

# Quinone platinum complex catalyzed hydrosilylation of alkenes and alkynes

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

## Abstract

The (bisvinyl)siloxane 2-methyl-1,4-naphthoquinone platinum complex **1** catalyzes the hydrosilylation of styrenes **2a–e** with triethylsilane. The  $\beta$ -silyl regioisomers are formed as major products along with minor amounts of  $\alpha$ -isomers and E- $\beta$ -silyl styrenes. Depending on the styrene substitution pattern, the turnover numbers range between 553 and 973. Trimethylvinylsilane undergoes regioselective  $\beta$ -silylation in good yields. A 8:1 regiopreference in favor of the  $\beta$ -silyl addition product is observed for 1-pentyne. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Homogeneous catalysis; Hydrosilylation; Platinum complexes; Quinones

## 1. Introduction

The hydrosilylation is an important industrial process which *inter alia* is used for the synthesis of polysiloxanes and polysilanes [1–3]. Moreover, it is applied to the reduction of ketones to secondary alcohols [4,5]. The most prominent catalysts for this reaction are based on platinum, and have been developed by Speier [6] and Karstedt [7]. Subsequently, additional transition metal systems predominantly containing Rh-, Pd- and Pt-centers, turned out to be efficient and have been used in specific reactions [8–12],<sup>1</sup> as well as, titanium systems which have been applied to the stoichiometric reduction of amides to aldehydes [13] or to the catalytic hydrosilylation of pyridines [14].

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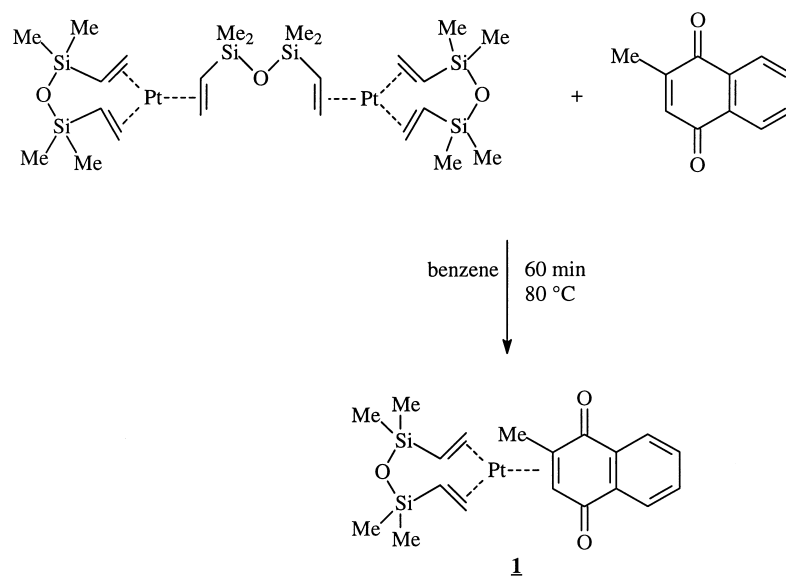
<sup>1</sup> For the enantioselective hydrosilylation with rhodium catalysts, see: [11,12].

Recently, Osborn synthesized a series of naphthoquinone platinum complexes derived from Karstedt catalyst and applied them to the hydrosilylation of trimethylvinylsilane [15]. Following our interest in quinone-based catalysts [16], we focused on the 2-methylnaphthoquinone platinum complex and screened it in the hydrosilylation of styrenes and terminal alkynes.

## 2. Experimental

All reactions were performed under argon. Solvents were dried and degassed, according to standard procedures. The yields were calculated on the basis of GC analysis with a Perkin Elmer Autosystem XL gas chromatograph having a flame ionization detector equipped with a J & W scientific fused silica column (30 m  $\times$  0.25 mm  $\times$  0.10  $\mu$ m); nitrogen served as carrier gas.

The hydrosilylation reactions were carried out in dried and degassed *n*-hexane. Samples for GC and

Scheme 1. Synthesis of catalyst **1**.

GCMS analysis were periodically taken from the reaction solution with a syringe. The hydrosilylation with the Speier catalyst was performed in tetrahydrofuran in the presence of air [17,18].<sup>2</sup>

2-Methylnaphthoquinone complex **1** was synthesized from Karstedt catalyst by substitution of the bridging siloxane ligand for the quinone (Scheme 1). Benzene (5 ml) and 2-methyl-1,4-naphthoquinone ( $0.62 \times 10^{-3}$  mol (0.107 g)) were added to a solution of the Karstedt catalyst (prepared from the reaction of 1 g  $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$  with  $3.86 \times 10^{-2}$  mol (8.85 ml) divinyltetramethylsiloxane in 8 ml EtOH) and the solution was warmed under reflux for 1 h. The solvent was removed under reduced pressure, and the yellow residue was washed with hexamethylsiloxane. The yield was 208 mg (60%).

