

Properties of $[\text{Pd}_2\text{X}_2(\text{dppm})_2]$ ($\text{X} = \text{Cl}, \text{SnCl}_3$, $\text{dppm} = \text{Bis}(\text{diphenylphosphino})\text{methane}$) Complexes on Porous Vycor Glass

Iara de Fátima Gimenez[#] and Oswaldo Luiz Alves*

Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13083-970 Campinas - SP, Brazil

Neste trabalho o vidro poroso Vycor foi utilizado como matriz para a imobilização de complexos contendo ligação metal-metal $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$, $[\text{Pd}_2(\text{SnCl}_3)\text{Cl}(\text{dppm})_2]$ e $[\text{Pd}_2(\text{SnCl}_3)_2(\text{dppm})_2]$. A elevada reatividade das ligações metal-metal em reações de inserção de moléculas como CO e SO_2 é preservada no meio poroso, sendo reversível sob vácuo. Os espectros de RMN MAS ^{31}P , refletância difusa no infravermelho e Raman indicaram que há uma gama de interações possíveis entre o vidro e as moléculas, como resultado da disponibilidade de diferentes grupamentos presentes nas moléculas, bem como de uma topologia porosa irregular. O caráter estático das moléculas no ambiente restrito impede movimentos do anel $\text{Pd}_2\text{P}_4\text{C}_2$ entre as conformações barco e cadeira, de modo que as moléculas confinadas podem ter diferentes conformações.

Porous Vycor glass (PVG) is used as a matrix for immobilization of complexes containing metal-metal bonds: $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$, $[\text{Pd}_2(\text{SnCl}_3)\text{Cl}(\text{dppm})_2]$ and $[\text{Pd}_2(\text{SnCl}_3)_2(\text{dppm})_2]$. The high reactivity of the metal-metal bonds in insertion reactions with small molecules such as CO and SO_2 is preserved in the pore medium, and is reversible under vacuum. ^{31}P MAS-NMR and Raman spectra indicate that there is a range of interactions between the glass and the adsorbed molecules as a result of the availability of different groups in the molecules and of the irregular pore topology as well. The static character of the molecules in the restrictive pore environment precludes motions such as flipping of the ring $\text{Pd}_2\text{P}_4\text{C}_2$ between boat and chair conformations and rotation of the phenyl rings, and the molecules may present a range of conformations.

Keywords: palladium complexes, Vycor, immobilization, ^{31}P NMR, Raman, metal-metal bond

Introduction

Many adsorption studies related to organometallic compounds and transition metal complexes on porous glasses have been performed with the purpose of applications such as catalysis^{1,2} and formation of nanoparticles by thermal decomposition or photolysis of the molecular species.³⁻⁷ In this area, a number of papers describe the immobilization of carbonyl complexes of iron³⁻⁷ and ruthenium⁸⁻¹⁰ onto porous glasses, since these complexes are good precursors to metallic or oxide particles via thermal and photochemical decomposition.

Immobilization studies of transition metal phosphine complexes were limited for many years by the lack of suitable characterization techniques. Infrared spectroscopy is very useful in the characterization of carbonyl complexes embedded in porous glasses, giving however spectra

dominated by the silica matrix bands in the case of phosphine complexes. The use of solid-state NMR techniques in addition to complementary vibrational measurements can be helpful in providing information about the structure and interactions between molecules and substrates.¹¹⁻¹³ Work by Fyfe and co-workers¹⁴ describes the use of ^{31}P MAS NMR spectroscopy for the study of phosphine complexes immobilized onto silica gel, in order to overcome the disadvantages in the characterization of such systems.

A family of highly reactive phosphine compounds, whose immobilization studies in solid substrates remain unexplored, is the series $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$, $[\text{Pd}_2(\text{SnCl}_3)\text{Cl}(\text{dppm})_2]$ and $[\text{Pd}_2(\text{SnCl}_3)_2(\text{dppm})_2]$. Holloway and co-workers first described complexes of the type $[\text{Pd}(\text{dppm})\text{X}]_2$ in 1976.¹⁵ These compounds take part in different types of reactions, such as additions, substitutions and insertions, owing to the presence of a single metal-metal bond, which acts as a nucleophilic center.¹⁶ The structure of the molecules comprises two Pd-Cl

