Synthesis of Poly(silyl ether)s by Rh(I)-NHC Catalysed Hydrosilylation: Homogeneous versus Heterogeneous Catalysis

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The preparation of 1-(3-triisopropoxysilylpropyl)-3-(2-methoxyethyl)-imidazolium bromide or chloride salts and their reaction with $[\text{Rh}(\text{COD})(\mu\text{-OMe})_2]$ (COD = 1,5-cyclooctadiene) to afford the corresponding $[\text{Rh}(\text{COD})(\text{NHC})\text{X}]$ (X = Br, Cl) (NHC = 1-(3-triisopropoxysilylpropyl)-3-(2-methoxyethyl)-2-ilydene-imidazol) species is described. These new compounds were used as catalysts precursors for acetophenone hydrosilylation. The higher activity of the rhodium-chlorido complex evidences a clear halide effect in the activation of the catalyst. Immobilization of the catalytic precursor $[\text{Rh}(\text{COD})(\text{NHC})\text{Cl}]$ on MCM-41 allows the preparation of the corresponding heterogeneous catalyst. Reduction of acetophenone to

$\text{PhMeCH-O-SiMe(OSiMe}_3)_2$ by hydrosilylation with 1,1,1,3,5,5,5-heptamethyltrisiloxane is effectively catalysed by both the homogeneous and the heterogeneous catalysts, being the homogenous system more active. Interestingly, the heterogeneous catalyst is reusable. Both homo- and heterogeneous catalysts are also effective for the copolymerization of terephthalaldehyde and 1,1,3,3,5,5-hexamethyltrisiloxane affording the corresponding poly(silyl ether), yielding the heterogeneous system polymers with higher molecular weights ($M_w = 94.000$) and a narrow molecular weight distribution ($\text{PDI} = 1.5 - 1.7$).

Introduction

Transition metal catalysed hydrosilylation can be considered one of the most fascinating chemical transformations in organometallic chemistry.^[1] The most efficient catalytic systems for hydrosilylation are based on Pt- or Rh-catalysts.^[1] However, such precious metal species are extremely expensive with diminishing reserves. Consequently, the development of highly selective and easily recyclable new catalysts is of great interest.

On the other hand, there is an increasing interest on the immobilization of homogeneous catalysts onto supports producing heterogeneous catalysts that could maintain the selectivity of the former homogeneous catalytic system and that would be easily recycled.^[2]

The use of N-heterocyclic carbenes (NHCs) as ligands has provided some significant improvements on the catalytic activity of several homogeneous systems.^[3] Pioneering work on homogeneous catalysts based on a transition metal-NHC species was reported by Herrmann's group in 1995.^[4] Since then, many transition metal complexes bearing NHC ligands have shown to be active homogeneous catalysts. In particular, rhodium complexes containing NHC carbenes demonstrated to be effective hydrosilylation catalysts.^[5] During the last decade, immobilisation of metal-NHC catalysts has become a field of great interest, being the immobilization of homogeneous catalysts without a decrease in the catalytic activity and selectivity of the active species a major goal.^[2,6]

Rh-catalysed hydrosilylation of ketones is a well-established process.^[1] However, further improvement of the catalytic activity and selectivity still remain a challenge.^[1,7] Catalytic hydrosilylation provides a convenient route for the synthesis of new functional materials^[8] such as poly(silyl ether)s.^[9] The backbones of poly(silyl ether)s contain Si-O-Si and Si-O-C bonds, being the latter hydrolytically more reactive.^[10,11] The hydrolytic reactivity of poly(silyl ether)s makes them attractive in many applications, such as, biodegradable materials or controlled release of drugs.^[12]

Poly(silyl ether)s have traditionally been prepared by polycondensation of dichlorosilanes, diphenoxysilanes or diaminosilanes with various diols.^[13] Lately, a number of poly(silyl ether)s have been obtained by metal-catalysed hydrosilylation using $[\text{Ru}(\text{CO})\text{H}_2(\text{PPh}_3)_3]$ as catalyst precursor.^[10,14] To the best of our knowledge, examples of rhodium-catalysed synthesis of poly(silyl ether)s have not yet been reported.

Recently, our research group has demonstrated that rhodium(I)-NHC complexes bearing hemilabile NHC ligands are efficient and selective catalysts for alkyne hydrosilylation^[15a] and hydrogen transfer hydrogenation.^[15b] In this context, a number of complexes containing O-, N-, or S-functionalized NHC hemilabile ligands have been synthesized, with an active role of the labile fragment in some catalytic processes.^[16]

As a variation of the work of our group on the chemistry of rhodium-NHC species,^[15,16a,17] here we report the synthesis and characterization of new rhodium-NHC complexes containing a doubly functionalized NHC ligand with a labile O-donor fragment and a triisopropoxysilyl tail group, O-donor-functionalized NHC ligand, together with the study of their activity as ketone hydrosilylation catalysts. Moreover, the new rhodium-NHC species was immobilized on MCM-41 in order to compare the effects exerted by the solid on the activity, selectivity and recyclability of the catalyst. Finally, we have studied the potential applicability of the new catalytic systems in the synthesis of poly(silyl ether)s by Rh-catalysed hydrosilylation.

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Results and Discussion

The synthesis of NHC ligands via deprotonation of the 2-carbon is one of the most important chemical applications of imidazolium salts.^[18] Particularly, Si(OR)₃-functionalized imidazolium salts have proved to be useful precursors to prepare Si(OR)₃-functionalized metal-NHC catalysts easy to immobilize on mineral supports.^[19,20,21]

The imidazolium salt 1-(3-triisopropoxysilylpropyl)-3-(2-methoxyethyl)-imidazolium bromide (**[2]Br**), used as precursor in this work, was synthesized by treatment of the 1-substituted imidazole **1** with 3-bromopropyltriisopropoxysilane in acetonitrile at 90 °C (Scheme 1). **[2]Br** was isolated as an off-white oily solid in 84 % yield according to Scheme 1. The off-white chlorido salt **[2]Cl** was prepared in good yield (≈ 90 %, Scheme 1) passing a dichloromethane solution of the imidazolium bromide salt **[2]Br** through an ion exchange column packed with Dowex® 1X8-100 chloride form resin. Both **[2]Br** and **[2]Cl** have been characterized by elemental analysis, mass spectrometry (ES⁺), ¹H and ¹³C{¹H} NMR spectroscopy.

