Rh(I)/(III)-N-Heterocyclic Carbene Complexes: Effect of Steric Confinement Upon Immobilization on Regio- and Stereoselectivity in the Hydrosilylation of Alkynes

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Abstract: Rh(I) NHC and Rh(III) Cp* NHC complexes (Cp*=pentamethylcyclopentadienyl, NHC= N-heterocyclic carbene = pyrid-2-ylimidazol-2-ylidine (Py–Im), thiophen-2-ylimidazol-2-ylidine) are presented. Selected catalysts were selectively immobilized inside the mesopores of SBA-15 with average pore diameters of 5.0 and 6.2 nm. Together with their homogenous progenitors, the immobilized catalysts were used in the hydrosilylation of terminal alkynes. For aromatic alkynes, both the neutral and cationic Rh(I) complexes showed excellent reactivity with exclusive formation of the β(E)-isomer. For aliphatic alkynes, however, selectivity of the Rh(I) complexes was low. By contrast, the neutral and cationic Rh(III) Cp* NHC complexes proved to be highly regio- and stereoselective catalysts, allowing for the formation of the thermodynamically less stable β-(Z)-vinylsilane isomers at room temperature. Notably, the SBA-15 immobilized Rh(I) catalysts, in which the pore walls provide an additional confinement, showed excellent β-(Z)-selectivity in the hydrosilylation of aliphatic alkynes, too. Also, in the case of 4-aminophenylacetylene, selective formation of the β(Z)-isomer was observed with a neutral SBA-15 supported Rh(III) Cp* NHC complex but not with its homogenous counterpart. These are the first examples of high β(Z)-selectivity in the hydrosilylation of alkynes by confinement generated upon immobilization inside mesoporous silica.

Introduction

Owing to the versatility, ease of handling, low toxicity, and reasonable stability relative to other vinyl-metal species, vinylsilanes are highly valuable building blocks in organic synthesis, polymer chemistry, and materials science.[1] The most straightforward and atom-economic approach to their synthesis is the transition metal-catalysed hydrosilylation of alkynes.[2] Predominantly Pt[3] and Rh-based catalysts[4] including nanoparticulate supported systems[5] have been used; however, alternative catalytic systems, for example based on ruthenium,[6] cobalt,[7] iron[8] or nickel[9] have been developed more recently. Generally, the hydrosilylation of terminal alkynes can yield different isomers (Figure 1). Thus, the reaction may proceed via anti-Markovnikov addition to afford the β(E)- and β-(Z)-vinylsilane stereoisomers (resulting from a syn- and anti-addition, respectively). Markovnikov addition results in the formation of the α-vinylsilane and the corresponding alkene, has been frequently observed for some catalysts. Consequently, the control of the

![Figure 1. Possible products of the hydrosilylation of terminal alkynes.](https://doi.org/10.1002/chem.202103099)
regio- and stereoselectivity along the H–Si addition process is a major issue.

Metal N-heterocyclic carbene (NHC) complexes have gained increasing importance in the hydrosilylation of alkynes. Co NHC complexes\(^{1a,2b}\) usually provide E/Z-mixtures of the anti-Markovnikov product, though in selected cases, high E-selectivity was observed.\(^{1b,3}\) In contrast, tailored Co bis(NHC) complexes and Co pincer complexes were reported to display high Markovnikov selectivity.\(^{1b,4}\) Detailed studies on Co(III) bis(NHC) complexes also revealed that bulky NHCs favour the formation of the anti-Markovnikov products in alkyne hydrosilylation.\(^{1c}\) Rh(I) NHC complexes provide high anti-Markovnikov selectivity in the hydrosilylation of alkenes.\(^{1a,5}\)

Despite the vast number of catalysts including Rh NHC complexes,\(^{1a,6}\) there is still need for the development of catalysts that allow for high stereo- and regioselectivity.\(^{1b,7}\,\,1c,7\) Also, while substantial efforts have been dedicated to the immobilization of organometallic catalysts over the last decades,\(^{1b,8}\,\,1c,9\,\,1d\) few studies on Rh-catalysed alkyn e hydrosilylations by supported catalysts with high regio- and stereoselectivity exist.\(^{1a,10}\) Indeed, reports on the hydrosilylation of alkynes with high β-(Z)-selectivity are scarce and so far required the use of cyclo-metalated Rh(III) Cp \(^*\) NHC complexes or complex heterogeneous hybrid analogues.\(^{1b,11}\)

We were interested in the question whether a specific environment provided by spatial confinement\(^{1b,12}\) inside porous silica supports allows for high β-(Z)-selectivity in the hydrosilylation of both aromatic and aliphatic 1-alkynes. To address this issue, both Rh(I) and Rh(III) catalysts containing N- or S-chelating NHCs were prepared and selectively immobilized inside the pores of mesoporous SBA-15. We used chelating NHCs since these usually display enhanced stability, the more if the bidentate ligand forms a five-membered metallacycle.

