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.
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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

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.

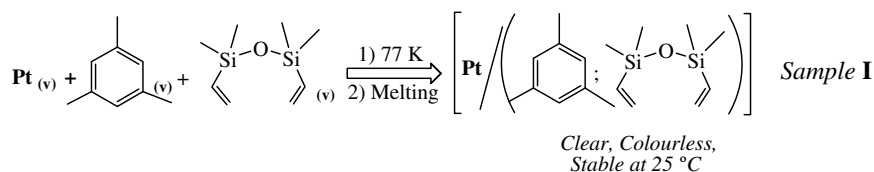### 2.2. NMR analyses of Pt/(DVS–mesitylene) system

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 commer-

cial 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.
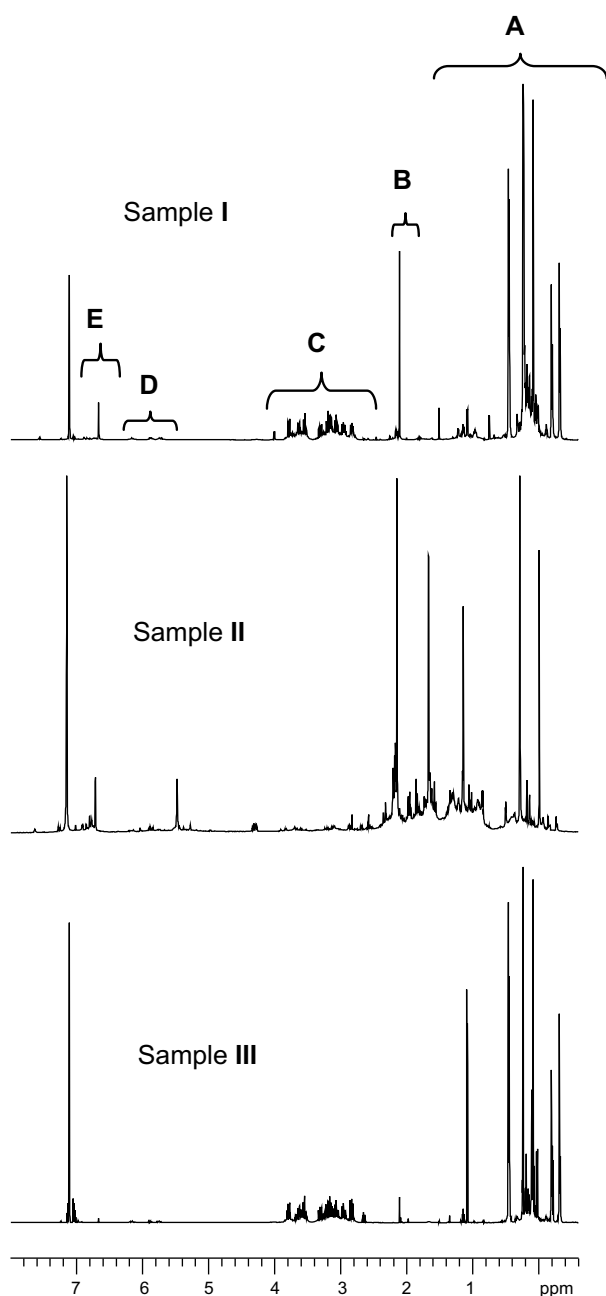
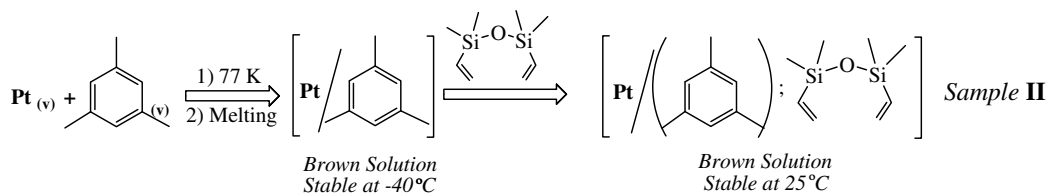*Clear, Colourless,
Stable at 25 °C*

Scheme 1.

Scheme 2.