Scheme 1.

The ¹H NMR spectra of cations **[2]⁺** depend on the counter ion which is in agreement with a weak C(2)-H...X (X = Br, Cl) interaction.^[22] The characteristic NCHN resonance appears downfield shifted as a singlet at δ 10.12 ppm (**[2]Br**) and δ 10.24 ppm (**[2]Cl**). The isopropoxy groups of the -(CH₂)₃Si(OⁱPr)₃ moiety are observed as a septuplet at around δ 4.2 ppm (CH-ⁱPrO) and as a doublet at around δ 1.2 ppm (CH₃-ⁱPrO) with a coupling constant of 6.0 Hz. The CH₂Si protons appear as a characteristic multiplet at around δ 0.5 ppm. The remaining resonances of the ¹H and ¹³C{¹H} NMR spectra are consistent with the structure proposed in Scheme 1 for such compounds. The most noticeable resonances in the ¹³C{¹H} NMR spectra are those due to the carbon atoms of the -(CH₂)₃Si(OⁱPr)₃ tail substituent, which are observed at around δ 8.5 ppm (CH₂Si), 25.7 ppm (CH₂), 51.8 (NCH₂) ppm, 65.5 ppm (CH-ⁱPr) and 25.6 ppm (CH₃-ⁱPr).

Preparation of Si(OⁱPr)₃-functionalized rhodium(I)-NHC complexes. Complexes [Rh(COD)(2-methoxyethyl-NHC-(CH₂)₃Si(OⁱPr)₃)X] (X = Br (**3a**), Cl (**3b**)) (NHC = 1-(3-triisopropoxysilylpropyl)-3-(2-methoxyethyl)-2-ilydene-imidazol) were prepared by treatment of the corresponding imidazolium salt with 0.5 equiv of [Rh(COD)(μ-OMe)]₂ (COD = 1,5-cyclooctadiene) in CH₂Cl₂ at room temperature (Scheme 2). The new Rh^I-NHC

complexes were isolated, after recrystallization, as pure yellow crystalline solids in ≈ 90 % yield according to Scheme 2.

Scheme 2.

Compounds **3a-b** were characterized by elemental analysis, mass spectrometry (ES⁺) and ¹H and ¹³C{¹H} NMR spectroscopy. Complex **3b** was further characterized by X-ray crystallography. A view of the molecular geometry of this compound is shown in Figure 1.

Figure 1. Molecular diagram of complex **3b**. Selected bond lengths (Å) and angles (deg) are: Rh1–Cl1, 2.4044(16); Rh1–C12, 2.033(7); Rh1–C71, 2.128(7); Rh1–C72, 2.099(7); Rh1–C75, 2.184(7); Rh1–C76, 2.193(7); Si1–C33, 1.845(7); Si1–O41, 1.618(5); Si1–O51, 1.610(6); Si1–O61, 1.634(6); C12–Rh1–Cl1 88.4(2); N11–C12–N13, 105.0(6); N11–C12–Rh1, 127.0(5); N13–C12–Rh1, 127.7(5).

The rhodium atom (Rh1) displays a slightly distorted square planar coordination. The COD ligand chelates two of the coordination positions (av. Rh1–C(COD) distance, 2.15 Å), while a chlorido ligand (Rh1–Cl1, 2.4044(16) Å) and a carbon atom (C12) of the NHC ligand (Rh1–C12, 2.033(7) Å) occupy the other two coordination sites. Considering the centroids of both CH=CH bonds of COD as formally binding sites at Rh1, the angle of Rh1 with *cis* positioned atoms or centroids deviates less than 4° from right angles (e.g., C12–Rh1–Cl1 88.4(2)°). Dihedral angle between the imidazole ring and the Rh coordination plane is 89.6(2)°. The geometry of the Rh^I(COD)Cl(NHC) fragment compares well with those reported for related complexes.^[15] Both substituents of the N atoms of the NHC ring are different, namely 2-methoxyethyl at N11, and (CH₂)₃Si(OⁱPr)₃ at N13. In the latter, silicon binds to C33 of a methylene group and three additional oxygen atoms of the isopropoxy groups, displaying a typical tetrahedral geometry. As expected, the Si1–C33 distance (1.845(7) Å) is longer in comparison to Si–O (Si1–O41,51,61 av., 1.62 Å).

The ¹H NMR spectra of complexes **3a** and **3b** show a typical pattern for the 2-methoxyethyl groups.^[15b] The resonances due to

the $-(CH_2)Si(O^iPr)_3$ fragment compare well for both complexes and are slightly shifted to lower field than those observed in the 1H NMR spectra of the corresponding imidazolium salts. The characteristic CH_2Si resonance appears at around δ 0.75 ppm and the resonances due to the isopropoxy group are observed at around δ 4.27 ppm ($CH-PrO$) and δ 1.22 ppm (CH_3-PrO). The $^{13}C\{^1H\}$ NMR spectra of complexes **3a** and **3b** exhibit a doublet resonance at around δ 183 ppm ($J_{Rh-C} \approx 51$ Hz) which proves the coordination of the carbene ligand to the rhodium center.^[15] The olefinic carbon atoms of the COD ligand in complexes **3a** and **3b** feature three doublet resonances: one at δ 97.6 ppm (**3a**) and at δ 98.1 ppm (**3b**) ($J_{Rh-C} \approx 7$ Hz) due the two olefinic carbon atoms situated *trans* to the carbene, and two at δ 68.6 ppm and δ 68.4 ppm (**3a**) and at δ 67.7 ppm and δ 67.3 ppm (**3b**) ($J_{Rh-C} \approx 14$ Hz), corresponding to the olefinic carbon atoms placed in relative *cis* position to the carbene ligand.^[15]

Immobilization of 3b on MCM-41. The new material **3b-MCM-41** was prepared by refluxing a mixture of the Rh^I -NHC complex **3b** and MCM-41 (Mobil Composition of Matter N° 41) in toluene for 24h (Scheme 3).^[21] The resulting off-white solid was characterized by elemental analysis, FT-IR, ^{13}C , ^{29}Si CP-MAS NMR and TEM.

