Hydrosilylation of Allyl Ethers in the Presence of Supported Sulfur-Containing Platinum(II) Complexes

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Received November 16, 2017

Abstract—Hydrosilylation of allyl ethyl, allyl butyl, allyl glycidyl, allyl benzyl, and allyl phenyl ethers by 1,1,3,3-tetramethyldisiloxane in the presence of supported sulfur-containing platinum(II) complexes with the general formula $[{SiO_2}O_2Si(Me)(CH_2)_3SR]_2PtCl_2$ (R = Bu, Hex, Bn; ${SiO_2}$ is silica surface) and side processes have been studied.

Keywords: hydrosilylation, allyl ethers, tetramethyldisiloxane, supported platinum(II) complexes

DOI: 10.1134/S107036321801005X

Organosilicon compounds have found wide application as specific materials since their commercial production in the 1940s. This was determined by their unique properties such as high thermal stability, chemical resistance to ozone, atomic oxygen, and oxygen plasma, excellent hydrophobicity, radiation stability, low glass transition temperature, low surface tension, low solubility, low dielectric constant, and nonflammability. Such properties as solubility, ionic conductivity, liquid crystallinity, etc., can often be modified by simple introduction of various functional groups to the silicon atom, and new materials with enhanced thermal and hydrolytic stability can be obtained [1–3].

Catalytic hydrosilylation of allyl ethers is one of the methods for the synthesis of organosilicon compounds, in particular epoxysilanes and epoxysiloxanes (hydrosilylation of allyl glycidyl ether) that are promising for industrial production of hybrid materials [4, 5]. The leading position among catalysts used for the hydrosilylation of allyl ethers is occupied by Speier's and Karstedt's catalysts [1, 2]; however, these catalysts are not free from a number of disadvantages related to difficult control of the reaction rate, necessity of using inhibitors, in some cases solidification of the reaction mixture *in situ*, and isomerization of multiple bond with subsequent acidic cleavage of functional group, which could impair properties of the products. Interest in the development of new catalytic systems does not diminish since there is a need to improve such parameters as catalytic activity, stability, selectivity, and the possibility of recycling. Up to now, examples of successful hydrosilylation of allyl ethers using rhodium siloxide complexes [6–8], including those immobilized in ionic liquids [9, 10] and silica-supported [11–13], silica-supported Karstedt's catalyst analog [14, 15], arsenide complexes of platinum(IV) [16] and rhodium(III) [17], phosphine rhodium(III) complexes [18], nitrogen-containing platinum(IV) complexes [19], chitosan platinum complexes [20–22], platinum, palladium, and rhodium complexes with a mercapto groups [23, 24], and sulfide rhodium complexes [25] have been reported.

On the other hand, sulfur-containing platinum(II) complexes are efficient homogeneous catalysts for hydrosilylation of C=C double bonds [25–31]. Hydrosilylation of allyl ethers over supported sulfur-containing platinum complexes has been poorly studied [1] despite known advantages of these catalysts [23, 24, 32–36]. Therefore, the aim of the present work was to study the catalytic activity of anchored sulfur-containing platinum(II) complexes with different substituents on the sulfur atom with the general formula [$\{SiO_2\}O_2Si(Me)(CH_2)_3SR]_2PtCl_2$ ([$(SiO_2)-2SR-PtCl_2$], R = Bu, Hex, Bn; $\{SiO_2\}$ is a modified silica surface [37]) in the hydrosilylation of allyl ethers

by 1,1,3,3-tetramethyldisiloxane, which was studied by us in detail previously by spectral methods [38]. The substrates were allyl ethyl (AllOEt), allyl butyl (AllOBu), allyl glycidyl (AllOGlyc), allyl benzyl (AllOBn), and allyl phenyl ethers (AllOPh).



General information on the reaction. The reactions of allyl ethers with 1.5 equiv of 1,1,3,3-tetramethyldisiloxane in the presence of $[(SiO_2)-2SR-PtCl_2]$ (R = Bu, Hex, Bn) can be successfully accomplished at 80– 100°C, i.e., under milder conditions than in the presence of most other supported metal complexes (120°C). The addition of the Si–H group to the allyl fragment follows two main pathways [38, 39]: predominant anti-Markovnikov (γ -addition) and Markovnikov (β -addition). Monoadducts with a reactive Si–H group fairly readily add to the second allyl ether molecule to give γ , γ - and β , γ -bis-addition products, whereas no β , β -adduct is formed (Scheme 1).