* e-mail: oalves@iqm.unicamp.br

[#] Present Address: Departamento de Química, Universidade Federal de Sergipe, Brazil (gimenez@ufs.br)

fragments directly bonded by a single metal-metal bond (bond length 2.699 Å) and two bridging dppm ligands.¹⁷⁻¹⁹ The arrangement around the palladium atoms is nearly planar and the conformation of the molecule is twisted with a dihedral angle of 39° between adjacent planes. For the palladium atoms the oxidation state I is considered low accounting for the reactivity of the compounds in insertion reactions into the metal-metal bond. Pd-Pd bond lengths were found to increase by 0.5 Å after insertion of molecules with withdrawing groups such as CO, SO_2 , methylene groups, and isocyanides.²⁰⁻²⁵ Adducts with A-frame structures such as $[\text{Pd}_2\text{Cl}_2(\mu\text{-SO}_2)(\text{dppm})_2]$ and $[\text{Pd}_2\text{Cl}_2(\mu\text{-CO})(\text{dppm})_2]$ can be prepared by bubbling the gases into solutions of the compound $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$, with observable color changes.

As far as the reactivity of single bonded Pd_2 moieties are concerned attempts previously reported to immobilize similar compounds onto polystyrene for application such as separation of gases were unsuccessful due to steric demands.²⁵ We were further interested in studying the reactions of the immobilized species with CO and SO_2 gases, having reported preliminary results for porous Vycor glass.²⁶

The main objectives of the present work have been to evaluate conditions for immobilization of $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$, $[\text{Pd}_2(\text{SnCl}_3)\text{Cl}(\text{dppm})_2]$ and $[\text{Pd}_2(\text{SnCl}_3)_2(\text{dppm})_2]$ complexes onto porous Vycor glass (PVG), to gain some insight into the nature of interactions responsible for the stabilization of the complexes in the PVG pores and the arrangement of the molecules in the restrictive pore space as well.

Experimental

Preparation and immobilization of the complexes

The solvents used in the experiments were dried over molecular sieves and the gases (White Martins) were used without further purification. The $[\text{Pd}_2\text{X}_2(\text{dppm})_2]$ complexes were synthesised according to the route described by Balch and Benner²⁷ and introduced into the pores of 1 mm thick polished Vycor 7930 glass plates. Immobilization experiments were carried out by immersion of glass plates with dimensions of 10 X 10 mm into 10 mL of 1.10^{-3} mol L^{-1} CH_2Cl_2 solutions of the $[\text{Pd}_2\text{X}_2(\text{dppm})_2]$ complex at room temperature for 24 h. The solvent was removed under vacuum and the glass plates containing the $[\text{Pd}_2\text{X}_2(\text{dppm})_2]$ complexes were stored in a desiccator.

The insertion reactions were carried out admitting the reagent gases in evacuated Schlenk flasks containing the adsorbed complexes and keeping the flasks closed for 1 h prior to measuring the UV-Visible absorption spectra.

Characterization by physical methods

The presence of the $[\text{Pd}_2\text{X}_2(\text{dppm})_2]$ complexes and the reactions with the gases whilst in the pores of PVG plates was detected by a set of spectroscopic techniques. UV-Visible Absorption Spectroscopy data were measured using a HP 8452A diode array spectrophotometer in the range 190 to 820 nm with spectral resolution of 2 nm. The Raman spectra were recorded on a Renishaw System 3000 Raman Imaging Microscope (*ca.* 1 μm spatial resolution) utilizing a diode laser (782 nm) and 8 mW laser power before the entrance optics. The measurements were performed on bulk and powdered samples. ^1H decoupled ^{31}P MAS NMR spectra were measured using a Bruker AC/300P instrument, with a spinning frequency of 15 kHz, relaxation delay (D1) of 80-100s and 85% H_3PO_4 as reference.

Results and Discussion

UV-Visible spectroscopy

After removal of the solvent, the behavior of the molecules in the glass pores was evaluated by successive measurements of UV-Visible spectra as a function of time, pointing out that only the compound $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$ is air stable for weeks. In the solid state, the compounds are long-term stable but in solution the characteristic absorption bands can be observed only up to three days, especially for concentrations lower than 10^{-4} mol L^{-1} . The glass plates containing the other two compounds studied presented spectral changes indicative of disruption of the SnCl_3 ligands.