Scheme 3.

We have determined for **3b-MCM-41** a rhodium loading of 1.63 wt% (Table 1) corresponding to 16.320 mg/g (this value corresponds to an average of two experiments). The FT-IR spectra of the new materials show the stretching vibration modes of the mesoporous framework (Si-O-Si) at around 1241 cm^{-1} , 1043 cm^{-1} and 800 cm^{-1} .^[20] The FT-IR spectra of the grafted materials exhibit an additional broad absorption corresponding to the $\nu(C=N)$ and $\nu(C=C)$ stretching modes of the ligand at around 1630 cm^{-1} .^[21]

The resonances observed in the ^{13}C CP-MAS solid state NMR spectra of **3b-MCM-41** compare well with those observed in the $^{13}C\{^1H\}$ NMR spectra of the parent complex **3b**. The ^{13}C CP-MAS solid state NMR spectra of **3b-MCM-41** are dominated by aliphatic resonances. The most evident resonances are those corresponding to the CH_{imd} (δ 122.5 ppm), $CH_2N(3)$ (δ 73.9 ppm), $CH_2N(1)$ (δ 50.7 ppm), CH_2O (δ 49.2 ppm) and $SiCH_2$ (δ 8.4 ppm) carbon atoms. The ^{29}Si CP-MAS solid state NMR spectra of **3b-MCM-41** exhibit resonances of great intensity corresponding to the silicon atoms of the parent MCM-41 (at around -92.5 ppm and -100.6 ppm) and a less intense broad resonance at around δ -57.5 ppm assigned to the CH_2Si silicon atom. As a whole, the above data confirm that complex **3b** has been effectively immobilized on MCM-41.

In addition, the transmission electron microscopy (TEM) of **3b-MCM-41** evidences that the new material keeps the long-range ordering of hexagonal symmetry with regular, monodirectional channels of the parent MCM-41 (Figure 2).

Figure 2. Transmission electron microscopy (TEM) of **3b-MCM-41**.

The results of N_2 -physisorption/desorption studies of MCM-41 and the material **3b-MCM-41** including BET surface area, total pore volume, and BJH pore size are shown in table 1. These results indicate that the surface area, pore volume and pore diameter of **3b-MCM-41** decrease, and confirm the inclusion of the rhodium complex inside the channels of the mesoporous material.

Table 1. N_2 -physisorption/desorption studies.				
Material	Rh (mg/g) ^[a]	S_{BET} (m ² /g) ^[b]	Vp (cm ³ /g) ^[c]	Dp (Å) ^[d]
MCM-41	-	1731	1.41	27.6
3b-MCM-41	16.32	1121	0.82	24.4

[a] ICP analysis. [b] surface area. [c] pore volume. [d] pore diameter.

Homogeneous versus heterogeneous catalytic hydrosilylation of acetophenone. 1,1,3,3,5,5-hexamethyltrisiloxane (HexMTS) is a potential co-monomer for the preparation of poly(silyl ether)s. Thus, the choice of 1,1,1,3,5,5,5-heptamethyltrisiloxane (HeptMTS) as hydrosilane for this catalytic study is justified by its analogy to HexMTS. Treatment of acetophenone with HeptMTS at 80°C for 8h using the rhodium chlorido species **3b** or **3b-MCM-41** as catalysts produces quantitatively the corresponding racemate PhMeCH-O-SiMe(OSiMe₃)₂ (**4**) (ee. $\approx$ 4%) (Scheme 4, Table 2 entries 2-3). A decrease of the reaction yield was observed (86 %, Table 2 entry 1) when the rhodium bromido complex **3a** is used as catalyst in accordance with a strong halide effect.^[23] Compound **4** has been isolated as a yellowish oil and characterized by mass spectrometry (ES⁺), 1H and $^{13}C\{^1H\}$ NMR spectroscopy.

Scheme 4.

Table 2. Catalytic reduction of acetophenone to 4 with HeptMTS			
Entry	Catalyst ^[a]	Yield ^[b]	cycles ^[c]
1	3a	86	-
2	3b	100	-
3	3b-MCM-41	100	Fresh catalyst
4	3b-MCM-41	100	1 recycling
5	3b-MCM-41	100	2 recycling
6	3b-MCM-41	98	3 recycling
7	MCM-41	0	-

[a] 1.0 % mol. [b] NMR yield after 8h. [c] only for the heterogeneous system.

The recyclability of the heterogeneous catalyst **3b-MCM-41** was tested four times (fresh catalyst plus three cycles). The results showed in Table 2 (Entries 3 to 6) clearly indicate that the heterogeneous catalyst is reusable, and allow concluding that no significant leaching of the metal species takes place during the catalytic process. A blank reaction using commercial MCM-41 as catalyst (Table 2, entry 7) showed no formation of **4**.

The catalytic reactions were monitored by Gas Chromatography (GC), the results of these studies are showed in Table 3 and Figure 3. In general, we have observed that the homogeneous catalyst **3b** is the most active species (Table 3, entry 2). Interestingly, the heterogeneous catalyst **3b-MCM-41** shows slightly lower activity (Table 3, entry 3) than that observed for **3b**, and as it was expected, species **3a** (Table 3, entry 1) is less active.

Table 3. Catalytic hydrosilylation of acetophenone with HeptTMS			
Entry	Catalyst	TOF(h ⁻¹ , 1h)	TOF(h ⁻¹ , 2h)
1	3a	22.0	11.4
2	3b	31.7	23.8
3	3b-MCM-41	27.5	18.2

Figure 3. Time dependency of the conversion of acetophenone into **4** when the species **3a**, **3b** or **3b-MCM-41** (1.0 % mol) are used as catalysts.

¹H NMR studies of the reaction in C₆D₆, using **3a** or **3b** (10 mol %) as catalysts, confirm that it is necessary to overtake a previous activation step since no reaction was observed below 80 °C (**3a**) or 60 °C (**3b**). These experiments showed complete conversion after 90 min at 80 °C when **3b** was used as catalyst. However, using **3a** under the same reaction conditions only 10% of conversion was observed after 4h. In both cases, formation of mixtures of not identified Rh-H containing species was observed.

