



Catalytic study of heterobimetallic rhodium complexes derived from partially alkylated s-indacene in dehydrogenative silylation of olefins

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ABSTRACT

This work describes the catalytic study of heterobimetallic rhodium compounds derived from partially alkylated s-indacene in dehydrogenative silylation of olefins in order to elucidate as much as possible the effects of: solvent, temperature, chemical substrates, olefin effect, silane effect, and secondary metallic fragment. The rhodium complexes, *anti*-[Cp*Fe-s-Ic'-Rh(COD)] **1**, *anti*-[Cp*Ru-s-Ic'-Rh(COD)] **2**, and *syn*-[Cp*Ru-s-Ic'-Rh(COD)] **2'** (with s-Ic': 2,6-diethyl-4,8-dimethyl-s-indaceneide) were previously synthesized and characterized, and were compared with the catalytic activity of the complexes previously reported; monometallic [(COD)Rh-s-Ic'H] **3**, and homobimetallic *anti*-[[(COD)Rh]₂-s-Ic'] **4**, and *syn*-[[(COD)Rh]₂-s-Ic'] **4'**.

The heterobimetallic complexes show a high activity and selectivity for the dehydrogenative silylation of styrene and these complexes show also the presence of a cooperative effect between both metallic centers, which is evidenced when compared with monometallic complex.

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1. Introduction

The dehydrogenative silylation (DS) reaction of olefins is less documented than hydrosilylation, despite the fact vinylsilanes present multiple applications together with its commercial interest [1–3].

The big value of vinylsilanes lies, amongst others, in the synthesis of natural products [4–7], substrates for the formation of polycarbosilanes [8,9] as well as siloxane polymers or copolymers [10,11]. The main inconvenient of the dehydrogenative silylation of olefins is the competition with the hydrosilylation reaction. The first example of a catalytic reaction leading to vinylsilanes took place in 1962, where trialkylsilanes and several olefins were made react with Fe(CO)₅ [12,13], several years before the studies include other metals in the early 1980s [14,15].

Despite the fact there have been articles which have reported catalytic runs at different temperatures, most of these have no comments whatsoever on a plausible explanation of which step (or steps) is (are) most sensitive to heating, or to the influence on

solvent [16,17]. Other than theoretical studies and their activation energies, to the best of knowledge of our lab group, temperature and solvent effects are minimally analyzed.

The product abundance strongly depends on the nature of the catalyst and its ligands, the silane and olefin used, etc. In most case with rhodium catalysts, the formation of a geminal-alkylated hydrosilylation product together with a *cis*-vinylsilane is detectable only in trace amounts, and very rarely isolated [18,19].

Previously, our research group published the results obtained for the heterobinuclear complex [Cp*Ru-Pentalene-Rh(COD)] [20], in which an X-ray structure determination shows a bonding mode for rhodium similar to that in [(CO)₃Cr-Indenyl-Rh(CO)₂] [21], bringing it closer to an allylic array. Analogous to the Cr–Rh complex, allylic bonding produced an enhanced reactivity at Rh in two cases, these being the exchange of COD for carbon monoxide, and also in the dehydrogenative silylation of styrene [20]. This exchange has motivated us to work on the design of catalysis using bridging ligands and varying the secondary metallic fragment, in addition to an ancillary on the Rh center.

Pentalene is a very unstable compound, and its synthesis is long and expensive [22]. Polyalkylated s-indacene is a better alternative because its effectiveness as spacer ligand has been well documented [23–27].

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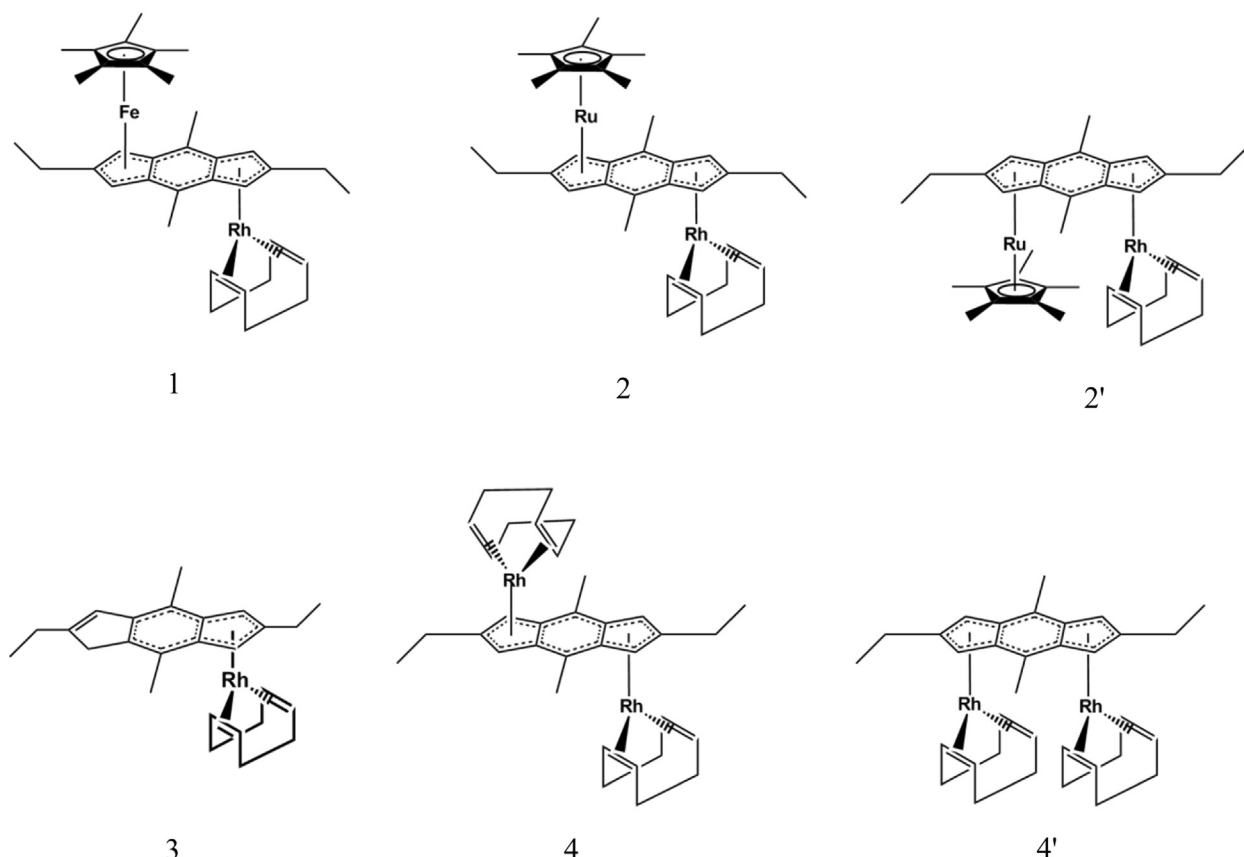


