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Dedicated to Prof. Bogdan C. Simionescu
on the occasion of his 75th anniversary

MOLECULAR AND SILICA-SUPPORTED METAL COMPLEXES AS NEW CATALYSTS FOR HYDROSILYLATION

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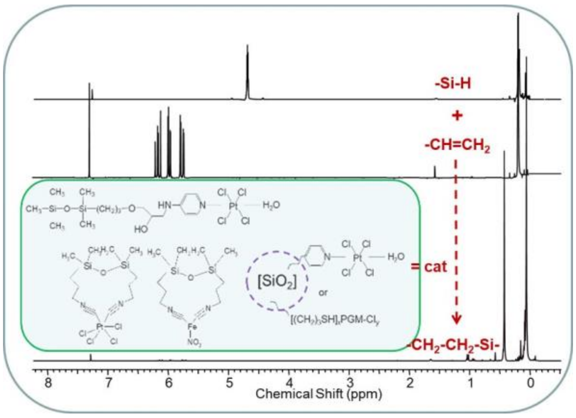
Two disiloxanes with pyridyl or isocyanide functional groups, as well as silica materials carrying pyridyl or thiol functionalities were used as ligands for Pt(IV) and Fe(III) ions. The molecular and silica-supported metal complexes were tested in a model hydrosilylation reaction between 1,3-divinyl tetramethyldisiloxane and 1,1,3,3-tetramethyldisiloxane, conducted in (pseudo)-heterogeneous conditions. The new hydrosilylation catalysts afforded 75–100 % conversion and 87–93 % selectivity, based on NMR data, while some of them presented recyclability; they were also successful in silicones crosslinking at room temperature. In particular, the iron-isocyanide disiloxane complex is proposed as a promising, cheap, unsophisticated and stable catalyst, capable to act in heterogeneous conditions, without the need of dry solvent or inert atmosphere. Silica-supported Pt or Pt/Pd catalysts, obtained with commercial or recovered noble metals precursors, presented high conversion and increased regioselectivity in the tested process, being reusable, and are efficient in other hydrosilylation reactions, useful in organic and silicon chemistry.



INTRODUCTION

The hydrosilylation reaction – the addition of Si–H bonds via an unsaturated C=C, C=O or C=N double bond – is common in organic chemistry and by far the most used in silicone chemistry for derivatization and crosslinking processes. In 1957 Speier discovered the catalytic activity of hexachloroplatinic acid $H_2[PtCl_6]$,[1] then in 1973 Karstedt’s catalyst $[Pt_2(dvtms)_3]$[2] practically revolutionized the silicone chemistry, including the industrial processes. Both Speier’s and Karstedt’s catalysts are Platinum complexes, the former with isopropanol and the latter with divinyldisiloxane as ligand. Since then, other catalysts containing noble metals have been proposed.[3-9] The platinum-based catalysts and their role in homogeneous and heterogeneous hydrosilylation have been described in comprehensive reviews.[10, 11]

There are several aspects regarding the hydrosilylation reaction that are still keeping up the research interest. The first concern is the scarcity of noble metals, pushing towards their recovery, which is not straightforward in homogeneous processes, but gains increasing attention in heterogeneous processes.[11-15] These ensure reaction

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products free of Pt particles, and economic benefits, due to easy removal and possible reuse of the catalyst. Alternatively, the replacement of platinum-based catalysts with equally efficient ones containing other metals is also a viable path.[16-19]

Leaching phenomena and formation of platinum black are undesired in silicones production, leading to contamination of the environment and the final materials. In this regard, a special attention gained the complexes with bulky ligands, as trialkylphosphine and N-heterocyclic carbenes,[10, 20, 21] which create kinetic barriers for agglomeration of Pt(0) species. Pt-supported catalysts, with good stability have also been proposed.[11,13]

Another aspect is regarding secondary reactions, regiospecificity and selectivity. It is well known that in classic hydrosilylation processes between a Si-H containing compound and a double bond, the anti-Markovnikov is the major product, but its regioisomer forms as well, being difficult to separate, and this aspect is unfortunately observed even in commercial reagents. On the other hand, in presence of proton-donating compounds, dehydrocoupling reactions occur between these and the Si-H groups, thus the desired addition compound requires anhydrous conditions and preliminary introduction of protective groups in double bond reagents containing labile protons. Other side reactions have been acknowledged[10,11] (such as alkene isomerization, dehydrogenative silylation, or crosslinking). On the other hand, these reactions which are unwanted from the viewpoint of hydrosilylation process, might bring benefits, for example in the synthesis of compounds with labile element-element bonds (*e.g.* silyl-ethers or silazanes).