The target process, hydrosilylation by tetramethyldisiloxane, is accompanied by allyl-propenyl isomerization, reduction of ether, disproportionation of tetramethyldisiloxane to $HMe_2Si(OSiMe_2)_nH$ (n = 2-4), and hydrosilylation of allyl ethers with siloxanes HMe₂Si(OSiMe₂)_nH by analogy with the hydrosilvlation by 1,1,3,3-tetramethyldisiloxane (Scheme 2). The qualitative and quantitative compositions of byproducts depend on the substrate structure and catalyst and will be discussed below. It should be noted that allyl-propenyl isomerization and reduction products were also formed in the reactions catalyzed by Speier's catalyst [40-44] and platinum(II) and rhodium(I) complexes $[Pt(L^1L^2)XY]$, $[Rh(Ph_3P)_3X]$ $(L^1, L^2 = cod,$ dmso, Py, Bn_2S , Ph_3P ; X, Y = Cl, $SnCl_3$) [45], and $[(diene)Rh(\mu-OSiMe_3)]_2]$ [6]; disproportionation products were detected when siloxide rhodium complexes, chloride and trichlorostannate platinum and rhodium complexes, and Speier's catalyst were used [6, 38, 42, 45], and hydrosilylation of allyl ethers by







 $R^1 = Et$, Bu, Glyc, Bn, Ph; $R^2 = Bu$, Hex, Bn.

 $H(Me_2SiO)_nSiMe_2H + H(Me_2SiO)_mSiMe_2H \rightleftharpoons H(Me_2SiO)_{(n+1)}SiMe_2H + H(Me_2SiO)_{(m-1)}SiMe_2H,$ m, n = 1-3.

hydrosiloxanes formed as by-products was observed in the reactions catalyzed by chloride and trichlorostannate platinum and rhodium complexes and Speier's catalyst [38, 40].

Other possible side reactions, such as oxirane ring opening and formation of glycidyl acrylate [3, 41], α -addition [38], dehydrogenative silylation (typical of rhodium and nickel catalysts) [6, 40], elimination of propylene [41], dimerization and polymerization of allyl ethers [6, 38, 44, 45], cyclization of siloxanes [46], etc., did not occur in our catalytic systems.

Hydrosilylation of allyl butyl ether. Analysis of the kinetic data for the hydrosilylation of allyl butyl ether by 1,1,3,3-tetramethyldisiloxane in the presence of [(SiO₂)-2SR-PtCl₂] showed the time necessary to attain maximum conversion of allyl butyl ether almost does not depend on the substituent R on the sulfur atom of the ligand; after 8 h at 80°C, the conversion was 98–99% for R = Bu, Hex, Bn (Fig. 1). In the early hydrosilylation stage, [(SiO₂)–2SHex–PtCl₂] is more active than [(SiO₂)-2SBn-PtCl₂] (1 h, conversion 42% against 35%); after 1.5 h, the conversion was the same in the presence of both catalysts; after 3 h, the conversion of AllOBu in the presence of [(SiO₂)-2SHex-PtCl₂] becomes lower than in the presence of $[(SiO_2)-2SBn-PtCl_2]$ (76% against 83%). If the catalytic activity is estimated by the time necessary for 50% substrate conversion, [(SiO₂)-2SHex-PtCl₂] and $[(SiO_2)-2SBn-PtCl_2]$ are more active than $[(SiO_2)-$ 2SBu-PtCl₂] (82 and 89 min against 143 min, respectively). Decrease the reaction temperature to 60°C considerably increased the reaction time: after 10 h in the presence of $[(SiO_2)-2SBu-PtCl_2]$, the conversion was 80%. Raising the temperature to 100°C shortened the reaction time almost twofold: the conversion was 52% after 1 h and 95% after 3.5 h (Fig. 1).

The selectivity with respect to the γ -adduct, i.e., the ratio of the yield of the γ -addition product (HMe₂Si)₂O to the overall yield of all products fromed from AllOBu {including by-products and products of monoand bis-addition products of HMe₂Si(OSiMe₂)_nH (n = 2, 3) to AllOBu} was 71.0, 74.4, and 76.3% (80°C) for [(SiO₂)–2SBn–PtCl₂], [(SiO₂)–2SBu–PtCl₂], and [(SiO₂)– 2SHex–PtCl₂], respectively, which was determined primarily by the side addition of the Si–H group of the monoadduct (Table 1). Unfortunately, published data very rarely include information on side processes accompanying hydrosilylation, whereas the selectivity is usually given as the ratio of γ - and β -adducts (regioselectivity). For example, the selectivity determined in such a way for the hydrosilylation of AllOBu by





Fig. 1. Variation of the conversion of allyl butyl ether with time in the hydrosilylation by $(HMe_2Si)_2O$ in the presence of platinum complexes (1, 4, 5) [$(SiO_2)-2SBu-PtCl_2$], (2) [$(SiO_2)-2SBu-PtCl_2$], and (3) [$(SiO_2)-2SHex-PtCl_2$] at (1) 100, (2, 3, 4) 80, and (5) 60°C; $c_{Pt} = 1.8 \times 10^{-4}$ M, molar ratio AllOBu–(HMe₂Si)₂O = 1 : 1.5.

