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Hydrosilylation of Cyclohexene and Allyl Chloride with Trichloro-, Dichloro(methyl)-, and Chlorodimethylsilanes in the Presence of Pt(0) Complexes

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Abstract—Hydrosilylation of cyclohexene and allyl chloride in the presence of Pt(0) complexes with tetramethyldivinyldisiloxane (Karstedt catalyst) and hexavinyldisiloxane was studied. It was shown that these catalysts are much more active in the hydrosilylation of cyclohexene with trichloro-, dichloro(methyl)-, and chlorodimethylsilane than the Pt(II)-containing Speier catalyst. In the hydrosilylation of allyl chloride in the presence of Pt(0) complexes, the ratio of the fraction of addition products to the fraction of reduction products increases from 5.7 (Speier catalyst) to 10–16. Quantum-chemical calculations showed that Pt(0) complexes are more active than Pt(II) complexes on the stage of formation of platinum silicon hydride complexes.

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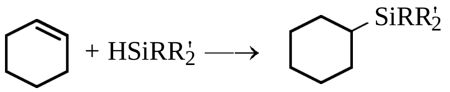
Previously [1] we showed that Pt(0) complexes with tetramethylvinyldisiloxane (Karstedt catalyst) and hexavinyldisiloxane are more active in hydrosilylation of ethylene with triethoxysilane than a solution of chloroplatinic acid in 2-propanol [Speier catalyst (**I**)]. The aim of this work was to assess the efficiency of these complexes in hydrosilylation of other unsaturated compounds, cyclohexene and allyl chloride, which are less active in addition reactions as compared to unsaturated compounds of the C_nH_{2n} homologous series. Sufficiently high yields in the hydrosilylation of cyclohexene with trichlorosilane and dichloro(methyl)silane in the presence of catalyst **I** could only be obtained at long reaction times, sometimes in sealed ampules or in autoclave. For example, the reaction of cyclohexene with trichlorosilane in the presence of catalyst **I** for 20 h at 100°C gave 78% of trichloro(cyclohexyl)silane [2]. Dichloro(cyclohexyl)methylsilane was obtained in 100% yield upon heating of starting materials in a sealed ampule on a water bath for 20 h [3]. No data on the hydrosilylation of cyclohexene with chlorodimethylsilane are available.

With the purpose to compare the activity of cyclohexene and hexane, we performed competing hydrosilylation of these compounds with trichlorosilane in the presence of Pd(0) hexavinyldisiloxane complex. After 16 h the reaction mixture contained 57.6% of trichloro(hexyl)silane and as little as 0.6% of trichloro(cyclohexyl)silane. We carried out hydrosilylation of cyclohexene with trichlorosilane, dichloro(methyl)silane, and chlorodimethylsilane.



(1)

IIa–IIc

R = R' = Cl (**a**); R = Me, R' = Cl (**b**); R = Cl, R' = Me (**c**).

The results of hydrosilylation are listed in Table 1. In the presence of Karstedt catalyst **III**, the yield of trichloro(cyclohexyl)silane under reflux for 1.5 h was 69.1%, and in the presence of platinum hexavinyldisiloxane complex **IV**, 93.8%. In the presence of catalyst **I** under the same conditions, no product was obtained. Chromatographic analysis and IR spectroscopy showed that the hydrosilylation of cyclohexene with trichlorosilane gives no dehydrogenative hydrosilylation by-products. Analogously in the presence of catalyst **I** the yield of dichloro(cyclohexyl)methylsilane is 92.4%, while in the presence of catalyst **I**, 95.4%. The hydrosilylation of cyclohexene with dichloro(methyl)silane, too, gives no dehydrogenative

Table 1. Hydrosilylation of cyclohexene with trichloro-, dichloro(methyl)-, and chlorodimethylsilane