The hydrosilylation mechanism has been introduced by Chalk and Harrod[22] in 1965. More recently, in-depth kinetic investigations, ^{195}Pt NMR studies[23] and DFT calculations[24] provided clarifications and additions to the Chalk-Harrod mechanism. It is however generally accepted that the main steps are the oxidative addition of a Si-H group to a metal-olefin complex, insertion steps and reductive elimination.[25] The formation of Pt(0) colloids /particles is generally associated with catalyst deactivation,[12] but the involvement of small Pt nanoparticles in certain hydrosilylation reactions has also been reported.[26]

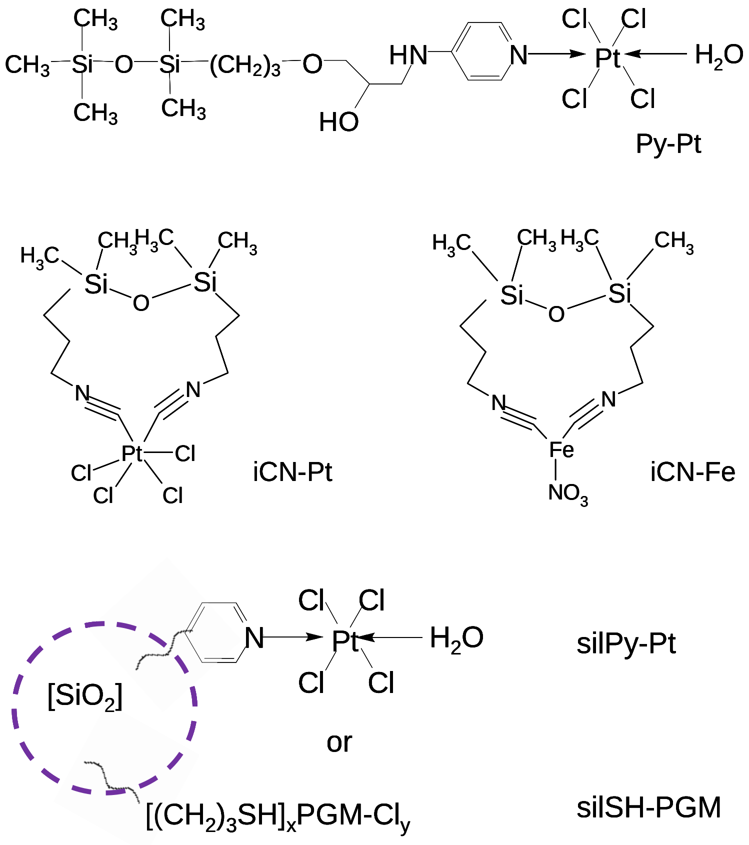
In previous studies,[29-31] several metal complexes, obtained in our laboratory with original siloxane-based ligands or functionalized silica have been presented, and their potential applications as catalysts for different types of reactions have been preliminary tested. These are Pt(IV) or Fe(III) molecular complexes based on pyridyl or isocyanide disiloxane ligands, and Pt or Pt/Pd complexes of pyridil- or thiol- modified silica, respectively. Herein these metal complexes are comparatively discussed from the perspective of their potential as new, stable and efficient hydrosilylation catalysts.