	-			=			-	-			-	
Allyl ether	Reaction time, h	Temperature, °C	Conversion of allyl ether, %	γ _Σ -Selectivity, %	γ/β, %	Product composition, %						
						product of (HMe ₂ Si) ₂ O addition				CH₃CH=CHOR'	others	
						β	γ	β,γ	γ,γ	-		
[(SiO ₂)–2SHex–PtCl ₂]												
AllOBu	8	80	99	94.7	96.3/3.7	3.0	76.3	1.1	12.3	0.8	6.5	
[(SiO ₂)–2SBn–PtCl ₂]												
AllOBu	8	80	99	92.6	96.3/3.7	2.7	71.0	1.0	12.5	1.1	11.7	
[(SiO ₂)–2SBu–PtCl ₂]												
AllOBu	1	100	52	96.3	96.2/3.8	3.4	87.2	0.5	7.1	0.3	1.5	
	8		99	96.0	96.2/3.8	3.1	77.8	1.2	15.2	0.3	2.4	
	8	80	99	94.9	96.3/3.7	2.9	74.4	1.2	13.1	1.4	7.0	
	10	60	80	96.0	96.6/3.4	2.9	83.0	0.9	10.6	0.4	1.9	
AllOBn		10 80	91	89.4	94.5/5.5	4.3	74.2	1.4	12.4	3.7	4.0	
AllOEt	10		74	92.1	95.5/4.5	3.8	79.7	1.4	9.9	3.1	2.1	
AllOPh			23	97.4	98.2/1.8	1.5	79.8	0.0	1.7	5.2	11.8	
AllOGlyc			79	84.1	91.8/8.2	6.5	70.7	0.0	8.3	5.0	9.5	

Table 1. Hydrosilylation of allyl ethers by 1,1,3,3-teramethyldisiloxane (HMe₂Si)₂O in the presence of $[(SiO_2)-2SR-PtCl_2]^a$

^a R = Bu, Hex, Bn; $c_{Pt} = 1.8 \times 10^{-4}$ M, molar ratio ether–(HMe₂Si)₂O = 1 : 1.5.

1,1,1,3,5,5,5-heptamethyltrisiloxane in the presence of $[Rh(cod)(\mu-OSiMe_3)]_2$ [6] was 98%, which may ensue from both lower reactivity of siloxane with an internal Si-H group in side processes [38] and ignoring processes accompanying hydrosilvlation. We estimated the regioselectivity of the addition of (HMe₂Si)₂O through the γ/β -adduct ratio at 96.3% for all the examined catalyst, i.e., it does not depend on the nature of substituent on the sulfur atom and is higher than in the hydrosilylation in the presence of homogeneous cyclooctadiene (85%), dibenzyl sulfide (87%), and dimethyl sulfoxide platinum complexes (84%); furthermore, it is comparable with the selectivity reached with the use of Wilkinson's catalyst [Rh(Ph₃P)₃Cl] (95%) and [Pt(dmso)₂(SnCl₃)Cl] (93%) [45]. On the other hand, it is interesting to evaluate the overall γ -addition (γ_{Σ} -selectivity, i.e., the contribution of all hydrosilylation products, including those derived from side siloxanes, and double addition products) in order to extrapolate the obtained data to oligomeric hydrosilylation by and polymeric hydrosiloxanes since siloxane disproportionation processes almost do not affect characteristics of the

final product. The reasonability of introducing this parameter is confirmed by the coincidence of the results obtained by GLC and 1H NMR. The γ_{Σ^-} selectivity was 92.6, 94.7, and 94.9% in the presence of [(SiO₂)-2SBn-PtCl₂], [(SiO₂)-2SHex-PtCl₂], and [(SiO₂)–2SBu–PtCl₂], respectively; i.e., it is slightly lower than the selectivity in the addition of exclusively (HMe₂Si)₂O due to increased contribution of βaddition of HMe₂Si(OSiMe₂)_nH (n = 2, 3) to AllOBu, which is proportional to the increase of the overall concentra-tion of the γ - and β -adducts of HMe₂Si· $(OSiMe_2)_n H$ (n = 2, 3) in the catalyst series [(SiO₂)-2SBu-PtCl₂] (4.1%), [(SiO₂)-2SHex-PtCl₂] (4.2%), and $[(SiO_2)-2SBn-PtCl_2]$ (6.9%). On the whole, siloxanes HMe₂Si(OSiMe₂)_nH formed as a result of disproportionation add to AllOBu with lower selectivity, which reduces the γ_{Σ} -selectivity.

The kinetic curves for free HMe₂Si(OSiMe₂)_{*n*}H (n = 2-4) and the corresponding hydrosilylation products smoothly ascend throughout the entire period of measurements (Fig. 2). After 5 h at 80°C, the yield of free HMe₂Si(OSiMe₂)_{*n*}H, e.g., in the presence of

