



Investigation of titanium-catalysed dehydrogenative coupling and hydrosilylation of phenylhydrogenosilanes in a one-pot process

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ABSTRACT

Titanium-catalysed dehydrocondensation and hydrosilylation of primary, secondary and tertiary phenylsilanes have been investigated in a one-pot process with $\text{Cp}_2\text{Ti}(\text{OPh})_2$ as catalyst by NMR studies. Only primary and secondary silanes were found to undergo simultaneous dehydrogenative coupling and hydrosilylation reactions to produce the functional polysilanes.

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1. Introduction

The search for efficient new materials with tailored properties is of significant interest for applications. Polysilanes figure among these materials which have long been synthesised and exploited mainly for their optical, electronic and chemical properties [1]. Among the various synthetic methods which exist [2], the dehydrocoupling polymerisation of silanes is one of the most interesting and effective way for preparing these polymers [3]. These reactions were initially performed following Harrod's pioneering work with titanium catalysts and in this field, new catalysts based on group 4 metallocenes afterwards proved to be the most active [4,5]. $\text{Cp}_2\text{Ti}(\text{OPh})_2$ [6] figures among these catalysts and gave interesting results in the polymerisation of PhSiH_3 and also of $\text{MeSiH}_2(\text{CH}_2)_2\text{SiH}_3$ [7]. We are interested in synthesising functional polysilanes and one possibility to achieve such materials involves the hydrosilylation of the Si–H groups. The main drawback of this route, until now, is the use of two different catalysts, one for the dehydrogenative coupling (usually a metallocene catalyst) and one for the hydrosilylation reaction (usually a platinum catalyst or AIBN [8]). Ti, Zr and Hf are also known to promote the hydrosilylation of olefins [9] but not as efficiently as platinum catalysts.

Although the two reactions have already been observed with a secondary silane (PhMeSiH_2) in the presence of an olefin [9c], no substituted polysilane was reported. Indeed, the formation of non hydrosilylated oligosilanes was observed with the $\text{Cp}_2\text{TiCl}_2/n\text{BuLi}$ catalyst employed. More recently the dehydrocoupling of PhSiH_3 , PhMeSiH_2 and Ph_2MeSiH was also studied in the presence of several group 4 metallocenes [10].

Following these reported results, we envisaged a one-pot reaction combining the dehydrocoupling of silanes and the hydrosilylation of an olefin with a titanocene derivative. We report here our study by solution NMR (^1H , ^{13}C and ^{29}Si) with a family of model compounds based on phenylsilanes. These compounds consist of a primary silane (PhSiH_3), a secondary silane (Ph_2SiH_2), a tertiary silane (Ph_3SiH) and a tertiary di-silane ($\text{Ph}_2\text{HSi-SiHPh}_2$).

2. Results and discussion

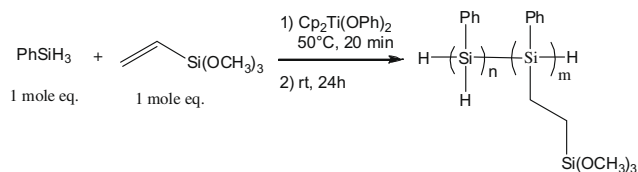
Vinyltrimethoxysilane and $\text{Cp}_2(\text{TiOPh})_2$ were selected as reagent and catalyst, respectively, for the hydrosilylation reactions with the four silanes mentioned above. The reactions were studied by solution NMR (^1H , ^{13}C and ^{29}Si).

2.1. Reaction with the primary silane, PhSiH_3

PhSiH_3 was mixed with the alkoxy silane (1/1 mole equivalent) and catalyst (3 mole%) and the resulting mixture was heated to

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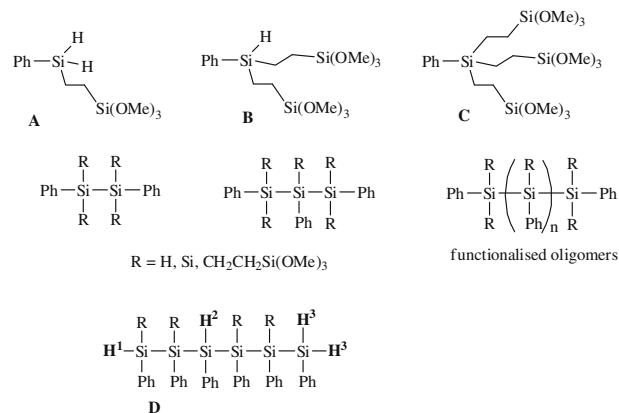
Scheme 1. Reaction with the primary silane, PhSiH₃.

50 °C for 20 min until the catalyst was activated. The initial orange solution turned dark blue. The reaction was monitored until the alkoxy silane had been consumed (Scheme 1).

2.1.1. ¹H NMR study

¹H NMR enabled the evolution of the characteristic chemical shifts of the reagents to be monitored. The chemical shifts of the two reagents (PhSiH₃ and vinyltrimethoxysilane) are depicted in spectra (a) and (b), respectively, while spectrum (c) shows the evolution of the reaction with time after complete consumption of the alkoxy silane.