Fig. 1. Mono- (**3**), homo- (**4** and **4'**) and heterobimetallic (**1**, **2** and **2'**) rhodium catalysts used in this work.

This contribution describes the results obtained by previously synthesized and characterized heterobimetallic rhodium catalysts *anti*-[Cp*Fe-*s*-Ic'-Rh(COD)] **1** [24], *anti*-[Cp*Ru-*s*-Ic'-Rh(COD)] **2**, and *syn*-[Cp*Ru-*s*-Ic'-Rh(COD)] **2'** [24] compare with the activity shown by [(COD)Rh-*s*-Ic'H] **3** [23], *anti*-[[(COD)Rh]₂-*s*-Ic'] **4** [23], and *syn*-[[(COD)Rh]₂-*s*-Ic'] **4'** [23] (with *s*-Ic' = 2,6-diethyl-4,8-dimethyl-*s*-indaceneiide) in the reaction of olefins with hydrosilanes. The main aim of this work is to elucidate as much as possible the effects of solvent, temperature, chemical substrates, olefin effect, silane effect, and secondary metallic fragment. These factors need to be assessed in order to determine if they have a direct influence on the selectivity of the different formed products, as well as with the reaction rate. All products were characterized in each case by GC–MS and by ¹H NMR, compared to literature [28].

2. Experimental

All manipulations were carried out under pure dinitrogen atmosphere using a vacuum atmosphere drybox equipped with a Model HE 493 Dri-Train purifier, or a vacuum line using standard Schlenk-tube techniques. Reagent grade solvents were dried using sodium and distilled under dinitrogen (tetrahydrofuran, toluene, petroleum ether). The synthesis of the following complexes has been reported previously: *anti*-[Cp*Fe-*s*-Ic'-Rh(COD)] **1** [24], *anti*-[Cp*Ru-*s*-Ic'-Rh(COD)] **2** [24], and *syn*-[Cp*Ru-*s*-Ic'-Rh(COD)] **2'** [24], [(COD)Rh-*s*-Ic'H] **3** [23], *anti*-[[(COD)Rh]₂-*s*-Ic'] **4** [23], and *syn*-[[(COD)Rh]₂-*s*-Ic'] **4'** [23]; with *s*-Ic' = 2,6-diethyl-4,8-dimethyl-*s*-indaceneiide. Styrene and triethylsilane were purchased from Aldrich and were degassed before use. ¹H and ¹³C NMR spectra were recorded on Bruker Avance 400 MHz. GC and GC–MS spectra

(EI, 70 eV) were recorded on HP 5890 series II and HP5889 A spectrometers.

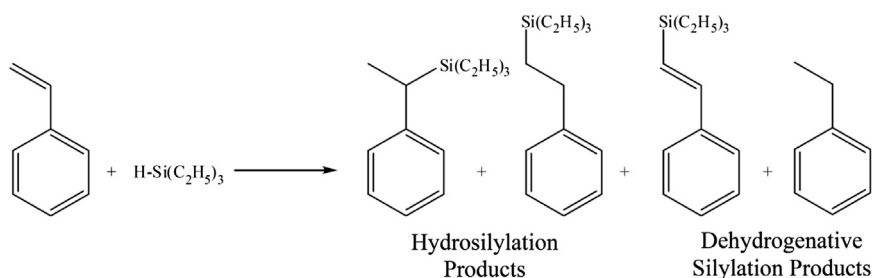
2.1. General procedure for the dehydrogenative silylation of styrene

A two-necked flask equipped with a magnetic stirring bar was charged with the catalytic amount of complex (0.015 mmol). The reactor was evacuated and filled with dinitrogen. Styrene (0.52 mL, 4.5 mmol) and toluene (5 mL) were added, and the mixture was stirred for 5 min. Then Et₃SiH (0.24 mL, 1.5 mmol) was added. The reaction flask was immersed in an 80 °C thermo-stabilized bath. The progress of the reaction was monitored by GC (disappearance of Et₃SiH). The products were identified by ¹H NMR, by GC–MS, and by comparison with the literature data [28].

