

Regioselectivity in the rhodium catalysed 1,4-hydrosilylation of isoprene. Aspects on reaction conditions and ligands

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Abstract

The regioselectivity in the Rh catalysed 1,4-hydrosilylation of isoprene was investigated. Variation of solvents and temperature did not significantly affect the isomer distribution between tail-product (**I**) and head-product (**II**). The choice of ligands had the greater influence, where Rh^I-based catalysts with the strong electron withdrawing ligand CO favoured production of isomer **II**, while Rh^I catalysts with strong electron donating ligands (for example triarylphosphines) gave isomer **I** as the main product. In contrast to the square planar carbonyl complex RhCl(CO)(PPh₃)₂, the square planar thiocarbonyl complex RhCl(CS)(PPh₃)₂, gave **I** as the major isomer.

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1. Introduction

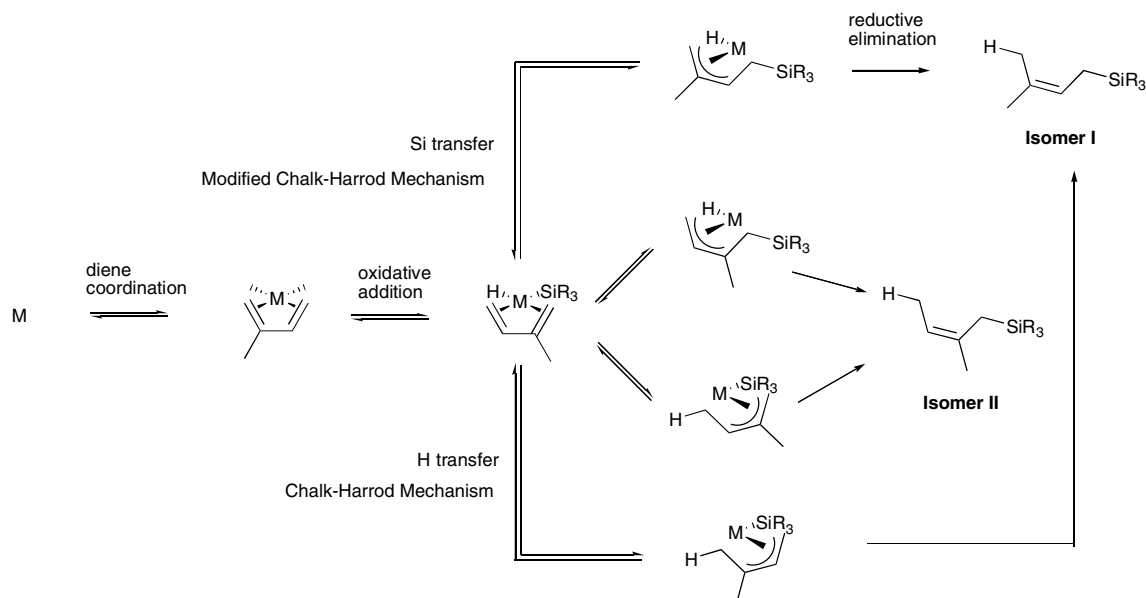
Transition-metal catalysed hydrosilylation of 1,3-dienes is a well-known reaction for the preparation of allylic silanes [1–7]. Complexes of many different metals such as Pt, Pd, Ni, Co, Rh and Ir have been used, but those based on Rh, Pd and Pt seem to be the most effective. The various complexes differ in reactivity as well as selectivity regarding 1,2- and 1,4-addition. One of the most effective catalytic systems, H₂PtCl₆ (heterogeneous), usually gives predominant 1,2-addition, while Wilkinson's catalyst, RhCl(PPh₃)₃ (homogeneous), predominantly gives 1,4-addition. When unsymmetric dienes are used, a mixture of regioisomers usually results. A typical example is the hydrosilylation of isoprene resulting in two regioisomers, tail-product (**I**) and head-product (**II**), *via* Z-specific 1,4-addition (Scheme 1). Depending on the actual catalyst, several different mechanisms for the rhodium-catalysed hydrosilylation of alkenes and dienes have been proposed [8–14]. The two most common ones for 1,3-dienes (Scheme 1)

[12–14], are based on the original proposal by Chalk and Harrod for the hydrosilylation of alkenes [15].