The comparison of these three spectra leads to two main observations. In spectrum (c), the chemical shifts at around 6 ppm (vinyl protons) disappeared completely and consequently signals between 0.5 to 1.2 ppm appeared. These are attributed to C-sp³ species bound to Si, which arise from quantitative hydrosilylation. The Si–H₃ signal at 4.25 ppm also completely disappeared and new chemical shifts were observed at 4.95 (predominant) and 4.85 ppm (Fig. 1, inset) which correspond to several new Si–H sites. Scheme 2 depicts a non-exhaustive list of different silicon sites likely to form during the reaction. The formation of mono- to tri-functionalised monomers (A–C), functionalised dimers and trimers, as well as a series of polyfunctionalised oligomers, are expected. Based on previous work [11], the predominant peak at 4.95 ppm may be attributed to Si–Si–H protons which are formed during the dehydrocoupling reaction (H² and H³ in molecule D – Scheme 2). The small triplet found at 4.85 ppm could correspond to a proton bonded to a monohydrosilylated silicon site (for example in molecule A and also H¹ in molecule D for R = CH₂CH₂Si(OMe)₃).



Scheme 2. Possible silicon sites obtained from reaction with PhSiH₃.

2.1.2. ¹³C NMR study

The ¹³C spectrum of the reaction mixture (Fig. 2) confirms the disappearance of the C-sp² peak associated with the vinylic group and also shows the formation of Si–CH₂ (3 peaks at around 5 ppm), as expected for the products of the hydrosilylation reaction. A sharp peak is observed at around 50 ppm corresponding to the carbon atoms of the methoxy groups on silicon atoms. The phenylic groups appear, as expected, as multiple peaks in the region of 125–135 ppm.

2.1.3. ²⁹Si NMR study

The ²⁹Si NMR spectrum (Fig. 3) exhibits several peaks, which are assigned as follows [12]:

- The peak at –2.9 ppm is assigned to a silicon atom bonded to the phenyl group and to three trimethoxysilyl ethenyl groups (Scheme 2, compound C). This compound results from complete hydrosilylation of the three H atoms of PhSiH₃
- The peak at –16.4 ppm corresponds to the chemical shift of a dihydrosilylated silicon atom bound to phenylene group and either (a) one H atom (Scheme 2, compound B) [13]; or (b) a Si atom arising the dehydrocoupling of the H atom [14].

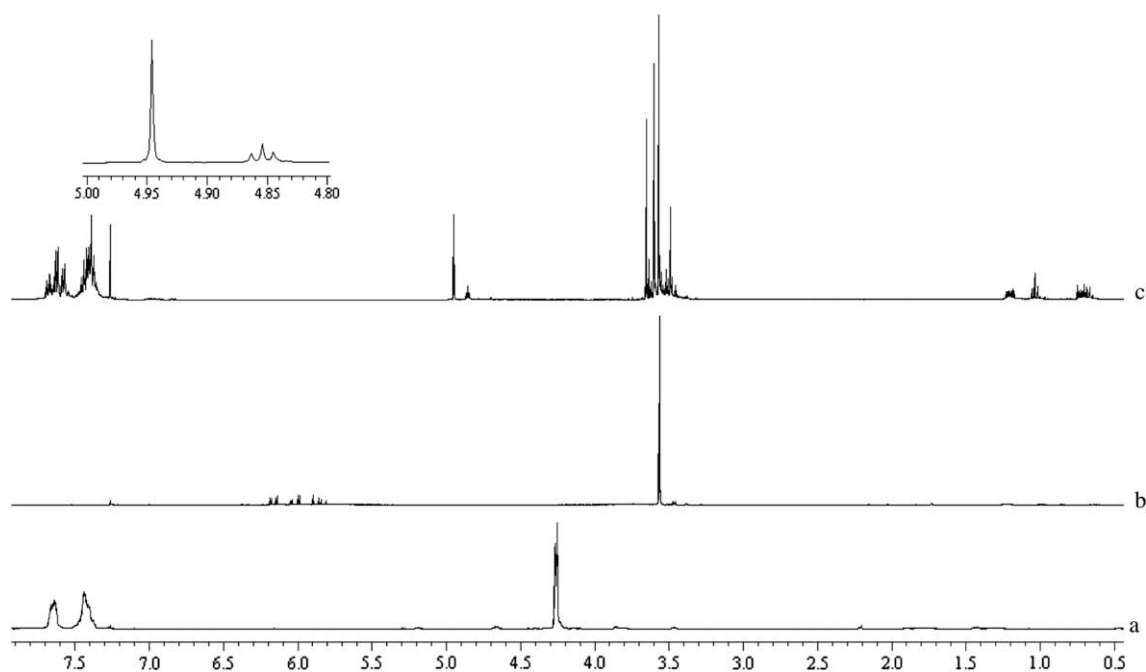


Fig. 1. ¹H NMR spectra of: (a) PhSiH₃, (b) vinylSi(OMe)₃, (c) reaction mixture of vinylSi(OMe)₃ with PhSiH₃ after 24 h.

