

Novel silica immobilized NCN-pincer palladium(II) and platinum(II) complexes: Application as Lewis acid catalysts

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Dedicated to Prof. B. Marciniec on the occasion of his 65th birthday.

Abstract

2,6-Bis[(dimethylamino)methyl]phenyl (NCN-pincer) palladium(II) and platinum(II) complexes tethered to a trialkoxysilane coupling agent through a carbamate linkage were immobilized on various types of silica using a grafting or a sol–gel process. The resulting hybrid materials were characterized by IR spectroscopy (DRIFT) and solid state CP/MAS NMR (^{13}C and ^{29}Si). Based on these analyses, H-bond interactions between the carbamate carbonyl group of the complex and the free silanol groups on silica surface were established. The palladium-based materials were tested for their activity as Lewis acid catalysts in the aldol reaction between methyl isocyanoacetate and benzaldehyde. It was found that these materials can indeed be applied as catalysts in this reaction. Their repetitive reuse showed an inferior catalytic efficacy, which presumably was caused by a reconstitution of the silica support. These studies also revealed that simple silver-based salts are active catalysts in this aldol reaction.

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1. Introduction

According to the principles of Green Chemistry catalytic systems are superior to the stoichiometric use of reagents [1]. In general, catalysts reduce the amount of reagents required and restrict waste generated in a reaction. They reduce energy requirements and decrease the number of separation steps due to increased selectivity [2]. Complex catalyst systems consisting of (precious) metals and laboriously synthesized (chiral) ligands are developed in homogeneous catalysis to meet these criteria. At the current state of art, recycling and reuse of these expensive catalyst systems become important aspects and the separation of catalysts from product streams poses an economical and environmental challenge [3].

In this respect, homogeneous and heterogeneous catalysts each fulfill some of the Green Chemistry criteria. Selectivity

and activity are better in the case of homogeneous catalysts [4] whereas product separation, catalyst recovery [5,6], and resistance to drastic operational conditions [7,8] are advantageous features of heterogeneous catalysts. Combination of these features would be desirable to arrive at an ideal catalyst system. This may be achieved by the immobilization of homogeneous catalysts on a solid support [9–15]. One approach to achieve this is to use homogeneous catalysts chemically bound to inorganic support materials like silica [16]. The properties of silica include thermal and chemical stability under reaction conditions, easily accessible and well-dispersed surface active sites (a high surface area $>100\text{ m}^2\text{ g}^{-1}$ is required), and a mesoporous structure which is a prerequisite for liquid phase processes (pore size $>20\text{ \AA}$ to avoid diffusion limitations) [17]. A wide range of homogeneous catalysts has been immobilized on silica and successfully recycled [18–33].

The actual immobilization of a homogeneous catalyst on a heterogeneous support can be achieved mainly by two different approaches. A transition metal is either complexed to ligands already chemically bonded (immobilized) to a sup-

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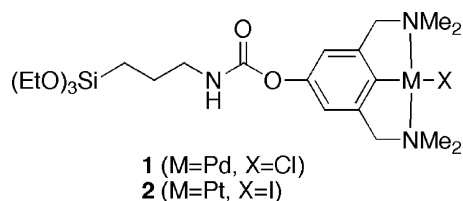


Chart 1. Siloxane-functionalized NCN-pincer complexes **1** and **2**.

port, or a metal complex containing an appropriate coupling agent is tethered to a support [6]. In the first approach, the coordination sphere around the metal center changes during immobilization via various ligand exchange processes and the average structural properties of this immobilized complex could be quite different from those of the homogeneous complex. In the second approach, such changes may be minimal provided that the metal ion is strongly complexed to the ligand and that this configuration remains intact during grafting [18,26,27].

In order to investigate the second approach, we decided to first obtain a fully characterized siloxane-functionalized metal complex which can be subsequently immobilized onto a silica support, and to study whether the heterogenized system formed has retained its initial metal–ligand configuration. For this study, we have used platinum and palladium complexes of so-called ‘pincer’ ligands of the ECE type (where ECE = [2,6-(ECH₂)₂C₆H₃][−], and E = NR₂, PR₂ or SR) [34] which can act as Lewis acid catalysts in aldol condensation reactions [35–40] and double Michael addition reactions [41–44]. The metal ion in these ECE-pincer metal complexes is strongly bound through a covalent M–C bond which is complemented by ortho-chelation of the two hetero atom containing substituents. This *mer*-ECE terdentate coordination provides considerable stability against metal leaching during catalysis [45,46]. In earlier efforts from our group, complexes of this type have been anchored to a variety of soluble supports like dendritic systems [35,42,47], hyperbranched polysilanes [38], methanofullerenes [43], etc., and were demonstrated to give stable, recyclable catalysts that show no leaching of metal, enabling the use of these systems in a membrane reactor for continuous operation [48]. Therefore, the metallo-pincer catalysts seem ideally suited for the grafting protocol to an insoluble support like silica as envisaged above. SCS- and PCP-type pincer palladium complexes have earlier been immobilized on silica and their use in aldol and Heck reactions was reported [20,23,32,49–51].

We have recently synthesized the siloxy-functionalized NCN-pincer palladium and platinum complexes **1** and **2** (Chart 1) from multipurpose, versatile *para*-OH functionalized NCN-pincer metal complexes, denoted as [MX(NCN-OH)] [52]. Here, we present our results on grafting these complexes on different types of amorphous silica surfaces. These immobilized complexes were characterized by various techniques such as IR spectroscopy (DRIFT) and solid-state CP/MAS NMR spectroscopy (¹³C and ²⁹Si). The immobilized palladium complexes were, furthermore, used in catalysis and the recyclability of these

catalysts in the aldol condensation reaction between benzaldehyde and methyl isocyanoacetate was investigated.