RESULTS AND DISCUSSION

Original proligands containing disiloxane moieties and pyridyl or isocyanide complexing groups have been reported by our group. The pyridyl – modified siloxanes have been synthesized by addition of 4-aminopyridine to epoxy-siloxanes.[27-29] The isocyanide disiloxane has been synthesized by Hofmann's modified carbylamine method, using a phase transfer agent.[30] Based on these proligands, Platinum(IV) and Iron(III) complexes have been prepared.[29,30] These were amorphous compounds, and in absence of clear structure assignment through single crystal X-ray diffraction, the most plausible structures have been proposed on the basis of mid- and far – FT-IR spectroscopy, UV-Vis titration, NMR spectroscopy, X-ray fluorescence spectroscopy (XRF), Energy-dispersive X-ray spectroscopy (EDX) and ESI-MS analyses. In Scheme 1, the assigned structures are represented, wherein the notations contain abbreviations of the proligands, based on the complexing moiety, *i.e.* pyridyl (Py) or isocyanide (iCN) and the metal (Pt or Fe). Two types of silica-supported platinum-containing catalysts are also discussed, coded herein as "silPy-Pt" and "silSH-PGM". The former is a modified silica, which was obtained by addition of 4-aminopyridine to a sol of hydrolyzed 3-glycidoxypropyltrimethoxysilane, condensation with Aerosil silica and reaction with H_2PtCl_6, and has an estimated Pt content of ca. 15 wt.%.[29] The latter was prepared from platinum group metals (PGM) recovered from a spent catalytic converter, by complexing with SH-functionalized mesoporous silica, and contains ca. 4 wt.% PGM (1.25 wt.% Pt and 2.75 wt.% Pd).[31]

In the previous articles, the catalytic potential of these metal complexes has been successfully tested in different processes: reduction of p-nitrophenol, oxidation of glucose and starch,[29] heterogeneous Fenton-like photodecomposition[30] and hydrosilylation reactions.[29-31] However, this aspect has been treated *inter alia* to suggest potential applications. Given our implication in silicon chemistry, we are particularly interested in new hydrosilylation catalysts with good efficiency, low production costs, better stability and hopefully selectivity than the widely available ones

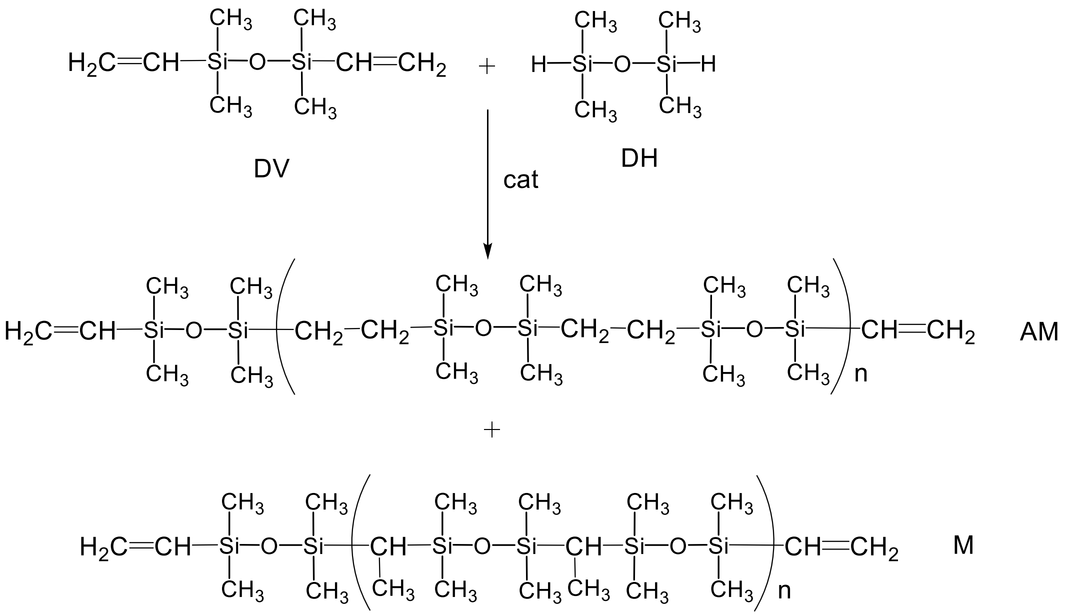
(Speier's and Karstedt's). The latter are indeed "hard to beat" in terms of efficiency, but require special conditions, in order to avoid secondary reactions and premature inactivation. Since promising results have been obtained with these complexes, they are herein compared and complementary data is included, in order to better estimate their performance. To this purpose, the hydrosilylation reaction between 1,3-divinyl tetramethyldisiloxane (DV) and 1,1,3,3-tetramethyldisiloxane (DH) – Scheme 2 – was followed by ^{1}H-NMR. As can be observed in Figure 1 for a representative example, the spectrum of the reaction product clearly showed formation of CH_2 groups with chemical shift at ~0.4ppm (anti-Markovnikov addition) and $CH\text{-}CH_3$ groups with chemical shift at 0.9–1 ppm (Markovnikov addition), disappearance of the Si-H signal from 4.7 ppm and presence of a residual signal at 5.6-6.1 ppm assigned to vinyl groups from the chain ends.