Fig. 1. ¹H NMR spectra (600 MHz, C₆D₆, 25 °C) of Pt/(DVS–mesitylene) system (sample **I**), Pt/(mesitilene) + DVS (sample **II**), and Pt-Karstedt catalyst (sample **III**). Five spectral regions were highlighted in the spectra: (E) aromatic protons of mesitylene, (D) free π-bonds, (C) coordinated π-bonds, (B) signals of methyl groups of mesitylene, and (A) methyl groups bonded to silicium and alkyl-metal species.
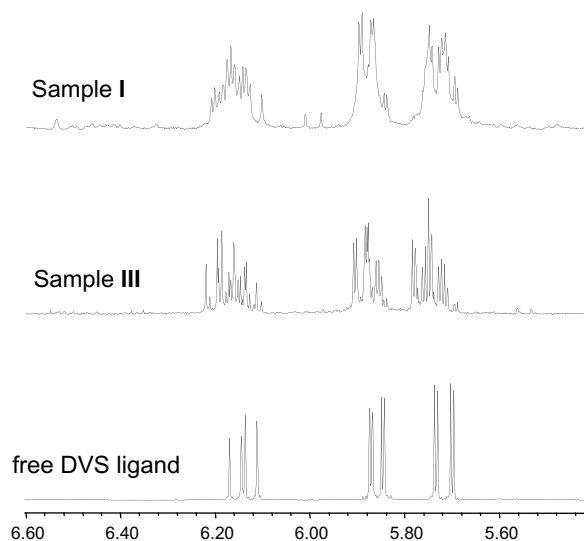

Fig. 2. Comparison of the ¹H NMR (600 MHz, C₆D₆, 25 °C) spectral regions corresponding to the free double bonds of: Pt/(DVS–mesitylene) (sample **I**), Pt-Karstedt catalyst (sample **III**) and free DVS ligand.

Thus sample **I** prepared by co-vaporization of platinum both with DVS and mesitylene contained species very similar to those detected for sample **II** prepared by adding DVS to solutions obtained by co-vaporization of Pt and mesitylene only [8]. However, as can be seen in Fig. 1, quite different integrated areas of the A and E spectral regions were observed. Previously discussed spectral assignments allowed us to establish that protons of double bonds of DVS contributed only to C and D regions and protons of mesitylene contributed only to E and B regions. A + B region has contributions only from the methyl resonances of mesitylene and from the methyl groups of DVS. Due to the fact that the integrated area of the region A + B exceeded the expect one on the basis of contributions from DVS and mesitylene, the excess of integrated area must be correspond to alkyl-metal species protons. Quantitative analyses of integrated areas of regions A–E led to the conclusion that sample **I** contained essentially DVS chelated (41%) and alkyls species (49%) bonded to platinum atoms and low amounts of mesitylene and DVS mono-coordinated Pt-species, whereas sample **II** had mesitylene and alkyls species in large quantities (53% and 40%, respectively) around platinum atoms (see Table 1). The same kind of spectral analysis of sample **III** (Karstedt catalyst) revealed an absence of Pt-alkyl species (Table 1).
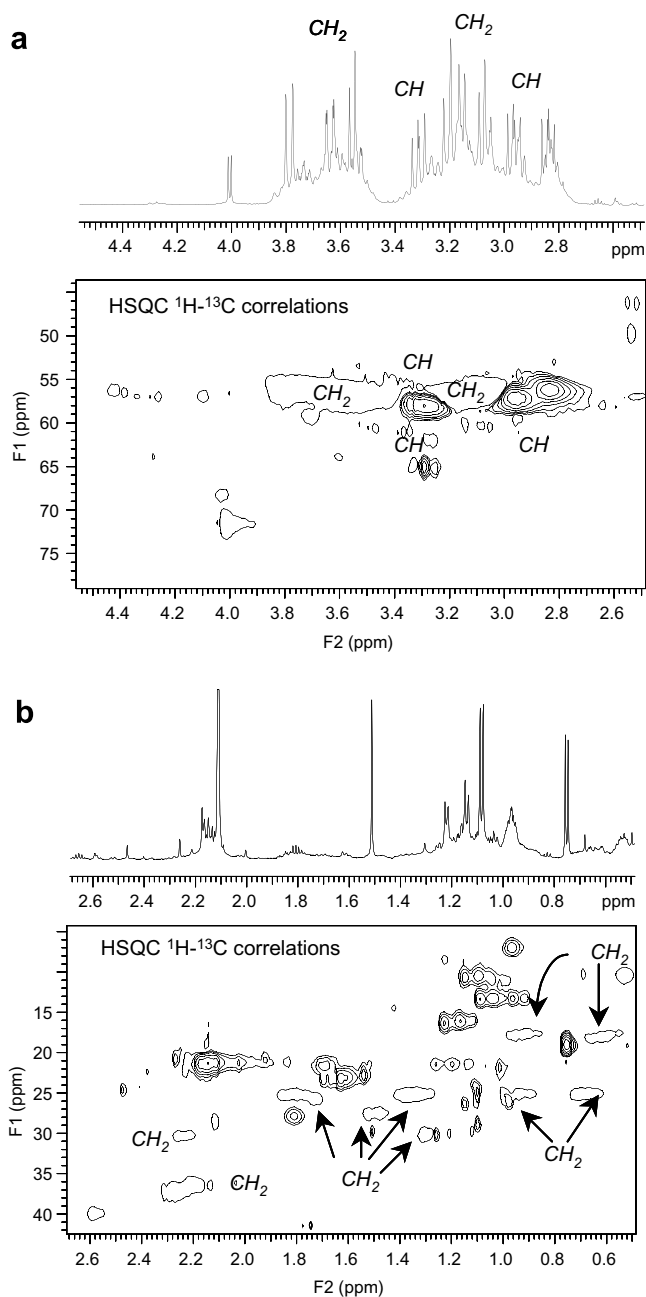
a

