Steric Effects in the Catalytic Tandem Isomerization-Hydrosilylation Reaction

Unai Prieto,[a] Susan Azpeitia,[a] Eider San Sebastian,[a] Zoraida Freixa,[a][b] María A. Garralda[a] and Miguel A. Huertos*[a][b]

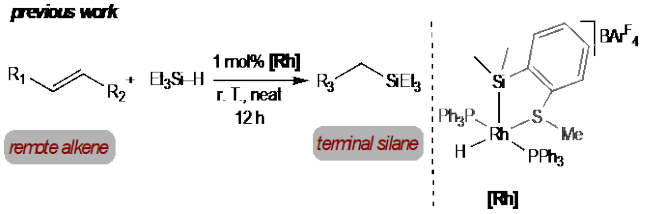
Abstract: The selective synthesis of linear silanes from remote alkenes is reported. Four new silane-thioether bidentate pro-ligands [$SiMe_2H(o\text{-}C_6H_4SR)$] (R = iBu, pentyl, benzyl, neopentyl) have been synthetized and used to form unsaturated and cationic 16 electron hydrido-silyl-Rh(III) complexes. These compounds are efficient catalysts for a tandem catalytic alkene isomerization-hydrosilylation reaction at room temperature under solvent-free conditions. The different size of the substituent on the sulphur atom results on a difference in the activity of this tandem reaction. Experimental observations demonstrate that the isomerization process is the rate-determining step of this catalytic transformation. This process would be of value to the chemical industry, because mixtures of internal aliphatic olefins are substantially cheaper and more readily available than the pure terminal isomers.

Introduction

Hydrosilylation represents one of the most important reactions in the silicon chemistry, and is extensively employed in industry to produce silicone polymers, useful as lubricants, water repellent coatings or resins.[1-3] It has also proved to be an efficient method for the formation of new organosilicon compounds, which can be used in fine chemical synthesis, as they participate in several important organic transformations.[4-5] The selectivity in the synthesis of linear alkylsilanes improved markedly in 1957 by using the transition metal compound $[H_2PtCl_6]\cdot H_2O$ (Speier's catalyst) as catalyst.[6, 7] The development of the platinum(0) $Pt_2[(Me_2SiCH{=}CH_2)_2O]_3$ compound, which is known as Karstedt's catalyst[8] in 1973 led to an important step forward in transition metal homogeneus catalysis. The aforementioned platinum based complexes have prevailed as the most employed catalysts in industry for decades due to their stability and high activity. The demand for cheaper catalysts has recently encouraged the study of first row transition-metal catalysts as a more accessible and sustainable replacement.[9-17] However, unwanted side reactions and the requirement of high temperatures are significant drawbacks for these systems.[18] Some recent reports show that by using iron catalysts some of these problems can be solved.[19-21] One important challenge for catalytic systems in alkene hydrosilylation is the formation of terminal silylated products from internal olefins or olefin mixtures.[22] The importance of this reaction is that internal olefin mixtures are more readily accessible and cheaper than pure terminal alkenes. For most common catalysts, the use of a terminal olefin is necessary to obtain a terminal silylated product. Therefore, final conversion of the substrate is reduced whenever there is concomitant α-olefin isomerisation. This limitation could be solved by a catalyst capable of tandem isomerisation-hydrosilylation of an internal alkene in which the previous isomerisation from internal to terminal olefins and subsequent α-olefin hydrosilylation is promoted by the same metal complex. Examples of efficient tandem isomerization-hydrosilylation of internal alkenes catalysed by transition metals such as cobalt,[23-25] nickel,[26,27] iron, [28] rhodium[29] or ruthenium,[29] or even metal nanoparticles[30, 31] have recently been reported. In most of these cases, large metal loadings or dual catalyst systems were necessary to achieve good results. Moreover, the hydrosilylation of remote internal olefins require in most cases additives or harder reaction conditions. In 1970, Chalk reported the slow isomerisation and subsequent hydrosilylation of cis-2-pentene by Wilkinson's catalyst, to give the linear pentylsilane in a low conversion (20 %).[32] In this context, Chalk and Harrod[33] proposed the formation of a rhodium(III) hydrido-silyl complex by oxidative addition of the silane to the catalyst. This silyl-hydride intermediate would be responsible for the isomerisation of the cis-2-pentene to 1-pentene, enabling the subsequent hydrosilylation of the terminal species to the pentylsilane product. We thought of interest to undergo the synthesis of this type of complexes to evaluate their behaviour as catalysts in the hydrosilylation of olefins with tertiary silanes.[34, 35] We have recently reported on a rhodium silyl complex containing a Si,S-chelating ligand, $[Rh(H)\{SiMe_2(o\text{-}C_6H_4SMe)\}(PPh_3)_2][BAr^F{}_4]$, as being a very efficient catalyst for tandem isomerization-hydrosilylation from internal alkenes to linear silanes under mild reaction conditions (Scheme 1).[34] These results prompted us to synthesize Si,S ligands with different substituents on the sulphur atom and evaluate the influence of the steric effects in the catalytic reactivity.

[a] U. Prieto, Dr. S. Azpeitia, Dr. E. San Sebastián, Prof. Dr. M. A. Garralda, Prof. Dr. Z. Freixa, Dr. M. A. Huertos
Department of Applied Chemistry
Faculty of Chemistry at San Sebastian
University of Basque Country
Pº Manuel Lardiazábal 3, 20018, San Sebastián
E-mail: migualangel.huertos@ehu.es

[b] Prof. Dr. Z. Freixa, Dr. M. A. Huertos
IKERBASQUE, Basque Foundation of Science
Bilbao

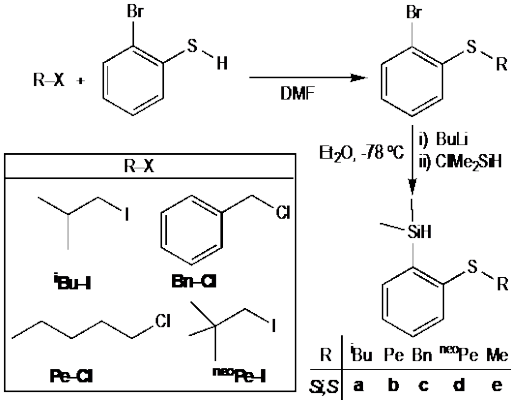


Scheme 1. Tandem isomerization-hydrosilylation reaction of a remote alkene catalysed by a previously reported silyl-thioether-Rh(III) compound.[34]

Results and Discussion

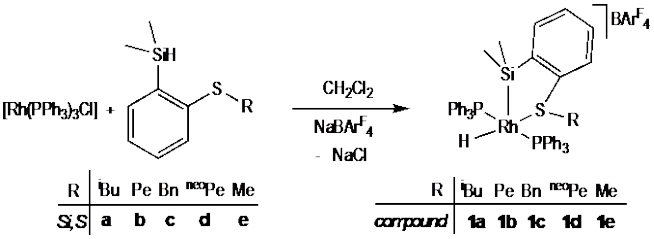
Synthesis of new silyl-thioether-Rh(III) compounds.