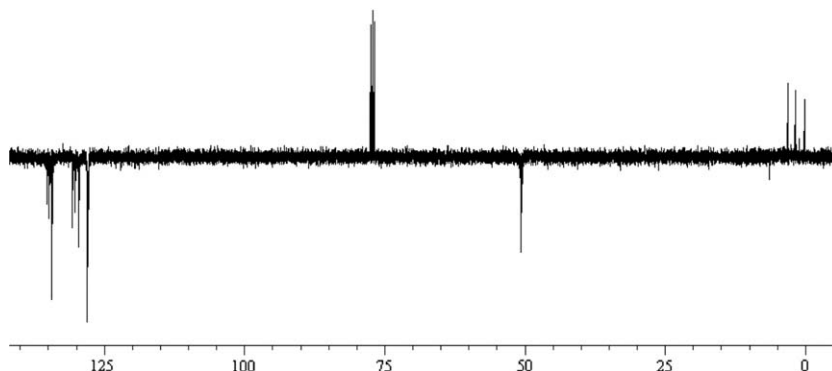


Fig. 2. ^{13}C NMR spectrum of the reacting mixture of the reaction with PhSiH_3 .

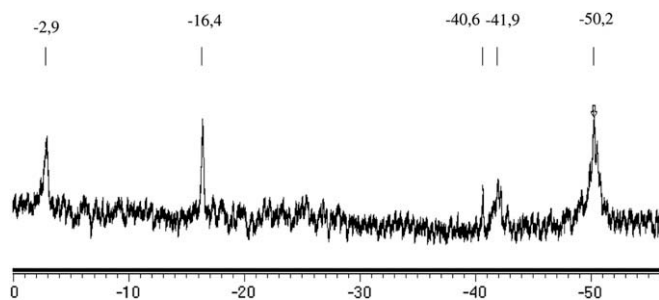


Fig. 3. ^{29}Si NMR spectrum of the reacting mixture of the reaction with PhSiH_3 .

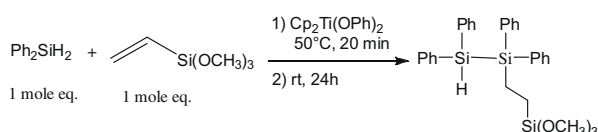
- The peaks at around -40 ppm are attributed to a silicon atom linked to three methoxy groups and one C-sp^3 , C-Si(OMe)_3 .
- The last peak at around -50 ppm is assigned to a monohydrosilylated silicon atom bound to a phenyl group and two X groups ($\text{PhSi}^*(\text{H})(\text{Si}/\text{H})\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$) ($\text{X} = \text{H}$ or Si) [15].

These observations from the ^{29}Si NMR spectrum gives evidence of the formation of several products consisting of different silicon sites which results from both the dehydrocoupling and the hydrosilylation reactions.

2.2. Reaction with the secondary silane, Ph_2SiH_2

The same procedures as above were used for studying the reactions of the secondary silane (Scheme 3) with stoichiometric quantities of diphenylsilane and alkoxy silane.

In this system, it has been reported that this secondary silane leads essentially to the dimer ($\text{Ph}_2\text{HSi-SiHPh}_2$) [16] by dehydrocoupling reaction. There are at least five possible compounds which may be formed in this reaction. Three compounds may be obtained consequently to dehydrogenative coupling: the dimer itself ($\text{Ph}_2\text{HSi-SiHPh}_2$), then $\text{Ph}_2\text{HSi-SiPh}_2\text{-CH}_2\text{-CH}_2\text{-Si(OMe)}_3$ and $[\text{SiPh}_2\text{-CH}_2\text{-CH}_2\text{-Si(OMe)}_3]_2$ resulting from a monohydrosilylation and a dihydrosilylation of the former. Moreover, the dimers ($\text{Ph}_2\text{HSi-SiHPh}_2$, and then $\text{Ph}_2\text{HSi-SiPh}_2\text{-CH}_2\text{-CH}_2\text{-Si(OMe)}_3$) may



Scheme 3. Reaction with the secondary silane, Ph_2SiH_2 .

also further polymerise into oligosilanes and polysilanes [17]. Two additional compounds may form from a monohydrosilylation and a dihydrosilylation of the initial silane which would lead to $\text{Ph}_2\text{SiH-CH}_2\text{-CH}_2\text{-Si(OMe)}_3$ and $\text{Ph}_2\text{Si-}[\text{CH}_2\text{-CH}_2\text{-Si(OMe)}_3]_2$, respectively.

2.2.1. ^1H NMR study

The ^1H spectra of Ph_2SiH_2 , vinyltrimethoxysilane and the corresponding reaction mixture are shown in Fig. 4.

As in the case of the primary silane, the complete disappearance of the protons (about 6 ppm) of the vinyl group of the alkoxy silane and the formation of Si-CH_2 (0.5–1.2 ppm) in spectrum (c) confirm the hydrosilylation of the double bonds. Moreover the chemical shift at 5.13 ppm (Si-H_2) is not observed. Only a new peak (4.94 ppm) appeared, corresponding to a Ph_2SiHC environment. This chemical shift may correspond to either (a) the proton of the monohydrosilylated secondary silane leading to the formation of $\text{Ph}_2\text{SiH-CH}_2\text{-CH}_2\text{-Si(OMe)}_3$ or (b) the product formed by monohydrosilylation of the dimer, $\text{Ph}_2\text{HSi-SiPh}_2\text{-CH}_2\text{-CH}_2\text{-Si(OMe)}_3$. The non-substituted dimer itself can be precluded since no signal corresponding to its Si-H proton (4.90 ppm) is observed. The peak at 0.5–1.2 ppm confirms the hydrosilylation reaction.