Scheme 1 – Chemical structures of the metal complexes used as catalysts.

In Table 1, the tested catalysts, their amounts, reaction conditions and outcome, based on NMR data are presented. The conversion was calculated based on the vinyl groups, given the fact that DH is more volatile than DV, while the Si-H groups might be involved in dehydrocoupling side reactions, since in most of these experiments, no dry solvent nor inert atmosphere were used. Although similar amounts of catalyst have been used, the content of metal, considered the active center, is rather different, depending on the molecular weight and composition of the materials. For a better comparison, the TON values were calculated as moles of DV per mole of metal center.

High conversion values were obtained based on NMR data, reaching total conversion for iCN-Pt in solvothermal conditions, and good selectivity, comparable with that of commercial catalysts. In addition, practically all the reactions proceeded in (pseudo-)heterogeneous catalysis conditions, due to lack of solvent or the use of a non-solvent (DMSO) for the reactants and the product. The obtained results in terms of conversion are thus very encouraging, especially in the case of iCN-Fe complex, since iron-based hydrosilylation catalysts are rather few[14]. Moreover, this catalyst was separated from the reaction product and used in a second cycle, with very good result (over 90% conversion, entry 5).



Scheme 2 – The hydrosilylation reaction.

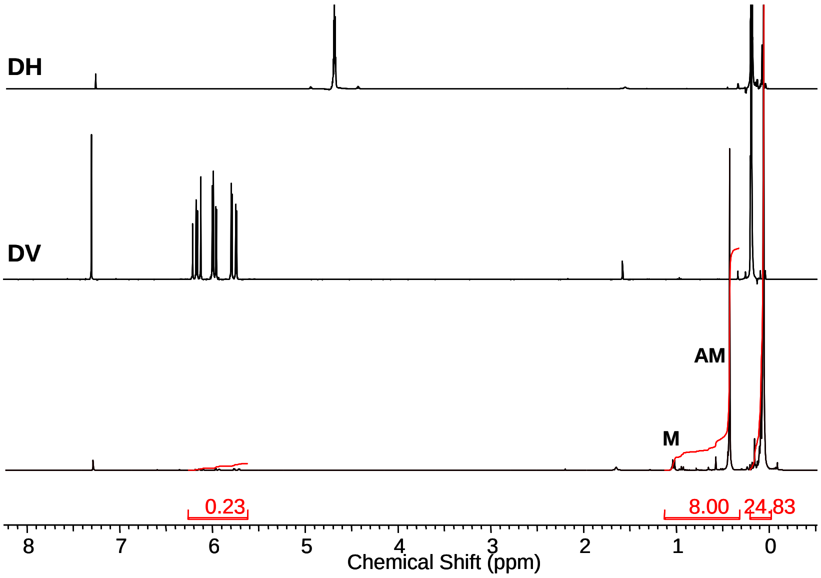


Fig. 1 – H-NMR spectra of the reactants and a final product (please refer to Scheme 2 for chemical structures).

Table 1

Conditions and outcome of hydrosilylation reaction between DV and DH

Entry	Catalyst, conc.	Metal wt%	Conditions	Vinyl groups conversion %	Regioselectivity (% AM)	TON[a]
1.	Py-Pt, 0.25 wt.% (in DMSO)	0.07	bulk, 60°C 2h + RT 20h	87	75	777
2.	Py-Pt, 2 wt.%, dispersed	0.55	bulk, 100°C (solvothermal), 2h	96.2	89	107
3.	iCN-Pt, 2 wt.%, dispersed	0.64	bulk, 100°C (solvothermal), 2h	100	87.5	94.7
4.	iCN-Fe, 2 wt.%, dispersed	0.29	bulk, 100°C (solvothermal), 2h	98	80	59
5.	iCN-Fe, 2nd cycle, 2 wt.%, dispersed	0.29	bulk, 100°C (solvothermal), 2h	93	84	56
6.	silPy-Pt, 1 wt.%	0.15	dry toluene, 60°C, 6h	100	90	406
7.	silPy-Pt, 2nd cycle, 1 wt.%	0.15	dry toluene, 60°C, 6h	98.3	76	399
8.	silSH-PGM, 1.5 wt.%	0.06	bulk, RT, 3 days	93.5	92	652[b]
9.	silSH-PGM, 2 wt.%	0.08	bulk, 100°C (solvothermal), 2h	90	92.7	470[b]

[a] Calculated as moles of DV/ mole of metal.

