Synthesis of platinum complexes containing (+)-bornyl- and (-)-menthylammonium in the outer coordination sphere and their catalytic activity in hydrosilylation reactions

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Optically active (+)-bornyl- and (–)-menthylammonium platinates were synthesized starting from H₂[PtCl₆]•4H₂O and hydrochlorides of the corresponding amines. Catalytic activity of the complexes in the hydrosilylation reactions of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane with 1,1,3,3-tetramethyldisiloxane and acetophenone with diphenylsilane was studied. The addition of the siloxanes leads to a predominant formation of β -adduct. Activity of the catalysts, evaluated on the 50% conversion of the substrate, decreases in the following sequence: (–)-(menthylNH₃)₂[PtCl₆] > (Et₃NH)₂[PtCl₆] > (+)-(bornylNH₃)₂[PtCl₄] > (+)-(bornylNH₃)₂[PtCl₆]. Asymmetric induction is observed in the hydrosilylation of acetophenone in the presence of (+)-(bornylNH₃)₂[PtCl_n] (n = 4, 6); (+)-(bornylNH₃)₂[PtCl₆] showed the highest catalytic activity and selectivity. The hydrosilylation of acetophenone gave 1-phenylethoxy(diphenyl)silane, 1-phenylvinyloxy(diphenyl)silane, and 2-phenylethyl-2-diphenylsiloxy(diphenyl)silane as the products.

Key words: terpenoids, asymmetric induction, hydrosilylation, acetophenone, siloxanes, platinates, (+)-bornylamine, (–)-menthylamine.

Optically active coordination compounds with nitrogen-containing ligands are widely used for the achievement of asymmetric induction in the catalyzed transformations of prochiral unsaturated compounds. In such catalysts, chiral centers are in the inner coordination sphere of the metal complex.^{1–3} Ionic coordinating compounds, forming intimate contact pair with the metal, belong to another promising type of optically active catalysts.^{4–11}

It is known^{12–14} that ammonium platinum complexes of the ionic type proved to be promising catalysts of hydrosilylation reaction. In this connection, it seemed reasonable to synthesize optically active ammonium platinates, containing a chiral center in the outer coordination sphere, to study their catalytic activity, and to estimate their ability for the asymmetric induction.

Results and Discussion

Synthesis of complexes. The reaction of aqueous hydrogen hexachloroplatinate with excess (+)-bornyl- or (-)-menthylammonium hydrochlorides at room temperature leads to the corresponding hexachloroplatinate(IV), gradually precipitating from the reaction mixture (the yield

was 50-55%) (Scheme 1). The yield of the target product can be raised up to 67-74% by the use of propan-2-ol solution of hydrogen hexachloroplatinate with subsequent precipitation of the product with diethyl ether.

Scheme 1

 $H_2[PtCl_6] \cdot 4H_2O + 2 RNH_2 \cdot HCl \longrightarrow (RNH_3)_2[PtCl_6]$

$$RNH_2 = \overset{\text{Me}}{\longrightarrow} \overset{\text{Me}}{\underset{\text{Me}}{\longrightarrow}} \overset{\text{Me}}{\underset{Me}}{\overset{\text{Me}}{\underset{Me}}{\underset{Me}}{\underset{Me}}{\underset{Me}}{\overset{\text{Me}}{\underset{$$

The complexes are virtually insoluble in acetone, benzene, dichloromethane, nitrobenzene, and ethanol; they are soluble in DMSO and DMF, however, a dissolution in DMSO can be accompanied by the partial changes in the coordination sphere (for example, it is known¹⁵ that the heating of [PtPy₄]Cl₂ or [PtPy₂Cl₂] in DMSO easily leads to *cis*- and *trans*-[Pt(DMSO)PyCl₂]). In our case, no incorporation of DMSO into the inner coordination sphere is observed upon keeping of the complexes at 20 °C for 3 h, however, a triplet signal of the coordinated DMSO

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at δ 3.4–3.6 appears in the ¹H NMR spectrum when the temperature is raised to 60 °C.

The IR spectra of (+)-(bornylNH₃)₂[PtCl₆] and (-)-(menthylNH₃)₂[PtCl₆] complexes contain characteristic absorption bands in the far IR-region: v(Pt-Cl) at 330 and 333 cm⁻¹.

The synthesis of bornyl- and menthylammonium tetrachloroplatinates(II) was accomplished by the action of aqueous hydrazine on the corresponding hexachloroplatinates(IV) according to the standard procedure.¹⁶ The reduction of (+)-(bornylNH₃)₂[PtCl₆] proceeds slowly and affords expected (+)-(bornylNH₃)₂[PtCl₄] (v(Pt-Cl) 316 cm⁻¹), whereas (-)-(menthylNH₃)₂[PtCl₆] complex is immediately reduced to platinum metal, which, probably, results from the high lability of (-)-(menthylNH₃)₂[PtCl₄] formed.

The absorption spectra of platinates(IV), differing only in the nature of the ammonium ligand, are very similar. Four absorption bands are presented in the available range (DMF) for (+)-(bornylNH₂)₂[PtCl₄] and (+)-(bornylNH₂)₂[PtCl₄] complexes, three bands, for (-)-(menthylNH₃)₂[PtCl₆] complex; positions and intensities of the bands are typical of the platinum(II) and (IV) complexes. In the circular dichroism (CD) spectrum of bornylammonium platinates(II) and (IV), a d-d-transition for platinum at $\lambda = 388$ nm is observed, which has a weak induced optical activity; for (-)-(menthyl- NH_{3} , $[PtCl_{6}]$, activity of this band turned out to be below the threshold of detection. This results from the fact that the rigid asymmetric bornyl framework is the better inductor of optical activity as compared with the conformationally labile menthyl structure.

The platinates(II) and (IV) obtained rotate the planepolarized light in the same direction as the bornyl- and menthylammonium hydrochlorides. However, the observed molar rotation of the platinates is lower than that of the corresponding hydrochlorides (for example, for (bornylNH₃)₂[PtCl₆], $[\Phi]_D^{20}$ in DMSO is +70.9°, for (bornylNH₃)₂[PtCl₄], +93.6°, and for bornylNH₂•HCl, +34.5°).

Hydrosilylation of siloxanes. 1,1,3,3-Tetramethyldisiloxane (HMe₂Si)₂O and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (VinMe₂Si)₂O (Vin is vinyl) have been chosen for the study of comparative catalytic activity of the obtained metal complexes in the hydrosilylation reaction. Disiloxanes (HMe₂Si)₂O and (VinMe₂Si)₂O besides the "modeling" of typical processes of solidifying of siloxanes by the hydrosilylation reaction, allow one to obtain siloxane monomers, containing active terminal Si—H or Si—Vin groups, as well as to synthesize carbosiloxane linear polymers.