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[(SiO₂)-2SBn-PtCl₂], is 0.8, 1.2, and 0.6%, and their overall yield (with account taken of their consumption for hydrosilylation) is 4.6, 2.9, and 0.9% for n = 2, 3, and 4, respectively. By the end of the reaction (8 h), the concentration of free siloxanes remains virtually unchanged (0.9, 1.6, and 0.9%), whereas the amount of the hydrosilylation products slightly increases (overall yield 5.3, 4.1, and 1.3%; Table 2). It should be noted that the amount of free HMe₂Si(OSiMe₂)₂H in the presence of [(SiO₂)-2SHex-PtCl₂] and [(SiO₂)-2SBu-PtCl₂] is higher than in the presence of [(SiO₂)-2SBn-PtCl₂]; the concentration of free HMe₂Si(OSiMe₂)₃H almost does not depend on the R substituent in the metal complex, while only traces of HMe₂Si(OSiMe₂)₄H were detected (or it was not detected at all); after 8 h at 80°C, the yield of free HMe₂Si(OSiMe₂)_nH in the presence of [(SiO₂)-2SHex-PtCl₂] and [(SiO₂)-2SBu- $PtCl_2$] was 4.2 and 1.5% or 4.0 and 1.9% at n = 2 and 3, respectively (Table 2). The amount of HMe₂Si. (OSiMe₂)₂H involved in side hydrosilylation in the presence of $[(SiO_2)-2SBn-PtCl_2]$ was larger (the siloxane conversion to hydrosilylation products was ~83%) than in the cases of $[(SiO_2)-2SHex-PtCl_2]$ and $[(SiO_2)-2SBu-PtCl_2]$ (30–31%), which suggests higher catalytic activity of [(SiO₂)–2SBn–PtCl₂]. Thus, the catalytic activity of supported platinum complexes in the side reactions of (HMe₂Si)₂O decreases in the series $[(SiO_2)-2SBu-PtCl_2] \approx [(SiO_2)-2SBn-PtCl_2] >$ [(SiO₂)–2SHex–PtCl₂] (Table 2).

Decrease the reaction temperature to 60°C reduces the yield of free HMe₂Si(OSiMe₂)_nH (n = 2-4) and the corresponding hydrosilylation products (Table 2). However, as we already noted, the target reaction also slows down (Fig. 1). The optimal temperature was 100°C. Under these conditions, the maximum conversion of AllOBu is attained in 5 h, and the overall yield of HMe₂Si(OSiMe₂)_nH is 3.4, 0.6, and 0.1% for n = 2, 3, and 4, respectively, which is lower than in 5 h at 80°C and all the more lower than by the end of the reaction at 80°C (8 h; Table 2).

Heating of $(HMe_2Si)_2O$ in the presence of $[(SiO_2)-2SBn-PtCl_2]$ without AllOBu at 80°C accelerates the formation of $HMe_2Si(OSiMe_2)_nH$ (n = 2-4), which is especially noticeable for $HMe_2Si(OSiMe_2)_2H$. For example, the yield of $HMe_2Si(OSiMe_2)_nH$ in 5 h is 7.6, 1.2, and 0.1% for n = 2, 3, and 4, respectively (Fig. 2). Similar results were obtained in the hydrosilylation catalyzed by homogeneous dibenzyl sulfide platinum complex *cis*-[Pt(Bn_2S)_2Cl_2] with the only difference that the amount of $HMe_2Si(OSiMe_2)_4H$ was larger



Fig. 2. Variation of the yield of HMe₂Si(OSiMe₂)₂H with time in the hydrosilylation of allyl butyl ether by (HMe₂Si)₂O in the presence of platinum complex [(SiO₂)–2SBn–PtCl₂] ($c_{\text{Pt}} = 1.8 \times 10^{-4}$ M, 80°C); (1) free and consumed for hydrosilylation HMe₂Si(OSiMe₂)₂H, (2) HMe₂Si(OSiMe₂)₂H consumed for hydrosilylation, (3) free HMe₂Si(OSiMe₂)₂H.

(yield 7.6, 1.2, and 1.4% for n = 2, 3, and 4, respectively; reaction time 5 h). Prolonged heating (15 h) favors formation of HMe₂Si(OSiMe₂)_nH, and this process is faster in the presence of the homogeneous platinum complex: yield 19.9, 3.6, and 0.7% over *cis*-[Pt(Bn₂S)₂Cl₂] against 11.5, 1.6, and 0.4% over [(SiO₂)–2SBn–PtCl₂] for n = 2, 3, and 4, respectively.

Side transformations of AllOBu in the hydrosilvlation by 1,1,3,3-tetramethyldisiloxane at 80°C, isomerization and reduction, were observed in the presence of $[(SiO_2)-2SHex-PtCl_2]$: the yield of isomeric propenyl butyl ethers was 0.8%, and of propyl butyl ether, 0.5%. Unlike [(SiO₂)–2SHex–PtCl₂], the hydrosilylation of AllOBu in the presence of [(SiO₂)-2SBu-PtCl₂] and [(SiO₂)-2SBn-PtCl₂] was accompanied by formation of only propenyl butyl ether isomers (isomerization, 1.1-1.4%). Raising the temperature to 100°C reduced the contribution of side process, and the yield of isomerization products in the presence of $[(SiO_2)-2SR-PtCl_2]$ (R = Bu, Hex, Bn) was 3-4 times lower (0.3%). When AllOBu was heated with [(SiO₂)-2SR-PtCl₂] in the absence of (HMe₂Si)₂O (8 h, 80°C), only isomeric propenyl butyl ethers were formed, and their yield in the presence of [(SiO₂)-2SHex-PtCl₂] was comparable with that obtained in the hydrosilylation (0.7%); however, in the case of [(SiO₂)-2SBu-PtCl₂] and [(SiO₂)-2SBn-PtCl₂] their yield was twice as low as that in the hydrosilylation