3. Results and discussion

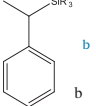
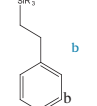
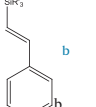
The dehydrogenative silylation reactions of organic compounds with silanes have emerged as a viable alternative for the synthesis of vinylsilanes [16]. These compounds are versatile intermediates in organic reactions, and their synthesis is catalyzed by transition metal complexes [18,29–31]. Considering that rhodium complexes have been reported to be effective catalysts [32–34], this prompted us to test the activity of the heterobimetallic complexes **1**, **2** and **2'** in dehydrogenative silylation of styrene and compare with the complexes **3**, **4** and **4'**. The Fig. 1 shows the catalyst used in this work.

Thus, the reaction of 1 equiv of triethylsilane (1.5 mmol) with 3 equiv of styrene (4.5 mmol) in the presence of a catalytic amount of heterobimetallic complexes (0.015 mmol) at 80 °C gave a mixture



Scheme 1. Reaction of triethylsilane with styrene. Reaction 1.

Table 1
Catalytic behavior for complex *anti*-[Cp*Fe-s-Ic'-Rh(COD)] **1** at different temperature values and solvents.

Entry	Silane consumption ^a (%)	Time (mins)	Solvent	Temperature (°C)			
1	42.9	100	THF	60	12.6	27.8	59.6
2	16.6	100	Hexane	60	0.5	27.0	72.5
3	20.1	100	Octane	60	0.8	23.1	76.1
4	12.2	100	Toluene	60	3.7	23.6	72.7
5	100.0	80	Toluene	80	1.3	12.9	85.9
6	100.0	100	Toluene	80	0.9	18.1	85.9
7	100.0	25	Toluene	120 (Reflux)	0.0	13.0	76.8
8	100.0	15	Octane	130 (Reflux)	0.9	22.3	76.8

^a Silane consumed %.^b Determined by GC.

of 1-phenyl-2-(triethylsilyl) ethane (hydrosilylation product) and (E)-1-phenyl-2-(triethylsilyl)ethene (dehydrogenative silylation product) with a product distribution of 13:87 for the silicon compounds (i.e., 0.29 and 1.31 mmol for hydrosilylation and dehydrogenative, respectively), Scheme 1.

3.1. Solvent and temperature effect

Several experiments were carried out in order to determine the ideal working solvent and temperature. Each run was performed for 100 min or until triethylsilane was fully consumed, whichever

would happen first. Table 1 summarizes the results of all experiments.

All tests and their results listed in Table 1 were performed using complex **1**, using 100 eqs. of triethylsilane, plus 300 eqs. of styrene, forming the product shown in reaction 1 (Scheme 1).

Solvent completed 5 mL of the mixture, and each solvent was distilled over sodium and degassed under vacuum and dinitrogen several times before usage. Working Temperatures were 60 °C in each case, as well as 80 °C and reflux temperatures for toluene and octane. These values were included as an attempt to understand and compare temperature effects.

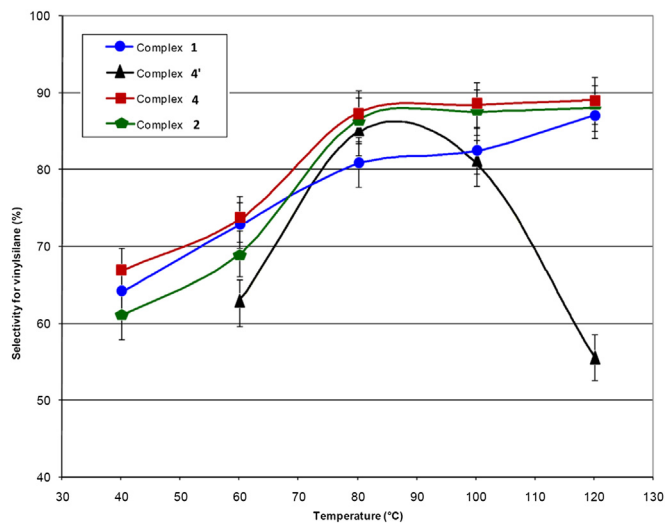


Fig. 2. Graph representing the selectivity for the vinylsilane of styrene at different temperatures and for different catalysts. Solvent, toluene. ○, *anti*-[Cp*Fe-s-Ic'-Rh(COD)] **1**; △, *anti*-[Cp*Ru-s-Ic'-Rh(COD)] **2**; □, *anti*-[[(COD)Rh]₂-s-Ic'] **4**; Δ, *syn*-[[(COD)Rh]₂-s-Ic'] **4'**.