Hydrosilylation in the $(HMe_2Si)_2O-(VinMe_2Si)_2O$ system with equimolar ratio of the reagents proceeds with the use of either one or two active groups (Si-H or

Si–Vin), giving products of α -, β -, and diaddition, which further are rapidly converted into the higher molecular weight adducts. Such a behavior is in a good agreement with the literature data^{17,18} on the hydrosilylation with three-molar excess (HMe₂Si)₂O. In the ¹H NMR spectrum of the reaction mixture, characteristic signals for the SiCH₂CH₂Si ethylene bridge (δ 0.42) and a doublet of the Me group of the SiCHMeSi fragment (δ 1.01, J = 7.5 Hz) are presented. The chromato-mass spectrometric data of the reaction mixtures confirm formation of the products of α -, β -, and the succeeding additions of the siloxanes. However, the retention times of the products differ from those given in the literature (for example, for α - and β -adducts, $t_r = 3.4$ and 3.3 min, whereas in Ref. 18, $t_{r} = 24$ and 22 min, respectively), as well as intensities of the base peaks, which can be explained by different conditions for the spectra recording. In the mass spectra of the GC peaks, the molecular ion signals are absent; the base peak depends on the structure and molecular weight of the compound (for the products, containing terminal Si-H and Si-Vin groups, the base peak, as a rule, is the ion with m/z 305 $([Me_2SiOSi(Me_2)CH_2CH_2Si(Me_2)OSi(Me_2)Vin - Me]^+$ or [Me₂SiCH₂CH₂Si(Me₂)OSi(Me₂)CH₂CH₂SiMe₂]⁺); if only terminal Si-H groups are present, the ion with m/z 293 ([Me₂SiOSi(Me₂)CH₂CH₂Si(Me₂)OSiMe₂]⁺) is the base one). The presence of the fragment with m/z 28, which we assigned to the $[CH_2CH_2]^+$ ion, serves as the

Scheme 2



β-Adduct



Scheme 3

main criterion allowing us to distinguish a direction of the addition: it is present when the β -addition occurs, but it is absent in the α -adduct.

According to the GLC data, an addition of one $(HMe_2Si)_2O$ molecule initially takes place, predominantly giving rise to the β -adduct (Scheme 2).

Then, in the presence of all the complexes under consideration, the formed monoadducts undergo further rapid transformations, leading mainly to the products of β , β -addition and, to a lesser extent, to the α , α - and α , β -adducts. Formation of the double-addition products with the equimolar ratio of reagents can take place owing both to the addition of another (HMe₂Si)₂O molecule to the vinyl group of the monoadduct (Scheme 3; the hydrosilylation of the β -adduct is shown as the example) and to the addition of the silicon-hydride fragment of the monoadduct to another (VinMe₂Si)₂O molecule (Scheme 4; see Ref. 18).

When the equimolar ratios of the reagents are used, both pathways are equally possible, however, a significant increase in the effective positive charge on the silicon atom of the Si—H group of the monoadducts as compared with $(HMe_2Si)_2O$, as it is known,¹⁹ should make difficult their addition to the vinyl group (according to the quantum chemical calculations for the β -adduct, the charge on the silicon atom is +0.982 as compared to +0.622 for $(HMe_2Si)_2O$ (see Ref. 20)).

The GLC analysis of conversions of the dihydro- and divinylsiloxanes shows that the conversion of $(HMe_2Si)_2O$ at least is not lower than the conversion of $(VinMe_2Si)_2O$ (for example, in the presence of (+)-(bornylNH₃)₂[PtCl₆] the conversion after 3.5 h is 95 and 88%, whereas in the presence of (+)-(bornylNH₃)₂[PtCl₄], 66 and 65% for $(HMe_2Si)_2O$ and $(VinMe_2Si)_2O$, respectively). Analysis of the side processes, occurring during the hydrosilylation, showed the presence of dehydrocondensation and disproportionation of $(HMe_2Si)_2O$, however, according to the GLC data, consuming of the latter in the side reactions (for example, in the presence of (+)-(bornylNH₃)₂[PtCl₆]) does not exceed 2% for 3.5 h. A slightly higher conversion



Scheme 4

of $(HMe_2Si)_2O$ (thus, if the consumption of $(HMe_2Si)_2O$ in the side processes is subtracted, the conversion of $(HMe_2Si)_2O$ in the presence of (+)-(bornylNH₃)₂[PtCl₆] is higher than that of $(VinMe_2Si)_2O$ by 5%) allows one to assume that the monoadducts are slightly more reactive in the reaction with $(HMe_2Si)_2O$ than with $(VinMe_2Si)_2O$.

Analysis of the chromato-mass spectra of the hydrosilylation products also confirms this assumption, since $H[Me_2SiOSi(Me_2)CH_2CH_2]_2Si(Me_2)OSi(Me_2)H$ siloxane with two terminal Si-H groups ($t_r = 4.8$ min) is the main product of the double addition, the scheme of decomposition of which agrees with that given in the literature.¹⁸

A prolonged keeping of the reaction mixtures under consideration ((HMe₂Si)₂O, (VinMe₂Si)₂O, and bornylor menthylammonium platinate) is accompanied by disappearance from the chromatography chart of signals of mono- and diaddition products due to the rapid more "deep" hydrosilylation, *i.e.*, further mutual addition of the mono- and diadducts. Such a behavior of the siloxane systems is characteristic of hydrosilylation in the presence of complexes with the outer-sphere ammonium ligands;^{12,18} and due to an increase in the molecular weights of the siloxanes formed, an increase in the viscosity of the reaction solution is observed (after 25 h in the presence of (+)-(bornylNH₂)₂[PtCl₄], the viscosity is 0.34 Pa s). Analysis of the chromato-mass spectra shows that the siloxane with two terminal Si-H groups ($t_r =$ 34.0 min), resulted from a sequential β -addition of the siloxanes, is the main product of the "deep" hydro-



Fig. 1. Changes in time of conversion of divinyltetramethyldisiloxane in the reaction with tetramethyldisiloxane (80 °C, $(HMe_2Si)_2O : (VinMe_2Si)_2O = 1 : 1 \text{ (mol.)})$ in the presence of $(bornylNH_3)_2[PtCl_6]$ (*I*-5), $(menthylNH_3)_2[PtCl_6]$ (6), $(Et_3NH)_2[PtCl_6]$ (7), and $(bornylNH_3)_2[PtCl_4]$ (8) complexes $(C = 1.88 \cdot 10^{-3} \text{ mol } L^{-1})$ after treatment with $(HMe_2Si)_2O$ (*I*) and $(VinMe_2Si)_2O$ (5), and without treatment (2-4, 6-8). The catalyst was used 3 (2), 2 (3), and 1 (4) times.

silylation. Products with the terminal Si—H and Si—Vin groups are presented in the reaction mixture in lower amounts (according to the chromatography data, the ratio siloxane with two Si—H groups : siloxanes with terminal Si—H and Si—Vin groups is 9 : 2).