Silane-thioether bidentate pro-ligands [$SiMe_2H$(*o*-C_6H_4SR)] (R = ^{i}Bu, pentyl, benzyl, neopentyl, **a**-**d**) containing different substituents on the sulphur atom were synthesized following synthetic procedures analogue to the one already described for the methylated derivative **d** (Scheme 2).[36] These compounds and their precursors were characterized by $^{13}C\{^1H\}$ and ^1H NMR spectroscopy (see Experimental Section and Sup. Info.). As expected, the ^1H NMR spectra show similar signals in the aromatic region, a septuplet around 4.6 ppm (due to Me_2Si–H proton), and the characteristic signals of the corresponding substituent (**a**, ^{i}Bu; **b**, pentyl; **c**, benzyl; **d**, neopentyl).



Scheme 2. Synthesis of silane-thioether pro-ligands.

Pre-ligands **a**-**d** were used for the synthesis of the corresponding Rh(III) complexes [Rh(H){$SiMe_2$(o-C_6H_4SR)}(PPh_3)$_2$][BAr^F_4] (R = ^{i}Bu, **1a**; Pe, **1b**; Bn, **1c**; ^{neo}Pe, **1d**) following the synthetic methodology described for the methylated derivative **1d** (Scheme 3).[32] Compounds **1a**-**1d** were characterized in solution by NMR spectroscopy and ESI-MS (see Sup. Info.). They all showed in the ^1H NMR spectrum a doublet of triplets at -9.8 {J_{Rh-H} = 23 Hz, J_{P-H} = 13 Hz} ppm assigned to the rhodium hydride, originated from the oxidative addition of the hydrosilane to the metal center. The signal is split by the metal center and two equivalent phosphorus. The equivalence of both phosphines in solution is confirmed by the presence of a doublet in the $^{31}P\{^1H\}$ NMR spectra at 42.5 {J_{Rh-P} = 118 Hz} ppm. All the spectroscopic data were consistent with square-pyramidal structures, with the strong σ-donor silyl fragment *trans* to the vacant octahedral site, as proposed in Scheme 3. Their composition was confirmed by ESI-MS analyses.



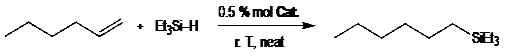
Scheme 3. Synthesis of cationic and unsaturated hydrido-silyl-thioether-Rh(III) complexes (**1a-e**).

Catalytic hydrosilylation of alkenes.

Initially, catalytic experiments were run using 1-hexene as substrate, to study the activity and selectivity of catalysts **1a**-**e** in the hydrosilylation of a terminal alkene in neat with Et_3SiH, using 0.5 mol% of catalyst loading.

The formation of hexyltriethylsilane was estimated by ^1H NMR spectroscopy after 30 and 60 minutes of reaction (Table 1). Analysis of the ^1H NMR spectra of the reaction mixtures showed, in all the examples, a complete anti-Markovnikov selectivity in the hydrosilylated product. Additionally, catalytic systems **1a** and **1d** outperform in terms of activity, showing a nearly complete conversion after 60 min (79% conversion for **1a** and 73 % for **1d** were observed at 30 min).

Table 1. Hydrosilylation of 1-hexene with Et_3SiH using catalysts **1a**-**1e** at different reaction times.



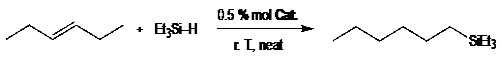
Entry[a]	Cat.	Time (min)	Yield (Select.)[b]
1	**1a**	15	55% (>99)
2	**1a**	30	79% (>99)
3	**1a**	60	96% (>99)
4	**1b**	30	66% (>99)
5	**1b**	60	84% (>99)
6	**1c**	30	61% (>99)
7	**1c**	60	74% (>99)
8	**1d**	30	73% (>99)
9	**1d**	60	90% (>99)
10	**1e**	15	47% (>99)
11	**1e**	30	64% (>99)
12	**1e**	60	78% (>99)

[a] Reaction conditions: alkene (0.25 mmol), Et_3SiH (0.25 mmol), catalyst 0.5 mol%, solvent-free, at room temperature. [b] Yields and selectivities calculated based on ^1H NMR ($CDCl_3$) analysis using dichloroethane as internal standard.

1b, **1c** and **1e** complexes also resulted active in the anti-Markovnikov hydrosilylation of 1-hexene. However, as shown in entries 4-7 and 10-12 of table 1, these precatalysts are less effective than **1a** and **1d**.

Next, the catalytic activity of complexes (**1a-1e**) was studied on a more challenging substrate, *trans*-3-hexene. The only silylated product formed in these reactions is hexyltriethylsilane. As with the substrate 1-hexene, compounds **1a** and **1d** result more active catalysts in the tandem isomerization-hydrosilylation reaction than **1b**, **1c** and **1e**. All these results are shown in Table 2.

Table 2. Hydrosilylation of *trans*-3-hexene with Et_3SiH using catalysts **1a-1d** at different reaction times.



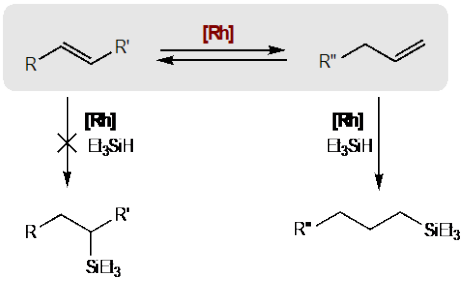
Entry[a]	Cat.	Time (min)	Yield (Select.)[b]
1	**1a**	60	75% (>99)
2	**1a**	120	93% (>99)
3	**1b**	60	35% (>99)
4	**1b**	120	68% (>99)
5	**1c**	60	34% (>99)
6	**1c**	120	51% (>99)
7	**1d**	60	67% (>99)
8	**1d**	120	84% (>99)
7	**1e**	60	39% (>99)
8	**1e**	120	71% (>99)

[a] Reaction conditions: alkene (0.25 mmol), Et_3SiH (0.25 mmol) with 0.5 mol % of catalyst, solvent-free, at room temperature. [b] Yields and selectivities determined by ^1H NMR ($CDCl_3$) by silane remaining using dichloroethane as internal standard.