## Results and Discussion

The precursors 1-(pyrid-2-yl)-1H-imidazole and 1-(thienyl)-1H-imidazole were synthesized using a modified Ullman-type coupling reaction of imidazole with 2-bromopyridine and 2-bromo thiazole, respectively, employing dimethyl sulfoxide (DMSO) as solvent and K\(_2\)CO\(_3\) as base.\(^{1b,13}\) The imidazolium salts L\(_1\) and L\(_3\) were obtained by reaction of 3-iodopropyltrimethoxysilane with 1-pyridyl-1H-imidazole and 1-(thienyl)-1H-imidazole, respectively. The ligand L\(_2\) was prepared according to the literature.\(^{1b,14}\)

### Rh(I)-NHC complexes

The rhodium complexes Rh\(_1\) and Rh\(_2\) were synthesized by deprotonating the imidazolium salts L\(_1\) and L\(_2\) with LiHMDS, followed by the addition of half an equivalent of the rhodium dimer [Rh(COD)Cl]\(_2\) (Scheme 1).

Under these reaction conditions we were unable to prepare the Rh(I) analogue of ligand L\(_3\) containing a thiophene instead of a pyridine donor group. The imidazolium salt L\(_3\) was therefore reacted with Ag\(_2\)O in CH\(_2\)Cl\(_2\) at room temperature followed by the addition of [Rh(COD)Cl]\(_2\) to yield Rh\(_5\). Reaction of complexes Rh\(_1\) and Rh\(_2\) with 1 equiv. of AgBF\(_4\) in CH\(_2\)Cl\(_2\) at room temperature resulted in the precipitation of AgCl and the formation of yellow to orange solutions from which the cationic complexes Rh\(_3\) and Rh\(_4\) were isolated in 67 and 74% yield, respectively. Complexes Rh\(_1\)–Rh\(_5\) were stable as solids under atmospheric conditions and were obtained as yellow to orange-coloured solids after recrystallization from CH\(_2\)Cl\(_2\)/diethyl ether.

#### Scheme 1. Synthesis of Rh(I)–NHC complexes Rh\(_1\)–Rh\(_5\).

The ¹³C NMR spectra displayed one doublet signal for the NHC’s C\(_2\)-carbon in the range of 173–184 ppm (\(\delta\)\(_{\text{C}}\) = 52 Hz) for complexes Rh\(_1\)–Rh\(_7\), which is in the usual range for Rh(I)–NHC complexes.\(^{1b,15}\) In Rh\(_3\) and Rh\(_4\), the pyridine fragment of the hemilabile NHCs coordinates to the metal. This chelation of the rhodium center in Rh\(_3\) by the pyridine fragment was confirmed by single-crystal X-ray analysis (Figure 2).

Complex Rh\(_3\) (Figure 2) crystallizes in the triclinic space group P\(_\text{I}1\). The Rh centre experiences a slightly distorted square planar geometry defined by the coordination of the metal to the two olefinic bonds of the cyclooctadiene ligand, the carbon atom of the NHC ligand and the nitrogen lone pair of pyridine fragment. The bite angle of the pyridyl-NHC ligand (C\(_1\)–Rh–C\(_2\)) is ca. 78.6°. The C(NHC)=Rh and N–Rh bond lengths are 202.5 and 211.0 pm, respectively, and are inconspicuous.\(^{16}\) The Rh–C(COD) distances (Rh\(_1\)–C\(_1\) = 223.2(7) pm and Rh\(_1\)–C\(_6\) = 217.5(7) pm) trans to the NHC’s C\(_2\)-carbon are slightly longer than the corresponding distances (Rh\(_1\)–C\(_9\) = 214.9(5) pm and Rh\(_1\)–C\(_{10}\) = 214.6(7) pm) cis to the NHC, reflecting the trans influence of the NHC.
While the reaction of Rh with AgBF₄ did not result in the clean formation of the cationic BF₄⁻ complex, the reaction of both Rh₁ and Rh₅ with NaB(Ar)₃ yielded the cationic analogues Rh₆ and Rh₇ (Scheme 2), which were isolated as microcrystalline, orange-coloured solids in 72% and 78% yield respectively. The solid-state structure of Rh₇ displays a dimeric structure with the Rh metal of one unit coordinated by a thiophene moiety of the second unit. Complex Rh₇ (Figure 3) crystallizes in the triclinic space group P-1 with both the Rh atoms having a distorted square planar geometry. The metal to carbene distances C22-Rh2 and C1-Rh1 are 200.7 and 209.6 pm, respectively, and are in good agreement with similar reported complexes. A trans influence of the NHC on one of the double bonds of cyclooctadiene was observed in case of Rh₇; the propyltrimetoxysilyl side arm was strongly disordered.