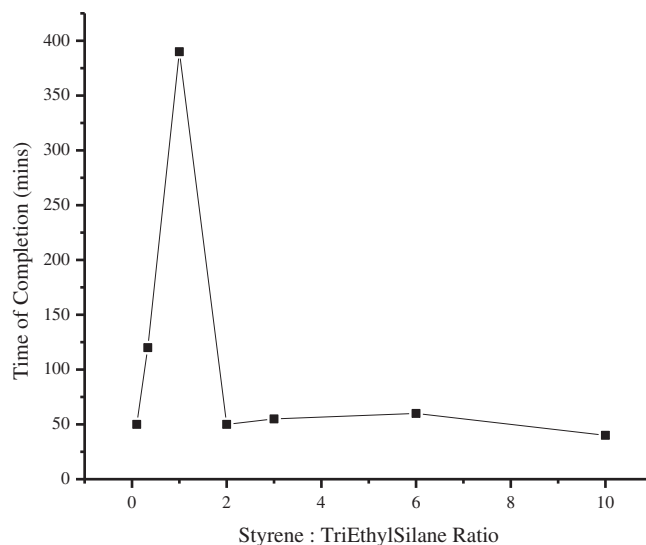


Fig. 3. Graph representing the reaction rate depending on the styrene:silane ratio.

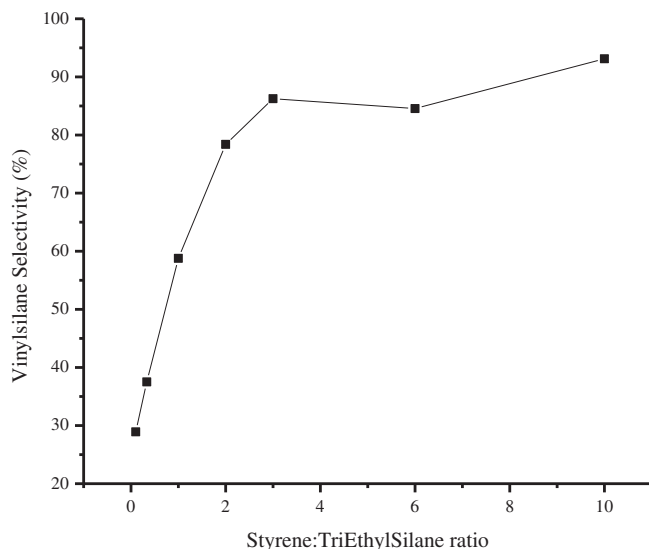


Fig. 4. Graph representing the vinylsilane selectivity depending on the substrates ratio.

Comparing the influence of the solvent at 60 °C, a coordinating solvent such as THF resulted in a higher silane consumption, compared to each of the other solvents at the same temperature. This took place against selectivity, highly favoring products of hydrosilylation rather than vinylsilane. A feasible explanation could be that since THF is a nucleophilic solvent, it might coordinate to the metallic center, decreasing its Lewis acid character, hence making it less favorable to abstract the β -hydrogen in the alkyl chain, necessary for the formation of a vinylsilane.

At 60 °C, the listed values of silane consumption and product selectivity are virtually identical. Hexane, octane and toluene are non-polar solvents, and their dielectric constants are very low; these similarities are reflected in the minimal differences in the outcome of each catalytic reaction. All other listed solvents probably have no other effect than to keep reagents and intermediates soluble at all times, in addition to delivering thermal energy to all substrates and active species to overcome the activation energy barriers for each relevant step of the catalytic cycle.

Temperatures of 80 °C and above are allowed only by toluene and octane, not only making the consumption of silane quantitative, but also greatly increasing the selectivity of vinylsilane formation. Temperatures higher than 80 °C reduce the time for complete silane consumption, although this does not increase or alter the selectivity values of any product, with the exception of octane at reflux temperature (130 °C). In this last entry of Table 1, a decreased percentile value of vinylsilane may indicate a possible decomposition of the catalysts at temperatures over 120 °C.

For the following catalytic reactions, toluene was chosen as solvent. Another test to determine the ideal working temperature

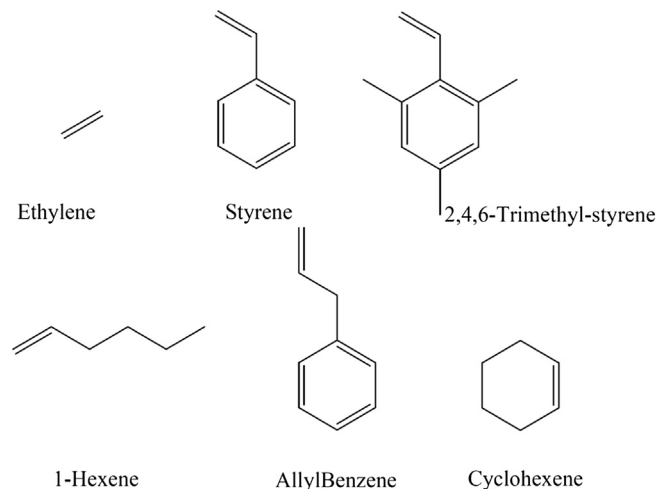


Fig. 5. Diagrams of all used olefins.

was carried out with complexes **4**, **4'**, **1** and **2** using temperatures from 40 to 120 °C. Experiments were also tried at 20 °C, but in all cases silane consumption was minimal, and there was either no product formation or simply trace amounts. Fig. 2 summarizes in a graph the effect temperature may have with each complex:

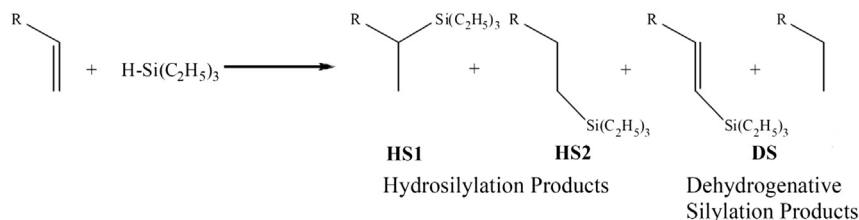
The above shown graph clearly reveals that at temperatures of 80 °C and above, there are only small changes selectivity regardless of the catalyst used, with the exception of Complex **4'**, which decreases the selectivity and the reaction rate of silane consumption at a given time. This may happen due to decomposition of the catalytic species, because of high steric crowding of both $-\text{Rh}(\text{COD})$ moieties which at high temperatures should reduce its effectiveness as a catalyst.