Table 2. Yields of HMe₂Si(OSiMe₂)_nH (n = 2-4) in the hydrosilylation of allyl ethers by 1,1,3,3-teramethyldisiloxane (HMe₂Si)₂O in the presence of [(SiO₂)-2SR-PtCl₂]^a

	R	Reaction time, h	Temperature, °C	Yield of HMe ₂ Si(OSiMe ₂) _n H, ^b %						
Allyl ether				n = 1	2	<i>n</i> =	= 3	<i>n</i> = 4		
				Ι	II	Ι	II	Ι	II	
	Bn	5	80	0.8	4.6	1.2	2.9	0.6	0.9	
		8		0.9	5.3	1.6	4.1	0.9	1.3	
	Hex	5		3.7	5.1	0.9	2.5	_	-	
		8		4.2	6.0	1.5	3.9	_	-	
AllOBu		5	60	1.3	1.5	0.2	0.3	0.1	0.1	
		8		2.5	3.0	0.3	0.5	0.1	0.1	
		5	80	3.1	4.6	0.9	2.2	_	Traces	
		8		4.0	5.8	1.9	4.2	0.3	0.6	
	Bu	5	100	2.6	3.4	0.3	0.6	0.1	0.1	
AllOEt				0.1	0.6	0.3	0.2	0.1	0.1	
AllOBn		10	80	0.6	1.0	0.7	1.2	-	0.4	
AllOPh				2.1	3.4	6.4	6.5	-	0.3	
AllOGlyc				0.6	3.5	0.6	0.9	-	-	

^a $c_{Pt} = 1.8 \times 10^{-4}$ M, molar ratio ether-(HMe₂Si)₂O = 1 : 1.5.

^b I: yield of free siloxane HMe₂Si(OSiMe₂)_nH; II: overall yield of free siloxane HMe₂Si(OSiMe₂)_nH and the corresponding hydrosilylation products.

(0.8 and 0.6%, respectively). Further rise in the reaction temperature (120°C, 8 h) did not affect the yield of propenyl butyl ether isomers, which was also lower $\{0.5\%, [(SiO_2)-2SBn-PtCl_2]\}$ than in the hydrosilylation. The observed reduction of the yield of propenyl butyl ether isomers in the absence of (HMe₂Si)₂O as compared to the hydrosilylation suggests participation of a silicon hydride intermediate in the isomerization process accompanying hydrosilylation.

The hydrosilylation of AllOBu with Si–Hcontaining monoadducts in the presence of $[(SiO_2)-2SR-PtCl_2]$ leads to the formation of γ,γ -bis-adducts [yield 12.3 (80°C) or 15.2% (100°C)] and β,γ -bisadducts ($\leq 1.2\%$). As a result, the yield of the target product decreases. In the reaction of AllOBu with (HMe_2Si)_2O catalyzed by $[(SiO_2)-2SBu-PtCl_2]$ and $[(SiO_2)-2SHex-PtCl_2]$, the yield of the target hydrosilylation product is 73.8 and 73.3%, respectively, while the yield of the γ -adduct in the presence of $[(SiO_2)-2SBn-PtCl_2]$ is slightly lower (70.7%) despite similar conversion of AllOBu. This suggests lower catalytic efficiency of the benzyl sulfide complex in the synthesis of the monoadduct. The yield of the γ addition product increases to 77.0% at 100°C in the presence of [(SiO₂)–2SBu–PtCl₂]. Analogous yields of the γ -adduct were achieved under conditions of homogeneous catalysis by [Pt(cod)Cl₂] (64.0%), [Pt(Bn₂S)₂(SnCl₃)Cl] (64.5%), [Pt(dmso)₂Cl₂] (65.9%), and [Pt(cod)(SnCl₃)Cl] (74.4%); rhodium complexes [Rh(Ph₃P)₃Cl] (88%) and [Rh(Ph₃P)₃(SnCl₃)] (90.5%) were more efficient [45].

Hydrosilylation of allyl ethyl ether. As in the reaction with AllOBu, the kinetic curve for the hydrosilylation of allyl ethyl ether by 1,1,3,3-tetramethyldisiloxane in the presence of $[(SiO_2)-2SBu-PtCl_2]$ (80°C) has logarithmic shape. The time necessary for 50% conversion of AllOEt (330 min) is considerably longer than in the hydrosilylation of AllOBu (143 min); after 10 h, the conversion of AllOEt reaches 74%, whereas the maximum conversion of AllOBu is attained in 8 h (99%, Fig. 3). The regioselectivity (95.5%) and γ_Σ-selectivity (92.1%) in the presence of $[(SiO_2)-2SBu-PtCl_2]$ are lower, while the selectivity for the γ-adduct is higher (79.7%, 80°C;

Table 1), than the corresponding parameters in the hydrosilvlation of AllOBu.

