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# A new platinum vapor-derived highly efficient hydrosilylation catalyst: NMR structural investigation

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**Abstract**

The structural features of a highly efficient hydrosilylation catalyst generated by reaction of Pt vapor and a mixture of mesitylene and 1,3-divinyltetramethyldisiloxane (DVS) were investigated by mono- and bidimensional NMR analyses. The structure around the Pt atoms was highlighted and compared with a commercial sample (Karstedt catalyst) and previously reported Pt vapor-derived system.


*Keywords:* Platinum; Hydrosilylation; NMR; DOSY

## 1. Introduction

The platinum-catalyzed addition reaction of hydrosilanes to unsaturated bonds (hydrosilylation reaction) is a versatile reaction for the synthesis of organofunctional silanes and polysiloxanes, for the cross-linking of polymers and for the manufacture of silicone-organic polymers [1].

Several decades ago Speier showed the activity of hexachloroplatinic acid ($H_2PtCl_6$) in hydrosilylation of unsaturated substrates [2], which led to the development of several Pt-based salts and complexes to add silanes to olefinic and acetylenic carbon–carbon bonds.

An important class of transition metal compounds used as hydrosilylation catalysts are Pt(0) complexes containing vinylsiloxane ligands [3], among which the most commonly used industrially is Karstedt's catalyst obtained by reaction of 1,3-divinyltetramethyldisiloxane (DVS) with hexachloroplatinic acid ($H_2PtCl_6$) [4]. A disadvantage of the resulting catalysts is the corrosive nature of the system, due to the formation of HCl, which can be removed through a base treatment [5], but under these conditions a reduction of catalytic activity and storage stability occurs [6].

Some years ago we reported the preparation of very active Pt-hydrosilylation catalyst using the metal vapor synthesis (MVS) technique, by co-condensation of Pt vapor and mesitylene vapor [7]. Unfortunately, the Pt/mesitylene solution was thermally unstable and brown in colour, making its use impractical in the industrial curing of polysiloxane resins, because of minimal shelf-life and undesired discolouring. Concerning the first problem, we demonstrated the usefulness of adding DVS stabilizing ligand to Pt/mesitylene solutions prepared by MVS in order to obtain highly stable solutions, containing species whose nature was established by NMR investigations [8]. The Pt solutions were, however, still coloured and not satisfactory for industrial application. More recently it was, however, possible to get round this problem with an alternative procedure in which Pt vapor was directly co-condensed with a mixture of mesitylene and DVS ligand. The resulting clear, colourless solution showed higher catalytic activity than

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commercially available platinum catalysts in curing process of polysiloxanes resins [9].

In this work, we report, therefore, the full details about the preparation of these new Pt-hydrosilylation catalyst and the structure around the Pt atoms, which was investigated by mono- and bidimensional NMR and compared with a commercial Karstedt catalyst and previously reported brown-coloured Pt MVS samples [8]. Moreover, the catalytic properties of the new Pt system were studied in the hydrosilylation reaction of allylamines and the results compared with the use of the commercial Karstedt catalyst.

## 2. Results and discussion

### 2.1. Preparation of Pt aggregates

The co-condensation of Pt vapor with DVS and mesitylene in great excess, at liquid nitrogen temperature, forms a frozen matrix which gives, on melting, a Pt-containing solution which is stable at room temperature and does not require purification (sample **I**, Scheme 1).

As anticipated, Pt/(DVS–mesitylene) sample **I** is in the form of a clear and colourless solution which can be stored at room temperature for several months, without changes in colour and without the formation of Pt metal. Moreover, the solid obtained by removing the volatiles from the Pt/(DVS–mesitylene) solution under vacuum can easily be redissolved in aromatic and aliphatic solvents. The role of both DVS and mesitylene in providing soluble colourless Pt species was further demonstrated by vaporization experiments of Pt and DVS without mesitylene: in these cases the formation of platinum powders was detected.

For comparison, the preparation of DVS stabilized Pt–mesitylene solution obtained by the previous described procedure [8] was also repeated, adding DVS ligand to the solution obtained by co-condensation of Pt vapors and mesitylene vapors (Scheme 2). The Pt/(mesitylene)DVS solution (sample **II**) was thermally stable and brown in colour.

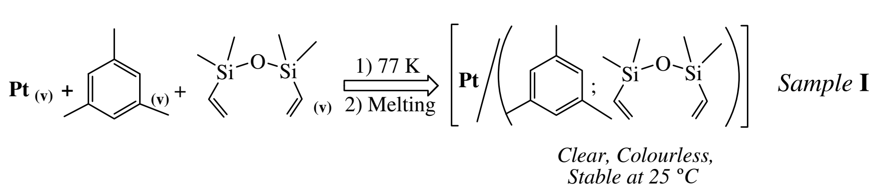
### 2.2. NMR analyses of Pt/(DVS–mesitylene) system

The $^{1}$H NMR spectra of the analysed samples was obtained keeping under vacuum a portion of the Pt solutions and dissolving the solid obtained in $C_6D_6$ (0.7 ml) containing 0.1% of TMS.

The $^{1}$H NMR spectrum of Pt/(DVS–mesitylene) (sample **I**) was compared with those of sample **II** and the commercial Pt-Karstedt catalyst (sample **III**) (Fig. 1). The spectrum of sample **I** was quite similar to those produced by samples **II** and **III**. Combined use of 1D and 2D NMR techniques (gradient Heteronuclear Single Quantum Coherence (gHSQC); TOtal Correlated SpectroscopY (TOCSY); Rotating-frame Overhauser Enhancement SpectroscopY (ROESY) and Diffusion-Ordered SpectroscopY (DOSY) [10]) involving the detection of scalar and dipolar couplings, as well as translational diffusion, provided information on the nature of the species, whose resonances contribute to the main spectral regions A–E (see Fig. 1), and on their average sizes.

HSQC analysis demonstrated that region E was constituted by methine protons which gave rise to, in the TOCSY map, long-range scalar correlations with methyl groups inside B region. Therefore region E can be unequivocally assigned to aromatic protons of mesitylene moieties. Spectral region D corresponded to methine and methylene vinyl moieties (HSQC) of DVS at chemical shifts very close (Fig. 2) to those of free DVS ligands. Thus, these signals were assigned to free double bonds not directly bonded to the metal, but included in its coordination sphere. As matter of fact, protons of region D gave ROE interactions with protons of C spectral region through space.

Region C (Fig. 1) contained protons giving direct $^{13}$C scalar correlations inside methine and methylene moieties (Fig. 3a), which were attributed, as for D region, to signals of double bonds. Their remarkable low frequencies shift was attributed to coordination with the metal, in accordance with the literature data [11]. Thus region C included π-bonded double bonds of DVS, part of which was assigned to DVS moieties with both double bonds complexed to the metal and with only one double bond complexed to the metal and the other one uncomplexed (region D, Fig. 1), as revealed by above-mentioned dipolar correlation occurring between protons of regions D and C. Moreover, some dipolar interactions were detected between DVS and mesitylene protons in regions E, C and E, A (Fig. 4) to indicate species in which DVS and mesitylene belong to the same coordination sphere of platinum. Finally region A included methyl groups of DVS species, but, surprisingly also showed the presence of highly shielded methylene moieties (HSQC) (Fig. 3b), which are unexpected in this region and can be reasonably assigned only to metal-alkyl species arising from the insertion of DVS into Pt–H bonds [12]. The sources of hydride species might be mesitylene solvent, since in the mixture dimeric 1,2-bis(3,5-dimethylphenyl)ethane was clearly identified by GC–MS analyses.




Scheme 1.