All other catalysts behave similarly, even $[\text{Cp}^*\text{Rh}(\text{COD})]$, which has a strict pentahaptoligand (Cp^*), and different only at lower temperatures at which the silane consumption is almost negligible. In conclusion, the ideal temperature for all catalysts is 80 °C, and their behavior at other temperatures is comparable.

3.2. Effect of chemical substrates

The nature of substrates is critical for the outcome of each experiment. For example, α -olefins may isomerize to internal olefins resulting in silicon isomers, whether in hydrosilylation or in dehydrogenative silylation products. Silanes also have a crucial role in product formation, as it is known that rhodium catalysts have a very low affinity for di- or trihydrosilanes, but react readily with trialkyl(mono hydro)silanes [35].

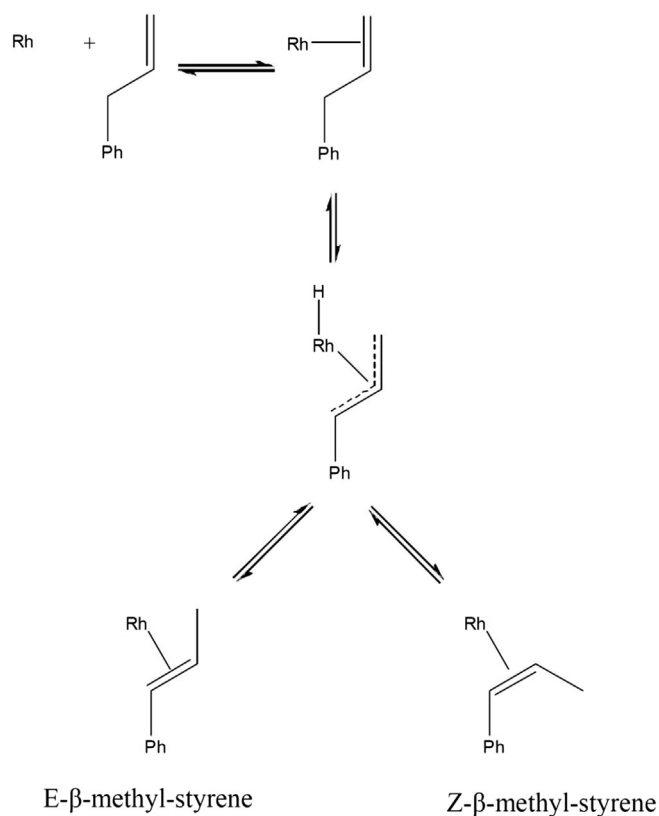
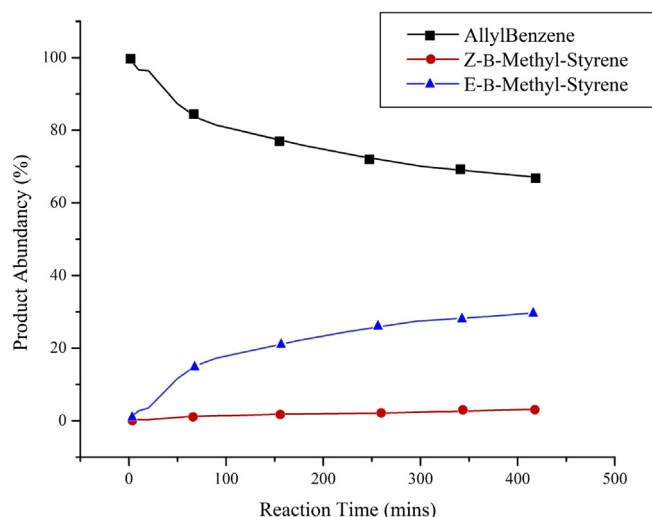
In the case of new silylated products, attempts to isolate each one were carried out by distillation at reduced pressure, and a later characterization by NMR and Mass Spectroscopy. Unless specified, most products were identified and compared to literature characterizations [4–7].



Scheme 2. Reaction of triethylsilane with different olefins. Reaction 2.

Table 2Results using different olefins (styrene, trimethylstyrene and ethylene).^a

Entry	Olefin used	Catalyst	Product		Abundance	Times (mins)	Silane consumption
			HS1 (%)	HS2 (%)	DS (%)		
1	Styrene	1	1.3	11.1	88.1	60	100%
2	Styrene	2	0.9	12.8	86.3	55	100%
3	2,4,6-Trimethylstyrene	1	0.0	14.1	85.9	420	71%
4	2,4,6-Trimethylstyrene	2	0.0	15.0	85.0	420	74%
5	Ethylene	1		59.6	40.4	100	100%
6	Ethylene	2		58.2	41.8	100	100%

^a Experimental conditions, solvent: Toluene; T: 80 °C.**Fig. 6.** Allylbenzene reacting with rhodium to form its respective isomers.**Fig. 7.** Graph representing the formation of allylbenzene isomers.