These facts are in agreement with a reaction mechanism analogous to that reported by Ojima *et al.* (Scheme 5).^[24] The active catalyst, a rhodium(I)-hydride species, is generated by reaction of the corresponding rhodium(I) precursor with the silane. The halide effect,^[23] demonstrated by NMR studies and by the lower reaction yield achieved when rhodium(I)-bromido species **3a** is used as catalyst precursor (Table 2, entry 1), supports a higher activation barrier for the rhodium(I)-bromido complex in comparison with its chlorido counterpart. Once the active catalyst has been generated, a rhodium(III)-dihydride-silyl species is formed by oxidative addition of the silane to the rhodium center (Scheme 5). Then, a molecule of acetophenone coordinates to the metal center and subsequently inserts into the rhodium-silicon bond to afford a rhodium(III)-alkyl-hydride intermediate species which, by reductive elimination of **4**, regenerates the rhodium(I)-hydride active species.

Synthesis of poly(silyl ether)s by catalytic hydrosilylation.

The ^1H NMR spectra of polymer **5** (Figure 4) are in agreement with the structure proposed in Scheme 6. These spectra show four singlet resonances at δ 7.29 ppm, δ 4.75 ppm, δ 0.14 ppm and δ 0.11 ppm corresponding to the aromatic, CH_2 , $\text{CH}_2\text{OSi}(\text{CH}_3)_2$ and $\text{OSi}(\text{CH}_3)_2\text{O}$ protons, respectively. The presence of benzaldehyde end groups in **5** is evidenced by the resonance of the CHO proton at δ 10.0 ppm and two doublets resonances at δ 7.84 and 7.49 ppm ($J_{\text{HH}} = (8 \text{ Hz})$) corresponding to the C_6H_4 protons, marked as (*) in Figure 4. The $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of **5** in CD_2Cl_2 show two singlet resonances at δ -11.45 ppm and at δ -20.82 ppm corresponding to the CH_2OSi and OSiO silicon atoms of the $-\text{CH}_2\text{OSiOSiOSiOCH}_2-$ moiety, respectively.

Figure 4. ^1H NMR spectrum of polymer **5** in CD_2Cl_2 .

The weight-average molecular weight (M_w) of polymer **5** depends on the catalytic system. The homogenous catalyst **3b** gave a polymer with an average $M_w = 5.184$ and a value of M_w/M_n (PDI) = 1.7. However, the freshly prepared heterogeneous catalyst **3b-MCM-41** gave a polymer with a bimodal distribution. One corresponds to the 22%wt of the total mass with an average $M_w = 93.970$ and PDI = 1.6 and the other corresponding to the 78%wt of the total mass, with a $M_w = 7403$ and PDI = 1.5. Interestingly, the recyclability studies of catalyst **3b-MCM-41** showed a drastic decrease of the average M_w to values in the range of 3600-1600. It is remarkable that the PDI values for **5** are in the range of 1.7-1.5, significantly lower than those reported for analogous copolymers prepared by Ru-catalysed hydrosilylation of terephthalaldehyde with 1,1,3,3-tetramethyldisiloxane (PDI = 2.74).^[14]

Figure 5. TGA analysis of samples of **5** obtained using **3b** or **3b-MCM-41** as catalysts.

Conclusion

The new rhodium(I) complexes [Rh(COD)(2-methoxyethyl-NHC-(CH₂)₃Si(OPr₃)₃)X] (X = Br (**3a**), Cl (**3b**)) have been synthesized and fully characterized. The study of their application as ketone hydrosilylation catalysts showed a clear halide effect, being the chlorido species **3b** more active than the bromido derivative **3a**. The most active species **3b** has been immobilized on MCM-41 to afford **3b-MCM-41**. The new material **3b-MCM-41** has been fully characterized. A comparative catalytic study indicates that **3b** and **3b-MCM-41** are effective catalysts for the hydrosilylation of acetophenone and, moreover the heterogeneous catalyst **3b-MCM-41** can be reutilized. Both species are also active for the preparation of poly(silyl ether)s, with a low PDI (1.7-1.5), by rhodium(I)-catalysed hydrosilylation of terephthalaldehyde. The copolymers with higher *M_w* were obtained using **3b-MCM-41** as catalyst. Further investigations regarding the design of more active catalyst for the preparation of poly(silyl ether)s are in progress.

Experimental Section

General information. All manipulations were performed with rigorous exclusion of air at an argon/vacuum manifold using standard Schlenk-tube techniques or in a dry-box (MB-UNILAB). Solvents were dried by the usual procedures and distilled under argon prior to use or taken under argon from a Solvent Purification System (SPS). (3-Bromopropyl)trichlorosilane, 4-dimethylaminopyridine, Dowex® 1X8-100 chlorido form resin, acetophenone, 1,1,1,3,5,5,5-heptamethyltrisiloxane, mesitylene, 1,1,3,3,5,5-hexamethyltrisiloxane and terephthalaldehyde were purchased from commercial sources and used without further purifications. The starting material [Rh(COD)(μ-OMe)]₂ was prepared according with methods reported in the literature.^[25] NMR spectra were recorded on a Varian Gemini 2000, Bruker ARX 300, Bruker Avance 300 MHz or Bruker Avance 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (¹H, ¹³C{¹H}). Coupling constants, *J*, are given in hertz. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectroscopy was measured on an Esquire 3000+ with Ion trap detector interfaced to an Agilent 1100 series HPLC system. FT-IR spectra were recorded on a Nicolet Nexus 5700 FT spectrophotometer equipped with a Nicolet Smart Collector diffuse reflectance accessory. Gas chromatography analyses were performed using an Agilent 6890N with FID detector equipped with a HP-1 column from J&W Scientific (30m, 0.25 mm i.d.). Parameters were as follows: Initial temperature 50 °C, initial time 5 min, ramp 30 °C/min, final temperature 250 °C, final time 5 min, injector temperature 250 °C, detector temperature 300 °C. TEM microscopy images were collected with a INCA 200 X-Sight from Oxford Instruments with a resolution in energy between 136 eV and 5.9 KeV. Isotherms were obtained on a Quantachrome AUTOSORB by measuring the volume of N₂ absorbed at relative pressures between 0.05 and 0.99 at 77.3 K after drying the sample at 120 °C *in vacuo*. Absolute Molecular weights of polymers were determined by GPC-MALS. Before injection all samples were filtered through 0.45 mm PTFE membranes. The column oven temperature was maintained at 35 °C during all the experiments. The measurements were carried out on a Waters 2695 autosampler equipped with three in line PLGel Mixed C (7.8x300 mm) columns and a Wyatt three detector setup (Minidaw TREOS® (MALS), Optilab Rex® (DRI) and Viscostar® Viscometer). The samples were eluted with THF at a rate of 1 mL/min. TGA of the polymers was measured on a TA Instruments SDT 2960 at a flow rate of 40 cm³ of nitrogen per min. The temperature program was 10 °C/ min from 25 to 850 °C. Tg of the polymer was determined by DSC on a TA instruments DSC Q1000 with liquid nitrogen cooling system. The temperature program for the analysis was begun at -120 °C and the temperature was increased at a rate of 10 °C/ min to 25 °C.