Kinetic curves of the hydrosilylation catalyzed by bornyl- and menthylammonium platinum complexes are characterized by an induction period (at the temperature below 80 °C) (Fig. 1), the presence of which is caused by the low solubility of these coordinating compounds in the reaction medium and by the formation of the "true" catalyst.

Catalytic properties of the complexes in the (HMe₂Si)₂O-(VinMe₂Si)₂O system significantly depend on the oxidation state of the complex-forming atom and on the nature of the ammonium counterion. Activity of the catalysts, evaluated by the time of 50% conversion of $(VinMe_2Si)_2O$ (see Fig. 1, curves 4, 6–8), decreases in the following sequence: (-)-(menthylNH₃)₂[PtCl₆] $(32 \text{ min}) > (\text{Et}_3\text{NH})_2[\text{PtCl}_6] (120 \text{ min}) > (+)-(\text{bornyl-})^2$ $NH_3_2[PtCl_4]$ (210 min) > (+)-(bornylNH_3_2[PtCl_6]) (233 min). The time to reach a complete conversion of (VinMe₂Si)₂O is the shortest in the case of $(Et_3NH)_2[PtCl_6]$ (470 min) and the longest, in the case of (+)-(bornylNH₂)₂[PtCl₄] (>10 h). Stability of the complexes in the reaction medium against decomposition to platinum metal decreases in the following sequence: $(+)-(bornylNH_3)_2[PtCl_6] >> (+)-(bornylNH_3)_2[PtCl_4] >$ $(Et_3NH)_2[PtCl_6] > (-)-(menthylNH_3)_2[PtCl_6]$. Menthylammonium hexachloroplatinate(IV) is reduced to platinum metal immediately, a decomposition of $(Et_3NH)_2[PtCl_6]$ starts in 10 min after the heating began, and (+)-(bornylNH₃)₂[PtCl₆] gives no platinum metal at all during the reaction (visual control). The selectivity of β -addition (determined from the correlation of the CH₂) and CH₃ groups in the ¹H NMR spectrum) changes in the following sequence: (+)- $(bornylNH_3)_2[PtCl_4]$ (96%) > $(+)-(bornylNH_3)_2[PtCl_6] (93\%) \approx (-)-(menthylNH_3)_2 [PtCl_{4}]$ (92%).

The high stability of the (+)-(bornylNH₃)₂[PtCl₆] complex against decomposition prompted us to estimate the possibility of its reuse. It was found that the three-time reuse of the catalyst in the $(HMe_2Si)_2O-(VinMe_2Si)_2O$ system increases its catalytic activity (see Fig. 1, curves 2–4). This can be explained by the gradual increase in the amount of "true" catalyst of hydrosilylation, which really participates in the formation of the reaction products.

For the preliminary activation of (+)-(bornyl-NH₃)₂[PtCl₆], *i.e.*, for the possible preparation of the "true" catalyst, we treated it with $(HMe_2Si)_2O$ or $(VinMe_2Si)_2O$ (80 °C, 5 h). It turned out that the heating of the complex in $(VinMe_2Si)_2O$ leads to a decrease of the induction period of the reaction with the parallel decrease in activity of the catalyst (see Fig. 1, curves 4 and 5). At

Scheme 5

the same time, (+)-(bornylNH₃)₂[PtCl₆] after the reflux with (HMe₂Si)₂O turned out to be the most active catalyst in the siloxane system (see Fig. 1, curve *I*), and an increase in activity of the catalyst causes only a slight decrease in the selectivity of its action (chromatography data): according to the ¹H NMR data, the share of β -addition in the hydrosilylation products formed is 92%, whereas the use of untreated (+)-(bornylNH₃)₂[PtCl₆] gives 95% of β -addition.

The reaction of (+)-(bornylNH₃)₂[PtCl₆] with (VinMe₂Si)₂O does not change the ¹H NMR spectrum. When $(HMe_2Si)_2O$ reacts with (+)- $(bornylNH_2)_2[PtCl_4]$, signals of the Me groups of such compounds as $H(Me_2)SiOSiMe_2$ (δ 0.06, 0.09, 0.16, and 0.17 (all s)) and $H(Me_2)SiOSi(Me_2)OSi(Me_2)H$ (δ 0.04 (s) and 0.17 (d, J = 2.5 Hz)), formed by the disproportionation and dehydrocondensation of tetramethyldisiloxane, as well as new signals at δ 0.04, 0.07, 0.12, 0.13, 0.18, and 0.19 are observed in the ¹H NMR spectrum. After 1.5 h, the reaction solution acquires yellow and then, green color. However, the isolation and characterization by spectroscopic methods of the colored compound were unsuccessful: attempted precipitation or high-vacuum low-temperature removal of the hydrosiloxanes solution lead to its rapid decomposition to bornylNH₂•HCl (NMR data) and, probably, colloidal platinum. The data obtained allow us to assume that formation of the "true" catalyst of hydrosilvlation occurs, in fact, under action of hydrosiloxane.

Asymmetric hydrosilylation of acetophenone. Hydrosilylation of acetophenone with diphenylsilane and subsequent hydrolysis of obtained silyl ethers 1 is one of the methods for the synthesis of *S*- or *R*-isomers of 1-phenylethanol 2 and it is widely used for the estimation of ability of a chiral catalyst to the asymmetric induction (Scheme 5).

Silver tetrafluoroborate or trifluoromethanesulfonate are used for the better activation of the hydrosilylation.²¹

Hydrosilylation of acetophenone with diphenylsilane in the presence of chiral metal complexes under consideration and $AgBF_4$ proceeds slowly. According to the ¹H NMR data, 1-phenylethoxy(diphenyl)silanes 1 (δ 1.62 (d, 3 H, Me, J = 6.4 Hz); 5.12 (q, 1 H, CH, J = 6.4 Hz); 5.55 (s, 1 H, SiH)) and 1-phenylvinyloxy(diphenyl)silane (3) $(\delta 4.87 (d, 1 H, CH_2, J = 2.2 Hz); 5.04 (d, 1 H, CH_2, J =$ J = 2.3 Hz); 5.74 (s, 1 H, SiH)) are the reaction products, which was observed previously²² for the hydrosilylation in the presence of rhodium complexes. In addition, signals at δ 1.50 (d, 1 H, CH₂, J = 5.4 Hz), 4.87 (dd, 1 H, CH, J = 5.4 Hz, J = 6.7 Hz), 5.68 (s, 1 H, SiH), and 5.78 (s, 1 H, SiH) are observed in the ¹H NMR spectrum, which we assigned to 2-phenylethyl-2-diphenylsiloxy(diphenyl)silane (4) (signal at δ 1.64 (d, 1 H, CH₂, J = 5.4 Hz) is shielded by the Me group of compound 1). At the same time, we did not observe an addition product of both SiH groups of diphenylsilane, the formation of which in the



presence of platinum complexes with the inner-sphere ligands was confirmed previously²² by the chromato-mass spectrometry.