2. Experimental

2.1. General procedures

Solvents were dried over appropriate materials and distilled prior to use in a dry N₂-atmosphere. All reagents were obtained from commercial sources and were used without further purification. All siloxane materials were stored under nitrogen atmosphere. Benzaldehyde and Hünig’s base were distilled prior to use. Silica was received from Engelhard De Meern B.V., The Netherlands, in a generous amount. Triethoxysilyl-functionalized NCN-pincer metal complexes **1** and **2** and [PdI(NCN-OH)] (**3**) were prepared as described previously [52]. ¹H (200 and 300 MHz) and ¹³C{¹H} (50.3 and 75.5 MHz) NMR spectra were recorded at room temperature on either Varian Mercury 200 or Varian Inova 300 spectrometers. ¹³C (75.5 MHz) and ²⁹Si (59.6 MHz) CP/MAS (cross-polarization/magic angle spinning) NMR spectra were recorded on a Varian Inova 300 spectrometer (Spinning rate 6000 Hz, contact time for ¹³C 1.50 ms and for ²⁹Si 3.0 ms, number of transients for ¹³C 6068 and for ²⁹Si 11336). FT-IR and DRIFT (Diffuse reflectance IR Fourier transformation) spectra were recorded using a Mattson Instruments Galaxy Series FTIR 5000 spectrometer with SPECAC diffuse-reflectance assembly. Gas chromatographic analyses were performed with a Perkin Elmer Autosystem XL GC using a 30 m, PE-17 capillary column with an FID detector. Microanalyses were obtained from H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany.

2.2. Synthesis of [PdI(C₆H₂{CH₂NMe₂})₂-2,6-{Me(CH₂)₂NHC(O)O}-4] (**4**)

n-Propyl isocyanate (25 μL, 0.25 mmol) was added to a solution of **3** (0.1 g, 0.23 mmol), triethylamine (35 μL, 0.25 mmol), and 4-(dimethylamino)pyridine (2 mg, 0.013 mmol) in dry CH₂Cl₂ (10 mL). This reaction mixture was then refluxed for 10 h after which a clear yellowish solution had formed. After allowing the reaction mixture to attain room temperature, all volatiles were removed in vacuo. The residue was washed with pentane (2 × 15 mL) and the product extracted from the residue by treating it with C₆H₆ (3 × 15 mL). The combined extracts were filtered over a small silica column to remove insoluble impurities and the solvent was evaporated in vacuo to obtain **4** as a yellowish solid (0.11 g, 90% yield). ¹H NMR (300 MHz, C₆D₆, 25 °C): δ = 0.70 (t, ³J(H,H) = 7.5 Hz, 3H, CH₃); 1.30 (mult., ³J(H,H) = 6.9, 7.5 Hz, 2H, CH₂); 2.65 (s, 12H, NCH₃); 3.00 (q, ³J(H,H) = 6.6, 6.9 Hz, 2H, NHCH₂); 3.22 (s, 4H, ArCH₂N); 4.85 (t, ³J(H,H) = 6.6 Hz, 1H, NH); 6.59 (s, 2H, ArH). ¹³C NMR (50 MHz, C₆D₆, 25 °C): δ = 11.25 (CH₃); 23.40 (CH₂); 43.10 (NHCH₂); 54.74 (NCH₃); 73.72 (ArCH₂N); 113.91, 146.25, 149.54, 154.93 (ArC); 155.81 (carbonyl). Anal. Calcd for C₁₆H₂₆IN₃O₂Pd (525.72): C, 36.55; H, 4.98; N, 7.99. Found: C, 36.43; H, 5.06; N, 7.85.

2.3. Grafting procedure

In a typical procedure, silica (1 g) was pretreated by heating it at 100 °C under vacuum for 2 h. After allowing it to cool to room temperature, a solution of **1** or **2** (0.2 mmol) in dry toluene (100 mL) was introduced. The resulting mixture was stirred to form a suspension and refluxed for 24 h, after which the silica was allowed to settle and the supernatant liquid was decanted. The silica was washed twice with dry CH₂Cl₂ (50 mL) and then it was subjected to Soxhlet extraction using CH₂Cl₂ for 16 h. Finally, it was dried under vacuum yielding about 1 g of material in each case.

Material 5: IR (KBr, DRIFT): $\tilde{\nu}$ (cm⁻¹) 2960, 2858 (C–H stretching), 1718 (C=O stretching), 1603, 1539 (CNH group), 1472, 1450 (N–H bending). ¹³C CP/MAS NMR (75.5 MHz, 25 °C): δ = 8.4 (SiCH₂); 15.3 (OCH₂CH₃); 24.6 (CH₂); 42.6 (NHCH₂); 51.1 (NCH₃); 58.3 (OCH₂); 73.4 (ArCH₂N); 114.36, 145.8, 148.4, 156.8 (ArC); 164.9 (carbonyl). ²⁹Si CP/MAS NMR (59.6 MHz, 25 °C): δ = -112.6, -103.1, -52.6. Anal. Found: C, 3.46; H, 0.75; N, 0.61; Pd, 1.63 (molar ratio of N/Pd 3; found 2.8).