Catalyst		Reaction time, h	Final temperature, °C	Yield of adduct, %	Method
comp. no	$M_{Pt} \times 10^6$				
		R = R' = Cl			
I	10.2	5	53	0	*a*, *b*
III	20.4	1.5	100	69.1	*b*
IV	10.2	5	116	93.8	*b*
IV	1.7	27	115	92.1	*b*
I + **V**	1.7	72	20	89	*c*
I + **V**	1.7	7	92	78.1	*b*
		R = Me, R' = Cl			
III	1.7	23.5	120	92.4	*d*
IV	1.7	8	64	41.4	*b*
IV	1.7	70[a]	64	81.2	*b*, *c*
IV	1.7	1152	20	95.4	*b*
I + **V**	1.7	6	20	13.4	*c*
I + **V**	1.7	24	20	53.3	*c*
I + **V**	1.7	48	20	80.1	*c*
I + **V**	1.7	72	20	93.2	*c*
		R = R' = Me			
II	1.7	34.5	105	18.6	*b*

[a] Including 62 h by procedure *c*.

hydrosilylation products. But in some experiments one additional product was formed boiling by about 30°C lower than the main compound. Evidently, it was chloro(cyclohexyl)methylsilane. The latter might form from chloro(methyl)silane generated by disproportionation of dichloro(methyl)silane.

$$2MeSiHCl_2 \longrightarrow MeSiH_2Cl + MeSiCl_3. \qquad (2)$$

The hydrosilylation of cyclohexene with trichlorosilane and dichloro(methyl)silane also easily proceeds in the presence of catalyst **I** plus allyl glycidyl ether (**V**). The yields of trichloro(cyclohexyl)silane and dichloro(cyclohexyl)methylsilane at room temperature within 72 h reach 89.0 and 93.2%, respectively.

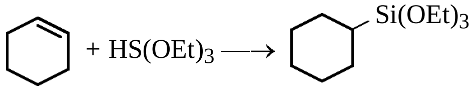
The hydrosilylation of cyclohexene with chlorodimethylsilane in the presence of catalyst **IV** was studied both at elevated and at room temperature. At room temperature, no changes were observed within one month. After 34.5 h under reflux, the final reaction temperature reached 105°C, and chloro(cyclohexyl)dimethylsilane was isolated in 18.5% yield. The resulting data show that the activity of silanes in cyclohexene hydrosilylation decreases in the series $HSiCl_3 \geq MeHSiCl_2 > Me_2HSiCl$.

The structure of cyclohexylsilanes was confirmed by NMR spectroscopy. The ^1H NMR spectrum of trichloro(cyclohexyl)silane contained two multiplets of ring protons at 1.2–1.4 and 1.7–2.0 ppm. The ^{13}C NMR spectrum contained cyclohexyl proton signals at 33.5 (C^1), 26.8 (C^2 or C^3), 26.0 (C^4), and 25.4 ppm (C^2 and C^3). The ^1H NMR spectrum of dichloro(cyclohexyl)methylsilane contained a singlet of the methyl group at 0.72 ppm and two complex signals at 1.2–1.3 and 1.7–1.9 ppm related to the cyclohexyl substituent. The ^1H NMR spectrum of chloro(cyclohexyl)dimethylsilane displayed two methyl singlets at 0.72 and 0.78 ppm and two complex signals at 1.2–1.3 and 1.7–1.9 ppm related to the cyclohexyl substituent. The ^{13}C NMR spectrum showed methyl carbon signals at 1.05 and 0.35 ppm, as well as signals at 28.18 (C^1), 27.54 (C^2 and C^3), 26.62 (C^4), and 26.36 ppm (C^2 and C^3), related to the cyclohexyl substituent.

Cyclohexyltriethoxysilane is usually prepared in two stages. The first stage involves hydrosilylation of cyclohexene with trichlorosilane, and the second, reaction of the resulting product with ethanol. With rhodium catalysts, the hydrosilylation of cyclohexene (80–100°C, 2–8 h) provides as little as 9% of cyclohexyltriethoxysilane [4]. No data on hydrosilylation in the presence of catalyst **I** were reported.