**Rh(III)–NHC complexes**

As depicted in Scheme 3 and Scheme 4, reaction of the imidazolium salts L₁–L₃ with Ag₂O at room temperature yielded the desired Ag–NHC intermediates, which upon in situ transmetalation with half an equivalent of [Rh(Cp*)Cl₆] yielded complexes Rh₈, Rh₉ and Rh₁₂. In case of the 1-mesityl-2-ylimidazolium-pyridine salt, reaction with [Rh(Cp*)Cl₆] produced a mixture of monodentate and bidentate complexes. Rh₉ was obtained in pure form after purification by column chromatography. However, isolation of Rh₈ proved to be extremely difficult and all attempts to synthesize the cationic analogue Rh₁₀ in situ was also not fruitful. Hence, complexes Rh₁₀ and Rh₁₁ were synthesized alternatively from the silver intermediates as shown in Scheme 3. Moreover, as depicted in Scheme 4, Rh₁₂ was also prepared via transmetalation from L₃ and [Rh(Cp*)Cl₆]₂ in good yields (68%). Notably, we were also
able to synthesize the cationic analogue \textit{Rh13} by reacting \textit{Rh12} with AgBF$_4$. Complexes \textit{Rh9–Rh13} were obtained as yellow-orange solids after recrystallization from a mixture of CH$_2$Cl$_2$ and diethyl ether. The carbon atoms bound to the Rh metal centres in \textit{Rh9–Rh13}, that is, the carbene and Cp* carbon atoms, exhibit a Rh–C coupling with coupling constants in the range of 51–58 and 7 Hz, respectively.

The molecular structure of \textit{Rh9} was confirmed by single-crystal X-ray analyses (Figure 4). \textit{Rh9} synthesized from ligand \textit{L2} was clean but, unfortunately, we could not obtain crystals suitable for X-ray analysis. However, when ligand \textit{L2} containing a chloride anion was replaced by one containing a bromide anion, the complex could be crystallized; nonetheless, the molecular structure featured a mixed set of halo ligands, with ~25% of the chloro positions occupied by bromo ligands. In the solid state, the rhodium is coordinated both to the NHC’s C$_2$ and carbon and the pyridine nitrogen. It adopts a three-legged piano-stool-type geometry as observed for other half-sandwich complexes. Complex \textit{Rh9} (Figure 3) crystallizes in the triclinic space group $P-1$ with distorted octahedral geometry at the metal centre. The bite angle of the pyridyl-NHC ligand is ca. 77.3° (C1–Rh–N3). The C1(NHC)–Rh and N–Rh bond lengths are 204.0 and 211.8 pm, respectively, which is in line with other complexes.

The molecular structure of \textit{Rh13} (Figure 5) displays a typical three-legged piano stool geometry with the rhodium metal centre coordinated by the cyclopentadienyl, monodentate NHC and bridging chlorine atom. The Rh–C$_{carbene}$ distances (206.0 pm) again lie in the typical range. As shown in the Figure 5, the two rhodium centers are connected by the bridging chlоро ligands. Complex \textit{Rh13} crystallizes in a triclinic crystal system in the space group $P-1$ with both the metal centres adopting the distorted octahedral geometry. The BF$_4$ anions and the propyl trimethoxysilyl sidearm were strongly disordered.