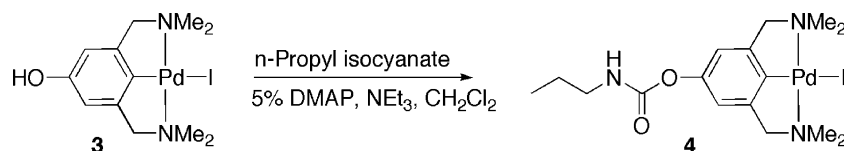
Material 6: IR (KBr, DRIFT): $\tilde{\nu}$ (cm⁻¹) 2986, 2930, 2891 (C–H, stretching); 1718 (C=O, stretching); 1525 (CHN group); 1454 (N–H, bending). Anal. Found: C, 1.13; H, 0.25; N, 0.27; Pt, 1.18 (molar ratio of N/Pt 3; found 3.2).

2.4. Protection of free silanol groups with trimethylsilyl groups

In a typical procedure, silica **5** (0.5 g) was treated with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (5 g, 31 mmol) in hexane (25 mL). The mixture was stirred for 24 h, after which the silica was washed with hexane (3 × 50 mL) and dried under vacuum yielding about 0.5 g silica **7**. IR (KBr, DRIFT): $\tilde{\nu}$ (cm⁻¹) 2960, 2901, 1736, 1521, 1450, 854, 765.

2.5. Synthesis of silica **10**; grafting by using amide linkage

Commercially available 3-aminopropyl functionalized silica **8** (2.4 g, loading ~1 mmol/g NH₂) was treated with a solution of organometallic activated ester **9** [53] (60 mg, 0.12 mmol) in CH₂Cl₂. The mixture was stirred at room temperature for 16 h. After centrifugation and decantation, the silica was washed successively with CH₂Cl₂, acetone, water, and then again with acetone and was finally dried in vacuo yielding about 2 g of material **10**. IR (KBr, DRIFT): $\tilde{\nu}$ (cm⁻¹) 2943, 2858 (C–H, stretching); 1658 (C=O, stretching); 1543 (CNH group); 1444 (N–H, bending). Anal. Found: C, 8.17; N, 2.27; Pd, 0.55.



Scheme 1. Synthesis of model complex **4**.

2.6. Synthesis of **5'**; grafting using ethanol

A mixture of silica (0.5 g), complex **1** (50 mg, 0.084 mmol) and triethylamine (1 mL, 7.2 mmol) in ethanol (20 mL) was stirred at ambient temperature for 16 h. Silica was filtered, washed with ethanol (3 × 20 mL) and dried in vacuo which gave 0.52 g of solid.

2.7. Synthesis of **5''**; grafting by sol–gel method

To a solution of NH₃ (29.3% aqueous NH₄OH solution, 7.25 mL) in ethanol (75 mL), complex **1** (95 mg, 0.16 mmol) and tetraethylorthosilicate (TEOS) (3.34 mL, 15 mmol) were added. This clear solution was stirred at ambient temperature. In about 10 min, fine gel particles precipitated out of the solution slowly. After stirring the mixture for 1 h, these particles were centrifuged off. Silica was washed with excess of ethanol and dried in vacuo. A 1.13 g of silica was obtained. IR (KBr, DRIFT): $\tilde{\nu}$ (cm⁻¹) 3230, 1638, 1464, 1059, 955, 796. Anal. Found for **5''**: Pd, 0.78.

2.8. Catalysis

The catalytic experiments were carried out using *i*Pr₂EtN (Hünig's base, 10 mol%) as a base, functionalized silica materials (approx. Pd content 1 or 2.5 mol%) as catalyst, and methyl isocynoacetate (1.6 mmol) and benzaldehyde (1.6 mmol) as reagents in CH₂Cl₂ (5 mL) at room temperature. Except for parallel screening, stirring was carried out using an overhead stirrer in order to avoid grinding of silica particles. The reaction progress was monitored by means of GC analysis using pentadecane as internal standard. After each run, the complete reaction mixture was centrifuged and the supernatant was separated. The remainders were washed with CH₂Cl₂ (2 × 20 mL) and dried in vacuo. The obtained solid was used for the next run.

3. Results and discussion

3.1. Siloxy-functionalized pincer complexes

The synthesis of **1** and **2** (Chart 1) was achieved by making use of [MX(NCN-OH)] pincer complexes as reported [52]. These complexes comprise both a trialkoxysilane and an organometallic fragment covalently connected through a carbamate linker. The *n*-propyl-functionalized complex **4** was prepared as a test compound in 90% yield in a similar fashion by refluxing [MX(NCN-OH)] pincer complex **3** with *n*-propyl isocyanate in the presence of a base combination comprising 0.05 equivalent of 4-(dimethylamino)pyridine (DMAP) and 1.1 equivalent of

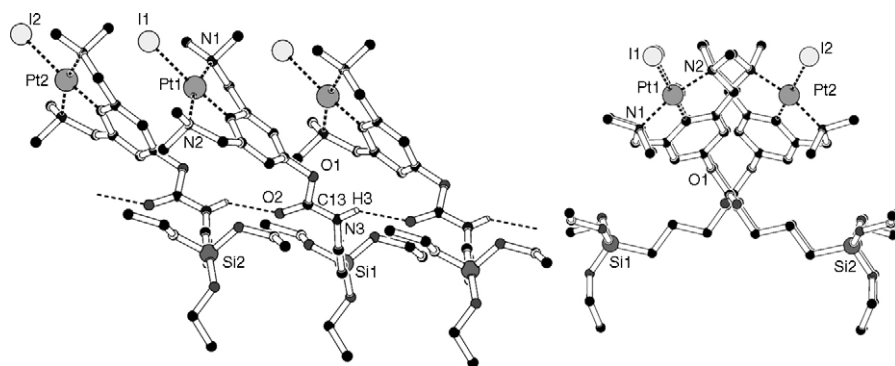


Fig. 1. Intermolecular H-bonding in **2**; lateral view (left) and axial view (right) (hydrogen atoms except those involved in the H-bonding have been omitted for clarity) [52].