Table 2. Total energies (E, kcal mol^{-1}), enthalpies (H, kcal mol^{-1}), Gibbs energies (G, kcal mol^{-1}), and entropies (S, cal mol^{-1} K^{-1}) of the intermediate and final products (platinum silicon hydride σ complexes) of reactions (5) and (6), in relation to reagents

System	ΔE, kcal mol^{-1}	ΔH, kcal mol^{-1}	ΔS, kcal mol^{-1} K^{-1}	ΔG, kcal mol^{-1}
Reaction (5), X = Cl				
Pt–H–Si complex	–5.43	–4.56	–25.35	3
Reaction products	–11.45	–10.01	–15.72	–5.32
Reaction (5), X = OCH_3 [C3 symmetry $HSi(OCH_3)_3$]				
Intermediate complex (Pt–H 3.2 Å)	–1.15			
Reaction products	–0.75	–0.08	–27.86	8.39
Reaction (5), X = Cl				
Intermediate complex (Pt–H 3.6 Å)	–6.15			
Reaction products	6.36	7.41	–34.30	17.64
Reaction (6), X = OCH_3 [C3 symmetry $HSi(OCH_3)_3$]				
Reaction products	–1.35	–0.35	–41.50	12.02



(3)

We carried out reaction (3) in the presence of catalyst **IV** at 95–100°C and atmospheric pressure. Monitoring by GLC showed that under these conditions only tetraethoxysilane and siloxanes were formed. Prolonged heating increased the fraction of tetraethoxysilane in the mixture.

$$7HSi(OEt)_3 \longrightarrow Si(OEt)_4 + (EtO)_3SiOSi(OEt)_3 + (EtO)_3SiOSi(OEt)_2OSi(OEt)_3 + 3EtH + 2H_2. \quad (4)$$

With the other platinum catalysts, analogous results were obtained. Gas chromatography–mass spectrometry revealed in the resulting mixture 25.1% of hexamethyldisiloxane {molecular ion peak with m/z 342 and a peak with m/z 297 $[M - OEt]^{+\cdot}$ (100%)} and 49.4% of octaethoxytrisiloxane {molecular ion peak is absent, peaks with m/z 405 $[M - C_2H_3 - OEt]^+$ (5.8%), 368 $[M - EtOEt - OH - H_2O]^{+\cdot}$ (23.1%), 281 $[EtO(Et)Si - OSi(OEt)_3]^{+\cdot}$ (56.9%), 253 $[EtO - SiH - O - Si(OEt)_3]^{+\cdot}$ (22.6%), and 207 $[EtOSi{=}Si(OEt)_2]^{+\cdot}$ (100%)}.

The ^{1}H NMR spectrum of siloxanes contained two triplets of methyl protons at 1.25 ppm, and two quartets of methylene protons at 3.85 ppm with the intensity ratio 3:2. The presence of two sets of signals can be explained by the formation of two different siloxanes, which agrees with the GC–MS data.

Triethoxysilane was found to disproportionate in the presence of catalyst **IV** under reflux. In the presence of cyclohexene this reaction proceeds 75% more actively. Therefore, we failed to hydrosilylate cyclohexene with triethoxysilane.

Note that despite of numerous studies of hydrosylylation many specific features of this process remain unclear, e.g., the higher activity of Pt(0) complexes compared to Pt(II) and of chlorosilanes compared to alkoxysilanes.

To find out the regularities and specific features of the hydrosilylation of unsaturated compounds with chlorosilanes and alkoxysilanes in the presence of Pt(0) and Pt(II) complexes, we carried out quantum-chemical calculations (GAUSSIAN-98, B3LYP/lanL2DZ) of the first reaction steps, that is, formation of platinum silicon hydride complexes. Model systems including Pt(0) and Pt(II) olefin complexes, trichlorosilane, and trimethoxysilane were studied.