[b] The number of moles of metal was calculated taking into account both Pt and Pd active species and their proportion.

In terms of turnover number, one can observe that better results may be obtained (elevated catalytic activity in smaller amount) when the catalyst is dissolved in a solvent, even if this is not miscible with the reaction mixture (entry 1), considered pseudo-heterogeneous catalysis, as opposed to "true" heterogeneous conditions in the other cases. Similar TON values were obtained with the two dispersed molecular catalysts containing Pt (entries 2 and 3), while slightly lower value resulted for iCN-Fe, due to lower atomic mass of iron.

In order to compare the two homologue complexes obtained with the same ligand, iCN-Pt and iCN-Fe, the GPC elugrams of the polymers obtained with these isocyanide-containing catalysts are overlaid in Fig. 2. The molecular masses and distributions, as determined by GPC in chloroform were: Mn = 12000 g/mol, PDI 1.8 for iCN-Fe and Mn = 15400 g/mol, PDI 2.3 for iCN-Pt. Thus, in the tested reaction conditions, the iron catalyst was very efficient, had good selectivity, comparable with the platinum catalysts, and yielded a narrower molecular mass distribution. So, this iron complex is a very promising, yet cheap and unsophisticated hydrosilylation catalyst, capable to act in heterogeneous conditions, without the need of dry solvent or inert atmosphere.

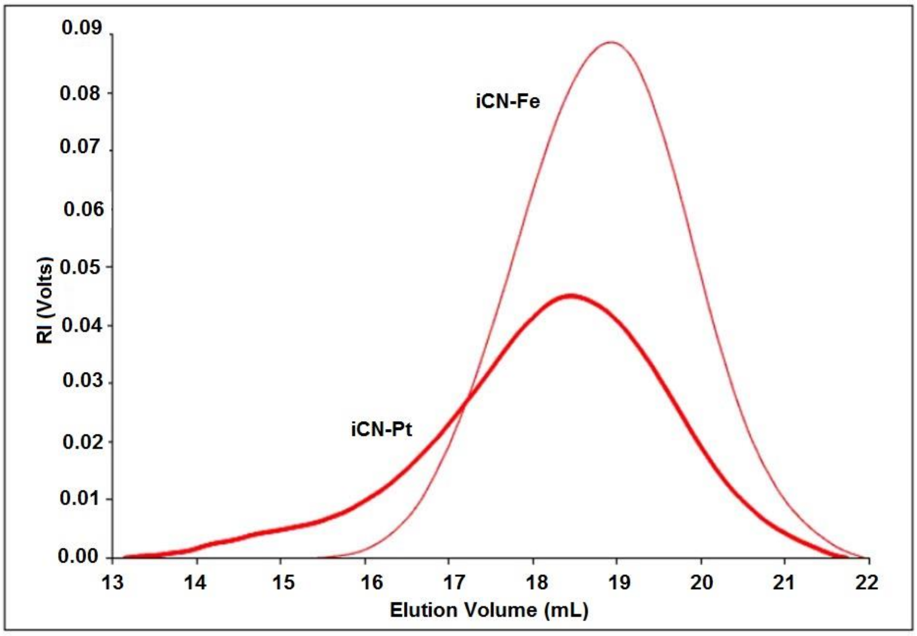


Fig. 2 – GPC curves of the polycarbosiloxanes obtained according to Scheme 2 with iCN-Pt and iCN-Fe as catalyst, respectively.