NEt_3 (Scheme 1). The employed base combination increases the rate of the reaction and drives it to completion. At the same time, product purification was much easier than when larger amounts of DMAP were used.

Detailed information on the structural aspects of the organometallic siloxanes **1** and **2** was earlier obtained through the single crystal X-ray structure of **2** [52]. The molecular units in this structure comprise an NCN-pincer Pt-complex with normal pincer-metal structural parameters connected to a triethoxysilane through a propyl carbamate linker that adopts an extended conformation. Interestingly, the molecular units are intermolecularly connected through a hydrogen bonding network involving the NH and carbonyl group of neighboring units (Fig. 1). As a result, all the NCN-pincer platinum units are arranged at one site and the $\text{Si}(\text{OEt})_3$ groups on the opposite site, creating a kind of model showing the possible arrangement of the NCN-pincer platinum groupings on a silica surface.

3.2. Grafting on silica

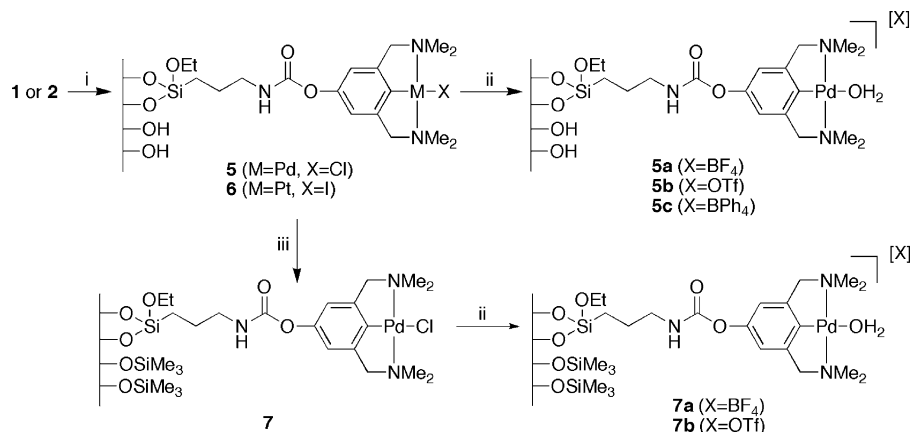
Silica with a particle size of 0.5–1.5 mm and pore diameter of 150 Å was used for the immobilization of **1** and **2**. In a typical process, silica was pre-treated by heating at 100 °C under vacuum for 2 h. It was then reacted with complex **1** or **2** in refluxing toluene for 24 h (Scheme 2). Continuous extraction (Soxhlet) of

the resulting material with CH_2Cl_2 was performed for 24 h in order to remove any non-covalently attached organic material. After drying in vacuo, the functionalized silicas **5** and **6** were obtained as off-white particles.

The results of DRIFT analysis of **5** indicated (vide infra) that some of the silanol groups on the silica had remained unreacted during the grafting procedure. To investigate the effect of such groups on catalysis, modified silica **5** was further treated with hexamethyldisilazane (HMDS) in hexane for 24 h at room temperature to obtain **7**, in which the remaining silanol groups were capped by trimethylsilyl groups (Scheme 2).

3.3. Characterization of hybrid materials

For the characterization of the modified silicas, various techniques such as IR spectroscopy (DRIFT), solid-state CP/MAS NMR spectroscopy (^{13}C and ^{29}Si), and elemental analysis were used. Comparison of the IR spectrum of plain silica with that of modified silica **5** showed a strong decrease in intensity of the signal for isolated silanol groups at 3742 cm^{-1} (Fig. 2). IR spectra of the homogeneous complex **1** and the hybrid material **5** were also compared (Fig. 2, Table S1). The signals corresponding to the C–H stretching, C=O stretching, CNH group, and N–H bending vibrations of **1** were observed in the spectrum of **5**. A further decrease in the isolated silanol signal at 3742 cm^{-1} was



Scheme 2. Immobilization and activation of **1** and **2** on silica: (i) silica, toluene, reflux, 24 h; (ii) AgBF_4 or TMSOTf in CH_2Cl_2 , or NaBPh_4 in acetone; (iii) HMDS, hexane, 24 h.