According to Ojima et al. [12–14] both mechanisms include the conventional oxidative addition/reductive elimination steps. An oxidative addition of the hydrosilane to a metal-diene complex, is followed by either a regiospecific hydrogen transfer (Chalk–Harrod) in the case of Pd(0)-phosphine catalyst (M = Pd in Scheme 1), or a non-selective silicon transfer (modified Chalk–Harrod) in the case of RhCl(PPh₃)₃ as catalyst (M = Rh in Scheme 1). Subsequent reductive elimination completes the catalytic cycle. On the other hand, Rh-carbonyl clusters as catalysts give results more in accordance with the Pd-cases. Here it is suggested that both pathways are operating *i.e.* initial H-transfer and Si-transfer are competing reactions. However, these proposals were based on product analysis without more detailed mechanistic investigations.

We have in our ongoing program been interested in the regio- [16,17] and stereoselectivity [18] problems in the hydrosilylation of different functionalised 1,3-dienes. When we attempted hydrosilylation of isoprene, using RhCl(PPh₃)₃ as catalyst, we observed considerable fluctuations in the isomer distribution from experiment to experiment. Most of the time under rigorous inert

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Scheme 1. Proposed schematic mechanisms for the hydrosilylation of 1,3-dienes (charges, oxidation states and geometries are omitted).

conditions, the ratios between **I** and **II** were as reported by Ojima et al. [12,13] (**I:II** 72:28 using Me_2PhSiH), but in a few cases (only successfully reproduced three times) we obtained isomer **I** exclusively. The isomer distribution varied between 2:1 and 9:1 under a variety of conditions. One important factor, the presence of molecular oxygen, changed the ratio in favour of isomer **II** as we previously reported [17].

Although numerous reports have appeared regarding the rhodium-catalysed hydrosilylation of 1,3-dienes, no general trends regarding the regioselectivity have emerged to our knowledge. The general impression from the literature is that the ligands on rhodium have the greatest influence on the selectivity [1]. Electron rich Rh^{I} complexes (e.g. $\text{RhCl}(\text{PPh}_3)_3$) gave **I** as the major isomer [12], while complexes with electron withdrawing ligands (e.g. $\text{RhCl}(\text{CO})(1,4\text{-diaz-}1,3\text{-butadiene})$) gave **II** as the major isomer [19].

In this communication we present the effect on the regio isomer distribution in the hydrosilylation of isoprene with respect to temperature, solvent, ligands and the presence of small amounts of other metals (metal cocatalysts). HSiMe_2Ph was used as the standard silane in all examples.

2. Results and discussion

2.1. Temperature effect

No large temperature effect was seen on the regioselectivity. Hydrosilylation at 0°C was slow and the yield of isolated products was close to zero, even after prolonged reaction time. In contrast to the reactivity-

selectivity principle [20], a lower regioselectivity was observed at 20°C as compared to 80°C (**I:II** 60:40 and 72:28 respectively) (Fig. 1) [21].

A tentative explanation of this phenomenon could be as follows: Wilkinson's catalyst catalyses the hydrosilylation reaction very slowly at lower temperatures. Since it is known that an equilibrium exists between the monomeric Wilkinson complex and the dimer $[\text{RhCl}(\text{PPh}_3)_2]_2$ (Eq. (1) + (2), Scheme 2) [22,23], it is possible that the proportion of the dimer is somewhat larger at a lower temperature. It is also possible that both monomer and dimer may act as catalysts in the present reaction. If the rate of formation of the dimer (k_2) is comparable with the rate of hydrosilylation catalysed by