In order to discuss the assignments of the absorption bands it is worth mentioning that owing to the electronic configuration $(d\sigma)^2(d\pi)^4(d\delta)^4(d\delta^*)^4(d\pi^*)^4(d\sigma^*)^0$, the complexes present one net metal-metal bond involving the palladium (I) atoms. The UV-Visible spectra of the three compounds, $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$, $[\text{Pd}_2(\text{SnCl}_3)\text{Cl}(\text{dppm})_2]$ and $[\text{Pd}_2(\text{SnCl}_3)_2(\text{dppm})_2]$, in CH_2Cl_2 consist of high energy bands at 290 nm and 340 nm, assigned to transitions of electrons from occupied σ and δ^* molecular orbitals to the unoccupied σ^* molecular orbital of the metal-metal bond, as elucidated by Alves and co-workers.¹⁹ Differences between the spectrum of $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$, $[\text{Pd}_2(\text{SnCl}_3)\text{Cl}(\text{dppm})_2]$ and $[\text{Pd}_2(\text{SnCl}_3)_2(\text{dppm})_2]$, respectively, are the bands at 415, 504 and 534 nm, assigned to electronic transitions from the π^* to the σ^* molecular orbital of the metal-metal bond. After removal of the solvent, the UV-Visible spectra of PVG plates, which were immersed in solutions of the complexes, closely resemble those previously obtained in solution by Olmstead and

co-workers.²³ All the spectra exhibit bands at 208 and 228 nm, assigned to the glass, along with bands of the adsorbed complexes, as can be seen in Figure 1.

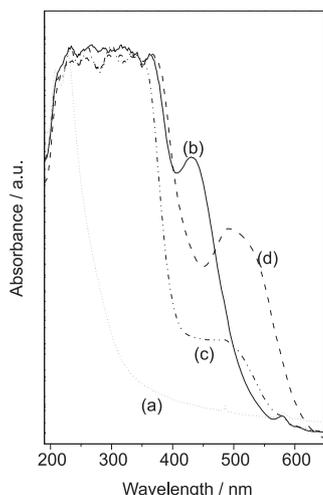


Figure 1. UV-Visible absorption spectra of PVG plates containing the immobilized complexes where (a) Porous Vycor glass, (b) $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$, (c) $[\text{Pd}_2(\text{SnCl}_3)\text{Cl}(\text{dppm})_2]$ and (d) $[\text{Pd}_2(\text{SnCl}_3)_2(\text{dppm})_2]$.

Raman spectroscopy

Figures 2 and 3 present Raman spectra of the complexes in the solid state and after immobilization onto Vycor glass plates, respectively.

For all complexes in the solid state the bands above 500 cm^{-1} can be interpreted in terms of vibrations of the phenyl rings from substituted phosphines $(\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_2)_n\text{P}(\text{C}_6\text{H}_5)_2$ ($1 < n < 4$). According to this

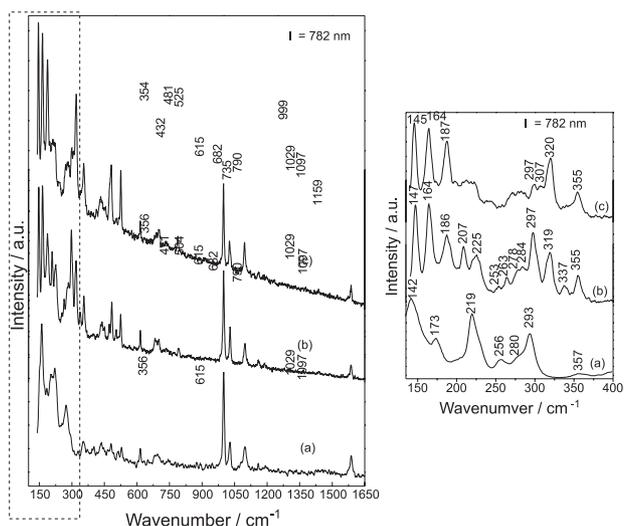


Figure 2. Raman spectra of crystalline specimens of the complexes where (a) $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$, (b) $[\text{Pd}_2(\text{SnCl}_3)\text{Cl}(\text{dppm})_2]$ and (c) $[\text{Pd}_2(\text{SnCl}_3)_2(\text{dppm})_2]$. The box on the right side shows a zoom of the region from 160 to 400 cm^{-1} .