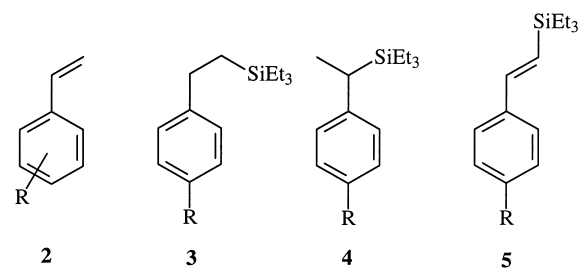
### 2.1. General procedure for the hydrosilylation

The substrate and  $\text{Et}_3\text{SiH}$  ( $1.5 \times 10^{-2}$  and  $7.5 \times 10^{-3}$  mol, respectively) were added to 10 ml *n*-hexane. The reaction mixture was warmed to 50°C, and a solution of 3.3 mg ( $6 \times 10^{-6}$  mol) of catalyst **1** in

10 ml *n*-hexane was added via a syringe. The standard workup was performed by Kugelrohr distillation, and the reaction products were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, GC and GCMS analysis.

### 3. Results

In all cases, except for *o*-methylstyrene (**2b**), the formation of the  $\beta$ -silylation product **3** was observed as the major product along with minor amounts of the  $\alpha$ -silylation product **4** and the  $\beta$ -silyl styrene **5**, arising from subsequent dehydrogenation of the  $\beta$ -silylation product **3** (Scheme 2, Table 1). During the

Scheme 2. Hydrosilylation of styrene derivatives **2** with triethylsilane catalyzed by **1**.

<sup>2</sup> For the oxygen effect (the presence of oxygen is important for the hydrosilylation) on the Speier catalyst, see [17,18].

Table 1

Yields of the platinum-catalyzed hydrosilylation of styrene derivatives after 50 h

R (2)	3 (%)	4 (%)	5 (%)
a: H	22.2	1	11.9
b: <i>o</i> -CH <sub>3</sub>	–	25.9	1.1
c: <i>p</i> -CH <sub>3</sub>	38.9	1.6	18.2
d: <i>p</i> -OCH <sub>3</sub>	28	0.8	8.3
e: <i>p</i> -Cl	22.8	1.1	15.8

hydrosilylation, the ratio of  $\beta$ -hydrosilylation product **3** and  $\beta$ -silyl styrene **5** remained constant (3:5  $\approx$  2:1) (Fig. 1).

The relative reactivity of the styrene derivatives towards hydrosilylation was screened by their turnover numbers (TON) after 50 h. The TON increased in the order of R = H < *p*-Cl < *o*-CH<sub>3</sub>  $\approx$  *p*-OCH<sub>3</sub> < *p*-CH<sub>3</sub> and increased from 553 (for styrene) to 973 (for *p*-methylstyrene) (Fig. 2). This sequence does not reflect the trend expected from the  $\sigma$ -Hammett constants; a significant deviation was found for the methoxy substituent and may be caused by a coordination of the heteroatom to the platinum center.

Attempts to extend the hydrosilylation to *trans*-1-phenyl-propene and  $\alpha$ -methylstyrene were unsuccessful and resulted only in traces of hydrosilylation

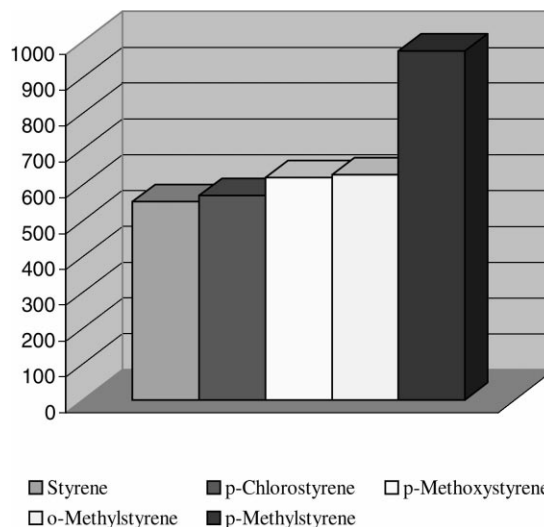


Fig. 2. TON's after 50 h for the hydrosilylation of styrene derivatives **2a–e**.

products after two days. These alkenes were similarly unreactive towards the Speier catalyst. This result may be rationalized in terms of the steric bulk arising from additional substitution of the vinylic C=C bond which hampers the coordination to the metal.