Plausible explanation of the catalytic activity considering the steric effects.

Catalytic tandem isomerization-hydrosilylation is effective only if the same catalyst is active in both reactions. Moreover, the catalyst should be ineffective in the direct hydrosilylation of internal alkenes leading to branched alkyl-silanes (Scheme 4).

Taking into account the structure of our precatalysts, 16e hydride-Rh(III) complexes, a reasonable assumption includes an isomerization process taking place through the well established hydride mechanism,[37, 38] while the anti-Markovnikov hydrosilylation reaction could be carried out through a σ-bond metathesis (σ-CAM) mechanism. [39, 40]



Scheme 4. Rhodium-catalysed tandem isomerization-hydrosilylation of olefins.

Experimental results show that bulky substituents on the sulfur atom yield higher catalytic activities. With the aim to analyze the catalytic pocket of the Rh(III) complexes and to compare the steric hindrance of the Si,S ligands, we studied the cationic complexes **1a** and **1e** using topographic steric maps (Figure 1).[41] As in the classical geographic physical maps, different colours are used to show the elevation of the ligands respect to the zero level fixed in the rhodium atom. The triphenylphosphine ligands are located on the y-axis, north and south of the map. At the western region is located the hydrido atom while the sulphur atom is on the east of the map, both on the x-axis. Finally, the silicon atom is placed bellow the rhodium atom. Comparison of steric maps of precatalysts **1a** and **1e** indicates some slight differences in the catalytic pocket for both pockets. The more intense red area for **1a** in the eastern region agrees with a larger steric hindrance due to the ^{i}Bu substituent.

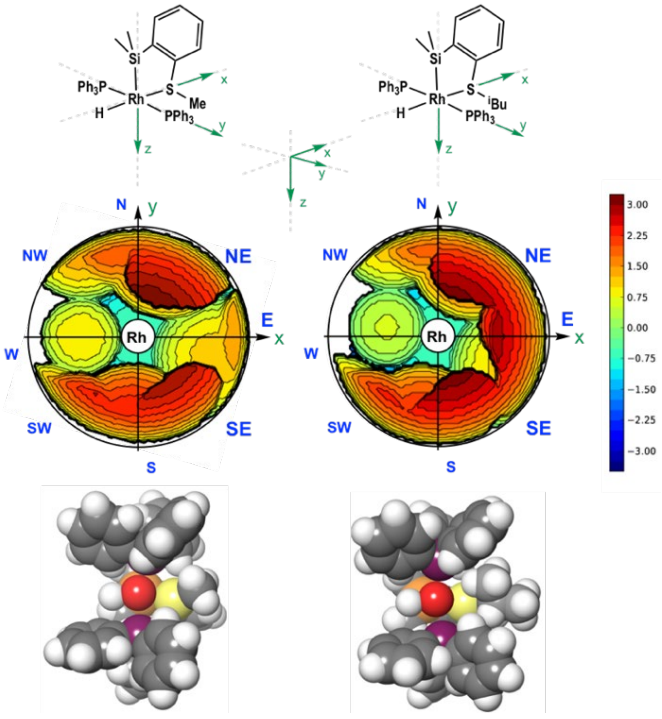


Figure 1. Steric maps of **1a** (right) and **1e** (left). The complexes are oriented according to the schemes on the top. Spacefill representation of **1a** and **1e** in the bottom of the Figure.

After demonstrating differences in the pocket size between catalysts **1a** and **1e**, we decided to study how this fact affects to the isomerization and hydrosilylation reactions independently. We reported in a previous work that complex **1e** is an efficient catalyst for the isomerisation of olefins leading to the corresponding thermodynamic mixture of terminal and internal alkenes.[34] Now, we have studied the isomerization of 1-hexene and 3-hexene catalysed by **1a**. When a NMR tube was charged with a solution of 1-hexene and 1 mol% of precatalyst **1a** in $CDCl_3$ and sealed, the isomerization reaction began readily. As in the **1e** catalysed isomerisation, after 45 min the isomerization reached the equilibrium and a mixture of hexene isomers, with a similar isomers distribution than the previously reported,[34] was obtained (Figure S36, Sup. Info.). The comparison of these results with those previously reported for **1e** confirms the slower isomerization reaction when **1a** is used as precatayst (Figure 2). In addition, the isomerization of trans-3-hexene in $CDCl_3$ is also catalysed by **1a**. As shown in Figure S.39b (Sup. Info.), this isomerization results, after 24h, in a mixture of 3-hexene, 2-hexene and a small amount of 1-hexene and appears faster than when using **1e** as catalyst (Figure S.39a in Sup.Info.). These results are important because the 1-hexene isomer is the only one active in the hydrosilylation reaction.

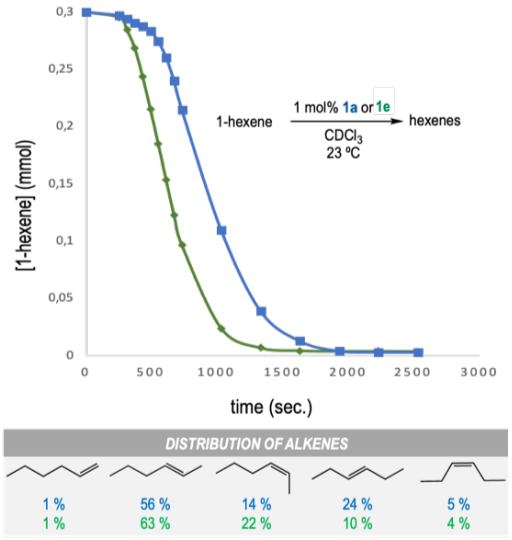


Figure 2. Decrease of 1-hexene, in the isomerization reaction, catalyzed by **1a** (blue) or catalyzed **1d** (green) over time and distribution of alkene isomers.