### Hydrosilylation of terminal alkynes

First, the Rh(I) NHC complexes \textit{Rh1–Rh5} were used as catalysts in the hydrosilylation of phenylacetylene and 1-octyne using HSiMe$_2$Ph and triethylsilane as silanes (Scheme 5, Figure S1, Table S1, Supporting Information). Reactions were conducted in CDCl$_3$ at 60°C with a standard catalyst loading of 1 mol% and...
monitored by $^1$H NMR and GC-MS using t-butylbenzene and n-dodecane, respectively, as internal standards. With all complexes, conversions ranged from 82–100%. Using phenylacetylene, a clear preference for the thermodynamically more stable $\beta$($E$)-isomer in the range of 40–100% was observed (Figure S1, Supporting Information). In addition, particularly the use of Rh2–Rh5 resulted in the formation of significant amounts of the $\beta$($E$) and $\alpha$-isomer. Using 1-octyne and HSiMe$_3$Ph, $\beta$($E$) selectivity was reduced, too, yielding substantial amounts of the $\beta$($Z$), along with minor amounts ($\leq 5\%$) of the anti-Markovnikov product ($\alpha$-isomer) owing to the increased bulkiness of the silane partner. Follow-up of the reaction of phenyl acetylene and HSiMe$_3$Ph in CDCl$_3$ by $^1$H NMR displayed only the formation of the $\beta$($E$)-isomer during the reaction, which rules out the formation of $\beta$($Z$)-isomer as an intermediate. Notably, for all complexes except for Rh4, no polymerization or dehydrogenative silylation was observed. However, hydroisilylation of 1-octyne with HSiMe$_3$Ph catalysed by Rh6 and Rh7 (Table 1, entries 9 and 10) displayed a similar selectivity in line with Rh3 but reaction times were quite extended (5 h and 8 h respectively). Moreover, terminal alkynes bearing hydroxy, chloro, methyl and methoxy groups were tolerated (Table 1, entries 14, 15, 18 and 20) when the reactions were performed with Rh1.

In contrast to the Rh(I) NHC complexes, the hydroisilylation reactions with Rh(III) Cp* NHC complexes could be performed at room temperature. Catalysts Rh9–Rh13 (Table 2) were highly active yielding exclusively the corresponding $\beta$($Z$)-isomers as observed for other Rh(III) complexes [18b] with full conversion to the desired products. However, Rh9 and Rh12 were found to be the slightly superior among the series. Rh12 was therefore also tested for other substrates. The set of aromatic alkynes that undergo Rh-catalysed $Z$-selective hydroisilylation is shown in Scheme 6. In general, a wide range of ethynylarenes containing electronically and sterically different aryl groups reacted smoothly in the presence of 1 mol% of Rh12 and HSiMe$_3$Ph at room temperature, affording the corresponding $Z$-vinylsilanes with complete conversion and excellent stereoselectivities ($Z$/$E = 89:11$) to $>99:1$). This $Z$-selective hydroisilylation showed good functional group tolerance for a wide range of reactive groups including ether, trifluoromethyl, halogen, unprotected hydroxy, unprotected primary aniline and NMe$_2$ moieties, which were all compatible with the reaction conditions. The conversion vs. time profiles for the hydroisilylation of the aromatic alkynes were all similar except for 4-aminophenylacetylene, which reacted much slower, yet reaching 99% conversion after 3 h (Figure S7, Supporting Information).

In addition, bulky t-butylacetylene was also tested for the hydroisilylation; the reaction yielded 89% of the $\beta$($Z$)-isomer. An attempt to reduce the catalyst loading to 0.1 mol% led to increased reaction times of up to 2 h to reach full conversion, yet without any effect on the selectivity.

Notably, the current catalytic system was also successfully applied to the hydroisilylation of internal alkynes. Thus, hydroisilylation of 3-hexyne with HSiMe$_3$Ph in the presence of Rh12 furnished a 1:1 mixture of the $E$ and $Z$ isomer.

While Rh13 is dimeric in the solid state, the active catalyst must be expected to be monomeric to fulfil the 18-electron rule. With Rh9, similar conversions and selectivities were observed in case triethyilsilane instead of dimethylphenylsilane was used in hydroisilylation (Figure S8–S11, Supporting Information).