The advantages of heterogeneous catalysis systems are well-known: easy removal, low contamination level in the case of metal-based catalysts, and absence of intensive workup like neutralization – thus leading to cleaner products –, as well as recyclability – leading to more economical processes. In the case of Pt and other rare elements, this aspect is very important, due to limited resources. It has been estimated that ca. 3% of the annual worldwide Pt production is lost due to consumption in the silicone industry[14]. Nevertheless, solid Pt hydrosilylation catalysts are less encountered in practice, in spite of intensive research work.[11] As mentioned, the discussed molecular complexes can act as heterogenous catalysts in bulk. On the other hand, true heterogeneous, silica-supported catalysts have also been obtained. By using a pyridyl-modified silica, a single-site heterogeneous catalyst (silPy-Pt) was prepared. In another approach, platinum group metals recovered from a spent catalytic converter were reused, by complexing with SH-functionalized mesoporous silica[31] (silSH-PGM). As can be observed in Table 1, very high conversion of vinyl groups has been registered with these silica-supported catalysts in various reaction conditions, as well as increased regioselectivity. The calculated TON values were found between 399 and 652, and were higher for the silica with recovered PGM, probably due to a synergistic effect of Pt and Pd. Moreover, the silica can be separated from the reaction mixture by centrifuge or filtration, and is reusable, thus ensuring superior valorization of scarcely available and expensive platinum metal. The reusability was proven by the very similar outcome obtained with silPy-Pt in a second cycle (entries 6 and 7 in Table 1). Another advantage of the heterogeneous catalysts is the limitation of product contamination, since the metals are chemically bonded with complexing groups.

The three molecular catalysts were further tested in the hydrosilylation crosslinking of a poly(dimethyl-methylvinyl)siloxane with ca. 9 mol% vinyl groups with a multifunctional crosslinker, pentamethylcyclopentasiloxane (D_5^H), at room temperature. To calculate the conversion, while avoiding false results given by side reactions involving D_5^H, the IR absorption band at 3055 cm^{-1}, corresponding to vinyl groups was followed, taking as reference the $Si\text{-}CH_3$ band at 1260 cm^{-1}. As can be observed in Fig. 3, the iCN-based catalysts ensured over 80% conversion of the vinyl groups within 45 minutes, and around 85% after 75 minutes, while Py-Pt presented an induction period, but yielded 95% conversion after 75 minutes. The latter can be regarded as a potential catalyst for hydrosilylation of vinyl-siloxanes with temperature-modulated rate,[29] thus being useful in certain silicone cross-linking systems without the need of inhibitors.[10] The obtained results confirm the very good catalytic activity of all the molecular complexes, even in ambient conditions.

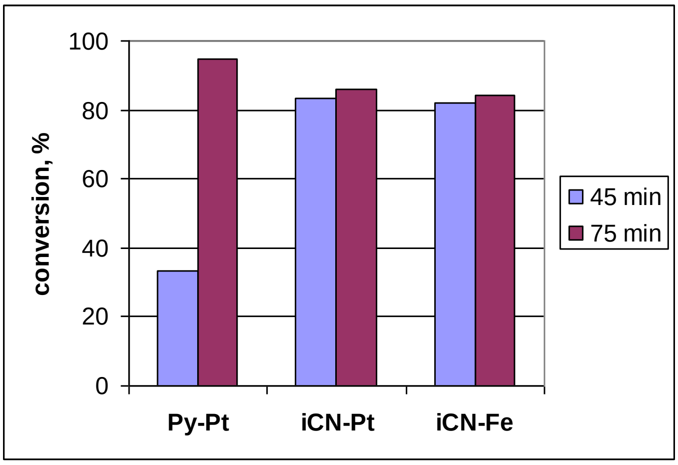


Fig. 3 – The hydrosilylation crosslinking process carried out in ambient conditions with the siloxane complexes as catalysts: conversion of vinyl groups followed by FT-IR.

Other hydrosilylation reactions have been tested with silSH-PGM[31]. Functionalization of tetramethyldisiloxane with allyl glycidyl ether gave 71% conversion after 2 h at 100°C with 2 wt% catalyst, in bulk. The reaction of tetramethyldisiloxane with 1-hexene gave ca. 90% conversion of Si-H groups after 12 h at 60°C, and a similar result was obtained for the hydroslylation of styrene with trimethoxysilane, both conducted in dry toluene.