3.2.1. Effect of substrate ratio

In this section, the ideal olefin:silane ratio was determined by using the same test as in reaction 1 (Scheme 1), with complex **2** in each case, and styrene:silane ratios ranging from 10:1 to 1:10.

Fig. 3 shows a high completion time (consumption of limiting substrates) with a styrene:triethylsilane ratio of one. Higher ratios dramatically increase reaction rates to almost the same value. Fig. 4 shows that both substrates affect product selectivity: the greater the concentration of olefin, the greater the amount of vinylsilane formed.

This tendency could be explained by the effect an olefin may have on the catalytic cycle. As it is known, the olefin also has the role of providing a lower energy path for the reductive elimination of hydrogen by acting as a hydrogen acceptor, boosting the consumption of the intermediate species, thereby yielding the desired vinylsilane. If the olefin is used in a low concentration, the role as a hydrogen acceptor is not carried out, hence the higher concentration of hydrosilylation products.

Also, at styrene:silane ratios greater than 3:1, the selectivity does not increase significantly. Therefore, the ideal condition is to use a substrate concentration of 300 equivalents of styrene and together with 100 equivalents of triethylsilane.

3.3. Olefin effect

The nature of the olefin may affect the catalytic cycle depending directly on the nature of the substituent group. Reaction 2 (Scheme 2) is an attempt to explain the olefin effect, using by varying the nature of the R group.

The products in reaction 2 are labeled HS1 for the geminal alkylated hydrosilylated product, HS2 for the lineal addition product, and DS for the vinylsilane and completely hydrogenated species.

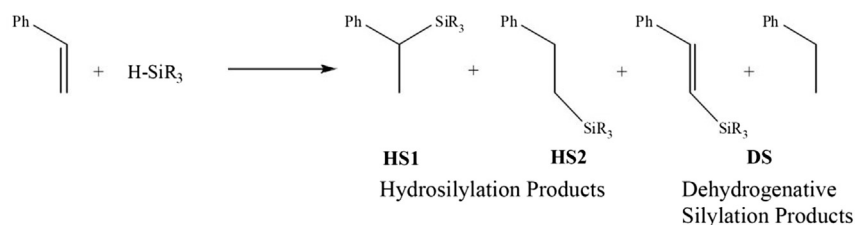
In each test, 300 equivalents of each chosen olefin together with 100 equivalents of triethylsilane, in toluene at 80 °C. In the case of ethylene, 1 bar of this olefin would be used instead. These olefins are diagramed in Fig. 5. Four different complexes were also included, in order to determine a possible greater affinity or reactivity of one particular catalyst for a certain olefin. These catalysts were **1** and **2**.

The above listed results in Table 2 show a fast consumption of triethylsilane for each entry, with similar values for selectivity.

Table 3Results using allylbenzene.^c

Entry	Complex used	Product selectivity				Time (mins)	Silane consumption
		Z ^a	E ^b	HS	DS		
1	1	4.7	75.4	6.9	13.0	350	80.5%
2	2	4.4	78.0	5.8	11.8	350	81.6%

^a Product Z-β-methyl-styrene.^b Product E-β-methyl-styrene.^c Experimental conditions, solvent: Toluene; T: 80 °C.



Scheme 3. Reaction of different trialkylsilanes with styrene. Reaction 3.

Table 4
 Results using different silanes.^a

Entry	Silane used	Catalyst	Product		Abundance	Times (mins)	Silane consumption
			HS1 (%)	HS2 (%)	DS (%)		
1		1	1.3	12.9	85.9	60	100%
2		2	0.9	12.8	86.3	55	100%
3		1	0.0	0.0	100	140	100%
4		2	0.0	0.0	100	150	100%
5		1	0.0	71.2	28.8	55	100%
6		2	0.0	73.8	26.2	60	100%
7		1	0.0	71.8	28.2	250	100%
8		2	0.0	73.4	26.6	250	100%

^a Experimental conditions, solvent: Toluene; T: 80 °C.

The electron-withdrawing groups, such as phenyl and trimethylphenyl, make a double bond a better hydrogen acceptor, explaining the high vinylsilane selectivity values for styrene and trimethylstyrene. The dramatic difference on the reaction rates could be easily explained by the steric hindrance of the methyl groups in positions 2 and 6 of 2,4,6-Trimethylstyrene, making more difficult the coordination of this olefin, together with delaying the insertion of the olefin whether into the M–H or to the M–Si bonds.

Allylbenzene increases the number of products. In this particular case, not all products were isolated and characterized, due to their large number.

Fig. 6 shows how the formation of β -methylstyrenes occurs, and may simultaneously react within the catalytic cycle.

The formation of these isomers was detected by GC, where the combination of the catalyst in the presence of the olefin in toluene would deliver one extra peak. These additional peaks were analyzed by mass spectroscopy, and by ^1H NMR, matching the molecular peaks and NMR peaks of both isomers, E- and Z- β -methylstyrene. Fig. 7 graphs the reagent and product abundance after a few hours of reaction [36].

Each different olefin, allylbenzene or its isomers, may present many different silylated products, though only two of these of unknown nature were detected. These products were identified only by means of mass spectroscopy, as when attempts to isolate them by means of silica column chromatography or reduced-pressure distillation would only present decomposition products as monitored by ^1H NMR, making it impossible to properly identify them. In Table 3, HS and DS stand for hydrosilylation and dehydrogenative silylation products, respectively, only that in this case, these were no means as to distinguish which particular product was formed.