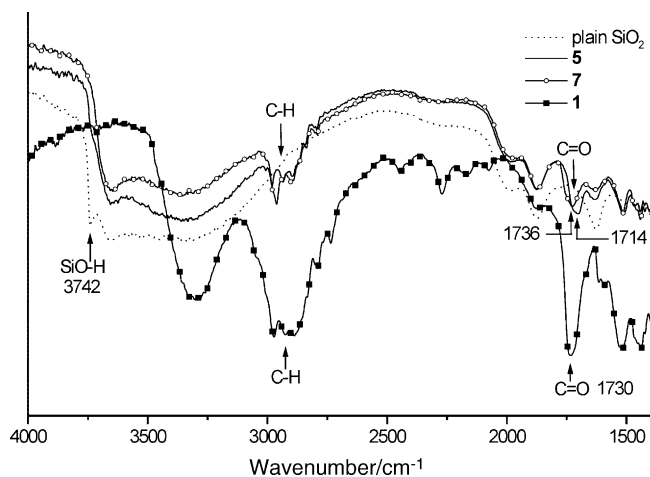


Fig. 2. IR spectra (DRIFT) of plain silica, silicas **5** and **7**, and homogeneous complex **1**.

observed after treatment of **5** with HMDS to obtain **7**. Additional signals corresponding to C–H stretching (2960 cm^{-1}), symmetric deformation of Si–CH₃ (1265 cm^{-1}), and Si–CH₃ rocking (860 and 765 cm^{-1}) vibrations were also observed for this material and appeared comparable to vibrations in the IR spectrum of plain silica after treatment with HMDS (Fig. 2, Table S1).

¹³C and ²⁹Si solid-state NMR spectroscopy on **5** provided further information on the structure of both the organic (spacer and metal-complex) and inorganic part of this hybrid material and is representative for all silica materials presented here. All peaks corresponding to the ¹³C NMR spectrum of homogeneous complex **1** were present in the ¹³C spectrum of **5** (Fig. 3). Signals corresponding to ethoxy groups on the silicon atom of **1** were present even after grafting (15.3 and 58.3 ppm). This suggests that not all ethoxy groups have reacted and that the covalent immobilization of this complex to the surface takes place via either one, two or three silyl ether linkages, i.e. the type of silicon atom of the grafted complex is best described as an average of T¹, T², and T³ types ($T^n = \text{RSi}(\text{OSi})_n(\text{OEt})_{3-n}$) [54]. This observation is supported by ²⁹Si NMR spectroscopy where a

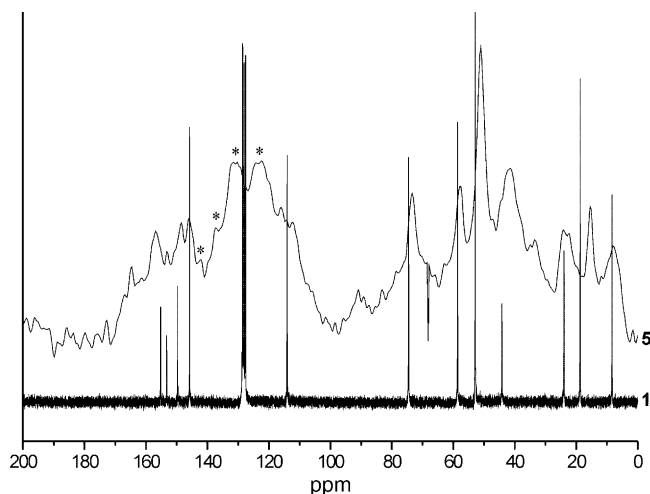


Fig. 3. CP/MAS ¹³C NMR spectrum of silica **5** and ¹³C NMR spectrum of homogeneous complex **1** (*spinning side-bands).

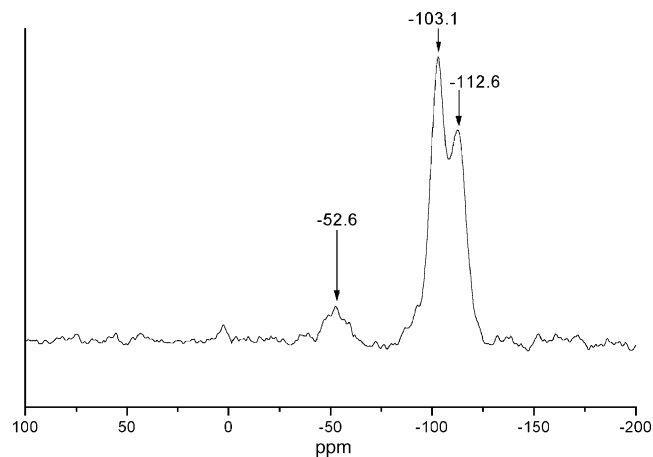


Fig. 4. CP/MAS ²⁹Si NMR spectrum of silica **5**.

broad signal is observed at -52.6 ppm for Tⁿ Si of the complex, corroborating the average of the three types of linkages to the support (Fig. 4). Furthermore, two strong signals were observed at -103.1 and at -112.6 ppm corresponding to Q³ Si and to Q⁴ Si from the support, respectively ($Q^n = \text{Si}(\text{OSi})_n(\text{OH})_{4-n}$).

According to elemental analysis, a loading of 1.63 weight % of Pd and 1.18 weight % of Pt is achieved for **5** and **6**, respectively. Comparison of the relative N and metal content showed their presence in the expected ratio of three according to the formulation of both **1** and **2**.

3.4. SO₂ binding test

Square planar NCN-pincer platinum halide complexes are known to reversibly bind SO₂ gas [55]. The adduct thus formed has a bright orange color whereas the SO₂-free complexes are colorless. Coloration tests with SO₂ can thus be used to detect and prove the presence of such complexes to a very low level of concentration and vice versa [56,57]. Conditions for SO₂ binding and colorization are that the Pt(II) ion is both cyclometallated by an NCN type pincer ligand and that it has a halide ion as its fourth ligand [58]. After immobilizing complex **2** on silica, the colorless, modified silica **6** was exposed to an SO₂ atmosphere upon which it turned orange. By applying vacuum, the silica turned back to colorless, displaying reversible binding of SO₂. These observations provide evidence for the successful grafting of the siloxane as well as for the presence and integrity of the NCN-pincer platinum halide complex on silica.