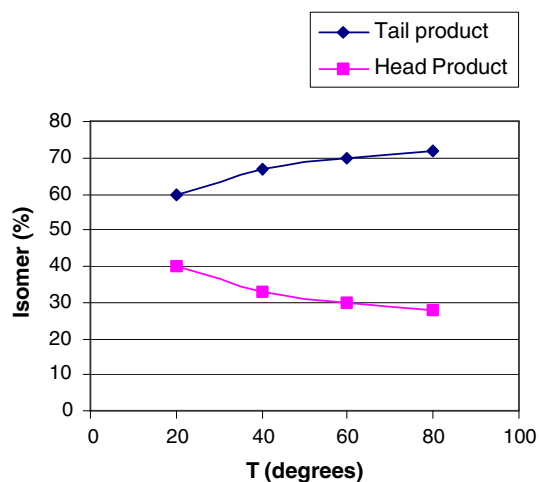
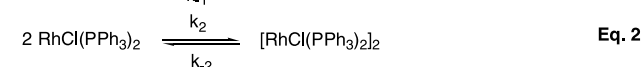
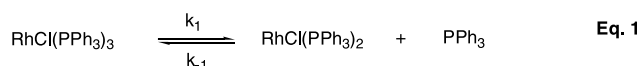


Fig. 1. Temperature dependence on the regioisomer distribution in the $\text{RhCl}(\text{PPh}_3)_3$ catalyzed hydrosilylation of isoprene with HSiMe_2Ph .



Scheme 2. A tentative explanation for the observed temperature effect. Temperature dependence, see Fig. 1.

$\text{RhCl}(\text{PPh}_3)_2$ (k_3), a competitive catalytic system will be present (Eq. (4)). If the dimeric catalyst has a more pronounced selectivity for **II**, a change in selectivity towards this isomer at lower temperatures would result, at least if k_4 is in the same range as k_3 . In fact, using the dimeric $[\text{RhCl}(\text{PPh}_3)_2]_2$ as the initial complex as catalyst resulted in lower amount of isomer **I** (**I:II** 58:42). Thus, the observed temperature effect may be a result of a shift of the catalyst monomer–dimer equilibrium (Eq. (2), Scheme 2) by temperature.

2.2. Solvent effect

Since the ligands have a strong influence on the regioselectivity of the reaction, we examined if a coordinating solvent could change the **I:II** ratio. In many experimental procedures the starting materials, the diene/alkene and hydrosilane, are mixed together with the catalyst without a solvent. Although no direct comparison has been made, it was indicated in the literature that there was little change in the results in the presence of a solvent as compared to the solventless reactions [13,17]. We therefore decided to make a more direct estimation by performing the hydrosilylation of isoprene in the solvents/solvent mixtures shown in Table 1 using dimethylphenyl silane and $\text{RhCl}(\text{PPh}_3)_3$ as catalyst.

Table 1
Isomer ratios in the $\text{RhCl}(\text{PPh}_3)_3$ catalysed hydrosilylation of isoprene using different mixtures of solvents

Entry	Solvent/solvent mixture	Isomer ratio (I:II)
1	THF	75:25
2	Diethyl ether	82:18
3	Heptane (dry) ^a	65:35
4	Heptane (wet) ^b	77:23
5	Heptane:PrOH (99:1)	66:34
6	Heptane:PrOH (90:10)	72:28
7	Heptane:PrOH (50:50)	83:17
8	Heptane:PrOH (10:90)	86:14 ^c
9	Heptane:BuOH (50:50)	72:28
10	Heptane:CyOH (50:50)	76:24
11	Benzene	74:26
12	No solvent	72:28

^a Dried over sodium metal.

^b One drop of water/100 ml heptane.

^c Competitive formation of silyl ether.

The best ratio between **I** and **II** (86:14) was achieved using a mixture of heptane (10%) and isopropanol (90%) (entry 8). Due to the high percentage of isopropanol, a major product was the corresponding isopropyl silyl ether. On reducing the proportion of isopropanol the degree of selectivity decreased, and in pure dry heptane the **I:II** ratio was only 65:35 (entry 3). A similar ratio (**I:II** 82:18) was obtained in diethyl ether. Reproducibility was a common problem and on one or two occasions the ratio between **I** and **II** was as good as 90:10. Chlorinated solvents like CH_2Cl_2 gave a lower ratio between **I** and **II**, but more importantly the reaction became sluggish. Even if some solvents gave a slightly improved ratio between **I** and **II**, the general impression is that they did not dramatically affect the regioselectivity.