**Table 1.** Hydroisilylation of terminal alkynes catalysed by the Rh(I) NHC complexes Rh1–Rh7.

| # | Substrate          | Catalyst, time$^a$ | Conv. [%] | $\beta$($Z$) [%] | $\beta$($E$) [%] | $\alpha$ [%] |
|---|--------------------|---------------------|-----------|-----------------|-----------------|-------------|
| 1 | 1-Hexyne, 2 h      | Rh1, 2 h            | 100       | 45              | 55              | –           |
| 2 | 1-Octyne, 2 h      | Rh3, 3 h            | 100       | 43              | 52              | 5           |
| 3 | 1-Octyne, 5 h      | Rh5, 3 h            | 96        | 67              | 27              | 6           |
| 4 | 2-Octyne, 2 h      | Rh1, 2 h            | 100       | 28              | 72              | –           |
| 5 | 2-Octyne, 2 h      | Rh2, 2 h            | 100       | 63              | 36              | 1           |
| 6 | 3-Octyne, 2 h      | Rh3, 2 h            | 100       | 38              | 58              | 4           |
| 7 | 4-Octyne, 2 h      | Rh4, 2 h            | 100       | 57              | 39              | 4           |
| 8 | 4-Octyne, 5 h      | Rh5, 3 h            | 90        | 67              | 28              | 5           |
| 9 | 5-Octyne, 5 h      | Rh6, 5 h            | 100       | 58              | 22              | 20          |
| 10| 7-Octyne, 5 h      | Rh7, 5 h            | 86        | 53              | 29              | 18          |
| 11| 1-Nonyne, 2 h      | Rh1, 2 h            | 100       | 43              | 57              | –           |
| 12| 1-Nonyne, 2 h      | Rh3, 2 h            | 100       | 60              | 31              | 9           |
| 13| 1-Nonyne, 3 h      | Rh5, 3 h            | 82        | 62              | 32              | 6           |

[a] Unless noted otherwise, all the reactions were performed employing 1.0 equiv. of alkyn, 1.5 equiv. of dimethylphenylsilane, 1 mol% of Rh catalyst, 0.5 mL of CDCl$_3$ at 60°C. [b] Triethyilsilane was used at 60°C.

**Table 2.** Hydroisilylation of terminal alkynes catalysed by the Rh(III) Cp* NHC complexes Rh9–Rh13.

| #  | Alkyne     | Catalyst, time$^a$ | Conv. (%) | $\beta$($Z$) [%] | $\beta$($E$) [%] | $\alpha$ [%] |
|----|------------|---------------------|-----------|-----------------|-----------------|-------------|
| 1  | 1-Hexyne   | Rh9, 30 min         | 98        | >99             | <1              | –           |
| 2  | 1-Hexyne   | Rh10, 2 h           | 100       | 99              | 1               | –           |
| 3  | 1-Hexyne   | Rh11, 2 h           | 92        | 95              | 5               | –           |
| 4  | 12-Octyne  | Rh12, 10 min        | >99       | 100             | 99              | 1           |
| 5  | 13-Octyne  | Rh13, 40 min        | >99       | 100             | 99              | 1           |

[a] Unless noted otherwise, all the reactions were performed employing 1.0 equiv. of alkyn, 1.5 equiv. of dimethylphenylsilane, 1 mol% of Rh catalyst, 0.5 mL of CDCl$_3$ at 25°C. [b] Reactions were performed at 60°C.

Immobilization of Rh(I) NHC and Rh(III) Cp* NHC catalysts on mesoporous SBA-15

Two different SBA-15 materials with defined average pore diameters of 5.0 and 6.2 nm, respectively, referred to as SBA-15$_{5.0}$nm and SBA-15$_{6.2}$nm were used for the immobilization of Rh1, Rh3, Rh5, Rh12 and Rh13 using the trimethoxysilyl moiety (Scheme 7).
A recently published synthetic protocol that allows for the selective immobilization inside but not outside the pores was used. The Rh content, determined by ICP-OES, was 9.7, 18.6, 2.9 and 16.4 μmol/g for Rh1@SBA-15 5.0 nm, Rh1@SBA-15 6.2 nm and Rh3@SBA-15 5.0 nm and Rh3@SBA-15 6.2 nm respectively. For Rh5@SBA-15 6.2 nm, Rh12@SBA-15 6.2 nm and Rh13@SBA-15 6.2 nm a loading of 3.6, 8.9 and 5.6 μmol/g was determined. For comparison, we also immobilized Rh1 on unmodified SBA-15 6.2 nm labelled as Rh1@SBA-15* 6.2 nm. ICP-OES measurements revealed a high Rh-loading of 204.1 μmol/g, due to the immobilization of Rh1 both inside and outside the mesopores of silica. Rh K-edge EXAFS analysis of Rh3@SBA-15 6.2 nm was conducted to confirm that the catalyst remains intact upon immobilization on SBA-15. The experimental spectra and the fit results are shown in Figure 6; structural parameters are summarized in Table 3. Six atoms are found in the first coordination shell, three at a distance of 2.06 Å and three at 2.20 Å. Both values are in the range of Rh–C and Rh–N bond distances, and in agreement with the crystal structure. As EXAFS cannot distinguish between light ligands, the type of atoms remains unknown, while the description of scattering paths in Table 3 refers to the parent catalyst Rh3. The differences in bond lengths in the first coordination shell did not
Hydrosilylation reactions and confinement effects