To study the extent of the competitive isomerization of the starting substrate under catalytic conditions, additional 1-hexene hydrosilylation reactions were performed and analysed at shorter reactions times. After 15 minutes of reaction, hexyltriethylsilane was obtained in 55% yield when **1a** was used as catalyst and 47% yield when the catalyst used was **1e**. The ^{1}H NMR spectrum of the reaction catalysed by **1a** shows that 1-hexene is the major hexene isomer after 15 minutes of reaction. In the case of the reaction catalysed by **1e**, after 15 minutes, most of 1-hexene had been isomerized to internal hexane isomers as shown the ^{1}H NMR spectra (see Section 2 in Sup. Info.). This indicates that the isomerization of 1-hexene to internal alkenes is slower when **1a** is used as catalyst also under catalytic reaction conditions.

Finally, in order to check the influence of the steric effect in the hydrosilylation reaction, the hydrosilylation of an unisomerizable olefin was carried out using **1a** and **1e**. Tert-butylethylene reacted with Et_3SiH in the presence of 0.5 mol% of **1a** or **1e** leading to (3,3-dimethylbutyl)triethylsilane, in 30 minutes with almost complete conversion in both cases (**1a**, 95 %; **1e** 99%; see Table 3 and Sup. Info. for more details). This shows a similar catalytic activity of **1a** and **1e** in the anti-Markovnikov hydrosilylation of terminal alkenes. These results are consistent with the isomerization being the rate-determining step of the tandem transformation, as has been previously suggested by other authors in similar processes,[26, 42]

Catalytic tandem isomerization-hydrosilylation reaction of internal alkenes.

On view of these results, we included other internal alkenes in our study. **1a** and **1d** were used as catalysts with the aim to compare if the difference in the activity shown in the isomerization-hydrosilylation of 1-hexene and *trans*-3-hexene can be extrapolated to other internal alkenes such as *trans*-2-hexene, *cis*-2-hexene, *trans*-4-octene, *cis*-4-octene, *trans*-3-octene, *trans*-2-octene and *cis*-2-octene. The hydrosilylation of these internal alkenes was performed using Et_3SiH and 0.5 mol% of the precatalysts (**1a** or **1e**) without solvent (Figure 3). The transformation into the terminal silylated product was calculated by ^{1}H NMR after 2 hours of reaction. The results obtained showed that, after 2 hours of reaction, cationic complex **1a** is more active than **1e** in the catalytic tandem isomerization-hydrosilylation of all the internal alkenes tested.

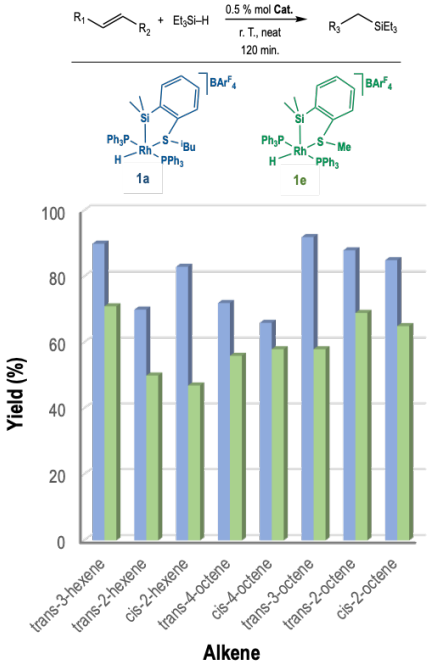


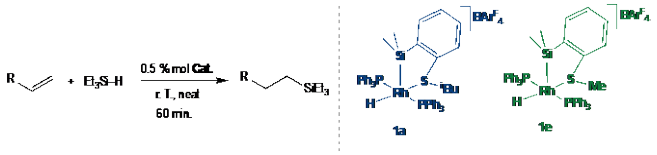
Figure 3. Comparison of precatalysts **1a** (blue) and **1e** (green) in the hydrosilylation of several alkenes. Reaction conditions: alkene (0.25 mmol), Et_3SiH (0.25 mmol) with 0.5 mol% of catalyst, solvent-free at room temperature. Yields determined by ^{1}H NMR ($CDCl_3$) by silane remaining after 120 minutes using dichloroethane as internal standard. Linear Selectivity was larger than 99% in all cases.

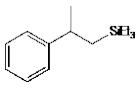
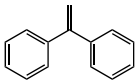
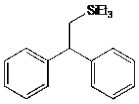
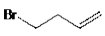
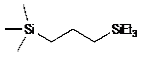
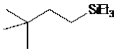
With the aim to prove that our precatalyst **1a** is able to convert a mixture of hexane isomers into a single product, the reaction of 1.25 mmol of 1-hexene, 1.25 mmol of cis-2-hexene, 1.25 mmol of trans-2-hexene and 1.25 mmol of trans-3-hexene with 5 mmol of Et_3SiH under the previously reported catalytic conditions (0.5 mol % of **1a** as catalyst, 2 h, room temperature and solvent-free) was performed. This reaction led to the formation of hexyltriethylsilane as the only silylated product in a 68 % of yield (683 mg).

Catalytic hydrosilylation of other alkenes.

To complete this study, the hydrosilylation of other alkenes with Et_3SiH was tested. In the hydrosilylation of unisomerizable and α-substituted styrenes such us α-methylstyrene and 1,1-diphenylstyrene, complex **1e** results more effective catalyst than **1a** (Table 3, entries 1 and 2). These results support the isomerization being the rate-determining step of the tandem process. The reaction of 4-bromo-1-butene with 1 equivalent of triethylsilane under the same reaction conditions gave the linear hydrosilylation product with 23 % conversion when **1a** is used and 15 % conversion when the precatalyst used was **1e** (Table 3, entry 3). Finally, Allyltrimethylsilane reacted with Et_3SiH in the presence of 0.5 mol% of **1a** or **1e** leading to the selective formation of (3,3-dimethylbutyl)triethylsilane with similar conversions (Table 3, entry 4).