2.3. Ligand effect

It is well known that the ligands in metal catalysed reactions have a strong influence on reaction rates, yields and selectivity. A useful way to characterize the ligands is to use the electronic (ν_{CO}) and steric (θ) parameters as described by Tolman [24,25]. To investigate what influence these parameters may have on the regioisomeric distribution, we first made a series of ligand exchange reactions on $[\text{Rh}(\text{COD})\text{Cl}]_2$ (Table 2, entries 1–6 and 9) using different phosphine and phosphite ligands. The COD was removed by hydrogenation. Entries 1–3 show the results of three monodentate ligands having different cone angles: PPh_3 (entry 1, $\theta = 145^\circ$, $\nu_{\text{CO}} = 2069 \text{ cm}^{-1}$), PBu_3 (entry 2, $\theta = 130^\circ$, $\nu_{\text{CO}} = 2060 \text{ cm}^{-1}$) and PMe_2Ph (entry 3, $\theta = 122^\circ$, $\nu_{\text{CO}} = 2065 \text{ cm}^{-1}$). When going from the ligand with the largest cone angle (PPh_3) to the ligand with the smallest cone angle (PMe_2Ph), the amount of regioisomer **II** increased at the expense of isomer **I** (PPh_3 75:25, PBu_3 65:35 and

Table 2
The effect on the regioselectivity in the hydrosilylation of isoprene with HSiMe_2Ph using different $\text{RhCl}(\text{PR}_3)_3$ (entry 1–6 and 9) or $[\text{RhCl}(\text{PPh}_3)_2\text{L}]$ (entry 7 and 8) complexes as catalysts^a

Entry	Ligand	Ratio (I:II) ^b	Yield I + II (%)
1	PPh_3	75:25	>99
2	PBu_3	65:35	>90
3	PMe_2Ph	50:50	>90
4	$\text{P}(p\text{-MeC}_6\text{H}_4)_3$	70:30	>90
5	$\text{P}(p\text{-ClC}_6\text{H}_4)_3$	74:26	>90
6	$\text{P}(p\text{-OMeC}_6\text{H}_4)_3$	65:35	>90
7	CO	15:85	>90
8	CS	70:30	>90
9 ^c	$\text{P}(\text{O}^i\text{Pr})_3$	40:60	>90

^a The reactions were performed in benzene at 80 °C.

^b The ratios were determined by ¹H-NMR.

^c Temperature 100 °C for prolonged time.

PMe₂Ph 50:50, respectively, at 80 °C [26]. Interestingly, when the catalyst was prepared differently (by adding six equivalents of PBu₃ to one equivalent of [Rh(COD)Cl]₂, without the hydrogenation procedure (see Section 4), the ratio between **I** and **II** increased to 89:11.

An attempt to isolate the electronic component was made using *p*-substituted triaryl phosphines ($\theta = 145^\circ$). The effects were small using the electron donating P(*p*-Me-C₆H₄)₃ (entry 4, $\nu_{\text{CO}} = 2067 \text{ cm}^{-1}$) and the electron donating P(*p*-OMe-C₆H₄)₃ (entry 6, $\nu_{\text{CO}} = 2066 \text{ cm}^{-1}$) and the electron withdrawing P(*p*-Cl-C₆H₄)₃ (entry 5, $\nu_{\text{CO}} = 2073 \text{ cm}^{-1}$). The observation was that an increase in electron density around the rhodium atom increased somewhat the formation of isomer **II** (compare entry 5 and 6). The stronger electron withdrawing ability of P(OPh)₃ (entry 9, $\theta = 128^\circ$, $\nu_{\text{CO}} = 2086 \text{ cm}^{-1}$) gave a 40:60 ratio between **I** and **II** (compare entry 2 and entry 9). This experiment was performed at elevated temperature (100 °C) due to low reactivity of the catalyst system. Further, the ligands PCl₃ and P(OEt)₃ gave no conversion at 80 °C and the bulky P(^tBu)₃ gave a complex mixture of isomers.