After 13 days (5 °C), the conversion of acetophenone in the presence of (+)-(bornylNH₃)₂[PtCl₆] reaches 86.3%, in the presence of (-)-(menthylNH₃)₂[PtCl₆], 73.5%, and in the presence of (+)-(bornylNH₃)₂[PtCl₄], only 52.5%. In this case, the yields of silyl ether **1** (¹H NMR data) were 79.4, 50.9, and 39.9%, of silane **3**, 3.0, 8.2, and 5.8%, of **4**, 3.9, 14.4, and 6.8% in the presence of (+)-(bornylNH₃)₂[PtCl₆], (-)-(menthylNH₃)₂[PtCl₆], and (+)-(bornylNH₃)₂[PtCl₄], respectively. Thus, (+)-(bornylNH₃)₂[PtCl₆] complex is the most active and chemoselective catalyst for the hydrosilylation of acetophenone, whereas (+)-(bornylNH₃)₂[PtCl₄] was the most selective in the hydrosilylation of (VinMe₂Si)₂O.

Stereoselectivity of hydrosilylation is usually determined from the structure of 1-phenylethanol, formed by the hydrolysis of the reaction mixture (after the 100% conversion of acetophenone is reached). In the presence of bornylammonium catalysts, the subsequent hydrolysis leads to a chiral 1-phenylethanol in all the cases, the absolute configuration of which depends on the platinum oxidation state: in the presence of (+)-(bornyl-NH₃)₂[PtCl₆], (-)-*S*-2 (*ee* 24%) is formed and in the presence of (+)-(bornylNH₃)₂[PtCl₄], (+)-*R*-2 (*ee* 11%). The (-)-(menthylNH₃)₂[PtCl₆] complex does not cause the asymmetric induction, which, apparently, results from its rapid and complete decomposition in the reaction medium to platinum metal.

As it is known,²³ the highest enantioselectivity of hydrosilylation is usually reached by the introduction into the reaction mixture of 2-13-fold excess of the chiral ligand relatively to the metal. An excess of the optically active ligand is especially important when complexes with the nitrogen-containing chiral ligands are used.²⁴⁻²⁶ Therefore, we also accomplished a hydrosilylation in the presence of 10-fold molar excess of the corresponding hydrochlorides (amines were not used, since they can enter the inner coordination sphere and thus in situ change the structure of the complex used). In case of $(+)-(bornylNH_3)_2[PtCl_4]$ and $(-)-(menthylNH_3)_2[PtCl_6]$, such an approach did not result in the asymmetric induction, whereas in the case of (+)-(bornylNH₃)₂[PtCl₆], (+)-R-2 (ee 24%) was the reaction product. Thus, an addition of the outer-sphere chiral counterion during the hydrosilylation, catalyzed by (+)-(bornylNH₂)₂[PtCl₄] complex, leads to the inversion of configuration of 1-phenylethanol formed.

Experimental

NMR spectra were recorded on a Bruker AC-200 and Bruker WM-400 spectrometers in CDCl₃ and (CD₃)₂SO (200.13, 400.14 (^{1}H) , and 50.33 MHz (^{13}C)) with the use of a signal of the deuterated solvent as the internal standard. IR spectra were recorded on a Shimadzu FTIR-8400S (4000-400 cm⁻¹) and Hitachi FIS-3 (400-100 cm⁻¹) spectrometers in KBr pellets. Elemental analysis was performed on a Leco CHN-932 C,H,Nanalyser. Polarimetric study was carried out on a Perkin-Elmer 241MC instrument in quartz thermostated cuvettes of 10 cm in length. CD spectra were recorded on a JACSO J-500 spectrometer (285-700 nm) in DMF with concentration of 5 mg mL⁻¹. Electronic absorption spectra were obtained on a Specord M-40 double-beam scanning spectrophotometer (250-900 nm) for solutions in DMF with concentration of 5 and 0.5 mg mL⁻¹ for the visible and near UV regions, respectively. Melting points were determined on the Kofler heating apparatus with the rate of heating 2.5 deg min^{-1} . Viscosimetric study was performed on a Rheotest 2 (VEB MLW) instrument.

Chromatographic analysis of hydrosilylation products was carried out on a Tsvet-100 chromatograph with the katharometer as the detector on a column (3000×4 mm) with SE-30 (10 wt.%) on Chromaton N-AW-DMCS; helium was the carrier gas (4 L h⁻¹), the bridge current was 100 mA. The injector temperature was 300 °C, the column temperature was varied

from 80 to 200 °C at 10 deg min⁻¹. The sequence of peaks on a chromatography chart: β -, α -, β , β -, β , α -, and α , α -adducts ($t_r = 14, 15, 26, 28, \text{ and } 29 \text{ min}, \text{ respectively}$). Assignment of the GC peaks of the adducts was made based on the data in Refs 17 and 18.

Hydrosilylation of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane was performed with equimolar amount of 1,1,3,3-tetramethyldisiloxane in the presence of the internal standard (octamethylcyclotetrasiloxane) in the sealed tubes with subsequent chromatography of the reaction mixture at arbitrary times. Concentration of the complexes in the reaction mixture was varied in the range $1 \cdot 10^{-4} - 2 \cdot 10^{-3}$ mol L⁻¹.

To recover the catalyst, after 100% conversion of $(VinMe_2Si)_2O$ was reached in the preceding cycle, the reaction mixture was cooled, the undissolved catalyst was filtered off, washed with dichloromethane, and added to a new reaction mixture, and the next hydrosilylation cycle was carried out according to the general procedure.

Hydrosilylation of acetophenone with diphenylsilane was carried out in THF in the presence of $AgBF_4$ according to the known procedure,²¹ the course of the reaction was monitored by NMR. 1-Phenylethanol was isolated by column chromatography, *ee* was determined by polarimeteric method from the observed angle of rotation of a mixture of enantiomers in toluene.

Commercial (+)-menthol, ethanol, propan-2-ol, toluene, diethyl ether, acetophenone, THF, DMF, DMSO, octamethyl-cyclotetrasiloxane, and $H_2PtCl_6 \cdot 4H_2O$ (all of chemically pure grade); 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, 1,1,3,3-tetramethyldisiloxane, and AgBF₄ (Aldrich); D-(+)-camphor and diphenylsilane (Acros); silica gel 60 (Merck) were used in the experiments; (Et₃NH)₂[PtCl₆] was obtained as described in Ref. 12.

Chromato-mass spectrometry study of the $(HMe_2Si)_2O-(VinMe_2Si)_2O$ reaction mixture (8 h, 80 °C, (+)-(bornyl-NH₃)₂[PtCl₆]) was performed on a Agilent 6890N chromatograph with an Agilent 5973N mass-selective detector and EI (70 eV) ionization. A DB-5MS quartz capillary column (60 m × 0.25 mm, the phase film thickness, 0.25 µm) was used; the injector temperature was 280 °C, the interface temperature was 290 °C, the temperature of the column was varied from 150 to 280 °C at 10 deg min⁻¹; helium was the carrier gas, separation of the flow, 1 : 20; a sample was 1 µL in volume. Suggested structures of the adducts, detected by the chromato-mass spectrometry study, are given below.