3.5. H-bonding

The crystal structure of the platinum-based complex **2** reveals the presence of intermolecular hydrogen bonds with the carbamate nitrogen as donor and the carbamate carbonyl of a neighboring molecule as acceptor (Fig. 1) [52]. In the IR spectrum of palladium-based complex **1** in the solid-state, the carbonyl stretching signal is found at 1730 cm^{-1} and the N–H vibration at 3313 cm^{-1} (broad), whereas a diluted solution of **1** in CH₂Cl₂ has these vibrations at 1737 and 3445 cm^{-1} (sharp), respectively, clearly indicating a decrease in H-bonding in solution. Upon

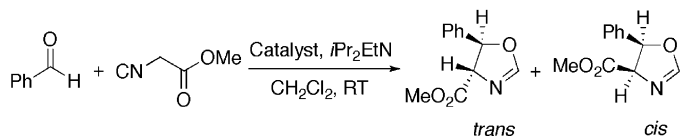


Plate 1.

immobilization of this complex on silica (**5**), the signal for the carbonyl group is shifted to 1714 cm⁻¹ (Fig. 2), indicating a stronger H-bonding for the immobilized complex with either a carbonyl moiety of a neighboring complex or, alternatively, with (isolated) silanol groups on the silica surface. Interestingly, when the isolated silanol groups were protected by trimethylsilyl groups (modified silica **7**), the signal for the carbonyl group shifted to the value observed for **1** in solution (1736 cm⁻¹), suggesting a decrease in the H-bonding (Fig. 2). In these silica samples, the N–H vibrations are obscured by vibrations from the support.

These observations are supported by the considerable shift observed in ¹³C solid-state NMR for the carbonyl carbon signal (from 155.6 for homogeneous complex **1** to 164.9 for grafted complex **5**), which points to stronger H-bonding in the grafted complex. The combined data suggest that isolated silanol groups from **5** may be involved in H-bonding as a H-bond donor with the carbamate moiety acting as a H-bond acceptor via its carbonyl group.

3.6. Catalysis

NCN-pincer palladium complexes are known to be excellent pre-catalysts for the formation of Lewis acid catalysts for the aldol condensation reaction between methyl isocyanoacetate (MI) and benzaldehyde to form oxazolines (Reaction 1) [59].

In all previous works, pre-catalyst NCN-pincer palladium halide complexes are activated by removal of the halide ligand in order to generate cationic Pd-aquo complexes, which are believed to be the active catalytic species [35–40]. In this study, we prepared various types of combinations of possible immobilized catalyst systems, each time starting from hybrid material **5** (Scheme 2). The materials thus obtained were tested in a parallel manner in the aldol condensation. The following protocols were considered for creating the catalyst systems: (i) use of an activating reagent to form the cationic palladium-center, either AgBF₄ or trimethylsilyl triflate (TMSOTf), and (ii) use of either TMS protection or non-protection of free silanol groups after immobilization of complex **1**.

The catalytic results are summarized in Table 1. After treatment with AgBF₄ and prior to use in catalysis, silicas **5a** and **7a** were rinsed with fresh CH₂Cl₂ several times with the aim to remove all silver salts. Interestingly, the reactivity of the obtained materials was found to be unusually high (Table 1, entries 1 and 2). Upon checking the activity of simple silver salts like AgCl and AgBF₄ for this aldol reaction, it was found that both silver salts are active catalysts [60]. This unexpected aspect had initially escaped our attention as well as that of previous researchers who used silver-based activating agents for the generation of both homogeneous [35–37,39,40,61] and het-

Table 1

Aldol reaction with cationic Pd materials obtained from **5**^a

Entry	Activation	Protection	Catalyst	Time (h)	Percentage of product	Percentage of trans
1	AgBF ₄	No	5a	2	70	63
2	AgBF ₄	Yes	7a	2	>80	66
3	TMSOTf	No	5b	6	38	68
4	TMSOTf	Yes	7b	6	38	67
5	NaBPh ₄	No	5c	6	18	70

^a 1 mol% Pd loading.

erogeneous [21,32] cationic palladium catalysts for this reaction. Our observation clearly points out that by the protocols followed, not all silver salts are completely removed from samples such as silicas **5a** and **7a**. In case of the homogeneous complexes, it is possible to separate insoluble silver salts by filtration, although, also in this case care must be taken that soluble AgBF₄ has been completely removed. However, in case of the heterogenized complexes, it is difficult to remove silver salts and consequently catalysis will be affected by their presence. Therefore, use of silver-based reagents should be avoided. Hence, silicas **5b** and **7b** were obtained via treatment of **5** and **7** with TMSOTf. In this case, the side product is TMSCl which can be easily removed by applying vacuum. These cationic complexes show palladium-based catalysis in the aldol condensation (Table 1, entries 3 and 4). It appeared that recycling of **5b** and **7b** was severely hampered, probably due to the generation of triflic acid, which induces the decomposition of the palladium complex to Pd(0) (silica turned grayish after treatment with TMSOTf).