The contribution of side processes related to transformations of HMe₂Si(OSiMe₂)_nH in the hydrosilvlation of AllOEt by 1,1,3,3-tetramethyldisiloxane in the presence of [(SiO₂)–2SBu–PtCl₂] is smaller than in the hydrosilvlation of AllOBu (after 10 h at 80°C, the overall yield of HMe₂Si(OSiMe₂)_nH with a correction for their consumption for hydrosilvlation was 0.6, 0.2, and 0.1% for n = 2, 3, and 4, respectively, i.e., 10–12 times lower than in the reaction with AllOBu; Table 2). The small contribution of the secondary transformations of (HMe₂Si)₂O in the hydrosilvlation of AllOEt in the presence of [(SiO₂)–2SBu–PtCl₂] increases the selectivity with respect to the γ -adduct, as compared to the reaction with AllOBu.

In contrast, isomerization of AllOEt in the hydrosilylation over $[(SiO_2)-2SBu-PtCl_2]$ is more significant than it would be expected on the basis of the data for AllOBu. The concentration of propenyl ethyl ethers reaches 3.1% which is twice as high as that of propenyl butyl ethers; in addition, traces of propyl ethyl ether were detected. Heating of AllOEt with $[(SiO_2)-2SBu-PtCl_2]$ in the absence of $(HMe_2Si)_2O$ (10 h, 80°C) afforded only traces of propenyl ethyl ether.

The overall concentration of products of AllOEt hydrosilylation by monoadducts containing active Si–H bonds in the presence of $[(SiO_2)-2SBu-PtCl_2]$ (10 h, 80°C) was slightly lower than in the reaction with AllOBu (9.9 and 1.4% of the γ , γ - and β , γ -bisadducts, respectively; Table 1) due to lower conversion of the initial ether.

Hydrosilylation of allyl benzyl ether. The hydrosilylation of allyl benzyl ether by 1,1,3,3tetramethyldisiloxane follows the same pattern as that established for AllOBu and AllOEt. In the reaction catalyzed by [(SiO₂)-2SBu-PtCl₂], allyl benzyl ether is considerably more reactive than AllOEt: the 50% conversion is achieved in 137 min against 330 min for AllOEt; after 10 h at 80°C, the conversion of AllOBn was 91%, while the conversion of AllOEt was 74% (Fig. 3, Table 1). During the first two hours, AllOBn was more reactive than AllOBu (in 1 h at 80°C, the conversion of AllOBn was 33% against 24% conversion of AllOBu), but the reaction slowed down when a conversion of 50% was reached; as a result, the conversion of AllOBu after 10 h was higher than that of AllOBn by 9% (Fig. 3).



Fig. 3. Variation of the conversion of (1) allyl butyl ether, (2) allyl benzyl ether, (3) allyl glycidyl ether, (4) allyl ethyl ether, and (5) allyl phenyl ether with time in the hydrosilylation by (HMe₂Si)₂O in the presence of platinum complex [(SiO₂)–2SBu–PtCl₂]; $c_{Pt} = 1.8 \times 10^{-4}$ M, molar ratio allyl ether–(HMe₂Si)₂O = 1 : 1.5, 80°C.

The selectivity for the γ -adduct in the presence of [(SiO₂)–2SBu–PtCl₂] was 74.2%, and the γ_{Σ} -selectivity, 89.4%. The regioselectivity of the addition of (HMe₂Si)₂O in the hydrosilylation of AllOBn in the presence of [(SiO₂)–2SBu–PtCl₂] (94.5%) was the lowest among the examined ethers.

The contribution of side processes (transformations of Si–H siloxanes) in the hydrosilylation of AllOBn in the presence of $[(SiO_2)-2SBu-PtCl_2]$ was smaller than in the hydrosilylation of AllOBu but greater than in the reaction with AllOEt; after 10 h, the concentration of all siloxane by-products did not exceed 2.6%. After 10 h at 80°C, the overall yield of HMe₂Si(OSiMe₂)_nH with account taken of their consumption for hydrosilylation was 1, 1.2, and 0.4% for n = 2, 3, and 4, respectively (Table 2).

The isomerization and reduction of AllOBn were twice as intense as the corresponding side processes in the hydrosilylation of AllOEt; after 10 h at 80°C in the presence of $[(SiO_2)-2SBu-PtCl_2]$, the overall concentration of the isomerization and reduction products was 5.7%. Therefore, the reaction selectivity for the γ -adduct was even lower than those found for AllOEt and AllOBu (Table 1). Heating of AllOBn in the presence of $[(SiO_2)-2SBu-PtCl_2]$ without (HMe₂Si)₂O (10 h, 80°C) gave 1.9% of isomeric propenyl benzyl ethers; i.e., their amount was almost twice as low as that obtained in the hydrosilylation.

The yield of the γ , γ -adduct in the reaction catalyzed by [(SiO₂)–2SBu–PtCl₂] (10 h, 80°C) almost coincided

with the results of hydrosilylation of AllOBu (12.4%), whereas the yield of the β , γ -adduct was twice as large (3.7%).