b

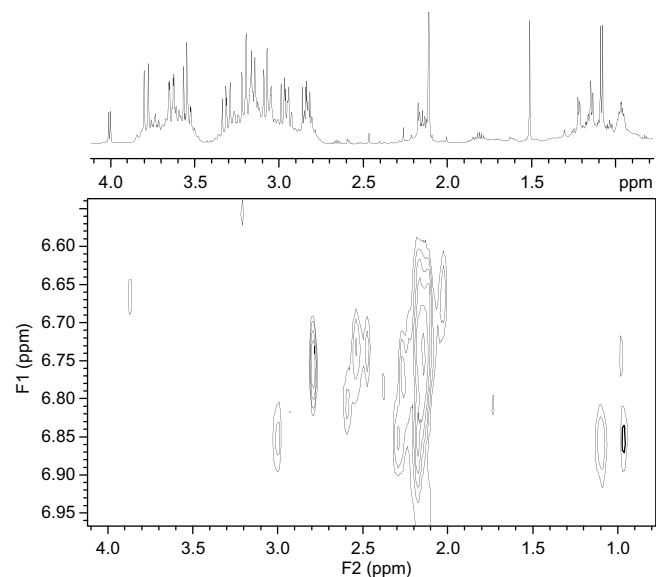Fig. 3. Expansions of HSQC map (600 MHz, C_6D_6, 25 °C) of Pt/(DVS–mesitylene) (sample **I**).

Fig. 4. Expansion of the ROESY map (600 MHz, C_6D_6, 25 °C, mix 0.6 s) corresponding to the spectral region of the aromatic protons of mesitylene of Pt/(DVS–mesitylene) (sample **I**).

Table 1
Quantitative analysis based on the ^1H NMR (600 MHz, C_6D_6, 25 °C) spectra of samples **I**, **II** and **III**

Ligand	Relative amounts of Pt-bounded species in solution (%)		
	Pt/(DVS–mesitylene) sample **I**	Pt/(mesitylene) DVS sample **II**	Pt-Karstedt catalyst sample **III**
Mesitylene	6	53	–
DVS mono-coordinated	4	–[a]	10
DVS chelate	41	7	90
Pt-alkyl	49	40	–

[a] Neglected as <1%.

7.4×10^{-10} m^2/s which, on the basis of Eq. (1), corresponds to hydrodynamic diameter of 0.9 nm. DOSY analysis carried out on Karstedt catalyst (sample **III**) revealed a similar diffusion coefficient of Pt species in solution (6.0×10^{-10} m^2/s) corresponding to hydrodynamic diameter of 1.1 nm. The same analysis for sample **II** showed diffusion coefficients ranging from 7.7 to 3.4×10^{-10} m^2/s corresponding to a wider platinum size distribution (0.9–2.0 nm in diameter) than the previous discussed samples (samples **I** and **III**). The results of the NMR structural investigation of the different Pt samples can be schematically represented as in Fig. 5.

As can be seen from the data shown in Fig. 5, there is a significant difference between samples **I** and **II** in the order of magnitude of the platinum atoms aggregation (number of Pt atoms ∼2, in sample **I**, 2–50 in sample **II**) [13]. Like sample **III**, sample **I** is colourless, while **II** is brown: the difference in the Pt size can satisfactory account of this variation in colour, in agreement with the literature [14].