Adduct $HMe_2SiOSi(Me_2)CH_2CH_2Si(Me_2)OSi(Me_2)-CH=CH_2. t_r = 3.3 min, the content in the mixture, 6.2%. MS,$ $<math>m/z (I_{rel}(\%)): 320 [M - H]^+ (4), 305 [M - H - Me]^+ (100), 291 [M - 2 Me]^+ (9), 277 (19), 263 [M - H - 2 Me - Vin]^+ (2), 249 [M - 3 Me - Vin]^+ (1), 235 [M - H - SiMe_2Vin]^+ (2), 219 [M - H - OSiMe_2Vin]^+ (32), 205 [M - H - SiMe_2Vin - 2 Me]^+ (6), 191 [M - 3 Me - SiMe_2Vin]^+ (9), 175 [Me_2SiOSi-(Me_2)CH_2CH_2Si(Me_2)O - 4 Me]^+ (2), 160 [Me_2SiOSiMe_2-CH_2CH_2]^+ (5), 145 [Me_2SiOSi(Me)CH_2CH_2]^+ and/or [MeSiOSi(Me_2)CH_2CH_2]^+ (53), 133 [HMe_2SiOSiMe_2]^+ (9), 117 [Me_2SiOSiMe]^+ (16), 103 [HMeSiOSiMe]^+ and/or [HSiOSiMe_2]^+ and/or [HMe_2SiOSi]^+ (2), 85 [SiMe_2Vin]^+ (4), 73 [HSiOSi]^+ (30), 59 [OSiMe]^+ (7), 45 [HSiO]^+ (3), 28 [CH_2CH_2]^+ (1).$

Adduct $HMe_2SiOSi(Me_2)CH(Me)Si(Me_2)OSi(Me_2)-CH=CH_2$. $t_r = 3.4$ min, the content in the mixture, 4.6%. MS, $m/z (I_{rel}(\%)): 320 [M - H]^+ (1), 305 [M - H - Me]^+ (100), 291$

$$\begin{split} & [M-2 \ Me]^+ \ (3), \ 277 \ (6), \ 263 \ [M-H-2 \ Me-Vin]^+ \ (2), \\ & 247 \ [M-HSiMe_2 - Me]^+ \ (1), \ 231 \ [M-HMe_2SiO - Me]^+ \\ & (2), \ 219 \ [M-H-OSiMe_2Vin]^+ \ (13), \ 205 \ [M-H-SiMe_2Vin]^+ \ (2), \\ & 219 \ [M-H-OSiMe_2Vin]^+ \ (13), \ 205 \ [M-H-SiMe_2Vin]^+ \ (6), \\ & 177 \ (2), \ 159 \ [M-H-4 \ Me-OSiMe_2Vin]^+ \ and/or \\ & [Me_2SiOSi(Me_2)Vin]^+ \ (2), \ 145 \ [Me_2SiOSi(Me)CHMe]^+ \\ & and/or \ [MeSiOSi(Me_2)CHMe]^+ \ (6), \ 133 \ [HMe_2SiOSiMe_2]^+ \\ & (5), \ 117 \ [Me_2SiOSiMe]^+ \ (4), \ 103 \ [HMeSiOSiMe]^+ \ and/or \\ & [HSiOSiMe_2]^+ \ and/or \ [HMe_2SiOSi]^+ \ (1), \ 85 \ [SiMe_2Vin]^+ \ (3), \\ & 73 \ [HSiOSi]^+ \ (17), \ 59 \ [OSiMe]^+ \ (5), \ 45 \ [HSiO]^+ \ (1). \end{split}$$

Adduct H[Me₂SiOSi(Me₂)CH₂CH₂]₂Si(Me₂)OSi(Me₂)H. $t_r = 4.8$ min, the content in the mixture, 1.7%. MS, m/z $(I_{rel}(\%))$: 305 $[M - 2 HMe_2SiO]^+$ (2), 293 $[M - H - HSiMe_2O^ Si(Me_2)CH_2CH_2]^+$ (100), 279 [M - HSiMe_2OSi(Me_2)CH_2CH_2 - Me_{1}^{+} (5), 263 $[M - HMe_{2}SiOSi(Me_{2})CH_{2}CH_{2} - 2 Me - H]^{+}$ (2), 249 $[M - HSiMe_2OSi(Me_2)CH_2CH_2 - 3 Me]^+$ (1), 233 $[M - HMe_2SiOSi(Me_2)CH_2CH_2 - 4 Me - H]^+$ (2), 219 $[M - HMe_2SiOSi(Me_2)CH_2CH_2Si(Me_2)O]^+$ and/or $[M - HMe_2SiOSi(Me_2)CH_2CH_2 - 5 Me]^+$ (56), 205 $[M - HSiMe_2OSiMe_2CH_2CH_2SiMe_2 - H - 2Me]^+$ (17), 191 $[HMe_2SiOSi(Me_2)CH_2CH_2Si(Me_2)O - 2 Me]^+$ (7), 177 (3), 159 $[M - HMe_2SiOSi(Me_2)CH_2CH_2Si(Me_2)O - 4 Me]^+$ (2), $147 (29), 133 [HMe_2SiOSiMe_2]^+ (70), 117 [Me_2SiOSiMe]^+ (12),$ 103 (3), 85 (2), 73 [HSiOSi]⁺ (28), 59 [OSiMe]⁺ (6), 45 [HSiO]⁺ (2), 28 $[CH_2CH_2]^+$, $[Si]^+$ (3).