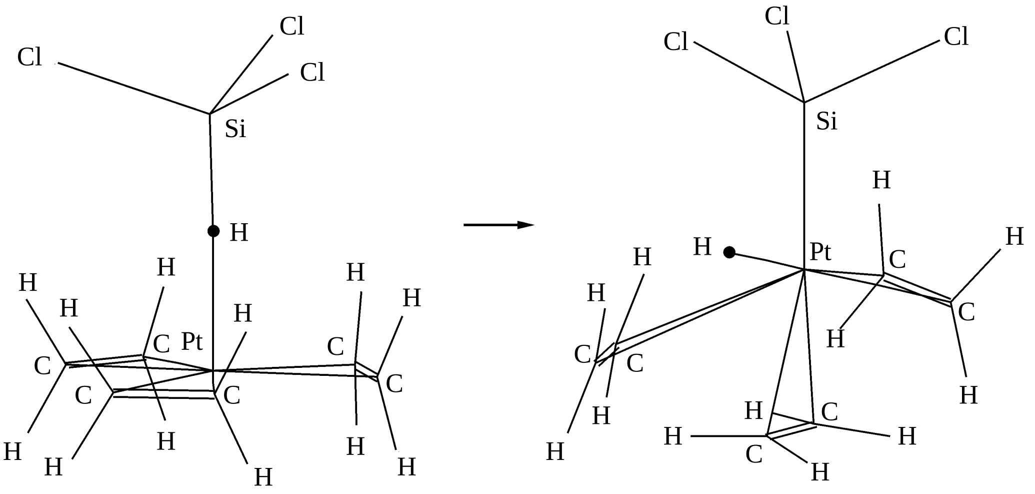
$$(C_2H_4)_3Pt^0 + H{-}SiX_3 \longrightarrow (C_2H_4)_3Pt^{-1}{-}H{-}SiX_3 \longrightarrow (C_2H_4)_3Pt^2H(SiX_3), \quad (5)$$

$$(C_2H_4)_2Pt^2Cl_2 + H{-}SiX_3 \longrightarrow (C_2H_4)_2Cl_2Pt^1{-}H{-}SiX_3 \longrightarrow (C_2H_4)_2Cl_2Pt^4H(SiX_3), \quad (6)$$

$$X = Cl,\ OCH_3.$$

The calculated parameters of the intermediate states and products of the platinum silicon hydride complex formation reactions are listed in Table 2.

New features of the structure and formation of ethylene and silicon hydride platinum complexes were revealed. Reaction (5) (X = Cl) can proceed through intermediate formation of a stable complex $(C_2H_4)_3Pt$–



Structures of the molecular systems on the separate steps of reaction (1) (GAUSSIAN-98, B3LYP/LanL2DZ)

$H{-}SiCl_3$ including a Pt–H–Si bridging three-center bond (see figure), and its subsequent rearrangement to a platinum silicon hydride complex. Finally, the most stable reaction product occurs to be a platinum silicon hydride complex with Pt–H and Pt–Si σ bonds. Therewith, one of the ethylene ligands leaves Pt and no longer coordinated to it (see figure). As follows from the total energy surface of the rearrangement of the $(C_2H_4)_3Pt{-}H{-}SiCl_3$ complex to $H{-}Pt{-}SiCl_3(C_2H_4)_3$, this reaction has a fairly low potential barrier (15–20 kcal mol^{-1}).

Characteristic changes take place in the type of intermediate structures and parameters of reaction products in the case of triethoxysilane and a Pt(II) complex. No stable bridge structures are formed. The minimum point on the coordinate of approach of two reaction centers corresponds to formation of van der Waals complexes at a distance of 3.2–3.6 Å. Further approach causes an exponential growth of the energy of the system. Analysis of the energy and thermodynamic parameters of platinum silicon hydride complexes with Pt–H and Pt–Si σ bonds points to their lower stability as compared to the initial system including isolated molecules (see Table 2).

Hence, the higher activity of Pt(0) complexes and trichlorosilane in hydrosilylation can be associated with the easier formation and higher stability of platinum silicon hydride complexes.