Table 3. Hydrosilylation of alkenes with Et_3SiH using catalysts **1a** and **1e**.[a]



Entry	Alkene	Product Yield (Select.)[b]
1		 **1a**: (25% (>99)); **1e**: (31% (>99))
2		 **1a**: (8% (>99)); **1e**: (15% (>99))
3		 **1a**: (23% (>99)); **1e**: (16% (>99))
4		 **1a**: (72% (>99)); **1e**: (73% (>99))
5[c]		 **1a**: (95% (>99)); **1e**: (99% (>99))

[a] Reaction conditions: alkene (0.25 mmol), Et_3SiH (0.25 mmol) with 0.5 mol % of catalyst, solvent-free, at room temperature. [b] Yields and selectivities determined by ^1H NMR ($CDCl_3$) after 60 minutes of reaction by alkene remaining using dichloroethane as internal standard. [c] Yield determined after 30 minutes of reaction.

Conclusions

Unsaturated and cationic hydrido-silyl-Rh(III) complexes, **1a-1e**, are efficient catalysts for the solvent-free tandem isomerization-hydrosilylation reaction of alkenes forming the anti-Markovnikov terminal silylalkanes as the only silylated products. This process permits the synthesis of terminal silanes from remote alkenes. Even if all the catalysts assayed showed good results in terms of selectivity, the results obtained evidenced a clear dependence of the activity of the process on the size of the alkyl substituent in the sulphur atom. The best results were obtained when catalysts **1a** and **1d** containing bulky ^{i}Bu and ^{neo}Pe substituents were used. According to our experimental results, the different reactivity most probably originates from steric effects on the isomerization process.

Experimental Section

Experimental Details. All manipulations, unless otherwise stated, were performed under an atmosphere of nitrogen, using standard Schlenk techniques. Glassware was oven dried at 80ºC overnight and flamed under vacuum prior to use. Dry and oxygen free solvents were employed. $[Rh(PPh_3)_3Cl]$,[43] $[NaBAr^F{}_4]$[44] and were prepared as previously described. $[SiMe_2H(o\text{-}C_6H_4SMe)]$ was prepared by an adaptation of the published route by using nBuLi as it was previously reported in our group.[36] Et_3SiH and alkenes were purchased from Aldrich. NMR spectra were recorded on Bruker Avance DPX 300 and Bruker Avance 400 MHz spectrometer. ^1H and ^{13}C NMR spectra were referenced to the residual solvent signals. Chemical shifts are quoted in ppm and coupling constants in Hz. Microanalysis was carried out with a LECO TRUSPEC microanalyzer. ESI-MS was recorded on a Bruker MicrOTOF instrument.

Synthesis and characterization of 2-RS(C_6H_4Br). These compounds were prepared by an adaptation of the published route for similar compounds.[45] To a Schlenk charged with a solution of 2-bromobenzenethiol (0.32 mL, 3.57 mmol), K_2CO_3 (0.74 g, 5.35 mmol) and Cs_2CO_3 (0.24 g, 0.75 mmol) in DMF (9 mL) was added the haloalkane (I-^{i}Bu, 0.47 mL, 4.12 mmol; Cl-pent, 0.50 mL, 4.12 mmol; Cl-benz, 0.47 mL, 4.12 mmol) at room temperature. The reaction mixture was stirred for 1 hour. The reaction was quenched with water and extracted with diethyl ether. The solvent was removed under vacuum to give the corresponding compound as a colourless oil. Yield (**2-(^{i}Bu)S(C_6H_4Br)**: 0.75 g (86%); **2-(Pe)S(C_6H_4Br)**: 0.67 g (73%); **2-(Bn)S(C_6H_4Br)**: 0.82 g (82%); **2-(^{neo}Pe)S(C_6H_4Br)**: 0.71 g (77%).

2-(^{i}Bu)S(C_6H_4Br). ^1H NMR (300 MHz, $CDCl_3$): δ 7.58-6.99 (4H, aromatics), 2.84 (d, J = 6.8 Hz, 2H, CH_2), 1.97 (m, J = 6.8 Hz, 1H, CH), 1.11 (d, J = 6.7 Hz, 6H, 2 CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 134-126 (4C, aromatics), 42.1 (1C, CH_2), 28.2 (1C, CH), 22.6 (2C, 2 CH_3).

2-(Pe)S(C_6H_4Br). ^1H NMR (300 MHz, $CDCl_3$): δ 7.60-6.98 (4H, aromatics), 2.95 (t, J = 7.5 Hz, 2H, CH_2), 1.74 (m, J = 7.6 Hz, 2H, CH_2), 1.54-1.31 (m, 4H, (2 CH_2, pent), 0.94 (t, J = 7.2 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 134-126 (4C, aromatics), 33.1 (1C, CH_2), 31.5 (1C, CH_2), 28.5 (1C, CH_2), 22.6 (1C, CH_2), 14.3 (1C, CH_3).

2-(Bn)S(C_6H_4Br). ^1H NMR (300 MHz, $CDCl_3$): δ 7.64-7.00 (9H, aromatics), 4.19 (s, 2H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 134-126 (4C, aromatics), 37.2 (1C, CH_2).

2-(^{neo}Pe)S(C_6H_4Br). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58-6.95 (4H, aromatics), 2.87 (d, J = 6.8 Hz, 2H, CH_2), 1.97 (m, J = 6.8 Hz, 1H, CH), 1.09 (9H, 3 CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 134-126 (4C, aromatics), 48.5 (1C, CH_2), 29.9 (1C, C), 29.4 (3C, 3 CH_3).

Synthesis and characterization of the proligands $SiMe_2H$(*o*-C_6H_4SR). These compounds were prepared by an adaptation of the published route for [$SiMe_2H$(*o*-C_6H_4SMe)].[36] To a Schlenk charged with a solution of 2-RS(C_6H_4Br) (**2-(^{i}Bu)S(C_6H_4Br)**, 221 mg, 0.9 mmol; **2-(Pe)S(C_6H_4Br)**, 233 mg, 0.9 mmol; **2-(Bn)S(C_6H_4Br)**, 251 mg, 0.9 mmol); **2-(^{neo}Pe)S(C_6H_4Br)** 200 mg, 0.7 mmol), in diethyl ether (5 mL) was added n-BuLi (1.58 mL of a 1.6 M solution in hexane, 0.99 mmol) at -78 ºC. The reaction mixture was stirred for 1 hour and $ClSiMe_2H$ was added dropwise (0.1 mL, 0.9 mmol). After being stirred at room temperature overnight, the reaction mixture was quenched with water and extracted with diethyl ether. The solvent was removed under vacuum to give the corresponding compound as a colourless oil. Yield (**a**: 149 mg (74%); **b**: 165 mg (77%); **c**: 177 mg (72%); **d**: 140mg (76%)).