Adduct H[Me₂SiOSi(Me₂)CH₂CH₂]₃Si(Me₂)OSi(Me₂)-**CH=CH₂**. $t_r = 12.0$ min, the content in the mixture, 7.3%. MS, $m/z (I_{rel}(\%))$: 539 [M – H – OSi(Me₂)Vin]⁺ and/or [M – Vin – HMe_2SiO]⁺ (0.5), 481 [M – H – Me_2SiOSi(Me_2)Vin]⁺ (1), 465 $[M - HMe_2SiOSi(Me_2)CH_2CH_2 - Me]^+$ (4), 451 $[M - H - H_2CH_2 - Me]^+$ $Me_2SiOSi(Me_2)Vin - 2 Me_1^+ and/or [M - HMe_2SiO - Me_2SiO - M$ $Me_2SiVin - 2Me_1^+$ and/or $[M - HMe_2Si - OSiMe_2Vin - 2Me_1^+]$ Me^{\dagger}_{1} (1), 407 $[M - HSiMe_2OSi(Me_2)CH_2CH_2SiMe_2 - Me^{\dagger}_{2}$ (1), 379 $[Me_2SiOSi(Me_2)CH_2CH_2Si(Me_2)OSi(Me_2)CH_2CH_2 Si(Me_2)$]⁺ (2), 363 (1), 335 (3), 320 [Me_2SiOSi(Me_2)CH_2CH_2- $Si(Me_2)OSi(Me_2)Vin]^+$ (13), 305 $[Me_2SiOSi(Me_2)CH_2^ CH_2Si(Me_2)OSi(Me_2)Vin - Me]^+$ and/or $[Me_2SiCH_2^ CH_{2}Si(Me_{2})OSi(Me_{2})CH_{2}CH_{2}SiMe_{2}]^{+}$ (100),291 $[Me_{2}SiOSi(Me_{2})CH_{2}CH_{2}Si(Me_{2})OSi(Me_{2})Vin - 2 Me]^{+} (7),$ 277 (6), 263 $[\tilde{C}H_2\tilde{C}H_2\tilde{S}i(Me_2)\tilde{O}Si(Me_2)\tilde{C}H_2CH_2Si(Me_2)O]^+$ (1), 247 $[CH_2CH_2Si(Me_2)OSi(Me_2)CH_2CH_2SiMe_2]^+$ (26), 233 [HMe₂SiOSi(Me₂)CH₂CH₂Si(Me₂)OSiMe₂ - 4 Me]⁺ (55), 219 [Me₂SiOSi(Me₂)CH₂CH₂SiMe₂]⁺ (31), 203 [HMe₂Si- $OSi(Me_2)CH_2CH_2Si(Me_2)OSiMe_2 - 6 Me]^+$ (8), 191 $[HMe_2SiOSi(Me_2)CH_2CH_2Si(Me_2)O - 3 Me]^+$ (11), 175 $[Me_2SiOSi(Me_2)CH_2CH_2Si(Me_2)O - 4 Me]^+$ (3), 159 $[Me_{2}SiOSi(Me_{2})Vin]^{+}$ (6), 145 $[Me_{2}SiOSi(Me)CH_{2}CH_{2}]^{+}$ and/or [MeSiOŠi(Me2)CH2CH2]+ (40), 133 [HMe2SiOŠiMe2]+ (10), 117 $[Me_2SiOSiMe]^+$ (15), 99 $[SiCH_2CH_2SiMe]^+$ (1), 85 $[Me_2SiVin]^+$ (6), 73 $[HSiOSi]^+$ (35), 59 $[OSiMe]^+$ and/or $[HMe_2Si]^+$ (3), 28 $[CH_2CH_2]^+$, $[Si]^+$ (2).

Adduct HMe₂SiOSi(Me₂)CH(Me)[Si(Me₂)OSi(Me₂)CH₂-CH₂]₂Si(Me₂)OSi(Me₂)CH=CH₂. $t_r = 12.9$ min, the content in the mixture, 1.7%. MS, m/z (I_{rel} (%)): 479 [M – 9 Me – Vin]⁺ (2), 465 [M – HMe₂SiOSi(Me₂)CHMe – Me]⁺ (7), 451 [M – H – 2 Me – Me₂SiOSi(Me₂)Vin]⁺ and/or [M – HMe₂SiO – Me₂SiVin – 2 Me]⁺ and/or [M – HMe₂Si – OSiMe₂Vin – 2 Me]⁺ (2), 407 [M – Me – HSiMe₂OSi(Me₂)CH(Me)SiMe₂]⁺ (2), 393 (3), 379 [Me₂SiOSi(Me₂)CH(Me)Si(Me₂)-OSi(Me₂)CH₂CH₂SiMe₂]⁺ (4), 365 (2), 349 (2), 333 (5), 319 [Me₂SiOSi(Me₂)CH₂CH₂Si(Me₂)OSiMe₂Vin]⁺ (11), 305

[Me₂SiOSi(Me₂)CH₂CH₂Si(Me₂)OSi(Me₂)Vin – Me]⁺ and/or $[Me_2SiCH_2CH_2Si(Me_2)OSi(Me_2)CH_2CH_2SiMe_2]^+$ and/or [Me₂SiCH(Me)Si(Me₂)OSi(Me₂)CH₂CH₂SiMe₂]⁺ (100),291 $[Me_2SiCH(Me)SiMe_2OSiMe_2CH_2CH_2SiMe_2O - 2 Me]^+$ (10), 277 (8), 263 $[MeCHSiMe_2OSi(Me_2)CH_2CH_2Si(Me_2)O]^+$ and/or $[CH_2CH_2SiMe_2OSi(Me_2)CH_2CH_2Si(Me_2)O]^+$ (3), 246 $[Me_2SiCH_2CH_2Si(Me_2)OSiMe_2Vin]^+$ (58), 233 $[HMe_2SiO_2Vin]^+$ $Si(Me_2)CH(Me)Si(Me_2')OSiMe_2 - 4 Me]^+$ (55), 219 [Me_2SiOSi(Me_2)CH_2CH_2SiMe_2]^+ (36), 203 [HMe_2SiO- $\operatorname{Si}(\operatorname{Me}_2)\operatorname{CH}(\operatorname{Me})\operatorname{Si}(\operatorname{Me}_2)\operatorname{OSi}\operatorname{Me}_2 - 6 \operatorname{Me}_2^+ (10), 191$ $[HMe_{2}SiOSi(Me_{2})CH(Me)Si(Me_{2})O - 3 Me]^{+} (4), 175$ $[Me_2SiOSi(Me_2)CH(Me)Si(Me_2)O - 4 Me]^+$ (4), 159 $[Me_2SiOSi(Me_2)Vin]^+$ (9), 145 $[Me_2SiOSi(Me)CH_2CH_2]^+$ and/or [MeSiOSi(Me2)CH2CH2]+ and/or [Me2SiOSi(Me)- $CHMe]^+$ and/or $[MeSiOSi(Me_2)CHMe]^+$ (38), 133 $[HMe_2SiOSiMe_2]^+$ (16), 117 $[Me_2SiOSiMe]^+$ (16), 103 $[HMeSiOSiMe]^+$ and/or $[HSiOSiMe_2]^+$ (2), 85 $[SiMe_2Vin]^+$ (10), 73 [HSiOSi]⁺ (45), 59 [OSiMe]⁺ (7), 43 [SiMe]⁺ (4), 28 $[CH_2CH_2]^+$, $[Si]^+$ (14).