Hydrosilylation of allyl phenyl ether. Allyl phenyl ether showed the lowest reactivity among the examined allyl ethers; after 10 h at 80°C, its conversion was as low as 23% (Fig. 3); correspondingly the reactivity series of allyl ethers in the presence of $[(SiO_2)-2SBu-PtCl_2]$ is as follows: AllOBu > AllOBn > AllOEt >> AllOPh. This series is hardly consistent with published data according to which there is no relation between the reactivity of allyl ethers in hydrosilylation and the structure of catalysts and Si-H reagents. The maximum yield of the target product in the hydrosilylation of AllOPh is often achieved in almost the same time as with other allyl ethers; in the presence of siloxide rhodium complexes, the hydrosilvlation of AllOPh is faster than the reaction with other ethers [6], whereas the reactivity of AllOPh in the presence of [(SiO₂)-2SBu-PtCl₂] is the lowest.

After 10 h, the selectivity in the hydrosilylation of AllOPh was 79.8% (conversion 23%), which coincided with the selectivity found for AllOEt but was higher than those for other ethers (70.7–74.4%); the γ_{Σ} -selectivity (97.4%) was slightly lower than that for AllOBu, and the regioselectivity of the addition of (HMe₂Si)₂O (98.2%) exceeded the corresponding values for the other ethers.

Despite low rate of hydrosilylation of AllOPh in the presence of [(SiO₂)-2SBu-PtCl₂], after 10 h the reaction mixture contained both free oligosiloxanes HMe₂Si(OSiMe₂)_nH (yield 2.1 and 6.4% for n = 2 and 3, respectively) and the corresponding hydrosilylation products. The overall yield of HMe₂Si(OSiMe₂)_nH (3.4, 6.5, and 0.3% for n = 2, 3, and 4, respectively) was comparable with that observed in the hydrosilylation of AllOBu (tabl. 2), and the amount of octamethyltetrasiloxane (n = 4) was the largest among all the examined catalytic systems. Side processes in the hydrosilvlation of AllOPh catalyzed by [(SiO₂)-2SBu–PtCl₂] included only the formation of propenyl phenyl ether isomers (0.4%) whose yield was 3-7 times lower than the yield of the corresponding isomeric ethers in the hydrosilylation of other allyl ethers.

Among all possible products of hydrosilylation by a reactive Si–H group of the monoadduct, only γ , γ -adduct was detected in the presence of [(SiO₂)–2SBu–

 $PtCl_2$] (its concentration was 1.7% after 10 h at 80°C and 8.5% after 22.5 h).

Hydrosilylation of allyl glycidyl ether. The reactivity of AllOGlyc in the hydrosilylation by 1,1,3,3tetramethyldisiloxane in the presence of $[(SiO_2)-2SBu-$ PtCl₂] was comparable with that of AllOEt: AllOBu > AllOBn > AllOEt \approx AllOGlyc >> AllOPh. The selectivity of $[(SiO_2)-2SBu-$ PtCl₂]-catalyzed hydrosilylation (70.7%), γ_{Σ} -selectivity (84.1%), and regioselectivity of the addition of (HMe₂Si)₂O (91.8%) were the lowest in the examined series of allyl ethers (Table 1).

The contribution of side processes in the hydrosilylation of AllOGlyc by 1,1,3,3-tetramethyldisiloxane in the presence of $[(SiO_2)-2SBu-PtCl_2]$ was larger than in the reactions with AllOEt and AllOBn but smaller than in the hydrosilylation of AllOBu and AllOPh; after 10 h at 80°C, the overall yield of HMe₂Si(OSiMe₂)_nH (including their consumption for hydrosilylation) was 3.5, 0.9, and 0% for n = 2, 3, and 4, respectively (Table 2). Correspondingly, the effect of initial allyl ethers on the side transformations of siloxanes [estimated by the overall yield of HMe₂Si (OSiMe₂)_nH at the maximum ether conversion] decreases in the series AllOPh > AllOBu > AllOGlyc > AllOBn > AllOEt.

Secondary transformations of AllOGlyc provide a larger contribution to the reduction of selectivity. The yield of propenyl glycidyl ether isomers reaches 5.0%, which is 3.5 times higher than, e.g., the yield of propenyl butyl ether isomers), and the yield of propyl glycidyl ether is 3.3%. Heating of AllOGlyc with [(SiO₂)–2SBu–PtCl₂] in the absence of (HMe₂Si)₂O for 10 h at 80°C afforded 2.3% of propenyl glycidyl ether, which is twice as low as in the hydrosilylation.

The hydrosilylation of AllOGlyc by Si–Hcontaining monoadducts in the presence of $[(SiO_2)-2SR-PtCl_2]$ (10 h at 80°C) produced exclusively the γ,γ -adduct whose concentration was 8.3%; it is slightly lower than in the reactions with AllOEt, AllOBu, AllOBn.

