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> LETTERS TO THE EDITOR

# Reactions of Silicon Hydrides Catalyzed by Rhodium(III) Sulfoxide Complexes

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**Abstract**—Dehydrocondensation reactions of silicon hydrides catalyzed by the rhodium(III) complex  $[RhCl_3(Me_2SO)_3]$  in the absence of the second substrate were studied. It was found that the complex  $[RhCl_3(Me_2SO)_3]$  catalyzed the dehydrocondensation reaction with the formation of compounds containing siloxane bonds. Analysis of NMR spectra has shown that the reaction of  $[RhCl_3(Me_2SO)_3]$  with silicon hydride includes sequential desoxygenation of sulfoxide ligands to sulfide ligands with the complex  $[RhCl_3(Me_2S)_3]$  formation.

**Keywords:** dehydrocondensation, silicon hydride, rhodium(III) complex, desoxygenation of ligands **DOI:** 10.1134/S1070363217080400

Rhodium complexes are widely used as catalysts for hydrosilylation and dehydrocondensation reactions of silicon hydrides. Coordination-unsaturated rhodium(I) complexes with phosphorus-containing ligands are prevailingly used for these purposes, whereas data on the catalytic activity of rhodium complexes in higher oxidation states are limited to singular examples [1, 2].

Recently we have shown that rhodium(III) sulfoxide complexes  $[RhCl_3(R_2SO)_3]$ , in spite of coordination saturation, are effective catalysts for reactions of diphenylsilane methanolysis [3] and styrene methyl-dichlorosilane hydrosilylation [4], being no worse than the traditional Wilkinson's catalyst  $[RhCl(Ph_3P)_3]$  and sometimes surpassing it in activity and selectivity.

This paper is devoted to the catalytic silicon hydride reactions in the absence of a second substrate

and to the elucidation of the possibility of the preparation of compounds with Si–Si bonds. It has been found that the complex [RhCl<sub>3</sub>(Me<sub>2</sub>SO)<sub>3</sub>] catalyzes the reaction of diphenylsilane dehydrocondensation in the absence of an alcohol at higher temperatures (40–50°C, the catalyst concentration  $10^{-3}$  mol/mol of diphenylsilane) with the hydrogen evolution and the formation of a solid reaction product (Scheme 1).

Bands of stretching Si–H vibrations in the region of 2100 cm<sup>-1</sup> and of bending vibrations in the region of 860 cm<sup>-1</sup> are absent from the IR spectrum of the resulting compound, but strong absorption bands in the range of 1000–1100 cm<sup>-1</sup> characteristic of the Si–O–Si bond appear. In the <sup>1</sup>H NMR spectrum resonance signals of Si–H protons in the region of 5 ppm also are not observed, which points to the complete consumption of silylhydride hydrogen atoms.



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To determine the compound structure, we have isolated its single crystals and studied them using X-ray diffraction analysis. According to the X-ray data, the compound is octaphenyltetracyclosiloxane (see the figure). Crystal structure of the siloxane is a triclinic modification previously described in [5, 6]. The independent part consists of two halves of siloxane molecules differing by the slope angles of the phenyl groups with respect to the siloxane ring (112.5°, 112.3° for the first molecule and 110.6°, 109.5° for the second molecule, respectively). The lengths of the Si-C bonds vary within the limits of 1.849–1.864 Å. The conformation of the siloxane ring is close to flat, the deviation of atoms from the ring plane for the both molecules not exceeding 0.08 Å. The Si–O bond lengths are within the limits of 1.617– 1.627 Å and are consistent with the average length of 1,630 Å for Si–O bonds in siloxanes.

According to the chromato-mass-spectrometry data, the dehydrocondensation of diphenylmethylsilane at



General view of the octaphenyltetracyclosiloxane molecule in a crystal.

 $40^{\circ}$ C in the presence of [RhCl<sub>3</sub>(Me<sub>2</sub>SO)<sub>3</sub>] gives two products: methyldiphenylsilanol and 1,1,3,3-tetraphenyl-1,3-dimethyldisiloxane in the ratio 25 : 75 (Scheme 2).





The complex  $[RhCl_3(Me_2SO)_3]$  also catalyzes the reaction of 1,1,3,3-tetramethyldisiloxane with the formation of a mixture of cyclic and linear oligomeric siloxanes.

We have studied [RhCl<sub>3</sub>(Me<sub>2</sub>SO)<sub>3</sub>] transformations on its reaction with silicon hydride by the NMR method. According to the X-ray data, the complex has the structure of *mer,cis*-[RhCl<sub>3</sub>(Me<sub>2</sub>SO)<sub>3</sub>], in which two sulfoxides are coordinated through the sulfur atom and one through the oxygen atom [7, 8].