It is known from the literature that allyl chloride reacts with trichloro-, dichloro(methyl)-, triethoxy-, and chlorodimethylsilane. Hydrosilylation of allyl chloride is accompanied by reduction leading to propylene and chlorosilane. Propylene enters hydrosilylation to form corresponding propylsilanes.

$$\begin{array}{lll} & \xrightarrow{1} & ClCH_2CH_2CH_2SiR_3, \\ ClCH_2CH{=}CH_2 + HSiR_3 & & \\ & \xrightarrow{2} & CH_3CH{=}CH_2 + ClSiR_3. \\ & & \quad\Big\downarrow HSiR_3 \\ & & \quad PrSiR_3 \end{array} \qquad (7)$$

The fraction of reduction products increases on methyl substituents for chlorine in the silicon hydride molecule [4].

It is known that decreased temperature decrease improves the yield of hydrosilylation products and suppresses reduction. The latter pathway is also suppressed when the reaction is performed at increased pressure (8 atm). Hence, the reaction of allyl chloride with trichlorosilane at atmospheric pressure provides 64% of the adduct and 36% of the reduction product (addition/reduction ratio 1.8 : 1). At increased pressure this ratio reaches 5.6 (83.5 : 16.5) [5]. Some additives to the Speier catalyst favor hydrosilylation. Addition of *N*,*N*-dimethylacetamide [6], tributylamine [7], triphenylphosphine [8] increases the yield of trichloro-(γ-chloropropyl)silane from 57–64% to 85%.

The data on the hydrosilylation of allyl chloride in the presence of catalyst **I**, Pt(0) complexes, and catalyst **I** plus triphenylphosphine and trichlorophosphine oxide are listed in Table 3. As seen, in the presence of catalysts **III** and **IV** the yield of trichloro-(γ-chloropropyl)silane increases from 62.2 to 67.5–75.0%, and the addition/reduction (A/R) ratio changes from 5.7 to 14.6–16.3. Triphenylphosphine and trichlorophisphine oxide additives to the Speier catalyst do not give a positive effect. The hydrosilylation of allyl chloride with chlorodimethylsilane in the presence of

Table 3. Hydrosilylation of allyl chloride with trichlorosilane and chlorodimethylsilane

R	Synthesis conditions		Content of products in the mixture, %		Yield, %	A/R [b]
	catalyst [a]	time, h	$C_3H_7SiR_2Cl$	$ClCH_2CH_2CH_2SiR_2Cl$		
Cl	**I**	4.2	10.8	61.6	62.2	5.7
Cl	**I** + PPh_3	5.5	15.9	62.4	62.9	3.9
Cl	**I** + $POCl_3$	8.25	2.9	30.8	31.0	10.6
Cl	**III**	5.6	5.1	74.4	75.0	14.6
Cl	**IV**	5.5	5.2	84.4	85.1	16.3
Me	**III**	8.2	7.0	75.7	80.6	11.5
Me	**IV**	10.5	6.6	71.2	75.7	10.8

[a] One drop (0.017–0.018 ml) of the catalyst was added. [b] Addition/reduction ratio.

catalyst **III** leads to high yields of (γ-chloropropyl)dimethylsilane (75.7–80.6%). The A/R ratio is 10.8–11.5.

EXPERIMENTAL

Gas chromatography was performed on an LHM-80 chromatograph with a thermal conductivity detector, carrier gas helium (30 ml $\min^{-1}$), 1000×3-mm stainless-steel column packed with 5% SE-30 on Chromaton N-AW-DMCS (0.25-0.31 mm). The oven temperature was programmed from 20 to 300°C at a rate 8 deg $\min^{-1}$, injector temperature 350°C, detector temperature 250°C.

The mass spectra were obtained on a Hewlett–Packard HP-5971A GC–MS system at an ionizing voltage of 70 V. Gas chromatography was performed on a 25000×0.32-mm quartz capillary column, stationary phase DV-5 (film thickness 25 nm). The oven temperature was programmed from 50 to 280°C at a rate 7°C $\min^{-1}$; carrier gas helium.