X-ray crystal data for **3b** were recorded at 100 K with a Bruker Kappa APEX2 diffractometer equipped with an area detector and graphite monochromated Mo Kα radiation (0.71073 Å). Data reduction was done with the APEX2 software.^[26] The structure was solved by direct methods and refined by full-matrix least-squares methods based on *F*² using SHELXL-97 and WinGX programs.^[27] Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were positioned geometrically and refined with isotropic displacement parameters according to the riding model. Distance and angle calculations were performed using the SHELXL-97 and WinGX programs.^[27] Refinement parameters are as follows: [C₂₆H₄₈ClN₂O₄RhSi] (**3b**), triclinic, *P*-1, *a* = 9.9500(18) Å, *b* = 13.003(2) Å, *c* = 13.349(2) Å, α = 107.377(2)°, β = 103.957(2)°, γ = 105.201(2)°, *Z* = 2, *M_r* = 619.11 g mol⁻¹, *V* = 1491.8(5) Å³, *D_{calcd}* = 1.378 g cm⁻³, λ(Mo Kα) = 0.71073 Å, *T* = 100 K, μ = 0.734 mm⁻¹, 11827 reflections collected, 5967 observed (*R_{int}* = 0.064), *R*1(*F_o*) = 0.0778 [*I* > 2σ(*I*)], *wR*2 (*F_o*²) = 0.1503 (all data), GOF = 1.096. CCDC: 879869.

Preparation of 1-(2-methoxyethyl)-2H-imidazole (1): NaOH (1.28 g, 320 mmol) was added to an acetonitrile (30 mL) solution of imidazole (1.088 g, 16.0 mmol) and the mixture was refluxed for 30 min. After that, 2-chloroethylmethylether (1.5 mL, 16.0 mmol) was added dropwise to the solution and the mixture refluxed for 16 h. The solution was filtered and the solvent was removed *in vacuo*. The oily residue was extracted with Et₂O (3 x 20 mL) and the solvent was removed *in vacuo* to afford yellowish oil. Yield 1.88 g (93 %). ¹H NMR (300 MHz, CDCl₃, 293 K): δ 7.50 (s, 1H, NCHN), 7.03 (vt, 1H, *J_{H-H}* = 1 Hz, CH_{imd}), 6.95 (vt, 1H, *J_{H-H}* = 1 Hz, CH_{imd}), 4.07 (t, 2H, *J_{H-H}* = 5 Hz, CH₂N), 3.61 (t, 2H, *J_{H-H}* = 5 Hz, CH₂O), 3.32 (s, 3H, CH₃O). ¹³C NMR (75 MHz, CDCl₃, 293 K): δ 137.5 (NCHN), 129.3 (CH_{imd}), 119.1 (CH_{imd}), 71.9 (CH₂O), 59.1 (CH₃O), 47.1 (CH₂N).

Preparation of Br(CH₂)₃Si(PrO)₃: To a solution of 1,8-Bis(dimethylamino)pyridine (3.20 g, 14.5 mmol) in ⁱPrOH (40 mL) Br(CH₂)₃SiCl₃ (0.75 mL, 4.8 mmol) was added dropwise at 0 °C. The resulting mixture was warmed to r.t. and stirred during 10 h to give a white suspension. The ⁱPrOH solution was filtered and the solvent removed *in vacuo* to afford a white oily residue which was extracted with hexane (2 x 20 mL). The solvent was removed *in vacuo* to give a pale yellow liquid. Yield 1.40 g, (89 %). ¹H NMR (300MHz, CDCl₃, 293 K): δ 4.19 (stp, 6H, *J_{H-H}* = 7 Hz, CH-ⁱPrO), 3.40 (t, 2H, *J_{H-H}* = 7 Hz, CH₂Br), 1.94 (m, 2H, -CH₂-), 1.17 (d, 18H, *J_{H-H}* = 6 Hz, CH₃-ⁱPrO), 0.69 (m, 2H, CH₂Si). ¹³C{¹H} NMR (300 MHz, CDCl₃, 293 K): δ 65.0 (CH-ⁱPrO), 36.9 (CH₂Br), 26.9 (-CH₂-), 25.5 (s, CH₃-ⁱPrO), 11.2 (s, CH₂Si). MS (ESI⁺): *m/z* 248.3 (M⁺).