Finally DOSY [10] analysis allows us to determine the diffusion coefficients of the species present in solution. Diffusion coefficients are correlated to molecular sizes on the basis of Eq. (1), strictly holding for medium to high-molecular weight and spherical molecules

$$D = \frac{kT}{6\pi\eta r} \tag{1}$$

where k is the Boltzmann constant, T the temperature, η the viscosity and r the hydrodynamic radius. The value measured for Pt/(DVS–mesitylene) revealed the presence of Pt species having an average diffusion coefficient at
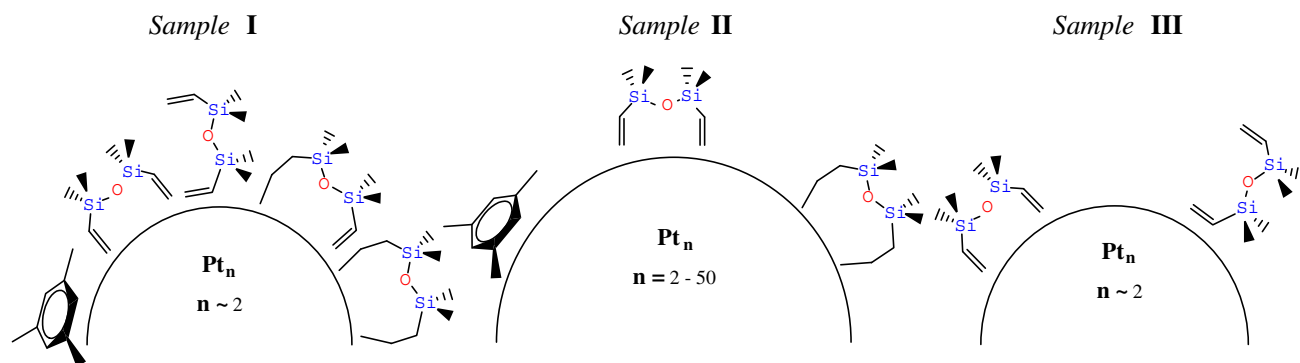
Fig. 5. Simplified schematic representation of kind of bonds on Pt atoms surface in samples **I**, **II** and **III**, respectively; *n* is the number of Pt atoms.

## 2.3. Catalytic hydrosilylation of allylamines

As anticipated, the Pt/(DVS–mesitylene) system (sample **I**) had already proved more active than commercially available Pt catalyst in the cross-linking of silicon materials [9]. In order to extend the comparison to low-molecular weight systems, the addition of diethoxymethylsilane to allylamines was studied in this work, in the presence of the platinum solution prepared by MVS (sample **I**) and with the commercially available Pt-Karstedt catalyst (sample **III**). In this respect it is interesting to note that the hydrosilylation of this class of functional unsaturated compounds with common Pt catalysts (Speier's and Karstedt's catalysts) has been reported to be problematic in the case of allylamines, because of poor reproducibility or low activity; to solve this problem the use of Pt/C or PtO₂ at 85 °C in a sealed tube under Ar was suggested [15].

In order to simplify the comparison with those results [15], samples **I** and **III** were tested under Ar in the hydrosilylation of N,N-dimethylallylamine or N-ethyl-2-methylallylamine (Table 2). Both Pt catalysts proved active even when the reactions were carried out at 0 °C or 25 °C, respectively and with a substrate/metal molar ratio = 10000. With respect to this, a referee noted that

for allyl hydrosilylations a problem may be the isomerization of the allyl group to an internal double bond, at a rate that is competitive with the hydrosilylation process. However, in the present case the reactions were remarkably clean, as confirmed by GLC analyses, where substrates **1**, **2**, **3a**, **3b** and mesitylene could account for >95% of the total area. Moreover, ^{1}H and ^{13}C NMR spectra of the crude products showed the resonances expected for the regioisomeric mixture **3a/3b**, with no signal of any double bond isomerization compound (e.g. N,N-dimethylprop-2-enylamine, N-isopropylideneethylamine or N-ethyl-2-methylprop-2-enylamine) [16]. By contrast, less than 5% conversion after 5 and 24 h, respectively, was obtained using of PtO₂ under the same conditions, demonstrating that for secondary and tertiary allylamines the soluble catalysts, samples **I** and **III**, are definitively more effective than the previously reported heterogeneous system.