In the <sup>1</sup>H NMR spectrum of [RhCl<sub>3</sub>(Me<sub>2</sub>SO)<sub>3</sub>] three signals are clearly observed, which correspond to three ligands: dimethylsulfoxide molecule bound through oxygen ( $\delta = 2.88$  ppm) and two dimethylsulfoxide molecules bound through sulfur (in the *trans*-position to chlorine,  $\delta = 3.46$  ppm, and in the *trans*-position to the ligand bound through oxygen,  $\delta = 3.65$  ppm). Signals of methyl protons of sulfoxides bound through sulfur, which were previously identified as singlets [9], are doublets with a constant  $J_{RhH} =$  of 0.5 Hz of splitting by the <sup>103</sup>Rh atom, as we have shown by applying algorithms of narrowing lines. The presence of these signals can be used as indicators for studying transformations of the initial metal complex.

The analysis of the NMR spectra has shown that the reactions of [RhCl<sub>3</sub>(Me<sub>2</sub>SO)<sub>3</sub>] with silicon hydrides include sequential deoxygenation of sulfoxide ligands to sulfide ligands with the final formation of a complex with three dimethylsulfide ligands (Scheme 3).

The product of full deoxygenation to the sulfide complex was obtained with a high yield by the reaction of  $[RhCl_3(Me_2SO)_3]$  with a tetramethyldisiloxane

#### Scheme 3.

$$[RhCl_3(Me_2SO)_3] \rightarrow [RhCl_3(Me_2SO)_2(Me_2S)]$$
$$\rightarrow [RhCl_3(Me_2SO)(Me_2S)_2] \rightarrow [RhCl_3(Me_2S)_3].$$

## Scheme 4.

$$[PtCl_2(Et_2SO)_2] \rightarrow [PtCl_2(Et_2SO)(Et_2S)]$$
$$\rightarrow [PtCl_2(Et_2S)_2] \rightarrow Pt \text{ colloid.}$$

excess. The structure of the complex was confirmed by the elemental analysis and also by NMR and IR spectroscopy. It should be noted that the oxidation state of the metal remains unchanged in this case. It follows from the analysis of the <sup>1</sup>H and <sup>13</sup>C NMR spectra of the resulting sulfide compound that in its structure two sulfide molecules are located in the *trans*position to each other [ $\delta_{H}$ , ppm: 2.54 d (6H, SCH<sub>3</sub>);  $\delta_{p}$ , ppm: 21.93 (2CH<sub>3</sub>)], and the third molecule,in the *trans*-position to Cl [ $\delta_{H}$ , ppm: 2.31 d (3H, SCH<sub>3</sub>);  $\delta_{C}$ , ppm: 21.03 (CH<sub>3</sub>)]. The structure of such octahedral complex obtained in a different way was studied earlier by the X-ray diffraction analysis [10].



Similar processes of deoxygenation of sulfoxide ligands by silicon hydrides were observed previously for platinum(II) complexes [11]. However, in the case of platinum complexes the reaction with tetramethyldisiloxane proceeds deeper to reduce a metal complex to a platinum colloid (Scheme 4).

Thus, the complex [RhCl<sub>3</sub>(Me<sub>2</sub>SO)<sub>3</sub>] catalyzes reactions of silicon hydrides with the formation of compounds containing siloxane bonds. No formation of products containing Si–Si bonds was not found.

Synthesis of  $[RhCl_3(Me_2S)_3]$ . Complex  $[Rh(Me_2SO)_3Cl_3]$ , 0.5 g (0.0011 mol), was partially dissolved in methylene chloride. 1,1,3,3-Tetramethyldisiloxane, 1 mL (0.0076 mol), was added to the solution. During stirring hydrogen was liberated and the reaction mixture self-heated; the solution turned dark cherry. The resulting solution was left for a day to complete the reaction. After 24 h a crystalline mass of cherry color and a viscous liquid were formed. To the mixture 20 mL of hexane was added, a precipitate was filtered off on a glass filter. The reaction product was washed with hexane and dried at 80°C. Yield 0.45 g (91%). IR spectrum v, cm<sup>-1</sup>: 1416 s (SC–H), 683 w (S–C). <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>),  $\delta$ , ppm: 2.54 d (6H, SCH<sub>3</sub>, <sup>3</sup>*J*<sub>RhH</sub> = 0.7 Hz), 2.31 d (3H, SCH<sub>3</sub>, <sup>3</sup>*J*<sub>RhH</sub> = 1.0 Hz). <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>),  $\delta_p$ , ppm: 21.03 (CH<sub>3</sub>) 21.93 (2CH<sub>3</sub>). Found, %: C 18.88; N 4.15; S 24.67. C<sub>6</sub>H<sub>18</sub>Cl<sub>3</sub>RhS<sub>3</sub>. Calculated, %: C 18.21; H 4.59; S 24.31.

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