Preparation of 1-(3-triisopropoxysilylpropyl)-3-(2-methoxy-ethyl)-Imidazolium bromide ([2]Br): To an acetonitrile (30 mL) solution of 2-methoxy-ethyl imidazole (0.31 g, 2.5 mmol) Br(CH₂)₃Si(PrO)₃ (0.98 g, 3.0 mmol) was added. The reaction mixture was stirred at 90 °C for 24 h. The solution was filtered through Celite and the solvent was removed *in vacuo*. The residue thus obtained was washed with hexane (2 x 20 mL) to give an off-white oily solid. Yield 0.94 g (84 %). Anal. Calcd for C₁₈H₃₇BrN₂O₄Si: C, 47.67, H, 8.22, N, 6.18. Found: C, 47.91, H, 8.35, N, 6.58. ¹H NMR plus COSY (300 MHz, CDCl₃, 293 K): δ 10.12 (s, 1H, NCHN), 7.60 (m, 1H, CH_{imd}), 7.29 (m, 1H, Hz, CH_{imd}), 4.60 (vt, 2H, *J_{H-H}* = 5, CH₂N⁽³⁾), 4.27 (vt, 2H, *J_{H-H}* = 7, CH₂N⁽¹⁾), 4.15 (spt, 3H, *J_{H-H}* = 6, CH-ⁱPrO), 3.74 (vt, 2H, *J_{H-H}* = 5, CH₂O), 3.32 (s, 3H, OCH₃), 1.95 (m, 2H, -CH₂-), 1.13 (d, 18H, *J_{H-H}* = 6 Hz, CH₃-ⁱPrO), 0.50 (m, 2H, CH₂Si). ¹³C{¹H} NMR plus HSQC (75.46 MHz, CDCl₃, 293 K): δ 137.4 (NCHN), 123.4 (CH_{imd}), 121.3 (CH_{imd}), 70.4 (CH₂O), 65.4 (CH-ⁱPrO), 59.0 (OCH₃), 51.8 (CH₂N⁽¹⁾), 49.9 (CH₂N⁽³⁾), 25.6 (CH₃-ⁱPrO), 24.6 (-CH₂-), 8.6 (CH₂Si). MS (ESI⁺): *m/z* 373.2 (M⁺-Br).

Preparation of 1-(3-triisopropoxysilylpropyl)-3-(2-methoxy-ethyl)-Imidazolium chloride ([2]Cl): A dichloromethane (5.0 mL) solution of [2]Br (0.45 g, 1.00 mmol) was passed through an ion exchange column packed with Dowex® 1X8-100 chloride form resin. The solvent was removed *in vacuo* and the oily residue washed with hexane (20 mL) to give an off-white oily solid. Yield 0.41 g (91 %). Anal. Calcd for C₁₈H₃₇ClN₂O₄Si: C, 52.85, H, 9.12, N, 6.85. Found: C,

52.56, H, 9.60, N, 6.58. ^1H NMR plus COSY (300 MHz, CDCl_3 , 293 K): δ 10.24 (s, 1H, NCHN), 7.67 (s, 1H, CH_{imd}), 7.35 (s, 1H, CH_{imd}), 4.64 (t, 2H, $J_{\text{H-H}} = 5$ Hz, $\text{CH}_2\text{N}^{(3)}$), 4.31 (t, 2H, $J_{\text{H-H}} = 7$ Hz, $\text{CH}_2\text{N}^{(1)}$), 4.19 (spt, 3H, $J_{\text{H-H}} = 6$ Hz, CH-PrO), 3.78 (t, 2H, $J_{\text{H-H}} = 5$ Hz, CH_2O), 3.35 (s, 3H, CH_3O), 1.99 (m, 2H, $-\text{CH}_2-$), 1.17 (d, 18H, $J_{\text{H-H}} = 6$ Hz, $\text{CH}_3\text{-PrO}$), 0.54 (m, 2H, CH_2Si). ^{13}C NMR plus HSQC (75 MHz, CDCl_3 , 293 K) δ 140.4 (NCHN), 123.3 (CH_{imd}), 121.0 (CH_{imd}), 70.7 (CH_2O), 65.5 (CH-PrO), 59.1 (CH_3O), 51.8 ($\text{CH}_2\text{N}^{(1)}$), 49.9 ($\text{CH}_2\text{N}^{(3)}$), 25.7 ($\text{CH}_3\text{-PrO}$), 24.7 ($-\text{CH}_2-$), 8.5 (CH_2Si). MS (ESI $^+$): m/z 373.3 ($\text{M}^+ - \text{Cl}$).

Preparation of (**3a**): CH_2Cl_2 (30 mL) was added to a mixture of [**2**]Br (0.45 g, 1.0 mmol) and $[\text{Rh}(\text{COD})(\mu\text{-OMe})_2]$ (0.24 g, 0.5 mmol). The reaction mixture was stirred at room temperature for 10 h. The solvent was removed *in vacuo* and the residue thus obtained extracted with hexane (2 x 20 mL) and washed with pentane (2 x 10 mL) to afford a yellow crystalline solid. Yield 0.62 g (93 %). Anal. Calcd for $\text{C}_{26}\text{H}_{48}\text{BrN}_2\text{O}_4\text{RhSi}$: C, 47.06, H, 7.29, N, 4.22. Found: C, 46.96, H, 7.24, N, 4.21. ^1H NMR (400 MHz, C_6D_6 , 298 K): δ 6.67 (d, 1H, $J_{\text{H-H}} = 2$ Hz, CH_{imd}), 6.30 (d, 1H, $J_{\text{H-H}} = 2$ Hz, CH_{imd}), 5.50 (s, 2H, CH_{COD}), 4.86 (ddd, 1H, $J_{\text{H-H}} = 14$ Hz, $J_{\text{H-H}} = 5$ Hz, $J_{\text{H-H}} = 3.5$ Hz, CH_2O), 4.58 (ddd, 1H, $J_{\text{H-H}} = 13$ Hz, $J_{\text{H-H}} = 9$ Hz, $J_{\text{H-H}} = 6$ Hz, $\text{CH}_2\text{N}^{(1)}$), 4.28 (spt, 3H, $J_{\text{H-H}} = 6$ Hz, CH-PrO), 4.25 – 4.12 (m, 1H, $\text{CH}_2\text{N}^{(1)}$; 1H, CH_2O), 3.75 (ddd, 1H, $J_{\text{H-H}} = 10$ Hz, $J_{\text{H-H}} = 9$ Hz, $J_{\text{H-H}} = 3.5$ Hz, $\text{CH}_2\text{N}^{(3)}$), 3.52 (ddd, 1H, $J_{\text{H-H}} = 10$ Hz, $J_{\text{H-H}} = 9$ Hz, $J_{\text{H-H}} = 3.5$ Hz, $\text{CH}_2\text{N}^{(3)}$), 3.31 (m, 2H, CH_{COD}), 2.98 (s, 3H, CH_3O), 2.41 – 2.13 (m, 4H, $\text{CH}_{2\text{COD}}$; 1H, $-\text{CH}_2-$), 2.05 (m, 1H, $-\text{CH}_2-$), 1.77 (m, 4H, $\text{CH}_{2\text{COD}}$), 1.23 (vdd, 18H, $J_{\text{H-H}} = 6$ Hz, $J_{\text{H-H}} = 3$ Hz, $\text{CH}_3\text{-PrO}$), 0.75 (m, 2H, CH_2Si). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 293 K): δ 183.0 (d, $J_{\text{Rh-C}} = 51$ Hz, $\text{RhC}_{\text{Carbene}}$), 122.0 (CH_{imd}), 120.0 (CH_{imd}), 97.6 (d, $J_{\text{Rh-C}} = 7$ Hz, 2C, CH_{COD}), 72.2 ($\text{CH}_2\text{N}^{(3)}$), 68.6 (d, $J_{\text{Rh-C}} = 14$ Hz, CH_{COD}), 68.4 (d, $J_{\text{Rh-C}} = 14$ Hz, CH_{COD}), 65.3 (CH-PrO), 58.6 (CH_3O), 53.4 ($\text{CH}_2\text{N}^{(1)}$), 50.9 (CH_2O), 33.3 ($\text{CH}_{2\text{COD}}$), 33.0 ($\text{CH}_{2\text{COD}}$), 29.7 ($\text{CH}_{2\text{COD}}$), 29.5 ($\text{CH}_{2\text{COD}}$), 25.9 ($\text{CH}_3\text{-PrO}$), 25.2 ($-\text{CH}_2-$), 10.0 (CH_2Si). MS (ESI $^+$): m/z 583.1 (M^+).