However, by comparing the Pt/(DVS–mesitylene) system (sample **I**) with the Karstedt catalyst (sample **III**), some differences could also be observed. In fact, although very similar regioselectivity values were obtained using samples **I** or **III** (regioisomer ratio **3a/3b** = 85/15 and >99/1 for N,N-dimethylallylamine and N-ethyl-2-methylallylamine, respectively), significantly larger conversions

Table 2
Hydrosilylation reaction of allylamines with alkyldialkoxysilane
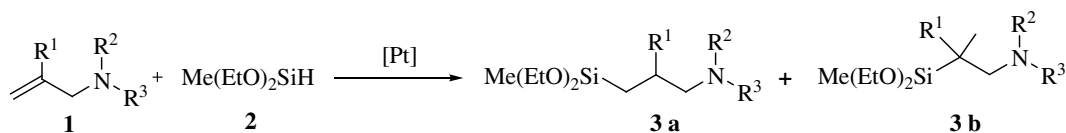
Entry	Substrate	Catalyst	T (°C)	t (h)	Conversion[a] (%)	Ratio[a] **3a/3b**
1	R¹ = H, R² = Me, R³ = Me	Pt/(DVS–mesitylene) sample **I**	0	0.4	90	85/15
2		Karstedt catalyst sample **III**	0	0.4	67	85/15
3		PtO₂	0	5	<5	–
4	R¹ = Me, R² = Et, R³ = H	Pt/(DVS–mesitylene) sample **I**	25	8	95	>99/1
5		Karstedt catalyst Sample **III**	25	8	65	>99/1
6		PtO₂	25	24	<5	–

Reaction conditions: molar ratio **1/2**/platinum = 10000/10000/1.

[a] Determined by GC and ^{1}H NMR analyses.

were obtained using the former catalytic system (Table 2, entries 1 *versus* 2 and 4 *versus* 5, respectively). As observed in the curing of vinyl silane resins [9], the Pt system obtained by MVS appears therefore more active than the Karstedt catalyst also in the hydrosilylation of low-molecular weight unsaturated compounds, containing amino groups. Interestingly, because both samples **I** and **III** solutions were evaporated under vacuum before the hydrosilylation runs, the variations in the catalytic activity cannot simply be ascribed to the "poisoning" due to the excess of free DVS in the commercial catalyst.

3. Conclusions

The Pt/(DVS/mesitylene) system (sample **I**) prepared by co-condensation of Pt vapor and a mixture of mesitylene and DVS ligand is very promising as a hydrosilylation catalyst, because of its catalytic activity, its stability at room temperature and its clear colourless appearance compared to the already reported MVS-derived sample **II**. As previously observed in the curing of vinyl silane resins [9], and, here demonstrated in the hydrosilylation of low-molecular weight unsaturated compounds such as allyl-amines, sample **I** showed higher catalytic activity than the Karstedt catalyst (sample **III**). The characterization of sample **I** by combined NMR approaches allowed us to relate its enhanced activity to the presence of Pt-alkyl species and Pt–mesitylene interactions (absent in the Karstedt catalyst), which could easily be replaced by the incoming unsaturated substrate [17].

The synthetic procedure proposed here, also makes it possible to obtain a greater control of the metal particle diameter leading to a narrower size distribution. With regards to this, the considerable value of NMR DOSY spectroscopy for the effective and reliable evaluation of particle sizes in solution must be stressed.

4. Experimental

4.1. General

All operations involving the metal vapor synthesis (MVS) products were performed under a dry argon atmosphere. Mesitylene (Aldrich product) was distilled from Na and stored under argon. 1,3-divinyl-1,1,3,3-tetramethylsiloxane (Aldrich product) was degassed and stored under argon. N,N-dimethylallylamine, N-ethyl-2-methylallylamine and diethoxymethylsilane (Aldrich products) were used as received. Platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Karstedt catalyst) 0.1 M in xylene was purchased from Aldrich and was used as received. Platinum(IV) oxide hydrate (Aldrich product) was used as received.

Atomic absorption spectrometry was performed with an electrothermally heated graphite furnace with a Perkin–Elmer 4100 ZL instrument with longitudinal Zeeman effect background corrector. GLC analyses were performed on a

Perkin–Elmer Autosystem gas chromatograph, equipped with a flame ionisation detector, using a SiO_2 "Wide Bore" column (DB-1, 30 m × 0.53 mm) and helium as carrier gas. The GC–MS analyses were carried out with a Perkin–Elmer Q-mass 910 spectrometer connected with a Perkin–Elmer gas chromatograph, equipped with a "split–splitless" injector, using a SiO_2 capillary column and helium as carrier gas.