$SiMe_2H$(*o*-$C_6H_4S(^iBu)$) (a). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58-7.00 (4H, aromatics), 4.59 (sept, J = 3.8 Hz, 1H, Si-H), 2.84 (d, J = 4.9 Hz, 2H, CH_2), 1.90 (m, 1H, CH), 1.06 (d, J = 6.7 Hz, 6H, 2 CH3), 0.43 (d, J = 3.8 Hz, 6H, 2 Si-CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 136-125 (4C, aromatics), 44.7 (1C, CH_2), 28.8 (1C, CH), 22.5 (2C, 2 CH_3), -2.8 (2C, Si-CH_3).

$SiMe_2H$(*o*-C_6H_4S(Pe)) (b). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60-6.98 (4H, aromatics), 4.59 (sept, J = 3.7 Hz, 1H, Si-H), 2.95 (t, J = 7.6 Hz, 2H, S-CH_2), 1.68 (m, 2H, CH_2), 1.50-1.25 (m, 4H, 2 CH_2), 0.92 (t, J = 3.7 Hz, 3H, CH_3), 0.43 (d, J = X Hz, 6H, 2 Si-CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 136-125 (4C, aromatics), 35.7 (1C, CH_2), 31.5 (1C, CH_2), 29.2 (1C, CH_2), 22.6 (1C, CH_2), 14.3 (1C, CH_3), -2.8 (2C, Si-CH_3).

$SiMe_2H$(*o*-C_6H_4S(Bn)) (c). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58-7.00 (9H, aromatics), 4.59 (sept, J = 3.7 Hz, 1H, Si-H), 4.14 (s, 2H, CH_2), 0.43 (d, J = 3.7 Hz, 6H, 2 Si-CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 136-126 (4C, aromatics), 41.1 (1C, CH_2), -2.8 (2C, Si-CH_3).

$SiMe_2H$(*o*-$C_6H_4S(^{neo}Pe)$) (d). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55-7.10 (4H, aromatics), 4.58 (sept, J = 3.7 Hz, 1H, Si-H), 2.90 (s, 2H, CH_2), 1.06 (s, 9H, 3 CH_3) 0.42 (d, J = 3.7 Hz, 6H, 2 Si-CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 136-125 (4C, aromatics), 50.7 (1C, CH_2), 32.7 (1C, C), 29.3 (3C, 3CH_3) -2.9 (2C, Si-CH_3).

Synthesis and characterization of the cationic Rh(III) compounds. To a Schlenk charged with [$Rh(PPh_3)_3Cl$] (30 mg, 0.032 mmol) in CH_2Cl_2 (3 mL), 1.5 equivalents of ligand (**a** (11 mg, 0.05 mmol), **b** (12 mg, 0.05 mmol) or **c** (13 mg, 0.05 mmol)) and 1.2 equivalents of $NaBAr^F{}_4$ (35 mg, 0.4 mmol) were added. The mixture was stirred for 30 minutes, filtered off via cannula and concentrated under vacuum. Addition of 15 mL of pentane gave a pale yellow precipitate that was washed with pentane and dried under vacuum. Yield (**1a**: 46 mg (84%); **1b**: 40 mg (72%); **1c**: 41 mg (73%); **1d**: 42 mg (75%)).

1a. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 8 H, $BAr^F{}_4$), 7.55 (s, 4 H, $BAr^F{}_4$), 7.53 – 7.10 (m, $H_{aromatics}$), 2.28 (d, $J_{H\text{-}H}$= 7.3 Hz, 2 H, S-CH_2, ^{i}Bu), 1.64 (m, 1 H, CH, ^{i}Bu), 0.73 (d, $J_{H\text{-}H}$= 6.6 Hz, 6 H, $(CH_3)_2$, ^{i}Bu) 0.19 (s, 6 H, Si-CH_3), -9.81 (dt, $J_{H\text{-}Rh}$= 22.9 Hz, $J_{H\text{-}P}$= 13.1 Hz, H-Rh). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 162.0 (q, $J_{F\text{-}C}$ = 50 Hz, $BAr^F{}_4$), 135.1 ($BAr^F{}_4$), 129.0 (q, $J_{F\text{-}C}$ = 12 Hz, $BAr^F{}_4$), 125.0 (q, $J_{F\text{-}C}$ = 273 Hz, CF_3), 117.8 (s, $BAr^F{}_4$), 135,0 – 128.2 (*aromatics*), 50.9 (S-*C*H_2, ^{i}Bu), 29.4 (*C*H, ^{i}Bu), 21.5 ($(CH_3)_2$, ^{i}Bu),10.4 (Si-*C*H_3). $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ 42.5 (d, $^1J_{Rh\text{-}P}$ = 118). ESI-MS (MeCN): calc, 851.20; found m/z 851.20, for $[Rh(H)[SiMe_2(o\text{-}C_6H_4S^iBu)](PPh_3)_2]^+$. Microanalysis for $C_{80}H_{62}BF_{24}P_2RhSSi$: Requires: C, 56.02; H, 3.64; S, 1.87. Found: C, 56.37; H, 3.72; S, 1.70.

1b. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.78 (s, 8 H, $BAr^F{}_4$), 7.60 (s, 4 H, $BAr^F{}_4$), 7.66 – 7.10 (m, $H_{aromatics}$), 2.38 (t, $J_{H\text{-}H}$= 7.9 Hz, 2 H, S-CH_2, Pe), 1.37 (m, 2 H, CH_2 , Pe), 1.10 (m, 2 H, CH_2 , Pe), 0.98 (m, 2 H, CH_2, Pe), 0.79 (t, $J_{H\text{-}H}$= 6.9 Hz, 3 H, CH_3, Pe) 0.24 (s, 6 H, Si-CH_3), -9.71 (dt, $J_{H\text{-}Rh}$= 23.0 Hz, $J_{H\text{-}P}$= 13.2 Hz, H-Rh). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 162.0 (q, $J_{F\text{-}C}$ = 50 Hz, $BAr^F{}_4$), 135.1 ($BAr^F{}_4$), 129.0 (q, $J_{F\text{-}C}$ = 12 Hz, $BAr^F{}_4$), 125.0 (q, $J_{F\text{-}C}$ = 273 Hz, CF_3), 117.8 (s, $BAr^F{}_4$), 148,0 – 128.2 (*aromatics*), 40.5 (S-CH_2, Pe), 31.0 (CH_2 , Pe), 29.5 (CH_2 , Pe), 22.4 (CH_2 , Pe), 13.7 (CH_3, Pe),10.4 (Si-*C*H_3). $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ 42.5 (d, $J_{Rh\text{-}P}$= 118 Hz, 2PPh_3) ESI-MS (MeCN): calc: 865.21.; found m/z 865.21, for $[Rh(H)[SiMe_2(o\text{-}C_6H_4Spent)](PPh_3)_2]^+$. Microanalysis for $C_{81}H_{64}BF_{24}P_2RhSSi$: Requires: C, 56.26; H, 3.73; S, 1.85. Found: C, 56.40; H, 4.02; S, 1.61.