Preparation of (**3b**): CH_2Cl_2 (30 mL) was added to a mixture of [**2**]Cl (0.41 g, 1.0 mmol) and $[\text{Rh}(\text{COD})(\mu\text{-OMe})_2]$ (0.24 g, 0.5 mmol). The reaction mixture was stirred at room temperature for 10 h. The solvent was removed *in vacuo* and the residue thus obtained extracted with hexane (2 x 20 mL) and washed with pentane (2 x 10 mL) to afford a yellow crystalline solid. Yield 0.54 g (52 %). Anal. Calcd for $\text{C}_{26}\text{H}_{48}\text{ClIn}_2\text{O}_4\text{RhSi}$: C, 50.44, H, 7.81, N, 4.52. Found: C, 50.5, H, 7.86, N, 4.32. ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 6.69 (d, 1H, $J_{\text{H-H}} = 2$ Hz, CH_{imd}), 6.35 (d, 1H, $J_{\text{H-H}} = 2$ Hz, CH_{imd}), 5.36 (s, 2H, CH_{COD}), 4.82 (ddd, 1H, $J_{\text{H-H}} = 14$ Hz, $J_{\text{H-H}} = 5$ Hz, $J_{\text{H-H}} = 4$ Hz, CH_2O), 4.52 (ddd, 1H, $J_{\text{H-H}} = 13$ Hz, $J_{\text{H-H}} = 9$ Hz, $J_{\text{H-H}} = 6$ Hz, $\text{CH}_2\text{N}^{(1)}$), 4.25 (m, 3H, CH-PrO and 1H, $\text{CH}_2\text{N}^{(1)}$), 1H CH_2O), 3.73 (ddd, 1H, $J_{\text{H-H}} = 10$ Hz, $J_{\text{H-H}} = 8$ Hz, $J_{\text{H-H}} = 4$ Hz, $\text{CH}_2\text{N}^{(3)}$), 3.52 (ddd, 1H, $J_{\text{H-H}} = 10$ Hz, $J_{\text{H-H}} = 5$ Hz, $J_{\text{H-H}} = 4$ Hz, $\text{CH}_2\text{N}^{(3)}$), 3.26 (m, 2H, CH_{COD}), 3.00 (s, 3H, CH_3O), 2.41 – 2.13 (m, 4H $\text{CH}_{2\text{COD}}$, 1H $-\text{CH}_2-$), 2.03 (m, 1H, $-\text{CH}_2-$), 1.80 (m, 4H, $\text{CH}_{2\text{COD}}$), 1.21 (vdd, 18H, $J_{\text{H-H}} = 6$ Hz $J_{\text{H-H}} = 3$ Hz, $\text{CH}_3\text{-PrO}$), 0.74 (m, 2H, CH_2Si). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 293 K): δ 183.2 (d, $J_{\text{Rh-C}} = 52$ Hz, $\text{RhC}_{\text{Carbene}}$), 122.0 (CH_{imd}), 120.0 (CH_{imd}), 98.1 (d, $J_{\text{Rh-C}} = 7$ Hz, 2C, CH_{COD}), 72.1 ($\text{CH}_2\text{N}^{(3)}$), 67.7 (d, $J_{\text{Rh-C}} = 14$ Hz, CH_{COD}), 67.3 (d, $J_{\text{Rh-C}} = 14$ Hz, CH_{COD}), 65.0 (CH-PrO), 58.6 (CH_3O), 53.5 ($\text{CH}_2\text{N}^{(1)}$), 51.0 (CH_2O), 33.6 ($\text{CH}_{2\text{COD}}$), 33.3 ($\text{CH}_{2\text{COD}}$), 29.5 ($\text{CH}_{2\text{COD}}$), 29.2 ($\text{CH}_{2\text{COD}}$), 25.9 ($\text{CH}_3\text{-PrO}$), 25.4 ($-\text{CH}_2-$), 10.0 (CH_2Si). MS (ESI $^+$): m/z 583.1 (M^+).