approach from a maximum of 30 bands expected in this region, only 6 were found to be dependent on the substituent mass.^{31,32} All bands observed in this region for the three compounds are very similar and show good agreement with those described by Whiffen and co-workers.^{31,32} Below 500 cm^{-1} , apart from bands at 145 cm^{-1} and 168 cm^{-1} , assigned to Pd-Pd and Pd-P stretching, respectively, the spectra of the three compounds present differences.¹⁹ For instance, bands in the region $253\text{--}284\text{ cm}^{-1}$, that can be assigned to Pd-Cl stretching are present in the spectra of both $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$ and $[\text{Pd}_2(\text{SnCl}_3)\text{Cl}(\text{dppm})_2]$, in contrast with the presence of bands at 207 cm^{-1} and 320 cm^{-1} assigned to Pd-Sn and Sn-Cl stretching, respectively, in the spectra of the compounds containing the SnCl_3 groups. For Vycor samples containing the complexes, the Raman spectra above 500 cm^{-1} are nearly free from interference of the spectroscopic features of the glass, presenting the same bands observed for the spectra obtained in solid state. Below 500 cm^{-1} the spectra show a strong interference from the glass bands, which appear in addition to broad bands assigned to the immobilized complexes. The typical spectroscopic features of the PVG/ $[\text{Pd}_2\text{X}_2(\text{dppm})_2]$ systems below 500 cm^{-1} in Figure 3 reflect the inherent complexity of the system relative to interaction and molecular arrangement. Most bands observed in Raman spectra of solid-state complexes are also present in the spectra of Vycor immobilized molecules. Despite band broadness in this region the similarity between wavenumbers observed in the glass and solid state spectra suggests that the molecular structures of the complexes have been preserved.

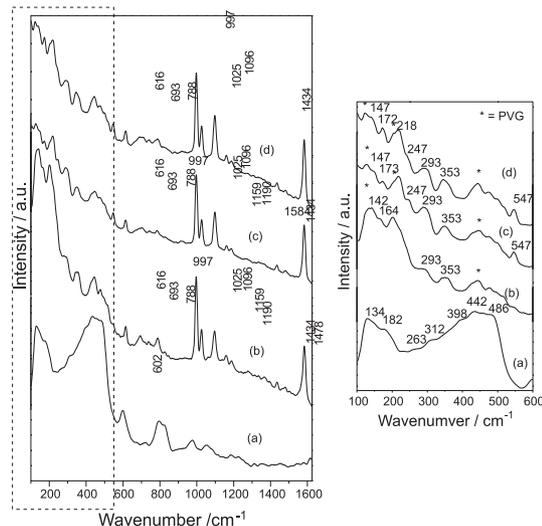


Figure 3. Raman spectra of PVG plates containing the immobilized complexes where (a) blank PVG (b) $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$, (c) $[\text{Pd}_2(\text{SnCl}_3)\text{Cl}(\text{dppm})_2]$ and (d) $[\text{Pd}_2(\text{SnCl}_3)_2(\text{dppm})_2]$. The box on the right side shows a zoom of the region from 100 to 600 cm^{-1} .

^{31}P MAS-NMR spectroscopy

^{31}P MAS-NMR measurements provided valuable information about the arrangement of $[\text{Pd}_2\text{X}_2(\text{dppm})_2]$ molecules in the glass pores (Figure 4). Since in these spectra the phosphorus resonances arise from the dppm ligands $[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}(\text{C}_6\text{H}_5)_2]$, the spectrum of this molecule immobilized onto Vycor glass has been measured as a model for the understanding of the spectra of the immobilized complexes. The resonance signal of phosphorus nuclei from the immobilized uncomplexed dppm ligands is relatively sharp and presents δ values similar to those described for the solution spectrum.³³ This is in contrast with the signal shape of samples containing the immobilized palladium complexes, which exhibit broad signals in addition to side bands. Several factors can account for the differences observed between the spectra of phosphorus nuclei from PVG/dppm and PVG/ $[\text{Pd}_2\text{X}_2(\text{dppm})_2]$. The higher spectral resolution of dppm phosphorus nuclei before complexation points out that coordination to Pd atoms strongly affects the magnetic environment of P atoms. Note that in the solid-state chemical and magnetic equivalence are not synonyms. Fyfe and co-workers¹⁴ described the ^{31}P solution spectrum of dppm where only one signal was observed at $\delta -23$, but in the solid state two signals are expected in the ^{31}P CP MAS spectrum of crystalline dppm. According to the crystallographic structure one entire molecule is present in the asymmetric unit (orthorhombic space group Pbca $Z = 8$) and the two P atoms are crystallographically inequivalent. For the sample containing dppm molecules adsorbed onto PVG, one signal is observed at $\delta -23$ in addition to an unresolved less intense signal at $\delta -30$. Certainly the reason for two signals is not the same as in the crystalline state but one possibility is that dppm molecules may interact with different groups of the glass (silanol and siloxanes) both *via* one or two P atoms.

