveals traces (< 5%) of styrene in exchange with both isomers of 2. Addition of further styrene and repetition of the exchange spectrum makes this exchange process more readily visible, see Fig. 4. The decision for SnCl₃⁻ exchange - and not deinsertion of SnCl₂, see scheme - assumes the validity of the



18e rule in combination with the observation that there is no $n^3 \rightarrow n^1$ allyl isomerization (as shown by following the transfer of magnetization from the individual syn and anti protons). If complex 2 were to lead to SnCl₂ + PtCl(SnCl₃)₂(C₄H₇)²⁻, the resulting dianion would still be coordinatively saturated and would not be expected to coordinate PhCH=CH₂. Consequently, despite the modest polarity of the solvent, we favor the formation of SnCl₃⁻.

Note a: The cross peak intensity will be proportional to the concentrations of the exchanging species. One of these may be present in negligible concentration; however, its cross peak can be readily observed.

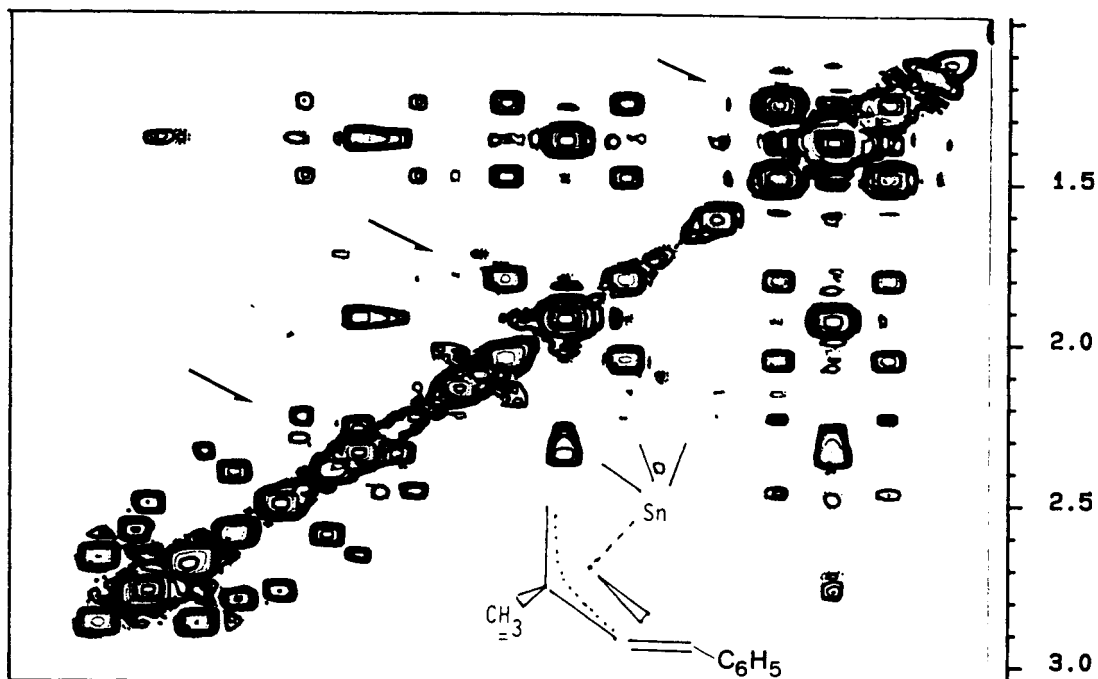
^1H -NOESY

Fig. 3 2-D NOESY for 2. Arrows indicate signals on diagonal involved in exchange.

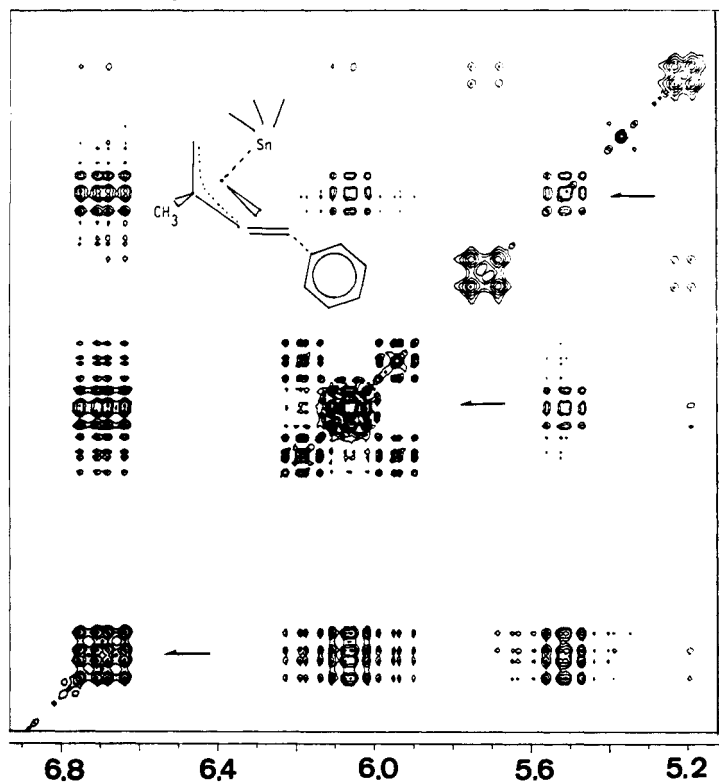
 ^1H -NOESY

Fig. 4 2-D NOESY for 2 with excess styrene. Arrows indicate $\text{PhCH}=\text{CH}_2$.

and an associated platinum cation. The dissociation of the PtSnCl_3 fragment into anions has been postulated as being an important feature of the $\text{PtCl}_2\text{L}_2/\text{SnCl}_2$ homogeneously catalysed hydroformylation (ref. 5). Our results represent one of the relatively few examples (ref. 5) where this possibility has been supported experimentally, and perhaps the only case where CH_2Cl_2 was used as solvent.

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