Inorganica Chimica Acta, *77* (1983) L17–L18

Solid State ^{13}C NMR Spectroscopy: the Isomer Distribution in the Solution and Solid Phases of Pd$Cl_2(PMe_2Ph)_2$

GEOFFREY BODENHAUSEN*, JANOS A. DELI*, CLEMENS ANKLIN** and PAUL S. PREGOSIN**

Physical and Inorganic Chemistry Laboratories, Eidgenössische Technische Hochschule, 8092 Zurich, Switzerland

Received February 3, 1983

Possible inequivalence between solution and solid phases is a perennial problem in structural chemistry. In many situations, evidence derived from diffraction methods must be compared with information obtained from solution-state spectroscopy. Such a comparison would be straightforward if conformational and configurational equilibria were retained during crystallisation. The combined use of high-resolution NMR in the solid and liquid states provides a simple test for the retention of such equilibria.

Using solid-state ^{13}C NMR we have found an example where discrepancies appear between the solution and solid states: specifically, the *cis*/*trans* equilibrium of the complex [$PdCl_2(PMe_2Ph)_2$]. In solution it is well known that complexes of this type exist as solvent-dependent mixtures of *cis* and *trans* isomers, with polar solvents favouring the *cis* species [1, 2], and the mechanism of isomerization has been investigated [3].

For room temperature solutions, we have determined a *cis:trans* ratio of 1.8:1 for a 0.07 *M* solution in chloroform, 6.2:1 for a 0.4 *M* solution in chloroform, and 10:1 for a saturated solution in ethanol, as evidenced by the signal areas in phosphorus-31 spectra. Selective inversion-recovery measurements indicate that the two isomers are in dynamic equilibrium. The predominance of the *cis* isomer in polar solvents is to be expected [3].

In the solid state, an X-ray diffraction study [4] of the complex indicates pure *cis* geometry. We believe this result may reflect either the procedure of crystallisation or the arbitrary choice of a suitable single crystal, since powder samples prepared in our laboratory by recrystallisation from ethanol contain *equal* amounts of *cis* and *trans* isomers.

Figure 1 shows a comparison of the solid-state carbon-13 spectrum of the title compound, obtained with cross-polarization [5] and magic-angle sample spinning [6, 7], and a high-resolution carbon-13 spectrum of a 0.07 *M* solution in chloroform. In the solid sample purified by recrystallisation from ethanol, the two CH_3 signals are separated by 11.2 ppm and the integrated peak areas indicate a 1:1 isomer ratio, in striking contrast to the 10:1 ratio in ethanol solution.

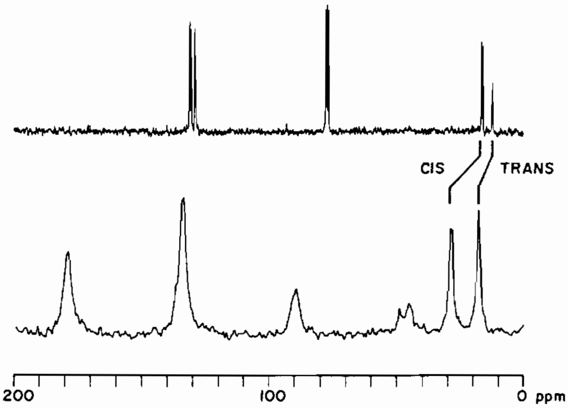

Fig. 1. Top: carbon-13 NMR spectrum of [$PdCl_2(PMe_2Ph)_2$] in 0.07 *M* $CDCl_3$ solution at 25 °C. The *cis* and *trans* methyl signals (15.9 and 11.9 ppm) appear as a doublet and triplet respectively (due to $^1J_{CP}$ and $^3J_{CPPdP}$ couplings) with integrated amplitude ratio 1.8:1. Below: solid-state carbon-13 magic-angle spectrum (spinner frequency 3435 Hz, cross-polarization time 1.5 ms) of the same complex recrystallized from ethanol, showing methyl resonances at 29 and 18 ppm with *equal* integrated signal amplitudes. The spectra were obtained with Bruker WM 250 and CXP 300 spectrometers.