Adduct H[Me₂SiOSi(Me₂)CH₂CH₂]₅Si(Me₂)OSi(Me₂)-CH=CH₂. $t_r = 24.5$ min, the content in the mixture, 5.6%. MS, $m/z (I_{rel} (\%))$: 480 [Me₂SiOSi(Me₂)CH₂CH₂Si(Me₂)OSi(Me₂)- $CH_2CH_2Si(Me_2)OSiMe_2Vin]^+$ (1), 465 $[Me_2SiOSi(Me_2) CH_2CH_2Si(Me_2)OSi(Me_2)CH_2CH_2Si(Me_2)OSiMe_2Vin - Me]^+$ $[Me_2SiOSi(Me_2)CH_2CH_2Si(Me_2)OSi(Me_2)-$ (3).451 $CH_{2}CH_{2}Si(Me_{2})OSi(Me_{2})CH_{2}CH_{2} - 2 Me]^{+}$ (1), 393 [Me₂SiO-Si(Me₂)CH₂CH₂Si(Me₂)OSi(Me₂)CH₂CH₂Si(Me₂)- $OSiMe_2 - 4 Me^{\dagger}$ (1), 379 [Me_2SiOSi(Me_2)CH_2CH_2] $Si(Me_2)OSi(Me_2)CH_2CH_2Si(Me_2)]^+$ (2), 363 (1), 349 (0.5), 333 (1), $3\overline{2}0$ [Me₂SiOSi(Me₂)CH₂CH₂Si(Me₂)OSiMe₂Vin]⁺ (16), $305 [Me_2SiOSi(Me_2)CH_2CH_2Si(Me_2)OSi(Me_2)Vin - Me]^+$ and/or $[Me_2SiCH_2CH_2Si(Me_2)OSi(Me_2)CH_2CH_2SiMe_2]^+$ 291 $[Me_2SiCH_2CH_2Si(Me_2)OSi(Me_2)CH_2CH_2]$ (80). $Si(Me_2)O - 2 Me]^+$ (6), 277 (5), 263 [CH₂CH₂Si(Me₂)- $OSi(Me_2)CH_2CH_2Si(Me_2)O]^+$ (1), 246 [Me_2SiCH_2CH_2-Si(Me₂)OSiMe₂Vin]⁺ **(**42), 233 [HMe₂SiOSi(Me₂)-CH₂CH₂Si(Me₂)OSiMe₂ 4 Me]⁺ (100),219 _ $[Me_{2}SiOSi(Me_{2})CH_{2}CH_{2}SiMe_{2}]^{+}$ (34), 203 $[HMe_{2}SiO Si(Me_2)CH_2CH_2Si(Me_2)OSiMe_2 - 6 Me]^+$ (10), 191 $[HMe_2SiOSi(Me_2)CH_2CH_2Si(Me_2)O - 3 Me]^+$ (8), 175 $[Me_2SiOSi(Me_2)CH_2CH_2Si(Me_2)O - 4 Me]^+$ (3), 159 $[Me_2SiOSi(Me_2)CH_2CH_2Si(Me_2) - 4 Me]^+$ (9), 145 $[Me_2SiOSi(Me)CH_2CH_2]^{\dagger}$ and/or $[MeSiOSi(Me_2)CH_2CH_2]^{\dagger}$ (55), 133 [HMe₂SiOSiMe₂]⁺ (9), 117 [Me₂SiOSiMe]⁺ (13), 97 (2), 85 $[Me_2SiVin]^+$ (8), 73 $[HSiOSi]^+$ (33), 55 $[SiVin]^+$ (3), 41 $[SiCH]^+$ (2), 28 $[CH_2CH_2]^+$, $[Si]^+$ (4).

Adduct HMe₂SiOSi(Me₂)CH(Me)[Si(Me₂)OSi(Me₂)CH₂-CH₂]₄Si(Me₂)OSi(Me₂)CH=CH₂. $t_r = 27.1$ min, the content in the mixture, 2.0%. MS, m/z (I_{rel} (%)): 536 [Me₂SiCH₂CH₂Si(Me₂)OSi(Me₂)CH₂CH₂Si(Me₂)OSi(Me₂)-CH₂CH₂Si(Me₂)OSi(Me₂)CH₂CH₂Si(Me₂)OSi(Me₂)-CH₂CH₂Si(Me₂)OSi(Me₂)OSi(Me₂)CH₂CH₂Si(Me₂)-OSi(Me₂)CH₂CH₂Si(Me₂)OSi(Me₂) - 9 Me]⁺ (2), 465 [Me₂SiOSi(Me₂)CH₂CH₂Si(Me₂)OSi(Me₂)CH₂CH₂Si(Me₂)-OSi(Me₂)CH₂CH₂Si(Me₂)OSi(Me₂)CH₂CH₂Si(Me₂)-OSiMe₂Vin - Me]⁺ (3), 451 [Me₂SiOSi(Me₂)CH₂CH₂Si(Me₂)-OSi(Me₂)CH₂CH₂Si(Me₂)OSi(Me₂)CH₂CH₂CH₂Si(Me₂)-OSi(Me₂)CH₂CH₂Si(Me₂)OSi(Me₂)CH₂CH₂ - 2 Me]⁺ and/or [Me₂SiOSi(Me₂)CH(Me)Si(Me₂)OSi(Me₂)CH₂-CH₂Si(Me₂)OSi(Me₂)CH₂CH₂ - 2 Me]⁺ (1), 414 (1), 406 [Me₂SiCH₂CH₂Si(Me₂)OSi(Me₂)CH₂CH₂Si(Me₂)OSi(Me₂)CH₂CH₂-Si(Me₂)OSiMe₂ - 4 Me]⁺ (9), 379 [Me₂SiO-

 $Si(Me_2)CH(Me)Si(Me_2)OSi(Me_2)CH_2CH_2Si(Me_2)]^+$ and/or $[Me_2SiOSi(Me_2)CH_2CH_2Si(Me_2)OSi(Me_2)CH_2CH_2Si(Me_2)]^+$ (4), 356 (3), 333 (4), 319 (11), 305 [Me₂SiOSi(Me₂)CH₂- $CH_2Si(Me_2)OSi(Me_2)Vin - Me]^+$ and/or $[Me_2SiCH_2CH_2 Si(Me_2)OSi(Me_2)CH_2CH_2SiMe_2]^+$ and/or $[Me_2SiCH(Me) Si(Me_2)OSi(Me_2)CH_2CH_2SiMe_2]^+$ (68), 291 [Me_2SiCH_2CH_2- $Si(Me_2)OSi(Me_2)CH_2CH_2Si(Me_2)O - 2 Me_1^+ and/or$ $[Me_2SiCH(Me)Si(Me_2)OSi(Me_2)CH_2CH_2Si(Me_2)O - 2 Me]^+$ (7), 277 (7), 263 [CH₂CH₂Si(Me₂)OSi(Me₂)CH₂CH₂- $Si(Me_2)O]^+$ and/or [MeCHSi(Me₂)OSi(Me₂)CH₂- $CH_2Si(Me_2)O]^+$ and/or $[CH_2CH_2Si(Me_2)OSi(Me_2)CH(Me)^ \operatorname{Si}(\operatorname{\tilde{M}e}_2)O^{\dagger}$ (3), 246 $[\operatorname{Me}_2\operatorname{Si}CH_2CH_2Si(\operatorname{Me}_2)OSi\operatorname{Me}_2Vin]^{\dagger}$ (100), $\overline{2}33$ [HMe₂SiOSi(Me₂)CH(Me)Si(Me₂)OSiMe₂ - 4 Me]⁺ (79), 219 $[Me_2SiOSi(Me_2)CH_2CH_2SiMe_2]^+$ and/or $[Me_2SiOSi(Me_2)CH(Me)SiMe_2]^+$ (45), 207 (18), 203 $[HMe_2SiOSi(Me_2)CH(Me)Si(Me_2)OSiMe_2 - 6 Me]^+ (13), 191$ $[HMe_2SiOSi(Me_2)CH(Me)Si(Me_2)O - 3 Me]^+$ (14), 175 $[Me_2SiOSi(Me_2)CH_2CH_2Si(Me_2)O - 4 Me]^+$ and/or $[Me_{2}SiOSi(Me_{2})CH(Me)Si(Me_{2})O - 4 Me]^{+}$ (5), 159 $[Me_2SiOSi(Me_2)Vin]^+$ (13), 145 $[Me_2SiOSi(Me)CH_2CH_2]^+$ and/or [MeSiOSi(Me2)CH2CH2]+, [Me2SiOSi(Me)CHMe]+ and/or [MeSiOSi(Me₂)CHMe]⁺⁻(65), 133 [HMe₂SiOSiMe₂]⁺ $(17), 117 [Me_2SiOSiMe]^+ (21), 109 (6), 95 (10), 85 [Me_2SiVin]^+$ (16), 73 [HSiOSi]⁺ (45), 55 [SiVin]⁺ (16), 43 [SiMe]⁺ (10), 28 $[CH_2CH_2]^+$, $[Si]^+$ (22).