4.2. NMR analysis

NMR measurements were performed on a Varian INO-VA-600 spectrometer operating at 600 MHz and 150 MHz for ^1H and ^{13}C, respectively. The temperature was controlled to ±0.1 °C. ^1H and ^{13}C NMR chemical shifts are referenced to TMS as internal standard. The 2D NMR spectra were obtained by means of standard sequences. The ROESY spectra were recorded in the phase-sensitive mode, with mixing time from 100 ms to 600 ms. The pulse delay was maintained at 5 s; 256 increments of four scans and 2 K data points each were collected. The data matrix were zero-filled to 2 K × 1 K and sinebell shifted functions were applied for processing in both dimensions. 2D TOCSY spectra were recorded acquiring 4 scans with a 2 s relaxation delay, 128 increments, 2 K data points and a mixing time of 120 ms.

The gradient ^1H, ^{13}C gHSQC spectrum was obtained in 32 transients per increment into a 2048 × 128 point data matrix. DOSY experiments were carried out by using a stimulated echo sequence with self-compensating gradient schemes, a spectral width of 8000 Hz and 64 K data points. Typically, a value ranging from 50 to 190 ms was used for Δ, 1.0 ms for δ, and g was varied in 30 steps (16 transients each) to obtain an approximately 90–95% decrease in the resonance intensity at the largest gradient amplitudes. The baselines of all arrayed spectra were corrected before the data were processed. After data acquisition, each FID was apodized with 1.0 Hz line broadening and Fourier transformed. The data were processed with the DOSY macro (involving the determination of the resonance heights of all the signals above a pre-established threshold and the fitting of the decay curve for each resonance to a Gaussian function) to obtain pseudo two-dimensional spectra with NMR chemical shifts along one axis and calculated diffusion coefficients along the other.

4.3. Preparation of Pt/(DVS–mesitylene) solution (sample I)

Pt vapor, generated by resistive heating of a tungsten wire surface coated with electrodeposited Pt (80 mg), was co-condensed with mesitylene (40 ml) and DVS (15 ml) in a glass reactor described elsewhere [18]. The reactor chamber was warmed at the melting point of the solid matrix (−40 °C), and the resulting pale yellow solution was siphoned and keep at room temperature (25 °C). The con-

tent of the metal, evaluated by atomic absorption analysis (AAS), was 1.2 mg/ml of solution.

4.4. Preparation of NMR samples

A portion of the Pt solution (10 ml of solution of sample **I**, 20 ml of sample **II** containing 0.5 mg/ml of platinum and 0.63 ml of solution of sample **III** containing 2.2% of Pt, respectively) was kept under vacuum at 5×10^{-5} mbar for 1 h at 25 °C. The solid thus obtained was dissolved in C_6D_6 (0.7 ml) containing 0.1% of TMS and solutions transferred into a NMR tube under argon atmosphere. TMS was used as internal standard both for ^1H NMR analyses and for NMR-DOSY analyses. Platinum concentration in the NMR tube for the three samples was 17.0 mg/ml.

4.5. Catalytic hydrosilylation of allylamines

All catalytic reactions were carried out under Argon atmosphere in a Schlenk tube, with magnetic stirring. 5×10^{-4} mg atom of Pt catalysts (0.09 ml of Pt/(DVS–mesitylene) solution, 1.2 mg/ml of Pt; 0.09 ml of Pt-Karstedt catalyst, 1.2 mg/ml in Pt, obtained by dilution with xylene of the starting solution (2.2% in Pt), 0.15 mg of platinum oxide hydrate, 81% in Pt) were introduced under argon, at room temperature. Subsequently, 5 mmol of allylamine (substrate/Pt molar ratio = 10 000) and 5.3 mmol of $(EtO)_2MeSiH$ (0.85 ml, $d = 0.83$ g/ml, MW = 108) were introduced. The mixture was kept at the temperature indicated in Table 2, then analysed by GLC (SiO_2) "Wide Bore" column, DB-1, 30 m × 0.53 mm and He as carrier gas (10 psi), [*N,N*-dimethylallylamine (3.5 min), *N*-ethyl-2-methylallylamine (3.8 min), diethoxymethylsilane (2.4 min), 3-(diethoxy(methyl)silyl)-*N,N*-dimethylpropan-1-amine (8.7 min), 2-(diethoxy(methyl)silyl)-*N,N*-dimethylpropan-1-amine (8.1 min), 3-(diethoxy(methyl)silyl)-*N*-ethylpropan-1-amine (9.5 min)] and ^1H NMR analysis.

Acknowledgement

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