1c. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.79 (s, 8 H, $BAr^F{}_4$), 7.61 (s, 4 H, $BAr^F{}_4$), 7.60 – 6.80 (m, $H_{aromatics}$), 3.73 (s, CH_2, Bn), 0.24 (s, 6 H, Si-CH_3), -9.78 (dt, $J_{H\text{-}Rh}$= 23.0 Hz, $J_{H\text{-}P}$= 13.5 Hz, H-Rh). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 162.0 (q, $J_{F\text{-}C}$ = 50 Hz, $BAr^F{}_4$), 135.1 ($BAr^F{}_4$), 129.0 (q, $J_{F\text{-}C}$ = 12 Hz, $BAr^F{}_4$), 125.0 (q, $J_{F\text{-}C}$ = 273 Hz, CF_3), 117.8 (s, $BAr^F{}_4$), 148,0 – 128.0 (*aromatics*), 44.4 (s, CH_2, Bn) 10.4 (Si-*C*H_3). $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ 42.7 (d, $J_{Rh\text{-}P}$= 117 Hz, 2PPh_3). ESI-MS (MeCN): calc: 885.18.; found m/z 885.18, for $[Rh(H)[SiMe_2(o\text{-}C_6H_4SBn)](PPh_3)_2]^+$. Microanalysis for $C_{83}H_{60}BF_{24}P_2RhSSi$: Requires: C, 56.99; H, 3.46; S, 1.83. Found: C, 57.15; H, 3.51; S, 1.75.

1d. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.73 (s, 8 H, $BAr^F{}_4$), 7.56 (s, 4 H, $BAr^F{}_4$), 7.55 – 7.25 (m, $H_{aromatics}$), 2.41 (s, 2H, CH_2, ^{neo}Pe), 0.78(s, 9H, CH_3, ^{neo}Pe) 0.14 (s, 6 H, Si-CH_3), -10.11 (dt, $J_{H\text{-}Rh}$= 23.0 Hz, $J_{H\text{-}P}$= 13.5 Hz, H-Rh). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ 162.0 (q, $J_{F\text{-}C}$ = 50 Hz, $BAr^F{}_4$), 135.1 ($BAr^F{}_4$), 129.0 (q, $J_{F\text{-}C}$ = 12 Hz, $BAr^F{}_4$), 125.0 (q, $J_{F\text{-}C}$ = 273 Hz, CF_3), 117.8 (s, $BAr^F{}_4$), 148,0 – 117.0 (*aromatics*), 57.9 (1C, CH_2, ^{neo}Pe), 32.4 (1C, C, ^{neo}Pe), 28.8 (3C, 3CH_3, ^{neo}Pe) 10.5 (2C, 2Si-*C*H_3). $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2): δ 41.6 (d, $J_{Rh\text{-}P}$= 118 Hz, 2PPh_3). Microanalysis for $C_{81}H_{64}BF_{24}P_2RhSSi$: Requires: C, 56.26; H, 3.73; S, 1.85. Found: C, 56.61; H, 3.82; S, 1.69.

Catalytic experiments. All catalytic reactions were performed under the same conditions: nitrogen atmosphere, room temperature and without solvent. The catalyst amount used was 0.5 mol%. Conversions were calculated by ^{1}H NMR ($CDCl_3$), based on the Si-H signal of the remainin silane, using 1,2-dichloroethane as internal standard (0.125 mmol of dichloroethane for 1 mmol of silane). In the ^{1}H NMR spectra, the signals integrate 2:1 for 1,2-dichloroethane and Si-H, respectively.

Topographic steric maps. Steric maps were evaluated with the SambVca 2.0 package using the following parameters: radius of the sphere around the centre atom (3.5 Å), mesh spacing (0.1 Å), H atoms omitted and atom radii: Bondi radii scaled by 1.17, as recommended by Cavallo.[41]

Acknowledgements

This research was supported by the Ministerio de Economía y Competitividad (PID2019-111281GB-100) and Gobierno Vasco (IT1880-19). The authors thank SGIker for technical and human support. Universidad del Pais Vasco (to U.P) and IKERBASQUE (to M.H. and Z.F) are acknowledged for personnel funding.

Keywords: Hydrosilylation • Isomerization • Rhodium • Silyl-Thioether Ligands • Steric Effects

[1] I. Fleming in *Comprehensive Organic Chemistry II* (Eds : D. Burton, W. D. Ollis), Pergamon Press, Oxford, U.K. **1979**, p 577.

[2] B. Marciniec in *Applied Homogeneus Catalysis with Organometallic Compounds,* Weinheim, Germany, **1996**, p 490.

[3] D. R. Thomas in *Comprehensive Organometallic Chemistry* (Eds : W. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, Oxford, U.K. **1995**, p 114.

[4] I. Fleming, A. Barbero, D. Walter, *Chem. Rev.* **1997**, *97*, 2063.

[5] S. E. Denmark, C. S. Regens, *Acc. Chem. Res.* **2008**, *41*, 1486.

[6] J. L. Speier in *Advances in Organometallic Chemistry, Vol. 17* (Eds : F. G. A. Stone, W. Robert), Academic Press, **1979**, p 407.

[7] J. L. Speier, J. A. Webster, G. H. Barnes, *J. Am. Chem. Soc.* **1957**, *79*, 974.

[8] P. B. Hitchcock, M. F. Lappert, N. J. W. Warhurst, *Angew. Chem. Int. Ed.* **1991**, *30*, 438.

[9] A. M. Schroeder, S. M. Wrighton, M *J. Organomet. Chem.* **1977**, *128*, 345.