After the selective immobilization\(^{[24]}\) of both Rh(I) and Rh(III) NHC complexes inside the mesopores of silica, the supported catalysts were used in the hydrosilylation of terminal alkynes; results were compared to those obtained with the corresponding homogeneous catalysts. In contrast to their homogeneous counterparts, the heterogeneous catalysts Rh1@SBA-15\(_{6.2\, \text{nm}}\), Rh3@SBA-15\(_{6.2\, \text{nm}}\) and Rh5@SBA-15\(_{6.2\, \text{nm}}\) yielded predominantly the \(\beta\)(Z)-isomer (up to 97\%, Table 4). Notably, the rhodium catalysts Rh1, Rh3 and Rh5 supported on modified SBA-15\(_{6.2\, \text{nm}}\) material showed much better \(\beta\)(Z) selectivity (Figure S12, Supporting Information) in the hydrosilylation reaction than the non-modified silica-supported analogue Rh1@SBA-15*\(_{6.2\, \text{nm}}\) (Table 4, entries 2, 7 and 13). This clearly points to a (steric) confinement effect of the mesopores onto the rhodium catalysts immobilized therein: the exclusive binding of both Rh1 and Rh3 inside the mesopores of SBA-15\(_{6.2\, \text{nm}}\) allows for high \(\beta\)(Z)-selectivity while catalysts supported outside the pores lack the necessary steric environment and cannot provide the same selectivity. Similarly, Rh5 immobilized on modified SBA-15\(_{6.2\, \text{nm}}\) showed high \(\beta\)(Z) selectivity with aliphatic alkynes, too (Table 4, entries 9 and 15). However, diffusion constraints of the substrates inside the SBA-15 pores limit activity, leading to longer reaction times.

On the expected lines, Rh1@SBA-15\(_{6.0\, \text{nm}}\) and Rh3@SBA-15\(_{6.0\, \text{nm}}\) (Table 4, entries 3 and 5) also showed excellent \(\beta\)(Z)-selectivity up to 95\% with aliphatic but not for aromatic alkynes (Table 4, entries 19, 22 and 25). Notably, the observed confinement effect was also observed in presence of functional groups such as chlorine and hydroxyl groups (Table 4, entries 16 and 17). In addition, a confinement effect could even be observed in the hydrosilylation of 4-aminophenylacetylene under the action of a supported Rh(III) Cp\(^+\) NHC catalyst. While homogeneous supports inside the SBA-15 pores limit activity, leading to longer reaction times. 

\[ \text{Rh(CO)}(\text{PhCN})_2\text{Ph} \equiv \text{Rh(CO)}(\text{PhCN})_2\text{Ph} + \text{H}_2 \]

### Table 3. EXAFS fitting results for Rh3@SBA-15\(_{6.2\, \text{nm}}\), including refined coordination numbers (N), Debye-Waller factors (\(\sigma^2\)) crystal structure bond lengths (\(R_{\text{r,cryst}}\)), refined bond lengths (\(R + \Delta R\)) and relative change of bond lengths upon EXAFS refinement.

| Path | N | \(\sigma^2\)/Å\(^2\) | \(R_{\text{r,cryst}}$/Å | \(R + \Delta R$/Å | \(R + \Delta R/R_{\text{r,cryst}}$/% |
|------|---|-------------------|------------------|-----------------|-----------------|
| Rh-C | 3.1(1) | 0.0041(12) | 2.025 | 2.061(9) | 102 |
| Rh-N | 3.4(1) | 0.0044(13) | 2.110 | 2.198(10) | 102 |
| Rh-C | 0.8(2) | 0.0035(19) | 2.157 | 2.491(26) | 118 |
| Rh-N | 1.0(4) | 0.0074(26) | 2.861 | 2.780(32) | 97 |
| Rh-C | 1.5(3) | 0.0062(18) | 3.003 | 2.917(26) | 97 |
| Rh-C | 1.8(4) | 0.0064(19) | 3.119 | 3.074(32) | 99 |
| Rh-C | 3.9(8) | 0.0083(27) | 3.312 | 3.760(23) | 114 |
| Rh-N | 8.4(1.6) | 0.0198(64) | 4.258 | 4.590(29) | 108 |