After 350 min, the main product is only the E form of methylstyrene. This may indicate the isomerization reaction has a much lower energy activation barrier which consumes most of allylbenzene forming its isomers, rather than reacting to form the silylated products. After each catalytic run was completed at the given time, almost 80% of allylbenzene had been consumed, thus explaining the high percentage of formation of the E isomer, plus a very low concentration of dehydrogenative silylation products.

Olefins such as 1-hexene and cyclohexene presented no silylated product. In each case, the silane consumption was below the values of 2%, which is clearly within the margins of the

Table 5
Cone angle and NMR shift for ^1H and ^{29}Si for the used silanes.

Entry	Silane	Angle (°)	δ (^1H) ppm	δ (^{29}Si) ppm	Selectivity for DS products
1		160	3.35	12.06	100%
2		132	3.68	0.53	88.1%
3		127	4.53	0.53	32.5%
4		110	4.49	−17.05	22.0%
5		–	4.44	−58.93	None
6		–	5.07	−35.74	None
7		–	3.84	−22.72	None

experimental error of the GC machine, used to monitor the disappearance of each substrate.

1-Hexene presented several other GC peaks in each chromatogram once started the catalytic run, which a mass spectrum corroborated these were only isomers, surely 2-hexene and 3-hexene. These two olefins were considered for our rhodium complexes as inactive. Hydrosilylation and dehydrogenative silylation of internal olefins is a much more complex procedure, which normally takes place by means of radical reactions, possibly providing a plausible explanation for the lack of reactivity for these olefins.

Table 6
Catalytic results for styrene and triethylsilane for rhodium complexes.^a

Entry	Catalyst	Time (mins)	Silane consumption	HS1 (%)	HS2 (%)	DS (%)
1	3^b	600	92.8	10.9	13.9	75.3
2	4^b	180	100	4.2	11.1	84.7
3	4^b	35	100	1.0	11.8	87.2
4	1	60	100	1.3	12.9	85.9
5	2	55	100	0.9	12.8	86.3
6	2'	280	100	0.5	13.8	85.7

^a Corrected product abundance, disregarding ethylbenzene formation. Conditions of reaction: 0.015 mmol of catalyst, 4.5 mmol of styrene, 1.5 mmol of triethylsilane, toluene as solvent, 80 °C.

^b Reference [23].

In general, according to these results, olefin isomerization reactions seemed to occur at much faster rates than the formation of silylated products, drastically restricting the number of adequate substrates that could be used for these Rh catalysts. These results indicate only olefins without hydrogen atoms in β position together with electron-acceptor groups seem to be suitable, such as styrene and trimethylstyrene.

3.4. Silane effect

Reaction 3 (Scheme 3) shows the products formed using styrene for olefin, in all catalytic tests using same catalysts as in the previous section. In most cases, product HS1 is undetectable, or in trace amounts which are only detectable by GC–MS, which are discarded in the value of selectivity.

Tables 4 and 5 show the results for all used trialkylsilanes, as those tests with dihydrosilanes, such as diethylsilane and diphenylsilane resulted in a complete lack of activity for all the listed rhodium catalysts.

A comparison between triethylsilane and tri(isopropyl)silane show a marked difference. Changing from a linear to a branched alkyl group boosts the selectivity to a quantitative consumption of the silane forming exclusively the respective dehydrogenative silylation products. There is a much higher reaction time with tri(isopropyl)silane than with triethylsilane, possibly explained by the greater difficulty of inserting an olefin group inside a Rh–Si(i-Pr)₃ bond owning a bulkier group.

Table 4 also shows the results for dimethylphenylsilane and triethoxysilane, respectively. These silanes strongly favor hydrosilylation products, together with a very much increased reaction time for triethoxysilane, indicating the lack of reactivity for this substrate.

When a silane has a large electronic density located on the silicon atom, this could form an “overly” stable Rh–Si bond which may decrease the feasibility of inserting the olefin in this bond, favoring the Chalk–Harrod mechanism. This may be the case with dimethylphenylsilane and triethoxysilane. Other failed experiments including different silanes are not listed in tables as results, as in these cases there was no activity whatsoever from the catalysts.

In general, silanes have a strong effect on the selectivity of the formed products.

This may happen due to the fact that the rate determining steps in the Chalk–Harrod and Modified Chalk–Harrod mechanisms involve a carbon silicon bond to form and undergo the migratory insertion of the relevant olefin.

According to a thorough theoretical study [37], the Chalk–Harrod mechanism has for rate determining step the reductive elimination of the Si–C bond. In the case of the Modified Chalk–Harrod mechanism, the rate determining steps are whether the insertion of ethylene into the Rh–Si bond, or oxidative addition of the silane. Therefore, in order to form a larger amount of vinylsilane, a silane should ideally have a fast oxidative addition together with a Rh–Si bond weak enough as to favor the migration of the trialkylsilyl group on the olefin, rather than the migration of the hydrogen group.

These results may be further explained with the data obtained from NMR tools and cone angles from each respective silane. In Table 5, a qualitative correlation between the selectivity value for dehydrogenative silylation products and the NMR chemical shifts

Table 7
Rhodium chemical shifts of the mono- and bimetallic complexes.