For the “classic” hydrosilylation catalysts, it is generally accepted that the platinum species undergo reduction with formation of Pt(0) coordinated to the double bond, and this is considered the active species. This preliminary process can explain the large induction period in the case of Py-Pt, for example. On the other hand, since the silPy-Pt catalyst was reusable, it is supposed that the reduced Pt species remain active, being stabilized by the complexing groups, which limits the formation of inactive clusters of platinum black. The stabilization of the active species has to be considered in the other cases as well, similar as with platinum carbene complexes,[10] while the formed Pt nanoparticles might also have a catalytic role also, according to literature.[26] The mechanism with the iron catalyst remains a challenge, since rather few such catalysts were reported and even fewer mechanistic studies. One can only suppose that the siloxane isocyanide ligand has a particular importance, as suggested in one case where such compounds have been introduced *in situ* with the role of “control agents”.[32]

One great advantage of the proposed catalysts is their stability in air, thus being easy to store and handle, contrary to $H_2PtC1_6 \cdot 6H_2O$, for example, which is hygroscopic. The preservation of the structure can be verified by comparing the FT-IR spectrum of old and new samples; as can be observed in Fig. 4, the spectra of iCN-Fe as measured initially and after more than one year of storing without precautions are practically identical. It has to be mentioned, however, that the catalysts have to be thoroughly dried before reaction, at 120°C.

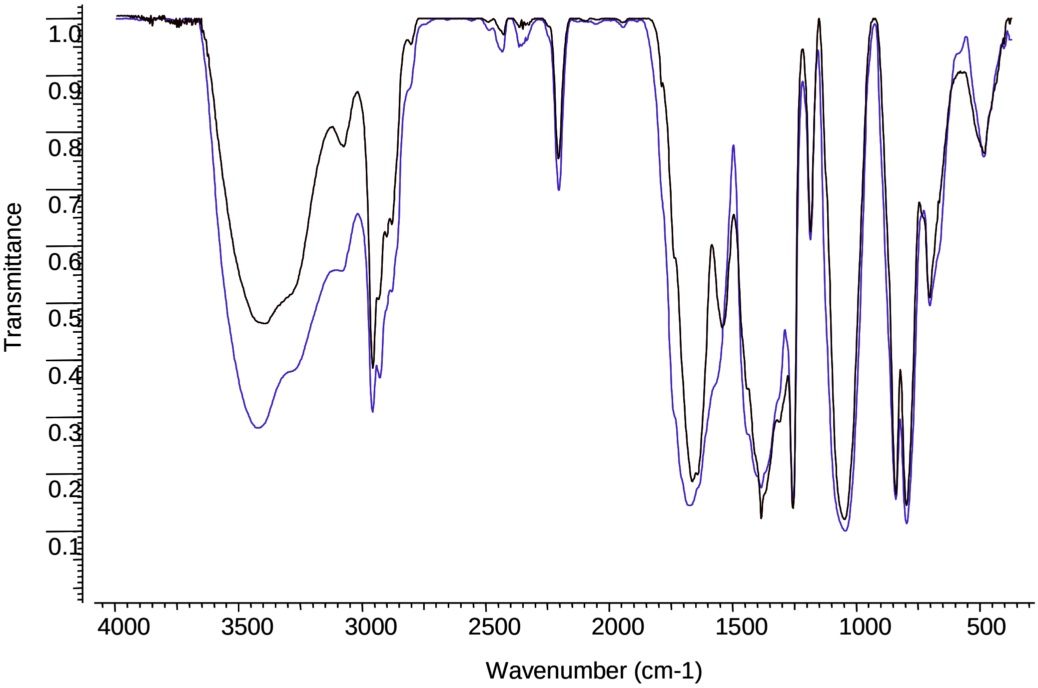


Fig. 4 – FT-IR spectrum of iCN-Fe: old sample in black line, new sample in blue line.

EXPERIMENTAL

Materials and methods. All chemicals were reactive grade commercial products and were used as received: pentamethyldisiloxane, 1,3-divinyl tetramethyldisiloxane, 1,1,3,3-tetramethyldisiloxane, pentamethylcyclopentasiloxan, allyl-glycidylether, 3-glycidoxypropyltrimethoxysilane, Aerosil 200, 4-aminopyridine, $H_2PtCl_6 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ (from Aldrich).