2.2.2. ^{13}C NMR study

In this case, the hydrosilylation is confirmed by the two peaks (2.3 and 3.4 ppm) observed due to the formation of $\text{Si-C(sp}^3\text{)}$. The peak at 50.9 corresponds to the carbon of the methoxy groups and the aromatic carbons are observed at 125–140 ppm (Fig. 5).

2.2.3. ^{29}Si NMR study

Four peaks can clearly be seen in the ^{29}Si spectrum, which are assigned as follows (see Fig. 6):

- The peak at -10.6 ppm is assigned to the completely-substituted compound resulting from the dihydrosilylation of the initial secondary silane. This chemical shift is quite similar to that described for $(\text{CH}_3)_2\text{SiPh}_2$ [16].
- The peak at -28.9 ppm is attributed to the silicon atom of the monohydrosilylated $\text{Ph}_2\text{SiH-CH}_2\text{-CH}_2\text{-Si(OMe)}_3$ [13,17].
- The two peaks at -40.6 and -42 ppm correspond to the silicon atoms bearing the methoxy groups.
- A small peak which is observed at -51.2 ppm may be attributed to the chemical shift of the monohydrosilylated and dihydrosilylated dimers (respectively $\text{Ph}_2\text{HSi-SiPh}_2\text{-CH}_2\text{-CH}_2\text{-Si(OMe)}_3$ and $[\text{SiPh}_2\text{-CH}_2\text{-CH}_2\text{-Si(OMe)}_3]_2$) [15]. This peak is very weak, suggesting that the hydrosilylation reaction is favoured over the dehydrocoupling reaction in this case.

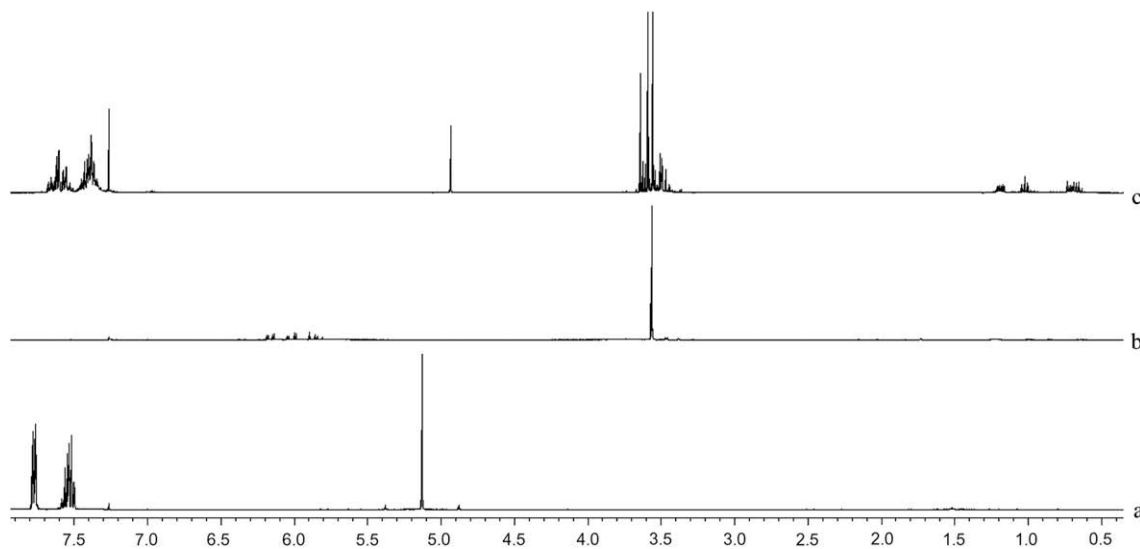


Fig. 4. ^1H NMR spectra of (a) Ph_2SiH_2 , (b) $\text{vinylSi}(\text{OMe})_3$, and (c) the reacting mixture of $\text{vinylSi}(\text{OMe})_3$ with Ph_2SiH_2 .

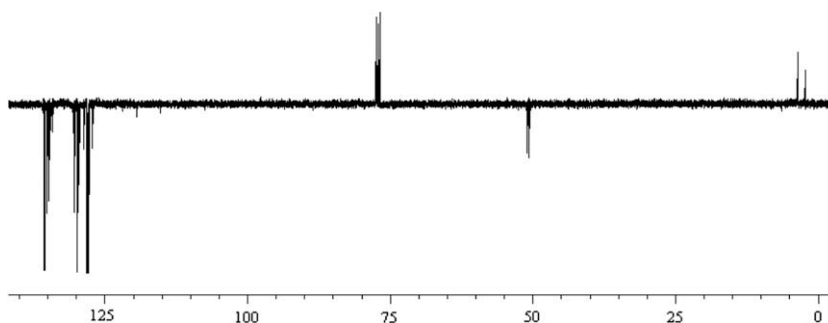


Fig. 5. ^{13}C NMR spectrum of the reaction mixture with Ph_2SiH_2 .