### Table 4. Hydrosilylation of terminal alkynes catalysed by the SBA-15 supported Rh(I) NHC and Rh(III) Cp\(^+\) NHC complexes Rh1@SBA-15\(_{6.2\, \text{nm}}\), Rh3@SBA-15\(_{6.2\, \text{nm}}\), Rh5@SBA-15\(_{6.2\, \text{nm}}\) and Rh12@SBA-15\(_{6.2\, \text{nm}}\). 

| # | Substrate | Rh@SBA-15\(_{6.2\, \text{nm}}\) time\(^{[a]}\) | Conv. (%) | \(\beta\)(Z) [%] | \(\beta\)(E) [%] | \(\alpha\) [%] |
|---|-----------|-----------------|------------|-----------------|-----------------|------------|
| 1 | 1-Hexyne | Rh1@SBA-15, 4 h | 95 | 95 | 3 | 2 |
| 2 | 1-Hexyne | Rh1@SBA-15*, 12 h | 90 | 72 | 28 | - |
| 3\(^{[b]}\) | 1-Hexyne | Rh1@SBA-15, 48 h | 94 | 95 | 3 | 2 |
| 4 | 1-Hexyne | Rh3@SBA-15, 32 h | 95 | 93 | 7 | - |
| 5\(^{[b]}\) | 1-Hexyne | Rh3@SBA-15, 48 h | 90 | 92 | 6 | 2 |
| 6 | 1-Octyne | Rh1@SBA-15, 40 h | 95 | 92 | 5 | 3 |
| 7 | 1-Hexyne | Rh1@SBA-15*, 12 h | 90 | 77 | 20 | 3 |
| 8 | 1-Hexyne | Rh3@SBA-15, 32 h | 100 | 93 | 5 | 2 |
| 9 | Rh5@SBA-15, 26 h | 63 | 90 | 9 | 1 |
| 10 | Rh1@SBA-15*, 4 h | 97 | 99 | 1 | - |
| 11 | Rh1@SBA-15, 4 h | 47 | 99 | 1 | - |
| 12 | 1-Nonyne | Rh1@SBA-15, 40 h | 95 | 97 | 3 | - |
| 13 | 1-Nonyne | Rh1@SBA-15*, 24 h | 97 | 96 | 3 | 2 |
| 14 | 1-Hexyne | Rh3@SBA-15, 32 h | 95 | 92 | 6 | 2 |
| 15 | Rh5@SBA-15, 26 h | 90 | 87 | 10 | 3 |
| 16 | Rh1@SBA-15, 24 h | 97 | 90 | 10 | - |
| 17 | 3-Hexyne | Rh1@SBA-15, 24 h | 35 | 77 | 23 | - |
| 18 | Rh1@SBA-15, 4 h | > 99 | 2 | 98 | - |
| 19\(^{[c]}\) | Rh1@SBA-15, 48 h | 60 | 18 | 73 | 9 |
| 20 | Rh1@SBA-15, 3 h | 94 | 100 | - | - |
| 21 | Rh1@SBA-15, 48 h | 69 | 100 | - | - |
| 22\(^{[c]}\) | Rh1@SBA-15, 3 h | 54 | 14 | 75 | 11 |
| 23 | Rh1@SBA-15, 3 h | > 99 | 1 | 99 | - |
| 24 | Rh1@SBA-15, 4 h | 60 | 99 | 1 | - |
| 25\(^{[c]}\) | Rh1@SBA-15, 48 h | 57 | 9 | 85 | 6 |
| 26 | Rh1@SBA-15, 3 h | > 99 | 99 | 1 | - |
| 27 | Rh1@SBA-15, 48 h | 78 | 100 | 1 | - |
| 28 | Rh1@SBA-15, 4 h | 93 | 100 | - | - |
| 29 | Rh1@SBA-15, 4 h | 58 | 100 | - | - |

[a] Unless noted otherwise, all the reactions were performed employing 1.0 equiv. of alkyne, 1.5 equiv. of dimethylphenylsilane, 0.5 mol% of Rh catalyst, 0.5 mL of CDCl\(_3\), at 60 °C. SBA-15\(_{6.2\, \text{nm}}\) was used throughout. [b] SBA-15\(_{6.0\, \text{nm}}\) was employed. [c] 1.5 equiv. of triethylsilane was employed.
Rh12 delivered only 85% β(Z) selectivity (Scheme 2), the heterogenous catalyst Rh12@SBA-15_{6.2 nm} again yielded exclusively the β(Z) isomer (Table 2, entry 29). Overall, β(Z) selectivity exceeded the one previously reported supported [Rh_{12}(CO)_{24}] clusters by far.\(^{[26]}\)