The abovedescribed findings prompted us to search for an alternative activating reagent. In this respect, NaOPh, NaBF₄, and NaBPh₄ were tested. With NaOPh, a Pd–OPh complex is formed [62] which is an active catalyst, but NaOPh at the same time reacts with silica to form basic sites, which themselves promote aldol reactions (plain silica treated with NaOPh was found to be active in the aldol reaction). NaBF₄ was ineffective as an activating agent for solubility reasons, whereas NaBPh₄ in acetone was found to be useful indeed to form cationic palladium centers (silica **5c**, Table 1, entry 5).

As a blank for the catalytic experiments, we also tested the palladium chloride silicas **5** and **7** without any further treatment. Surprisingly, these materials were also found to be effective catalysts (Table 2) [59]. A considerable improvement of the activity of silica **5** was obtained through the protection of silanol groups present in this material by capping them with trimethylsilyl groups (**7**). Silicas **5**, **5c** and **7** were used in subsequent recycling experiments.

Table 2

Aldol reaction with silica immobilized NCN-pincer palladium halide complexes^a

Entry	Catalyst	Time (h)	Percentage of product	Percentage of trans
1	5	6	18	68
2	7	6	42	70
3 ^b	7	3	84	70

^a 1 mol% Pd loading.^b 2.5 mol% Pd loading.

Table 3
Recycling of catalysts^a

Entry	Catalyst	Run 1	Run 2	Run 3	Run 4
1	5	60 (6, 71%)	42 (6, 74%)	26 (6, 77%)	
2	7	84 (3, 70%)	42 (4, 73%)	22 (4, 76%)	15 (4, 77%)
3	5c	60 (23, 70%)	43 (23, 71%)	25 (23, 71%)	23 (23, 76%)
4 ^b	5'	45 (5)	17 (5)		
5 ^c	10	50 (20, 79%)	30 (20, 78%)	30 (20, 81%)	
6 ^d	5''	44 (70, 81%)	38 (70, 80%)		

^a % conversion (time in hours and % trans), amount of Pd 2.5 mol%.

^b Silica obtained by grafting of **1** in ethanol.

^c Amount of Pd = 0.75 mol%.

^d Silica obtained by using **1** in a sol–gel process.

3.7. Recycling

Recycling studies with catalysts **5**, **5c** and **7** were carried out using overhead stirring and overall 2.5 mol% Pd per catalytic run, following a strict protocol for the work-up of the reaction mixture and recycling. After each run, the reaction vessel was centrifuged to settle the silica. Subsequently, the supernatant reaction mixture containing the reaction product was carefully decanted. The remaining silica was washed twice with CH₂Cl₂ and dried in vacuo. It was then used for the next run. From these experiments (Table 3, entries 1–3), it was obvious that while these catalysts do show activity during the first few runs, their activity drops gradually after each run.

To understand this deactivation, we considered several aspects. First of all it is possible that some sort of catalyst decomposition occurs during catalysis, even though pincer palladium complexes are known for their stability. To test this possibility, a second run was carried out without removing catalyst **5** from the reaction mixture after the first run, simply by adding more substrate to the product mixture. No decrease in activity was observed over the complete reaction time (Fig. S1), which suggested that the overall activity of the palladium sites present at the start of the catalytic runs did not change over time. Another possible reason for the reduced activity upon recycling may be that part of the palladium sites were removed from the reaction mixture as a result of the chosen work-up procedure. This would either suggest that not all silicious material had settled during the centrifugation protocol or that soluble palladium containing species/particles were formed. In general, immobilized catalysts can leach from the surface mainly by two processes, (a) cleavage of the linker, and (b) cleavage of Si–O–Si bonds from the

Table 4
Loss of catalyst **5** determined by ICP elemental analysis of supernatants (without silica) after each run^a

Run	Catalyst (mol%) ^b	Si (ppm)	Pd (ppm)	Si/Pd molar ratio in the washings ^c	Catalyst weight decrease (%) ^d	Activity decrease (%)
1	2.4	2700	1200	8.5	10.4	
2	2.15	2500	800	11.8	7.6	30
3	1.99	1500	500	11.3	5.3	40

^a Silica was centrifuged and supernatant filtered over a cotton plug before analysis.

^b At the beginning of the run.

^c Theoretical value in **1** is one.

^d At the end of the run.

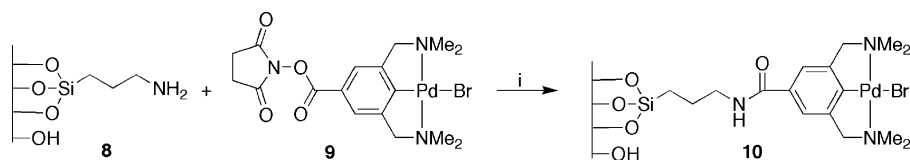
Table 5
Catalytic conversion for Reaction (1) using various silicas differing in particle size and pore diameter^a

Entry	Silica		Run 1	Run 2	Run 3
	Particle size	Pore diameter (Å)			
S1	0.5–1.5 mm	150	50 (68)	25 (73)	18 (74)
S2	50–200 μm	300	70 (69)	25 (74)	18 (77)
S3	50–200 μm	500	55 (70)	20 (75)	14 (79)
S4	60 μm	500	45 (71)	12 (77)	11 (82)

^a Amount of silica 100 mg in each case; amount of Pd may vary for each silica due to difference in surface area and hence the ability to immobilize the catalyst; reaction time 5 h, % conversion (% trans product).