2.3. Reaction with the tertiary silane, Ph_3SiH

It is known that tertiary silanes do not readily undergo dehydrocoupling [16b]. However it was of interest to see if hydrosilylation could occur in this case with the titanocene complex.

The same procedure as above was used with a 1/1 molar amount of the silane and the alkoxy silane (Scheme 4).

Despite the drastic conditions used (higher reaction temperature at 70°C for 24 h) no reaction occurred, and only the two starting reagents were observed by NMR. This confirms that the titanium complex is not a convenient catalyst for the hydrosilylation reaction in the case of a bulky tertiary silane. (see Scheme 4).

2.4. Reaction with tertiary disilane, $\text{Ph}_2\text{HSi-SiHPh}_2$

Since the secondary silane Ph_2SiH_2 dimerises to form $\text{Ph}_2\text{HSi-SiHPh}_2$ it was of interest to investigate if this dimer, which is considered to be a tertiary silane, could be hydrosilylated (Scheme 5). If so, then at least two compounds may be obtained in this reaction with monohydrosilylation and dihydrosilylation of the dimer leading to $\text{Ph}_2\text{HSi-SiCH}_2\text{CH}_2\text{Si}(\text{OMe})_3\text{Ph}_2$ and $[\text{SiCH}_2\text{CH}_2\text{Si}(\text{OMe})_3\text{Ph}_2]_2$, respectively. Again according to the literature, the monohydrogenosilane $\text{Ph}_2\text{HSi-SiCH}_2\text{CH}_2\text{Si}(\text{OMe})_3\text{Ph}_2$ can polymerise to form oligosilanes. The same reaction conditions were used as for the primary and the secondary silanes with stoichiometric (1/1) quantities of the disilane and alkoxy silane.

2.4.1. ^1H NMR study

Fig. 7 shows the ^1H NMR spectra of the disilane, the alkoxy silane and the reaction mixture.

In this case, hydrosilylation does occur, since the NMR spectrum of the reaction mixture (Fig. 7, spectrum c) exhibits no chemical shift at around 6 ppm (vinylic protons) whereas Si- CH_2 protons appear at 0.5–1.2 ppm. Moreover, the Si-H signal of the starting dimer disappears completely and a new signal (4.94 ppm) is observed. The chemical shift of this Si-H peak is similar to that observed in the case of the secondary silane, Ph_2SiH_2 , and could correspond to the monohydrosilylated compound, $\text{Ph}_2\text{HSi-SiCH}_2\text{CH}_2\text{Si}(\text{OMe})_3\text{Ph}_2$.

2.4.2. ^{13}C NMR study

The ^{13}C spectrum of the reaction mixture is presented in Fig. 8 and exhibits Si-C sp^3 chemical shifts at 2.34 and 3.52 ppm. The peak at 51.3 ppm is attributed to the methoxy groups and shifts associated with the phenylene groups are observed at 125–140 ppm. These observations give clear evidence that the disilane can undergo hydrosilylation.

2.4.3. ^{29}Si NMR study

In this case the ^{29}Si spectrum exhibits several peaks (Fig. 9) which may be assigned as follows:

- The peak at -28.9 ppm is attributed to the monohydrogenosilicon atom of the $\text{Ph}_2\text{SiH-SiPh}_2[\text{CH}_2\text{-CH}_2\text{-Si}(\text{OMe})_3]$ [13,17].

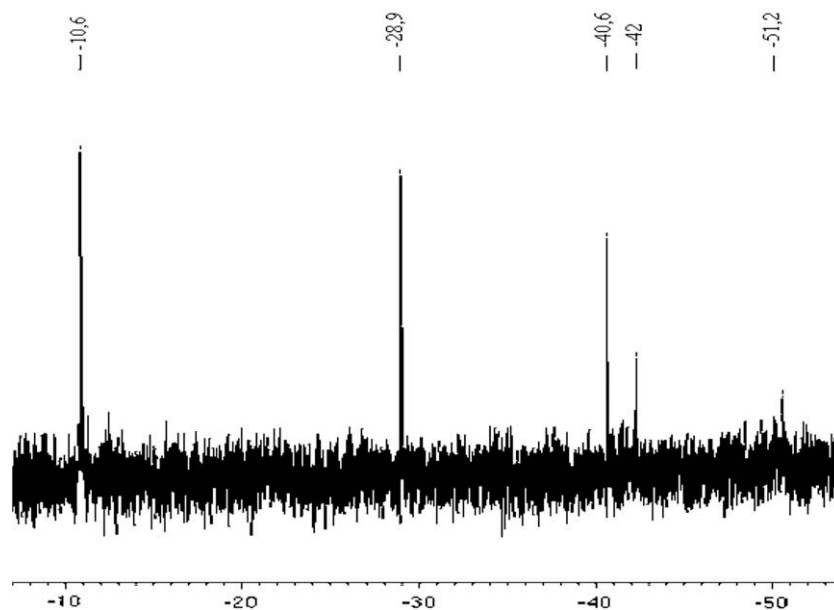
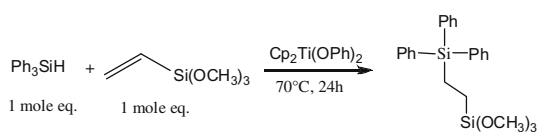
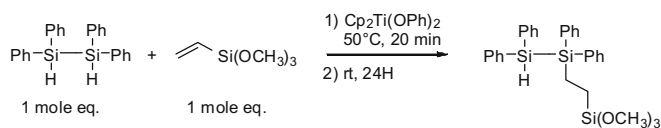


Fig. 6. ^{29}Si NMR spectrum of the reaction mixture with Ph_2SiH_2 .