The NMR spectra were taken on a Bruker AM-360 Fourier spectrometer (360 MHz for ^{1}H and 90 MHz for ^{13}C).

The Karstedt catalyst was prepared by the procedure in [9], catalyst **I** with the allyl glycidyl ether additive was heated for 0.5 h at 50°C prior to use.

Hydrosilylation of unsaturated compounds. *a*. A mixture of 0.03 mol of unsaturated compound and 0.033 mol of hydrosilane was treated with a catalyst and heated to slight reflux. In the course of the reaction increase in the boiling point of the mixture was observed. After it reached 120°C, the reaction mixture was kept at this temperature for 1 h and then cooled. If the temperature of the reaction mixture did not reach 120°C. it was kept for 1 h at the highest reached temperature and then cooled.

b. One drop (0.017–0.018 ml) of a 0.1 M solution of platinum catalyst was treated with 1/10 of a mixture of 0.03 mol of unsaturated compound and 0.033 mol of hydrosilane. The resulting mixture was heated to reflux, and the residual reagent mixture was added in portions after the temperature of the reaction mixture reached 80°C. The mixture was refluxed until it reached 120°C and then kept at this temperature for 1 h and cooled. If the temperature did not reach 120°C, the reaction mixture was kept at the highest reached temperature for 1 h and then cooled.

c. A mixture of 0.03 mol of unsaturated compound, 0.033 mol of hydrosilane, and one drop of catalyst (0.017–0.018 ml) was kept at room temperature and then analyzed.

d. One drop (0.017–0.018 ml) of a 0.1 M solution of platinum catalyst was mixed with unsaturated compound (0.03 mol), and the mixture was heated to 80°C. In the course of the heating, 0.033 mol of hydrosilane was added in 6 equal portions.

The final reaction mixtures were fractionated by distillation.

Trichloro(cyclohexyl)silane. Distillation of the mixture resulting from the reaction of cyclohexene with trichlorosilane gave a fraction with bp 92–95°C (20 mm Hg), containing 97.7% of trichloro(cyclohexyl)silane, n_D^{20} 1.228; MR_D 50.18; calc. MR_D 50.76. Published data [10]: n_D^{20} 1.4774; d_4^{20} 1.2211. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.2–1.4 m (6H), 1.7–2.0 m (5H). ^{13}C NMR spectrum ($CDCl_3$), δ_Cm ppm: 33.5 (C^1), 26.8 (C^2 or C^3), 26.0 (C^4), 25.4 (C^2 or C^3) (all signals belong to the cyclohexyl substituent).

Dichloro(cyclohexyl)methylsilane: bp 100°C (20 mm), n_D^{20} 1.4722, d_4^{20} 1.091; MR_D 50.63, calc. MR_D 50.64. Published data [11]: n_D^{20} 1.4724; d_4^{20}

1.0953. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.72 s (3H, Me), 1.2–1.3 m (4H), 1.7–1.9 m (5H).

Chloro(cyclohexyl)dimethylsilane: bp 72–74°C, n_D^{20} 1.4620; d_4^{20} 0.955; MR_D 50.88, calc. MR_D 51.16. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.34 s (6H, Me), 1.2–1.3 m (5H), 1.7–1.9 m (6H).

Reaction of cyclohexene with triethoxysilane. Syntheses were carried out in the presence of catalysts **II** and **III** by procedures *a*, *b*, and *c*. No changes were observed in the reaction mixture at room temperature. The mixtures resulting from the syntheses were fractionated by distillation to obtain a fraction with bp 118°C (3 mm Hg), n_D^{20} 1.406, and d_4^{20} 0.983, containing 21.5% of hexamethyldisiloxane, 49.4% of octaethoxytrisiloxane, and unidentified admixtures.

The hydrosilylation of allyl chloride was carried out by procedure *a*.

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