Several reasons should be considered to account for the differences in the NMR spectra of PVG/dppm and PVG/ $[\text{Pd}_2\text{X}_2(\text{dppm})_2]$. First, broad signals are commonly observed in the ^{31}P NMR spectrum of immobilized phosphine metal complexes as a consequence of the amorphous character of the substrates. Substantial dispersion of ^{31}P chemical shifts must be anticipated in amorphous systems where a given type of phosphorus atom may be present in a wide variety of environments.¹⁴ This broadening due to environmental effects will not be further reduced by any line-narrowing technique. The absence of ordered arrays of molecules, such as those observed in crystalline packing, in addition to fractal topology of pore surfaces, can account for the transference of some

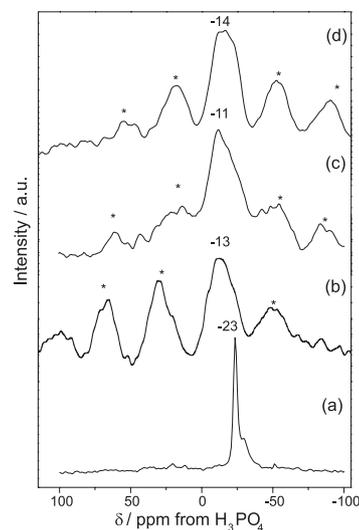
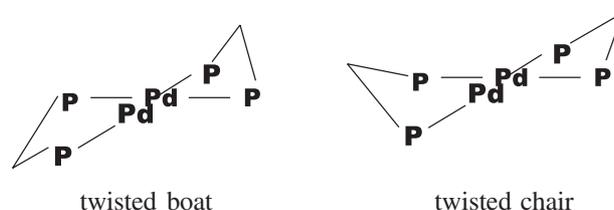


Figure 4. ^{31}P MAS-NMR spectra PVG plates containing (a) the uncomplexed dppm ligands and the immobilized complexes where (b) $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$, (c) $[\text{Pd}_2(\text{SnCl}_3)\text{Cl}(\text{dppm})_2]$ and (d) $[\text{Pd}_2(\text{SnCl}_3)_2(\text{dppm})_2]$.

amorphous character from the glass. Additionally, the broadness of the signal suggests a range of interactions between the glass and the adsorbed molecules, which is thought to reflect differences in the local topology and/or the availability of free and associated silanol groups at the individual adsorption sites.

Another important aspect is the role of packing on the conformational structure of the complexes. The importance of packing for related palladium dimers such as $[\text{Pd}_2(\text{dppm})_2(\text{OAr})_2]$ and $[\text{Pd}_2(\text{dppm})_2(\text{OCOCF}_3)_2]$ was studied by Krafft and co-workers through the crystal structure determination of these compounds.³⁴ Unlike the dihalide dimers $[\text{Pd}_2\text{Br}_2(\text{dppm})_2]$ and $[\text{Pt}_2\text{Cl}_2(\text{dppm})_2]$, which exhibit a “twisted chair” conformation of the $\text{Pd}_2\text{P}_4\text{C}_2$ ring system, the phenoxides and carboxylates exhibit a “twisted boat” conformation.



Although still not fully understood, the importance of steric or crystal packing effects in imposing the conformations is evident and illustrates the structural flexibility of this family of molecules. In solution, twist motions such as ring flipping between boat and chair conformations and rotation of the phenyl rings take place rapidly and the effect on the chemical shift is averaged to

the isotropic value. When confined in the glass pores, the molecules are neither free to move, as in solution, nor orderly packed as in the crystal. In the latter the molecules are found to show well-defined conformations, which might not be the case for the adsorbed molecules.