Scheme 4. Reaction with the tertiary silane, Ph_3SiH .



Scheme 5. Reaction with the tertiary di-silane, $\text{Ph}_2\text{HSi}-\text{SiHPh}_2$.

- The peaks at -39.9 and -42.1 ppm are assigned to the silicon atoms bearing three methoxy groups.
- The peak at -50.6 ppm is attributable to the monohydrosilylated and dihydrosilylated dimers ($\text{Ph}_2\text{HSi}-\text{SiPh}_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OMe})_3$ and $[\text{SiPh}_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OMe})_3]_2$, respectively) and also to the silicon atoms of the oligomers which may form [17]. Indeed this peak is relatively intense compared to the corresponding feature in the spectrum of the secondary silane. It may be considered that oligomerisation of the dimer occurs more readily than with the secondary silane in which the dehydrocoupling is somehow inhibited due to the formation of $\text{Ph}_2\text{Si}-[\text{CH}_2-\text{CH}_2-\text{Si}(\text{OMe})_3]$ by dihydrosilylation.
- Moreover no peak at -10.7 ppm is observed which is expected since no dihydrosilylation can occur.

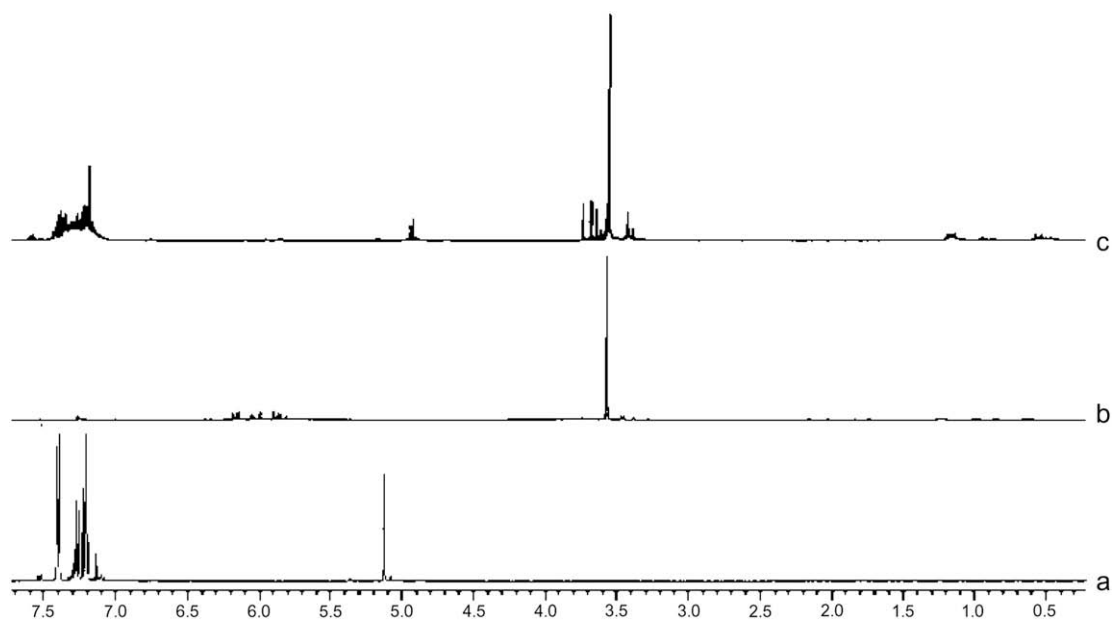


Fig. 7. ^1H NMR spectra of (a) $(\text{Ph}_2\text{SiH})_2$, (b) $\text{vinylSi}(\text{OMe})_3$ and (c) the reaction mixture of $\text{vinylSi}(\text{OMe})_3$ with $(\text{Ph}_2\text{SiH})_2$.

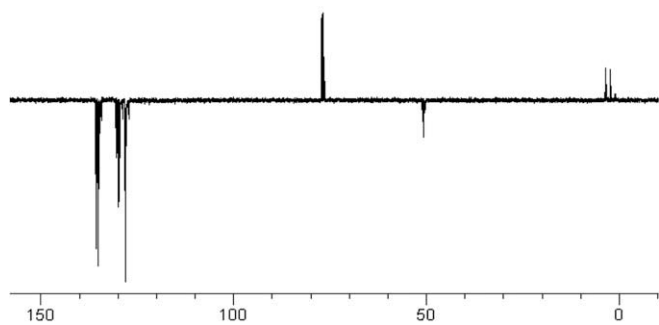


Fig. 8. ^{13}C NMR spectrum of the reaction mixture with $(\text{Ph}_2\text{SiH})_2$.