Surprisingly, a large difference was observed for the complexes RhCl(CO)(PPh₃)₂ and RhCl(CS)(PPh₃)₂. The former gave a 15:85 ratio of **I:II**, while the latter gave 70:30 (Table 2, entry 7 and 8, respectively). This change in selectivity is hard to explain since the complexes seem to be similar. However, a general opinion is that the thiocarbonyl ligand exhibits both stronger σ -donation as well as π -accepting properties than CO [27]. Overall, this results in a stronger electron withdrawing effect for CS, thus making the rhodium centre in the thiocarbonyl complex more electron-deficient than the corresponding carbonyl complex [28,29].

It is conceivable that the above mentioned carbonyl and thiocarbonyl Rh-complexes could form metal hydrides when treated with silanes similar to RhCl(PPh₃)₃ (hydride resonance at -15.3 ppm [30]). However, this was not the case. No hydride resonance was observed for the CX-complexes when treated with HSiMe₂Ph in the temperature interval +30–90 °C. Thus, different mechanisms may operate for the CX-complexes as compared to the Wilkinson complex.

Catalysts containing the bidentate ligands DPPE and DPPP gave more of isomer **II** (approximately **I:II** 40:60). Further, replacing the chloride of the Wilkinson complex with other ligands had little influence on the isomer distribution. Both the nitroso and hydroxy complexes Rh(NO)(PPh₃)₃ and Rh(OH)(PPh₃)₃ gave **I:II** 60:40 respectively, while the cationic complexes Rh(PPh₃)₃⁺BF₄⁻ and Rh(PPh₃)₃⁺ClO₄⁻ both gave similar ratios as the Wilkinson complex, **I:II** 72:28.

Change in the electronic properties of the hydrosilane had only minor effect on the isomer distribution, which was demonstrated by a similar **I:II** ratio, using *p*-CF₃C₆H₄Si(H)Me₂ and *p*-OMeC₆H₄Si(H)Me₂.

Table 3
Hydrosilylation of isoprene using different doped RhCl(PPh₃)₃ catalysts

Entry	Additive ^a	Ratio I:II	Yield (%)
1	None ^b	74:26	>90
2	NiCl ₂ · H ₂ O	72:28	>90
3	PdCl ₂ · H ₂ O	73:27	>90
4	PtCl ₂ · H ₂ O	74:26	>90
5	CoCl ₂ · H ₂ O	72:28	>90

^a 5 mol% used in the synthesis of the catalysts.

^b Recrystallisation of the Wilkinson catalyst several times did not improve the selectivity.

At this stage it is premature to draw any conclusions regarding the origin of regioselectivity. When altering ligands around the metal nucleus, equilibrium and rate constants may change (i.e. Scheme 2) and this may be one reason for the change in **I:II** ratio. So far, spectroscopic studies of the carbonyl complexes utilizing ³¹P- and ²⁹Si-NMR spectroscopy under a wide temperature range have not revealed any details of intermediates or complexes.

2.4. Metal cocatalyst

Rhodium is a rare metal comprising 0.0001-ppm of the earth's crust and it is found in ores associated with the platinum metals. To investigate if traces of metal impurities could be responsible for the variation in selectivity, different batches of "doped" Wilkinson's catalyst were prepared. A standard procedure for the preparation of RhCl(PPh₃)₃ was followed, in which NiCl₂, CoCl₂, PdCl₂ and PtCl₂ in amounts corresponding to a 5% concentration with respect to RhCl₃ · H₂O were added to each batch, respectively. When the different batches of doped Wilkinson's catalyst were used no dramatic change of the isomer distribution was noticed. The ratio between **I** and **II** was approximately 70:30 in all cases (Table 3), which excluded one of the potential other transition metal impurities being responsible for the earlier observed completely regioselective reaction. Prolonged storage (>4 years) of the catalysts resulted in a slightly worse **I:II** ratio (60:40). Repeated recrystallization of commercially available RhCl(PPh₃)₃ (and also freshly prepared as described in [30]) afforded only a modest increase in selectivity between **I** and **II**.

3. Conclusions

The effect of various solvents and temperature was small regarding the isomer distribution between tail-product (**I**) and head-product (**II**) in the hydrosilylation of isoprene. Greatest influence had the choice of ligand.