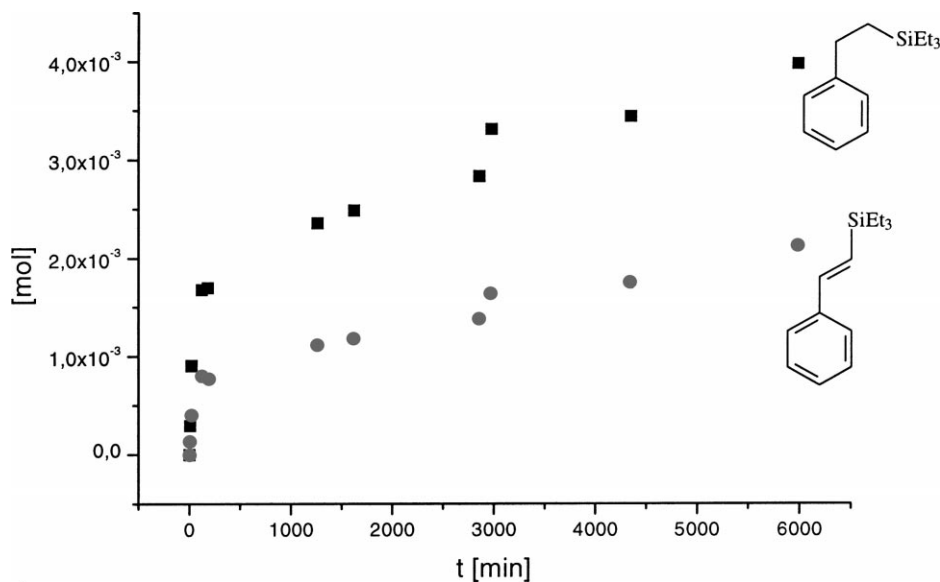
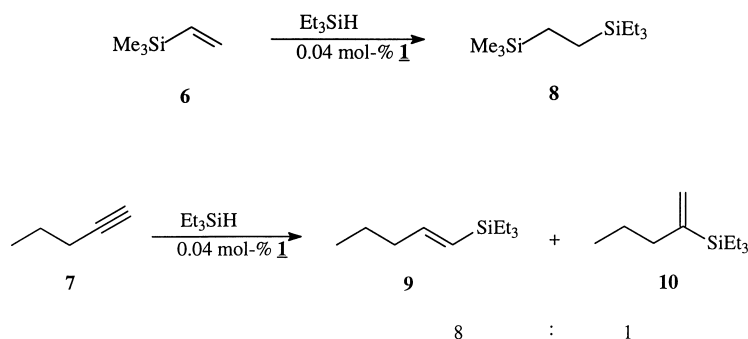


Fig. 1. Ratio 3:5 for the hydrosilylation of styrene with triethylsilane.

Scheme 3. Hydrosilylation of trimethylvinylsilane (**6**) and 1-pentyne (**7**) with catalyst **1**.

The order of reactivity observed for the hydrosilylation of styrenes with triethylsilane by catalyst **1** parallels that previously reported for the Karstedt catalyst applied to the addition of triethoxysilane [19]; the Karstedt catalyst, however, allowed higher turnover numbers (e.g. 99.7% conversion of *p*-methylstyrene).

Catalyst **1** was also applied to the hydrosilylation of trimethylvinylsilane (**6**) and 1-pentyne (**7**). Trimethylvinylsilane gave the highest yields of all tested substrates. After 5 h, we observed 60% conversion of substrate **6** to 1-triethylsilyl-2-trimethylsilyl ethane (**8**). 1-Pentyne (**7**) produced a 22% yield of a 8:1 mixture of 1-triethylsilyl-1-pentene (**9**) and 2-triethylsilyl-1-pentene (**10**) (Scheme 3).

#### 4. Conclusion

The hydrosilylation of styrene derivatives **2a–e** with triethylvinylsilane is catalyzed by naphthoquinone platinum complex **1** and affords predominantly the  $\beta$ -hydrosilylation products **7**. Yields and turnover numbers generally parallel the trend expected from the  $\sigma$ -Hammett constants, provided the substituent is unable to coordinate to platinum. At low catalyst concentration, complex **1** is also effective in the hydrosilylation of trimethylvinylsilane and 1-pentyne. In contrast to the Speier and the Karstedt catalysts the naphthoquinone catalyst **1** allowed homogeneous reactions without any formation of platinum colloids [20,21].<sup>3</sup>

<sup>3</sup> For a discussion on the nature of the platinum catalyst, see [20,21].

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