The catalysts were prepared according to previously reported methods, as follows. Py-Pt was obtained by reaction of $H_2PtCl_6 \cdot 6H_2O$ with pentamethyldisiloxane-1-propoxy-3-(pyridin-4-ylamino)propan-2-ol.[29] Silica-supported silPy-Pt was obtained in one-pot modification of Aerosil with a sol derived from 3-glycidoxypropyltrimethoxysilane reacted with 4-aminopyridine, and subsequent complexation with hexachloroplatinic acid.[29] iCN-Pt and iCN-Fe were synthesized starting from 1,3-bis(isocyanopropyl)tetramethyldisiloxane and $H_2PtCl_6 \cdot 6H_2O$ or $Fe(NO_3)_3 \cdot 9H_2O$, respectively[30]. The silica-supported Pt/Pd catalyst (silSH-PGM) was obtained by reaction of a thiol-modified mesoporous silica with an acidic solution containing platinum group metals (PGM) recovered from a spent catalytic converter.[31]

Medium IR spectra were recorded on a Bruker Vertex 70 FT-IR spectrometer (Bruker Optics, Ettlingen, Germany), in transmission mode, in the range 4000–400 cm^{-1}, at room temperature, with a resolution of 2 cm^{-1} and accumulation of 32 scans. ^1H -NMR measurements were done in $CDCl_3$ on a Bruker NEO-1 400 MHz spectrometer equipped with a 5 mm four nuclei ($^1H/^{13}C/^{19}F/^{29}Si$) direct detection probe. GPC measurements were done in chloroform on a Gel-permeable chromatograph Brookhaven WGE SEC 3010 equipped with full multiple detection: refraction index, viscosity, light diffusion MALS (7 different angles) and UV.

General procedures for the hydrosilylation reactions. In a typical example, the reagents 1,3-divinyl tetramethyldisiloxane and 1,1,3,3-tetramethyldisiloxane were mixed in 1:1 mole ratio without solvent in a screw vial, then the freshly dried catalyst was added, generally in solid state, unless otherwise stated. The vial was heated for 2 h at 100°C in a solvothermal oven without stirring. Alternatively, the reagents were dissolved in dry toluene, and the reactions proceeded at 60°C under argon. Modifications of the procedure and catalyst proportions are summarized in Table 1.

Hydrosilylation of allyl glycidyl ether with 1,1,3,3-tetramethyldisiloxane was done similarly in solvothermal conditions. Hydrosilylation of 1-hexene or styrene was conducted in dry toluene at 60 or 70°C, respectively, using freshly dried (silSH-PGM) as heterogeneous catalyst.[31]

Cross-linking by hydrosilylation was done using a poly(dimethyl-methylvinyl)siloxane with ca. 9 mol% vinyl groups as the substrate and pentamethylcyclopentasiloxane (D_5^H) as the cross-linker. The reagents were mixed in a small amount of chloroform, the catalyst was added as isopropanol solution, then solvents were removed by stirring and the mixture was analyzed from time to time by FT-IR.

CONCLUSIONS

Functionalized disiloxanes and silica have been used as ligands in combination with hexachloroplatinic acid or iron nitrate, to obtain new hydrosilylation catalysts. The molecular and silica-supported metal complexes have been tested in a model hydrosilylation reaction between 1,3-divinyl tetramethyldisiloxane and 1,1,3,3-tetramethyldisiloxane, conducted in (pseudo)-heterogeneous conditions. High conversion and selectivity were obtained, based on NMR, while some of these catalysts presented recyclability. The three molecular catalysts were tested in the hydrosilylation crosslinking of a poly(dimethyl-methylvinyl)siloxane, affording 85–95% conversion after 75 minutes at room temperature. In particular, an iron-based catalyst is very promising, cheap, unsophisticated and stable, capable to act in heterogeneous conditions, without the need of dry solvent or inert atmosphere. In the tested hydrosilylation reaction, it provided 98% conversion in the first cycle and 93% in the second one, over 80% selectivity, and yielded a narrower molecular mass distribution of the polycarbosiloxane, and similar efficiency as the platinum homologue in silicone cross-linking. Its mechanism of action remains to be studied. Silica-supported Pt or Pt/Pd catalysts, obtained with commercial or recovered noble metals precursors, presented high conversion and increased regioselectivity in the hydrosilylation reaction, being reusable. These catalysts were also successfully tested on other hydrosilylation reactions, useful in organic and silicon chemistry.

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