surface and the catalyst (apart from metal leaching). To check the stability of the carbamate linker, we designed a model compound **4** with an *n*-propyl carbamate linker instead of the siloxy carbamate one in **5** (Scheme 1). No degradation of the carbamate linker was observed (from NMR studies) when this compound was tested under catalytic conditions. Instead, ICP analysis on the supernatants combined with work-up washings of three consecutive runs using **5** as the catalyst provided compelling evidence for substantial loss of catalytic material (Table 4). Furthermore, the observed molar ratio of Si to Pd in the washings amounted to 8.5–11.8, indicating that cleavage of Si–O–Si bonds between silica and the organometallic fragment could not alone account for this ratio (note that the Si/Pd molar ratio would be expected to be close to one for the leached but intact catalyst). On the other hand, surface reconstitution of silica under the reaction conditions could have taken place forming small, inseparable particles. Clearly, the discrepancy between the total loss in material weight after work-up and the loss in catalyst activity seems to point to surface reconstitution as the main catalyst deactivation process.

Four types of silicas differing in pore size and particle diameter (Table 5) were then used for the immobilization of NCN-pincer palladium complex **1**. Unreacted silanol groups were capped with trimethylsilyl groups. Aldol reactions using these modified silicas as catalysts were carried out in the same manner as before. Results showed that although all of these materials were active, the activity of each silica decreased considerably after the first run. From the series of silicas tested, no indication could be derived for a relation between the structural properties of the support material and its stability under the catalytic conditions.



Scheme 3. Silica immobilization of an NCN-Pd halide complex via an amide linkage: (i) CH_2Cl_2 , 16 h.

3.8. Alternative grafting procedures

Finally, we have tested a number of alternative grafting methods for the synthesis of amorphous silica hybrids containing a grafted NCN-pincer palladium complex. The first protocol involved stirring of silica with a solution of **1** in ethanol at room temperature in the presence of a catalytic amount of NEt_3 for 20 h. The resulting solid was washed thoroughly with ethanol and dried in vacuo to yield a colorless material (**5'**). The catalytic activity of this material is comparable to that of **5**, but again upon reuse, substantial decrease in activity was observed (Table 3, entry 4).

A second protocol involved the change of the nature of the linker to the complex (Scheme 3). Modified silica **10**, with the NCN-pincer Pd moiety attached to silica via an amide type of linkage, was prepared from commercially available propylamine functionalized silica **8** and an activated ester functionalized NCN-pincer palladium complex **11** [53]. The results of three subsequent runs (Table 3, entry 5) revealed that the activity decreased gradually per cycle.

In a third protocol, a mixture of **1**, TEOS, and NH_3 (29.3% NH_4OH solution) in ethanol was stirred at ambient temperature [63]. Fine gel particles precipitated out of the solution slowly, which were centrifuged to obtain a modified Stöber silica (**5''**). From elemental analysis a palladium content of 0.78% w/w was found for this material. Surface area analysis by N_2 adsorption indicated **5''** to have a smaller surface area than that of commercial silica ($23.6 \text{ m}^2/\text{g}$ against $215.5 \text{ m}^2/\text{g}$). Consequently, the catalytic activity of material **5''** was observed to be lower (Table 3, entry 6); interestingly, it presented only a small decrease in activity during the second run suggesting better recycling properties.

4. Conclusion

This study shows that new organometallic silica hybrids are accessible via the grafting of discrete organometallic siloxane precursors onto commercially available silicas. Analysis of the resulting hybrid materials confirmed the full integrity of both the tether linkage and the organometallic NCN-pincer palladium fragment. The physico-chemical properties of the pincer metal complexes allow for a 'hands-on' structural analysis via reversible colorization of pincer platinum materials by SO_2 binding and, in addition, offer various opportunities in catalysis as exemplified by the corresponding pincer palladium materials described in this study. Moreover, the NCN-pincer manifold can be replaced by PCP, SCS, or a variety of other pincer-type combinations and together with specific choices of the metal site this gives access to a variety of catalysts for notable conversions in organic synthesis [20,23,32,45,64].

Catalytic testing of the pincer palladium hybrid materials in an aldol condensation reaction initially suffered from drawbacks in terms of insufficient pre-catalyst activation due to the heterogeneous reaction conditions. Serendipitously, the studies revealed that simple silver halide salts are very active catalysts themselves in this aldol condensation reaction. A more detailed analysis of the catalytic activity of silver halide salts can be found in Ref. [60]. Furthermore, it was established that the neutral NCN-pincer palladium halide complexes do not need activation by Ag-based reagents in order to apply them as catalysts in the aldol reaction [59]. Recycling studies on the hybrid materials therefore concentrated on these NCN-pincer palladium halide materials. Although poor recyclability was observed, sufficient evidence was obtained to conclude that detrimental side-reactions involving either the organometallic fragment or its linkage to the silica support are not playing a prominent role in catalyst deactivation. Finally, leaching experiments led us to conclude that reconstitution of the silica surface forming soluble, inseparable species is the main cause of the decrease of catalytic activity of these hybrid materials.

Current efforts focus on the use of organometallic pincer-siloxane reagents for surface modification and on the use of pincer-metal silica hybrid materials for other catalytic conversions (e.g., C–C and C–X bond formation) [45,64–69]. The integrity and stability of the silica support will be another important aspect of these studies. A preliminary sol–gel type of grafting method described here already hints at the formation of hybrid materials with increased stability as compared to the (pre-formed) amorphous silicas used in the present study.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.05.063.

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