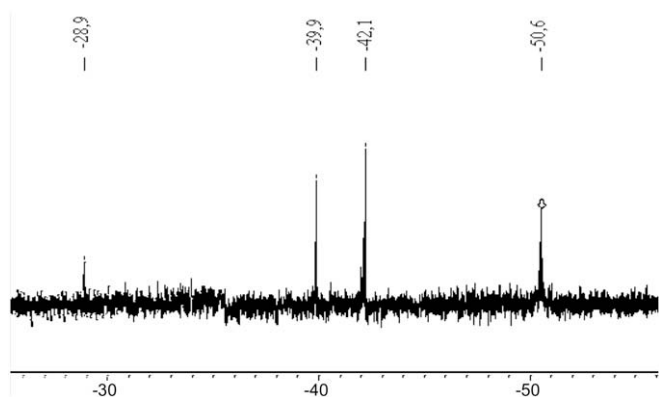


Fig. 9. ^{29}Si NMR spectrum of the reaction mixture with Ph_2SiH_2 .

3. Conclusions

In conclusion, we report a one-pot synthesis of functional polysilanes using $\text{Cp}_2\text{Ti}(\text{OPh})_2$ as catalyst. The latter promoted the dehydrogenative coupling of the silanes which simultaneously react with vinyltrimethoxysilane via a hydrosilylation reaction. These reactions readily occur with primary and secondary silanes, where the dehydrocoupling step is favourable. It does not appear to occur with tertiary silanes, which do not undergo any of the two reactions even under more drastic conditions. However, it was shown that the dimer $\text{Ph}_2\text{HSi}-\text{SiHPh}_2$ bearing the Si–Si bond undergoes the hydrosilylation reaction and oligomerisation. From these studies it appears that the formation of Si–Si bonds through the catalysed dehydrocoupling of hydrogenosilanes is the key step favouring the simultaneous hydrosilylation reaction. Although it is possible that the Si–Si bond may facilitate the hydrosilylation reaction, it is also possible that the disilane may first react directly with the titanium catalyst to generate sufficiently reactive species that subsequently participate in the hydrosilylation reactions.

4. Experimental

4.1. General and techniques

All reactions were carried out under a nitrogen atmosphere using vacuum line and Schlenk techniques. The reagents were purchased from Aldrich or Alfa Aesar. Karstedt and Speier catalysts were obtained from ABCR and Aldrich, respectively. $\text{Cp}_2\text{Ti}(\text{OPh})_2$ was synthesised according to the literature [6].

Melting points were determined on an electrothermal apparatus (IA9000 series) and are uncorrected. Elemental analyses were undertaken by the "Service Central d'Analyse du CNRS" at Vernai-

son (France). ^1H and ^{13}C NMR solution spectra were recorded on Bruker AC-200 spectrometers at 200 and 50 MHz, respectively. ^{29}Si NMR solution spectra were recorded on a Bruker AC-250 or AC-400 and CDCl_3 was used as a solvent. All chemical shifts are reported as δ values in parts per million relative to Me_4Si (δ 0 ppm for ^1H).

4.1.1. Dimerisation of Ph_2SiH_2 [16]

Ph_2SiH_2 (2.00 g, 10.9 mmol) and $\text{Cp}_2\text{Ti}(\text{OPh})_2$ (8.0 mg, 2.2 μmol) were mixed in a flask under argon. The mixture, upon heating at 100 $^\circ\text{C}$, turned dark blue and hydrogen was evolved. After 15 h, the mixture was cooled to room temperature. Crystallisation from pentane gave 0.85 g of Ph_2SiH_2 . (Yield 22%. mp = 79 $^\circ\text{C}$ (literature [16] 78 – 80 $^\circ\text{C}$. ^1H NMR (CDCl_3): δ = 7.56–7.35 (m, 20H, Ph-H), 5.27 (s, 2H, SiH)).

4.2. Reaction of the phenylsilanes and vinyltrimethoxysilane with $\text{Cp}_2\text{Ti}(\text{OPh})_2$

4.2.1. PhSiH_3 + vinyltrimethoxysilane

PhSiH_3 (300 mg, 2.77 mmol), vinyltrimethoxysilane (411 mg, 2.77 mmol) and $\text{Cp}_2\text{Ti}(\text{OPh})_2$ (30 mg, 0.083 mmol) were mixed in a flask under argon. The solution was heated to 50 $^\circ\text{C}$. After 20 min at 50 $^\circ\text{C}$, the solution colour changed from yellow to dark blue and H_2 was released, indicating the commencement of the dehydrocondensation reaction. The solution was stirred at room temperature for 24 h until the vinylic protons were no longer evident in the ^1H NMR spectrum, indicating that the hydrosilylation was complete.