**Time-dependent selectivity**

Notably, neither Rh12, nor Rh12@SBA-15_{6.2 nm}, showed any β(Z) to β(E) isomerization, neither for phenylacetylene nor for 1-octyne within reasonable times after the complete consumption of the alkyne. The monitoring of hydrosilylation of phenylacetylene with HSiMePh at 298 K showed that the reaction was completed within 10 min and 40 min for Rh12 and Rh12@SBA-15_{6.2 nm}, respectively, yielding exclusively the β(Z) isomer (Figure S13, Supporting Information). Similar was observed for aliphatic alkynes; again, no noticeable β(Z) to β(E) isomerization was observed as shown for 1-octyne (Figure S14, Supporting Information). By contrast, in the reaction of 4-ethynylanisole with HSiMePh, β(Z) to β(E) isomerization was observed, though only after prolonged reaction times (Figure S15–S17, Supporting Information).

**Mechanism**

Based on the above-observed results and earlier reports on the modified Chalk-Harrod mechanism,\(^{[8a]}\) a plausible mechanism for regioselectivity that accounts for the observed formation of all the three isomers catalysed by Rh(I) NHC complexes is depicted in Scheme 8. Initial rhodium hydride formation is followed by alkyne coordination. Insertion of the alkyne into the Rh–Si bond yields the (Z)-silylvinyldiene intermediate and, subsequently, the E-vinylsilane. However, the (Z)-silylvinyldiene intermediate can isomerize to the thermodynamically favourable (E)-silylvinyldiene owing to the steric repulsion between the substituents at the rhodium centre and the silyl group. At this point, the steric confinement, whether provided by the Cp^* and NHC ligand in the Rh(III) complexes or by the pore wall in case of the supported Rh(I) complexes, becomes effective. Particularly, the increased β(Z)-selectivity of the supported catalysts in comparison to their homogenous counterparts is attributed to an enhanced steric congestion inside the mesopores in which the pore wall exerts additional steric stress on the metal centre.

**Recyclability and leaching**

To demonstrate the sustainability of the catalytic system, five consecutive hydrosilylation reactions of 1-octyne with dimethylphenylsilane were carried out using the same batch of an immobilized Rh-NHC catalyst, i.e., Rh12@SBA-15_{6.2 nm}. At the end of each run, the silica-bound catalyst was recovered by simple filtration, washed repeatedly with chloroform, dried in vacuo, and reused in the next reaction. Gratifyingly, the catalytic performance of Rh12@SBA-15_{6.2 nm} remained constant over the course of the experiments, with no detrimental effect on selectivity and reactivity (Figure S18, Supporting Information). Noteworthy, recycling of the catalyst neither required purification nor any reactivation steps. Leaching of the catalyst was also tested by a hot filtration test (80 °C) under similar reaction conditions. The reaction mixture was filtered through celite, and the filtrate was analysed by ICP-OES. ICP analysis demonstrated no rhodium leaching.

**Conclusions**

β(Z)-Selectivity in the hydrosilylation of 1-alkynes is strongly governed by steric effects at the metal centre. Such confinement can to some extent be generated with Rh(III) complexes bearing a chelating N-heterocyclic carbene (NHC) in combination with bulky silanes. However, only Rh(III) pentamethycyclopentadienyl complexes containing a chelating NHC provide sufficient steric confinement and allow for high β(Z)-selectivity, both with aromatic and aliphatic alkynes. Alternatively, artificial confinement generated by the immobilization of Rh(I) NHC complexes in mesoporous supports allows for high β(Z)-selectivity, too. In selected cases, the high β(Z)-selectivity of Rh(III) Cp^* NHC complexes can also be further increased by immobilization inside mesoporous SBA-15.

**Experimental Section**

Deposition Number(s) 2082933 (Rh3), 2103708 (Rh7) 2082934 (Rh9) and 2086994 (Rh13) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Experimental procedures and spectral data for all the new complexes are available in the Supporting information.
Conflict of Interest

The authors declare no conflict of interest.

Keywords: alkenes · hydrosilylation · N-Heterocyclic carbones · rhodium · steric confinement

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Conflict of Interest

The authors declare no conflict of interest.
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