Immobilization of **3b** on MCM-41: To a suspension of MCM-41 (0.50 g) in wet toluene (10.0 mL) a solution of **3b** (50 mg) in toluene (5.0 mL) was added. The reaction slurry was refluxed and stirred for 24 h. The resulting mixture was cooled down to r.t. The solid was separated by decantation and washed with toluene (10 mL), dichloromethane (2x10 mL) and diethylether (10 mL) and dried *in vacuo* at 60 °C to afford an off-white solid. Yield 0.484 g (96.8%). Found: C, 6.23, H, 1.14, N, 0.43, Rh, 1.63 (16.320 mg/g). FT-IR: 1636 cm^{-1} (br.), $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$, 1241 cm^{-1} , 1043 cm^{-1} , 800 cm^{-1} $\nu(\text{Si-O-Si})$. ^{13}C -RMN CP-MAS: δ 122.5 (CH_{imd}), 86.4 (CH_{COD}), 73.9 ($\text{CH}_2\text{N}^{(3)}$), 69.8 (CH_{COD}), 66.9 (CH_{COD}), 57.1 (CH_3O), 50.7 ($\text{CH}_2\text{N}^{(1)}$), 49.2 (CH_2O), 36.0-18.0 ($\text{CH}_{2\text{COD}}$ and $-\text{CH}_2-$), 8.4 (CH_2Si).

Synthesis of $\text{PhCHMeOSi}(\text{OSiMe}_3)_2\text{Me}$ (**4**): A mixture of 1,1,1,3,5,5,5-heptamethylsiloxane (1.0 mL), acetophenone (1.0 mmol, 0.12 mL) and the corresponding catalyst (0.01 mmol) was stirred under argon at 80 °C for 16h. After cooling to room temperature methanol (5 mL) and water (2 mL) were added. The mixture was extracted with diethyl ether (3 x 5 mL), and the resulting diethyl ether solution was dried over anhydrous MgSO_4 . The solution was filtered through silica and the solvent removed *in vacuo* to afford yellowish oil. ^1H NMR (300 MHz, CDCl_3 , 298 K): δ 7.39-7.30 (m, 4H, CH), 7.25-7.20 (m, 1H, CH), 5.04 (q, 1H, $J_{\text{H-H}} = 7$ Hz, CHO), 1.48 (d, 3H, $J_{\text{H-H}} = 7$ Hz, CH_3CHO), 0.12 (s, 6H, SiCH_3), 0.07 (s, 6H, SiCH_3), 0.04 (s, 3H, SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3 , 293 K): δ 146.2 (C_{ipso}), 128.0 (2C, CH), 126.6 (CH), 125.3 (2C, CH), 70.0 (CHO), 26.6 (CH_3CHO), 1.7 (2C, SiCH_3), 1.6 (2C, SiCH_3), -3.2 (SiCH_3). MS (ESI $^+$): m/z 373.2 (M^+).

Hydrosilylation of acetophenone: homogeneous catalysis: A mixture of 1,1,1,3,5,5,5-heptamethylsiloxane (2 mL), the corresponding catalyst (13.3 mg (**3a**), 12.4 mg (**3b**), 0.02 mmol), acetophenone (0.234 mL, 2 mmol) and mesitylene (0.234 mL, 2 mmol, internal standard) was stirred at 80 °C. Samples were taken at regular time intervals and analyzed by gas chromatography.

Hydrosilylation of acetophenone: heterogeneous catalysis: A mixture of 1,1,1,3,5,5,5-heptamethylsiloxane (2 mL), **3b-MCM-41** (14.8 mg, 0.002 mmol), acetophenone (0.023 mL, 0.2 mmol) and mesitylene (0.0234 mL, 0.2 mmol, internal standard) was stirred under argon at 80 °C. Samples were taken at regular time intervals and analyzed by gas chromatography.

NMR studies of the hydrosilylation of acetophenone: An NMR tube was charged under argon with 1,1,1,3,5,5,5-heptamethylsiloxane (0.271 mL, 1.0 mmol), the corresponding catalyst (66.4 mg (**3a**), 62.0 mg (**3b**), 0.1 mmol) acetophenone (0.120 mL, 1.0 mmol) and C_6D_6 (0.5 mL). The reaction was monitored by ^1H NMR from 25°C to 90°C.

Recycling of the heterogeneous catalyst: The reaction mixture was centrifuged and **3b-MCM41** separated from the product by decantation, dried *in vacuo* and reused without further purifications.

Co-polymerization by homogeneous catalytic hydrosilylation: **1,4**-Dioxane (2 mL) was added to a mixture of 1,1,3,3,5,5-hexamethylsiloxane (0.254 mL, 1 mmol), terephthalaldehyde (134.13 mg, 1 mmol) and **3b** (12.4 mg, 0.02 mmol). The reaction mixture was stirred at 110 °C for 4 days. The resulting mixture was filtered through celite and the solvent removed *in vacuo* to afford orange oil. Yield 330 mg (96 %).

Co-polymerization by heterogeneous catalytic hydrosilylation: 1,4-Dioxane (2 mL) was added to a mixture of 1,1,3,3,5,5-hexamethylsiloxane (0.025 mL, 0.1 mmol), terephthalaldehyde (13.4 mg, 0.1 mmol), and **3b-MCM-41** (14.8 mg, 0.002 mmol). The reaction mixture was stirred at 110 °C for 4 days. The resulting mixture was filtered through celite and the solvent removed *in vacuo* to afford orange oil. Yield 30.8 mg (90 %).

Data for polymer **5**: ^1H NMR plus COSY (400 MHz, CD_2Cl_2 , 298 K): δ 7.29 (s, 4H, CH), 4.75 (s, 4H, CH_2), 0.14 (s, 12H, SiCH_3), 0.11 (s, 6H, SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR plus APT (101 MHz, CD_2Cl_2 , 298 K): δ 140.31 (2C, C_{ipso}), 126.99 (4C, CH), 64.44 (2C, CH_2), 1.18 (2C, CH_3), -0.72 (4C, CH_3). ^{29}Si NMR (60 MHz, CD_2Cl_2 , 298 K): δ -11.45 (2 Si, $\text{Si}(\text{CH}_3)_2$), -20.82 (1 Si, $\text{Si}(\text{CH}_3)_2$).

Acknowledgements

Financial support from the Spanish "Ministerio de Economía y Competitividad" projects CTQ2010-15221, CSD2009-00050 CONSOLIDER INGENIO-2010, CTQ2011-27593, "Ramon y Cajal"

program (P. J. S. M.), "Juan de la Cierva" program (M. I.) and "Diputación General de Aragón" group E07 is acknowledged.

Keywords: Poly(silyl ether)s • Hydrosilylation • Rhodium-NHC • Homogeneous Catalysis • Heterogeneous Catalysis

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