Complex	3	4	4'	1	2	2'
Chemical shift (ppm):	−486	−334	−261	−275	−271	−245

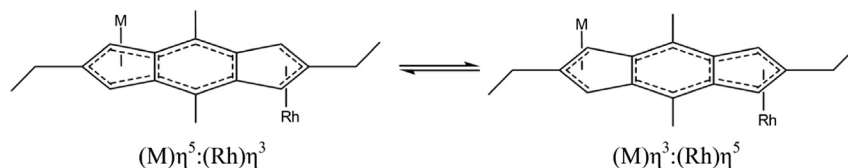


Fig. 8. Diagram of the equilibrium between the two possible bonding modes for each metallic fragment.

for proton and silicon nuclei can be evidenced, indicative that these rhodium catalysts boost their selectivity values when working with silanes with a dipole moment with a negative charge centered on the hydrogen atom and a positive charge on silicon, as in $\text{Si}^{\delta+}-\text{H}^{\delta-}$. The three last entries in Table 5 present a dipolar moment of the silicon–hydrogen bond closer to: $\text{Si}^{\delta-}-\text{H}^{\delta+}$, possibly hardening the oxidative addition process on the Rh center. Nevertheless, Table 5 also lists some cone angles for some trialkylsilanes (corresponding to each respective phosphine analog [38], revealing both factors, steric and electronic are responsible for the outcome of product selectivity, though steric influence seems to be the most significant factor when determining product selectivity.

Therefore, these catalysts seem capable of presenting very high selectivity values with a fairly limited number of silanes, more specifically, trialkylsilanes. Aryl and Alkoxy groups seem unsuitable, at least for these Rh catalysts.

3.5. Effect of the secondary metallic center

Several rhodium-based complexes, which differ only by the main ligand, have been tested [16,39–42]. Comparison between catalytic results of runs with mono- and binuclear complexes show that in the latter case, the second metallic center created a remarkable effect, the most pronounced consequence being on the activity of the catalyst. Indeed, concentration of Rh was kept constant for all catalytic tests and, this allowed direct assessment of relative activity. Mononuclear complexes **3** presented a reaction time of 600 min (see Table 6), while complete silane consumption is observed within 35 and 180 min, for **4** and **4'**, respectively. The strong electronic interaction between both metals channeled through the bridging ligand can be invoked to account for the higher activities of dinuclear complexes. The differences of efficiency between **4** and **4'**, can be rationalized in terms of steric hindrance due to the proximity of the two Rh(COD) entities in the syn isomer.

The selectivity was also found to depend on the nature (mono- vs. bimetallic) of the catalyst. Indeed, homobinuclear compounds lead to similar product distribution, i.e., 85–88% and 12–15% of dehydrogenative silylation and hydrosilylation products, respectively. In contrast, the selectivity of the reaction in the presence of mononuclear complex **3** drops to 75%. However, these differences remain weak and hazardous to rationalize. Thus, the difference of activity provides direct evidence for the involvement of cooperative effect between both metal centers during the catalysis. Dehydrogenative silylation and hydrosilylation products result from two competitive catalytic cycles and electronic communication may have stabilized intermediaries, which may have not taken place with mononuclear complexes. Detailed mechanism remain to be clarified and in particular, the precise role of the electronic communication during the reaction. Further exploration in this direction is currently in progress.

Both syn isomers (complexes **4'** and **2'**) have higher reaction times compared with the *anti*-isomers (complexes **4**, **1**, and **2**). This difference can be explained due to steric hinderance, concealing rhodium with the secondary metallic fragment, hardening the

entry of the each analyzed substrates, whether the silane in an oxidative addition plus the coordination of styrene.

The remaining complexes, the *anti* isomers, all have identical behavior, if taken into consideration the fact that complex **4** has two rhodium centers that may equally react within the catalytic cycle, thus shortening the reaction time. A similar catalytic test with half the concentration of this catalyst (considering equivalents of rhodium instead), required 65 min for reaction time. This result may allow us to consider the behavior of all *s*-indacendiide catalysts similar, if not identical.

If the ^{103}Rh -NMR chemical shifts for mono- and bimetallic rhodium complexes (Table 7) are taken into consideration, these have similar bonding modes between all complexes to the five membered ring. This can imply that rhodium is not severely affected when changing the secondary metallic group to another, which can explain the catalytic results in Table 6, and their similarities.

Because of this, it is feasible to assume the existence of a cooperative effect in these heterobinuclear complexes in the form of a metallic fragment forcing rhodium to have a greater ring slippage, thus bonding closer to an allylic towards *s*-indacene, similar to the effect seen in literature [21,20,43] and also shown in Fig. 8. This reaction is surely favoring a $(\text{M})\eta^5:(\text{Rh})\eta^3$ configuration.

4. Conclusion

These studied catalytic systems shown a high selectivity to dehydrogenative silylation (DS) of olefins, particularly with styrene and tri(isopropyl)silane, at 80 °C. Only olefins with electron-acceptor groups seem suitable for these organometallic rhodium complexes, together with only trialkylsilanes. These results prove neutral rhodium complexes are equally effective (if not more) than other cationic species, unlike what has been previously reported. Also, each previously listed catalyst have turnover values over 2000 in each case, data which have not been reported for simple complexes, also indicative of the presence of a very active catalytic species.

Binuclear complexes showed the presence of a cooperative effect between both metallic centers, which is clearly evidenced when compared with complex **3**, possibly explained to the different bonding mode Rh has towards indacene once a secondary metallic fragment is bonded to the spacer ligand, regardless of the different behavior these present in ESR and cyclic voltammetry tools.

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