^1H NMR (CDCl_3): δ = 0.5–1.2 (m, $\text{PhSiCH}_2\text{CH}_2\text{Si}$), 3.51–3.63 (m, OCH_3), 4.85 (t, $\text{Ph}(\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3\text{SiHSi})$), 4.95 (s, Si–SiH), 7.32–7.81 (m, Ph-H); ^{13}C NMR (CDCl_3): δ = 0–3.7 (SiCH_2), 50.4 (OCH_3), 127–136 (Ph and catalyst); ^{29}Si NMR (CDCl_3): δ = –50.2 ($\text{PhSi}^*(\text{H})(\text{Si}/\text{H})\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$), –41.9 and –40.6 ($\text{Si}(\text{OCH}_3)_3$), –16.4 ($\text{PhSi}^*(\text{Si}/\text{H})(\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3)_2$), –2.9 ($\text{PhSi}^*[\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3]_3$); Anal. Found for $\text{C}_{5.27}\text{H}_{8.47}\text{O}_{1.33}\text{Ti}_{0.02}\text{Si}$: C, 51.79; H, 6.98; O, 17.43; Ti, 0.84; Si, 22.96%.

4.2.2. Ph_2SiH_2 + vinyltrimethoxysilane

Ph_2SiH_2 (300 mg, 1.63 mmol), vinyltrimethoxysilane (242 mg, 1.63 mmol) and $\text{Cp}_2\text{Ti}(\text{OPh})_2$ (18 mg, 0.049 mmol) were mixed in a flask under argon. The solution was heated to 50 $^\circ\text{C}$. After 20 min at 50 $^\circ\text{C}$, the colour of the solution changed from yellow to dark blue with evolution of H_2 . The solution was stirred at 50 $^\circ\text{C}$ for 24 h until the vinylic protons were no longer evident in the ^1H NMR spectrum, indicating that the hydrosilylation was complete.

^1H NMR (CDCl_3): δ = 0.5–1.2 (m, $\text{Ph}_2\text{SiCH}_2\text{CH}_2\text{Si}$), 3.49–3.63 (m, OCH_3), 4.92 (m, SiH), 7.36–7.68 (m, Ph-H); ^{13}C NMR (CDCl_3): δ = 2.3 and 3.4 ($\text{SiCH}_2\text{CH}_2\text{Si}$), 50.9–51.1 (OCH_3), 127.8–134.8 (Ph and catalyst); ^{29}Si NMR (CDCl_3): δ = –51.2 ($\text{Ph}_2(\text{H})\text{Si}^*\text{Si}(\text{Ph}_2)\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$), –42 and –40.6 ($\text{Si}(\text{OCH}_3)_3$), –28.9 ($\text{Ph}_2(\text{H})\text{SiSi}^*(\text{Ph}_2)\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$), –10.6 ($\text{Ph}_2\text{Si}^*(\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3)_2$); Anal. Found for $\text{C}_{9.05}\text{H}_{10.8}\text{O}_{1.44}\text{Ti}_{0.02}\text{Si}$: C, 63.28; H, 6.34; O, 13.45; Ti, 0.58; Si, 16.35%.

4.2.3. $(\text{Ph}_2\text{SiH})_2$ + vinyltrimethoxysilane

$(\text{Ph}_2\text{SiH})_2$ (150 mg, 0.41 mmol), vinyltrimethoxysilane (61 mg, 0.41 mmol) and $\text{Cp}_2\text{Ti}(\text{OPh})_2$ (5 mg, 0.012 mmol) were mixed in a flask under argon. The solution was heated to 50 $^\circ\text{C}$. After 20 min at 50 $^\circ\text{C}$, the colour of the solution changed from yellow to dark blue with evolution of H_2 . The solution was stirred at 50 $^\circ\text{C}$ for 24 h until the vinylic protons were no longer evident in the ^1H NMR spectrum, indicating that the hydrosilylation was complete.

^1H NMR (CDCl_3): δ = 0.5–1.23 (m, $\text{Ph}_2\text{SiCH}_2\text{CH}_2\text{Si}$), 3.34–3.63 (m, OCH_3), 4.9 (s, SiH), 7.29–7.56 (m, Ph-H); ^{13}C NMR (CDCl_3):

$\delta = 2.2$ and 4.2 ($\text{SiCH}_2\text{CH}_2\text{Si}$), 50.3 and 50.7 (OCH_3), 126.9 – 137.3 (Ph and catalyst); ^{29}Si NMR (CDCl_3): $\delta = -50.6$ ($\text{Ph}_2(\text{H})\text{Si}^* - \text{Si}(\text{Ph}_2)\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$), -42.1 and -39.9 ($\text{Si}(\text{OCH}_3)_3$), -28.9 ($\text{Ph}_2(\text{H})\text{SiSi}^*(\text{Ph}_2)\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$); Anal. Found for $\text{C}_{9.78}\text{H}_{9.98}\text{O}_{0.74} - \text{Ti}_{0.01}\text{Si}$: C, 69.83; H, 5.98; O, 7.07; Ti, 0.43; Si, 16.69%.

4.2.4. Ph_3SiH + vinyltrimethoxysilane

Ph_3SiH (100 mg, 0.38 mmol), vinyltrimethoxysilane (57 mg, 0.38 mmol) and $\text{Cp}_2\text{Ti}(\text{OPh})_2$ (4.5 mg, 0.011 mmol) were mixed in a flask under argon. Although the solution was heated at 70°C for 24 h. no reaction occurred.

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