Reused of the $[(SiO_2)-2SR-PtCl_2]$ catalysts resulted in gradual reduction of their activity (3 cycles, TOF_{AllOBu} 0.1794 s⁻¹, TOF_{AllOBn} 0.2105 s⁻¹, TOF_{AllOGlyc} 0.0958 s⁻¹, TOF_{AllOEt} 0.0938 s⁻¹, TOF_{AllOPh} 0.0398 s⁻¹, TON > 2560), and the ether conversion decreased in the catalyst series $[(SiO_2)-2SBn-PtCl_2] > [(SiO_2)-2SHex-PtCl_2] > [(SiO_2)-2SBu-PtCl_2]$, the reaction time being the same. Neither selectivity nor regioselectivity nor γ_{Σ} -selectivity changed to an appreciable extent upon catalyst recycling; the amount of by-products resulting from secondary transformations of siloxanes and allyl ethers also remained virtually unchanged.

Interaction between the catalysts and reactants. In order to understand the catalytic mechanism we studied the reactions of [(SiO₂)–2SBu–PtCl₂] with 1,1,3,3-tetramethyldisiloxane and allyl butyl ether, and the obtained products were involved in comparative hydrosilylation.

The IR spectrum of the platinum complex treated with (HMe₂Si)₂O and then thoroughly washed with methylene chloride displayed a new absorption band at 2146 cm⁻¹, which can be assigned to Si-H stretching vibrations of the siloxane; simultaneously, the intensity of bands at 2931 and v_{as} (C–S) 2858 cm⁻¹ typical of the initial complex decreased. The catalytic activity of the preliminarily treated complex (2 h at 80°C) was higher than before the treatment; after 2.5 h at 80°C, the conversion of AllOBu was 55 against 38% (when both reactants were added simultaneously). The reaction selectivity with respect to the γ -adduct was significantly lower (46.5%) due to increased yield of the γ,γ -adduct (by a an order of magnitude, 33%); the regioselectivity slightly decreased (95.1 against 96.3%), and the γ_{Σ} -selectivity insignificantly increased (from 94.9 to 96.6%).

Analogous treatment of $[(SiO_2)-2SBu-PtCl_2]$ with allyl butyl ether produced no appreciable changes in the IR spectrum, but the conversion of AllOBu increased as compared to the untreated complex (41% after 2.5 h). In this case, the selectivity with respect to the γ -adduct, regioselectivity, and γ_{Σ} -selectivity were lower by 1.4, 2.7, and 2.6%, respectively, due to larger contribution of secondary transformations of AllOBu (the yields of propenyl butyl and propyl butyl ethers were 12.0 and 2.9%, respectively).

Taking into account the known concept of the hydrosilylation mechanism, the results of our study suggest that the initial platinum complex reacts with both allyl ether and 1,1,3,3-tetramethyldisiloxane. Primary coordination of allyl ether facilitates isomerization of the double bond, and the subsequent attack of the intermediate complex by siloxane promotes reduction of the unsaturated ether. In its turn, primary formation of silicon hydride complex is the key stage of hydrosilylation and side transformations of siloxanes.

EXPERIMENTAL

The IR spectra (4000–400 cm⁻¹) were recorded in KBr on a Shimadzu FTIR-8400S spectrometer. The product mixtures were analyzed by GLC on an Agilent 7890A chromatograph equipped with a thermal detector; DB-1 capillary column, conductivity 30 m×0.32 mm, film thickness 1 μ m; sample volume 0.5 µL; injector temperature 250°C. The reaction mixtures obtained from AllOPh and AllOBn were analyzed under temperature programming from 150°C (4 min) to 290°C at a rate of 42 deg/min, followed by 35 min at 290°C; carrier gas helium, split ratio 1:300. The reaction mixtures obtained from AllOEt, AllOBu, and AllOGlyc were analyzed under temperature programming from 70°C (5 min) to 200°C at a rate of 5 deg/min and then to 225°C at a rate of 25 deg/min, followed by 45 min at 225°C; carrier gas helium, split ratio 1:250.

The hydrosilylation of allyl ethers was carried out in ampules at 60–100°C. An ampule was charged with a required amount of catalyst, and a preliminarily prepared mixture of 1,1,3,3-tetramethyldisiloxane, allyl ether, and toluene at a molar ratio of 6:4:1 was added; the concentration of platinum in the reaction mixture was $(1.8-5) \times 10^{-4}$ M, and the platinum content of the supported catalyst was $c_{\text{Pt}} (2.8-4.1) \times 10^{-5}$ mol/g. The conversion and selectivity were determined by GLC from the kinetic data using toluene as internal standard according to the procedure described in [38]. Secondary catalytic transformations of (HMe₂Si)₂O and allyl ethers were studied by analogy with the main hydrosilylation process.

Commercial 1,1,3,3-tetramethyldisiloxane, allyl glycidyl ether (Acros Organics), allyl butyl, allyl phenyl, and allyl benzyl ethers (Aldrich), allyl ethyl ether (Fluka), and toluene and methylene chloride of analytical grade were used. The complexes $[(SiO_2)-2SR-PtCl_2]$ (R = Bu, Hex, Bn) were synthesized as described in [37], and *cis*-[Pt(Bn₂S)₂Cl₂] was prepared according to [47].

ACKNOWLEDGMENTS

This study was performed in the framework of state assignment of the Ministry of Education and Science of the Russian Federation (project no. 11.5362.2017/8.9) and the integrated program for the development of high tech production of the Ministry of Education and Science (contract no. 03.G25.31.0237).

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