Other factors such as the presence of residual second-order quadrupolar coupling in the ^{31}P MAS NMR spectra (peculiar to solid-state spectra) due to the ^{105}Pd nuclei ($I = 5/2$ and natural abundance of 22.2%) could be present causing line broadening. Komoroski and co-workers¹² considered that this effect might be expected in the ^{31}P MAS NMR spectra of silica-immobilized mononuclear palladium complexes but in that case a short T_1 (spin-lattice relaxation time for ^{105}Pd) leads to self-decoupling of the dipolar interaction between ^{105}Pd and ^{31}P , so the effect can be intrinsically suppressed. In the present case detailed calculations must be carried out in order to confirm this phenomenon.

Reactivity of metal-metal bonds

In order to verify if the reactivity of the metal-metal bond is preserved when inside PVG, glass samples containing the organometallic molecules have been exposed to different gases such as SO_2 and CO , since solution reactions are well known to take place.²⁰⁻²⁴ In general, color changes upon gas exposure have been observed for all samples, indicating insertion of gas molecules into the Pd-Pd bonds. Evidences for the insertion reactions were provided by UV-Visible spectroscopy and after gas exposure new bands can be observed in Figure 5. These new bands appear at the same wavenumbers observed when the reactions are carried out in solution.²⁰⁻²⁴ Additional characterization, such as Raman spectroscopy, was not possible owing to the dilute character of the A-frame adducts in the glass. However, measurements of the intensities of color change by UV-Visible spectroscopy may be the basis for use of this material in gas detection.

Previous studies related to reactions of species adsorbed onto PVG with gaseous reagents revealed the possibility of two kinetic reaction modes.³⁵ With low gas pressures, the diffusion of the gases through the pores is sufficient to ensure successful collisions between the adsorbed complexes and the gaseous reagents. As the pressure increases, co-adsorption and condensation of the gases take place on the pore surface and, in this case, the reaction occurs with a co-adsorbed mobile reagent. In the present work, as low gas pressures are used, we consider that the first situation described above predominates; nevertheless some co-adsorption cannot be ruled out. In the case of carbonyl type organometallics, substitution reactions may

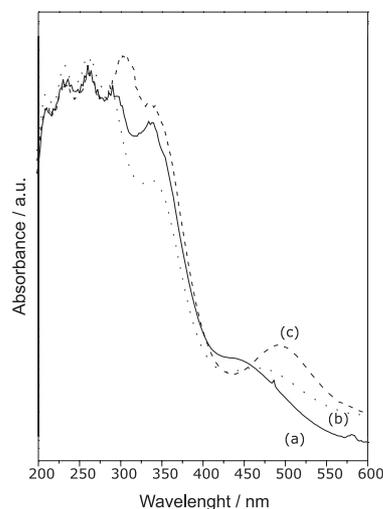


Figure 5. UV-Visible absorption spectra of PVG plates containing the complex $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$ (a) before and after exposure to (b) CO and (c) SO_2 gases.

take place between a silanol and a carbonyl ligand to account for the immobilization in glass pores, with the possibility of further substitution of CO ligands by the gaseous reagent. In the present case, the preservation of the reactivity of the metal-metal bond is ensured by interactions with silanol groups via the phenyl and/or methylene groups, leaving the Pd-Pd bonds available for further interactions. The chlorine atoms could also interact with silanol groups since it was found that this is a real possibility for organochlorinated molecules adsorbed onto silica gel.³⁰

It has been described that, in solution, the insertion can be reversed upon heating under reflux or an inert gas flow.²³ In the glass pores, we observed that spontaneous de-insertion takes place slowly but can readily occur under vacuum. Probably this is due to the absence of crystal stabilization or solvation effects.

Conclusions

This work has shown that immobilization of the complexes $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$, $[\text{Pd}_2(\text{SnCl}_3)\text{Cl}(\text{dppm})_2]$ and $[\text{Pd}_2(\text{SnCl}_3)_2(\text{dppm})_2]$ is carried out in porous Vycor glass though only the compound $[\text{Pd}_2\text{Cl}_2(\text{dppm})_2]$ is air stable in the pores for weeks. The other two compounds studied presented spectral changes indicative of disruption of the SnCl_3 ligands. It was shown by spectroscopic techniques that the structural flexibility of the compounds allows the necessary distortions of the molecular structure in order to be stabilized in the pores. In the restrictive pore environment motions such as ring flipping between boat and chair conformations are hindered and the molecules may present a range of conformations. The reactivity of

the compound [Pd₂Cl₂(dppm)₂] with CO and SO₂ in insertion reactions into the Pd-Pd bond has been preserved inside the glass pores, pointing out potentialities for application as gas detection devices.

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