Rh^I-based catalysts with strong donating ligands (for example PAr₃) gave isomer **I** as the main-product (typical ratio **I**:**II** was 70:30). Change in the electronic nature of *p*-substituted triaryl phosphine ligands had little influence on the regioselectivity, although a tendency towards an increased formation of isomer **II** was seen using more electron donating groups (*p*-Cl compared to *p*-OMe). RhCl(CO)(PPh₃)₂ favoured production of isomer **II** (**I**:**II** 15:85), while the corresponding thiocarbonyl complex, RhCl(CS)(PPh₃)₂, gave **I** as the major isomer (**I**:**II** 70:30).

4. Experimental section

GC analyses were performed on a Varian 3400 gas chromatograph using a SPB-5 column (Supelco, 30 m × 0.25 mm i.d. × 0.25 μm film thickness). NMR spectra were recorded at 400 MHz (Bruker DRX spectrometer), if nothing else is mentioned. Preparative chromatographic separations were performed on Matrex Amicon normal phase silica gel 60 (0.035–0.070 mm). Thin-layer chromatography was performed on Merck precoated TLC plates with Silica gel 60 F-254, 0.25 mm. After elution, the TLC plates were visualized with UV light followed by spraying with a solution of *p*-methoxybenzaldehyde (26 ml), glacial acetic acid (11 ml) concentrated sulfuric acid (35 ml), and 95% ethanol (960 ml) followed by heating. All solvents were dried over 4A ms (5% m/w) for 24 h prior to use, unless otherwise mentioned. The molecular sieves were activated at 400 °C for 6 h and then allowed to cool under argon. All solvents were thoroughly degassed by purging with argon. RhCl(PPh₃)₃ [31], [RhCl(COD)]₂ [32], RhCl(CS)(PPh₃)₂ [33], RhCl(CO)(PPh₃)₂ [34], Rh(NO)(PPh₃)₃ [35], Rh(OH)(PPh₃)₃ [36], HSiMe₂(*p*-CF₃C₆H₄) [37] and HSiMe₂(*p*-OMeC₆H₄) [37] were prepared according to literature procedures. 1-[Dimethyl(phenyl)silyl]-3-methyl-but-2-ene (**I**) and (*Z*)-1-[dimethyl(phenyl)silyl]-2-methylbut-2-ene (**II**) had identical spectroscopic data with those previously reported [12].

4.1. Typical procedure for the hydrosilylation reaction

Benzene (15 ml) was thoroughly degassed by purging with argon. RhCl(PPh₃)₃ (10 mg, 0.01 mmol), HSiMe₂Ph (0.50 g, 3.6 mmol) and isoprene (0.50 ml, 5.1 mmol) were added sequentially, after which the reaction vessel was sealed with a screw cap and heated at 60 °C. After 2 h the reaction mixture was allowed to cool to RT. Removal of the catalyst by filtration through a column of silica gel and evaporation of the solvent afforded the crude product, which was analysed by GLC. Isolated yields based on the silane are given in Tables 2 and 3.

4.2. Synthesis of rhodium (I) complexes of the type RhCl((*p*-X-C₆H₄)₃P)₃ X = Cl, Me, OMe and H and the following hydrosilylation of isoprene

[RhCl(COD)]₂ (2.5 mg, 0.01 mmol) and the respective ligand (0.06 mmol) were mixed in benzene. Hydrogenation of the reaction mixture for 10 h (3 atm) resulted in slightly yellow solutions. Argon was thoroughly bubbled through the solution for 5 min, whereafter HSiMe₂Ph (0.50 g, 3.6 mmol) and isoprene (0.50 ml, 5.1 mmol) were added sequentially. Workup as described above gave the yields reported in Table 2.

4.3. Synthesis of “doped” Wilkinson’s catalyst

A standard procedure described in [31] was followed. The respective transition metal chloride (5%) was added to each preparation. The isolated catalyst batches had a similar (reddish) colour as the non-doped RhCl(PPh₃)₃. The only exception was when CoCl₂ was used. In that case, the colour shifted towards red-orange.

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