In the solid-state spectrum, the large chemical shift anisotropy of the phenyl carbons gives rise to a family of sidebands centered at 135 ppm. No such problem arises for the two methyl signals, since the spinner frequency exceeds their anisotropy. We have verified that the relative signal areas are not affected by T_1 relaxation in the solution or by T_{IS} in the solid. Although solid state effects can result in equivalent chemical environments showing separate NMR resonances, these effects are usually small for ^{13}C [9] relative to the 11.2 ppm separation of the CH_3 signals.

We have also measured the solid state ^{13}C spectrum for the known *cis* and *trans*-[$PdCl_2(PMePh_2)_2$] mixture. Once again we find approximately equal amounts of both isomers based on the ^{13}C signals of the methyl groups (separated by 10.4 ppm), and this ratio is now in agreement with the solution data (*cis*/*trans* ~ 0.45/0.55 [1–3]). Note that if solid state effects were significant, more than two signals would be likely.

---

*Physical Laboratory.

**Inorganic Chemistry Laboratory.

0020-1693/83/$3.00

One explanation for the 1:1 ratio for the PMe_2Ph case in the powder could be the formation of mixed crystals, where *cis* and *trans* isomers would occupy alternating positions in the lattice. We have attempted to obtain a measure of microscopic homogeneity by investigating spin diffusion between dilute carbon-13 nuclei with solid-state NMR [10–12]. No conclusive evidence of intimate coupling between methyl nuclei belonging to *cis* and *trans* isomers could be found, possibly because spin-diffusion rates are too slow compared to spin-lattice relaxation in the solid phase (T_1^{cis} = 2 s, T_1^{trans} = 0.9 s). We intend to measure spin diffusion between inequivalent phosphorus-31 nuclei in the solid in the hope of supporting the mixed crystal hypothesis.

Our solid state measurements clearly reveal a very different picture for solid and solution-state isomer ratio, and suggest that a) one cannot be too careful in extrapolating structural knowledge derived from diffraction studies to solution-state chemistry, b) the nature and presence of a solvent is crucial when discussing the stability of a complex, and c) solid-state NMR of powders will prove to be a useful complement to X-ray crystallography.

Experimental

The *cis* and *trans* mixture of $[PdCl_2(PMe_2Ph)_2]$ was prepared as follows. To a suspension of $PdCl_2$ (0.642 g, 3.62 mmol) in 30 ml acetone, was added a solution of phosphine (7.25 mmol) in 5 ml acetone. Stirring for 12 h was followed by removal of the solvent *in vacuo*. Extraction with CH_2Cl_2, filtration through celite and concentration of the solvent gives the compound as a yellow solid which may be recrystallized from ethanol [13]. The micro-analytical data are: C, calc (found): 42.36 (42.44), H: 4.89 (4.88), Cl: 15.63 (15.58). The yields were of the order of 70%.

References

1 D. A. Redfield and J. H. Nelson, *Inorg. Chem., 12,* 15 (1973).
2 A. W. Verstuyft and J. H. Nelson, *Inorg. Chem., 17,* 1501 (1975).
3 D. A. Redfield and J. H. Nelson, *J. Am. Chem. Soc., 96,* 6219 (1974).
4 L. L. Martin and R. A. Jacobson, *Inorg. Chem., 10,* 1795 (1971).
5 A. Pines, M. G. Gibby and J. S. Waugh, *J. Chem. Phys., 59,* 569 (1973).
6 E. R. Andrew, *Progr. Nucl. Magn. Reson. Spectrosc., 8,* 1 (1971).
7 J. Schaefer, O. Stejskal and R. Buchdahl, *Macromolecules, 8,* 291 (1975).
8 M. M. Maricq and J. W. Waugh, *J. Chem. Phys., 70,* 3300 (1979).
9 N. Zumbulyadis and H. J. Gysling, *Inorg. Chem., 21,* 564 (1982).
10 N. M. Szeverenyi, M. J. Sullivan and G. E. Maciel, *J. Magn. Reson., 47,* 462 (1982).
11 D. Suter and R. R. Ernst, *Phys. Rev., B25,* 6038 (1982).
12 P. Caravatti, J. A. Deli, G. Bodenhausen and R. R. Ernst, *J. Am. Chem. Soc., 104,* 5506 (1982).
13 An infra-red spectrum (CsBr) shows a band at ~343 cm^{-1}, which may be attributed to the *trans* isomers; see D. M. Adams, 'Metal–Ligand and Related Vibrations', Edward Arnold Ltd., London, 1967, pp. 74–75.