[10] N. J. Archer, R. N. Haszeldine, R. V. Parish,. *J. Chem. Soc, Dalton Trans.* **1979**, 695.

[11] M. Brookhart, B. E. Grant, *J. Am. Chem. Soc.* **1993**, *115*, 2151.

[12] J. F. Harrod, A. H. Chalk, *J. Am. Chem. Soc.* **1965**, *87*, 1133.

[13] F. Kakiuchi, Y. Tanaka, N. Chatani, S. Murai, *J. Organomet. Chem.* **1993**, *456*, 45.

[14] Z. Mo, J. Xiao, Y. Gao, L. Deng, *J. Am. Chem. Soc.* **2014**, *136*, 17414.

[15] C. L. Reichel, M. S. Wrighton, *Inorg. Chem.* **1980**, *19*, 3858.

[16] F. Seitz, M. S. Wrighton, *Angew. Chem. Int. Ed.* **1988**, 27, 289.

[17] L. Yong, K. Kirleis, H. Butenschön, *Adv. Synth. Catal.* **2006**, *348*, 833.

[18] P. Jiajian, B. Ying, L. Jiayun, L. Guoqiao, *Curr. Org. Chem.* **2011**, *15*, 2802.

[19] S. C. Bart, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2004**, *126*, 13794.

[20] A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, P. J. Chirik, *Science* **2012**, *335*, 567.

[21] J. Y. Wu, B. N. Stanzl, T. Ritter, *J. Am. Chem. Soc.* **2010**, *132*, 13214.

[22] D. Peng, Y. Zhang, X. Du, L. Zhang, X. Leng, M. D. Walter, Z. Huang, *J. Am. Chem. Soc.* **2013**, *135*, 19154.

[23] C. Chen, M. B. Hecht, A. Kavara, W. W. Brennessel, B. Q. Mercado, D. J. Weix, P. L. Holland, *J. Am. Chem. Soc.* **2015**, *137*, 13244.

[24] D. Noda, A. Tahara, Y. Sunada, H. Nagashima, *J. Am. Chem. Soc.* **2016**, *138*, 2480.

[25] C. C. H. Atienza, T. Diao, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, J. L. Boyer, A. K. Roy, P. J. Chirick, *J. Am. Chem. Soc.* **2014**, *136*, 12108.

[26] I. Buslov, J. Becouse, S. Mazza, M. Montandon-Clerc, X. Hu, *Angew. Chem. Int. Ed.* **2015**, *54*, 14523.

[27] V. Srinivas, Y. Nakajima,, W. Ando, K. Sato, S. Shimada, *Catal. Sci. Tecnol.* **2015**, *5*, 2081.

[28] X. Jia, Z. Huang, *Nat. Chem.* **2016**, *8*, 157.

[29] B. B. Sarma, J. Kim, J. Amsler, G. Agostini, C. Weidenthaler, N. Pfänder, R. Arenal, P. Concepción, P. Plessow, F. Studt, G. Prieto,

[30] I. Buslov, F. Song, X. Hu, *Angew. Chem. Int. Ed.* **2016**, *55*, 12295. *Angew. Chem. Int. Ed.,* **2020**, *59*, 5806.

[31] M. Jakoobi, V. Dardum, L. Veyre, V. Meille, C. Camp, C. Thieuleux, *J. Org. Chem.* **2020**, *85*, 11732.

[32] A. J. Chalk, *J. Organomet. Chem.* **1970**, *21*, 207.

[33] A. J. Chalk, J. F. Harrod, *J. Am. Chem. Soc.* **1965**, *87*, 16.

[34] S. Azpeitia, M. A. Garralda, M. A. Huertos, *ChemCatChem* **2017**, *9*, 1901

[35] S. Azpeitia, A. Rodriguez-Dieguez, M. A. Garralda, M. A. Huertos, *ChemCatChem* **2018**, *10*, 2210

[36] S. Azpeitia, B. Fernández, M. A. Garralda, M. A. Huertos, *E. J. Inorg. Chem.* **2015**, 5451.

[37] E. Larinov, H. Li and C.Mazet, *Chem. Comm.* **2014**, 50, 9816

[38] S. M. M. Knapp, S. E. Shaner, D. Kim, D. Y. Shopov, J. A. Tendler, D. M. Pudalov, and A. R. Chianese, *Organometallics*, **2014**, 33, 473.

[39] M. Brookhart and B. E. Grant, *J. Am. Chem. Soc.,* **1993**, *115*, 2151–2156

[40] R. N. Perutz and S. Sabo-Etienne, *Angew. Chem. Int. Ed.,* **2007**, 46, 2578.

[41] L. Falvine, R. Credencino, A. Poater, A. Petta, L. Serra, R. Oliva, V. Scarano, L. Cavallo, *Organometallics* **2016**, *35*, 2286.

[42] J. V. Obligación, P. J. Chirik, *J. Am. Chem. Soc.* **2013**, *135*, 19107.

[43] J. A. Osborn, F. H. Jardine, J. F. Young, G. Wilkinson, *J. Chem. Soc. A* **1966**, 1711.

[44] M. Brookhart, B. Grant, A. F. Volpe Jr., A. F. *Organometallics* **1992**, *11*, 3920

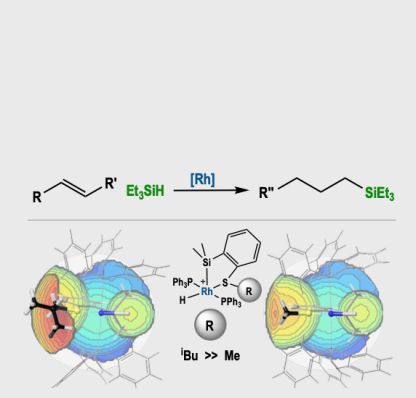
[45] A. Szadkowska, A. Makal, K. Wozniak, R. Kadyrov, K. Grela, *Organometallics*, **2009**, *28*, 2693.

Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

The bigger the better: four new hydrido-silyl-Rh(III) complexes have been used as efficient catalysts for a tandem catalytic alkene isomerization-hydrosilylation reaction. Small changes in the structure of the complex results on differences in the catalytic activity.



*Unai Prieto, Susan Azpeitia, Eider San-Sebastián, María A. Garralda, Zoraida Freixa, Miguel A. Huertos**

Page No. – Page No.

Steric Effects in the Catalytic Tandem Isomerization-Hydrosilylation Reaction