Adduct H[Me₂SiOSi(Me₂)CH₂CH₂]₆Si(Me₂)OSi(Me₂)H. $t_r = 34.0$ min, the content in the mixture, 55.7%. MS, m/z $(I_{rel} (\%))$: 480 [HSiMe₂OSiMe₂CH₂CH₂SiMe₂OSiMe₂- $CH_2CH_2SiMe_2OSiMe_2CH_2CH_2SiMe_2 - 4 Me]^+$ (1), 379 $[Me_2SiOSi(Me_2)CH_2CH_2Si(Me_2)OSi(Me_2)CH_2CH_2Si(Me_2)]^+$ (1), 319 [SiMe₂CH₂CH₂SiMe₂OSiMe₂CH₂CH₂SiMe₂O- $SiMe_2 - 4 Me_1^+$ (1), $305 [Me_2SiCH_2CH_2Si(Me_2)OSi(Me_2) \begin{array}{c} CH_{2}CH_{2}SiMe_{2}]^{+} & (12), \quad 293^{2} \quad [Me_{2}SiOSi(Me_{2})CH_{2}CH_{2}^{-}\\ Si(Me_{2})OSiMe_{2}]^{+} & (100), \quad 277 \quad (3), \quad 261 \quad (1), \quad 247 \end{array}$ $[CH_2CH_2Si(Me_2)-OSi(Me_2)CH_2CH_2SiMe_2]^+$ (3), 233 $[HMe_{2}SiOSi(Me_{2})CH_{2}CH_{2}Si(Me_{2})OSiMe_{2} - 4Me]^{+} (31), 219$ $[Me_{2}SiOSi(Me_{2})CH_{2}CH_{2}SiMe_{2}]^{+} (82), 207 (5), 191$ $[HMe_2SiOSi(Me_2)CH_2CH_2Si(Me_2)O - 3 Me]^+$ (4), 175 $[Me_2SiOSi(Me_2)CH_2CH_2Si(Me_2)O - 4 Me]^+$ (1), 159 $[Me_2^SiOSi(Me_2)CH_2CH_2SiMe_2 - 4 Me]^+ (3), 145$ $[Me_2SiOSi(Me)CH_2CH_2]^+ and/or [MeSiOSi(Me_2)CH_2CH_2]^+$ (34), 133 [HMe₂SiOSiMe₂]⁺ (21), 117 [MeSiOSiMe₂]⁺ (7), 86 $[Me_2SiCH_2CH_2]^+$ (2), 73 $[HSiOSi]^+$ (16), 59 $[OSiM\bar{e}]^+$ (1), 28 $[CH_2CH_2]^+$ (1).

(1*R*)-(–)-Menthylamine. The product was synthesized from (+)-menthol according to the known procedure,²⁷ the yield was 38%, $[\alpha]_D^{20}$ –24.0 (neat). ¹H NMR spectrum (CDCl₃) agrees with the literature data.²⁸ ¹³C NMR (CDCl₃), δ : 14.6 (CH<u>C</u>H₃); 20.5, 21.5 (CH₃CH<u>C</u>H₃); 22.4 (<u>C</u>H₂CH₂CH); 25.1 (CH₃<u>C</u>HCH₃); 31.2 (<u>C</u>HCH₃); 34.1 (CH₂<u>C</u>H₂CH); 44.7 (<u>C</u>H₂CHN); 49.6 (N<u>C</u>H); 50.7 (CH₃<u>C</u>HCH).

(1*R*)-(+)-Bornylamine. The product was obtained from (+)camphor according to the known procedure,²⁹ the yield was 27%, $[\alpha]_D^{20}$ +22.9 (*c* 0.2, EtOH); +32.6 (*c* 0.1, CHCl₃) (*cf.* Ref. 30: $[\alpha]_D^{20}$ +22.7 (EtOH)), m.p. 159–160 °C (*cf.* Ref. 31: m.p. 158–160 °C; *cf.* Ref. 29: m.p. 162.5–164 °C). ¹H NMR spectrum (CDCl₃) agrees with the literature data.²⁹ ¹³C NMR (CDCl₃), δ : 13.0 (CH₃); 18.1, 19.9 (CH₃C<u>C</u>H₃); 26.2 (CH₂); 28.0 (CH₂); 38.2 (<u>C</u>H₂CHN); 44.6 (CH₂<u>C</u>HCH₂); 48.0 (CH₃<u>C</u>CH₃); 48.6 (CH₃<u>C</u>CH₂); 56.3 (N<u>C</u>H). (1*R*)-(-)-Menthylamine hydrochloride. A mixture of (-)-menthylamine (0.5 g) and 0.1 *M* hydrochloric acid (10 mL) was kept for 0.5 h and the solution was concentrated by the air flow to 2 mL. A precipitate formed was filtered off and dried in air to obtain a white substance (0.57 g, 92%), $[\alpha]_D^{20}$ -27.1 (*c* 0.15, EtOH) (*cf.* Ref. 28: $[\alpha]_D^{20}$ -38 (PrⁱOH)), m.p. 288–289 °C (*cf.* Ref. 32: m.p. 289.5–291 °C). ¹H and ¹³C spectra in CDCl₃ correspond to the literature data.²⁸ IR, v(δ)/cm⁻¹: 3203 (v(N-H), δ (N-H)); 13033, 2960, 2932 sh, 2874, 2800 sh (v(N-H), v(C-H)); 1605 (δ_{as} (N-H)); 1516, 1504 (δ_{s} (N-H)); 1460 (δ (C-H) ring); 1392 (δ (NC-H)); 1369 (δ (C-H) ring); 1393 (δ (C-H)); 1087 (v(C-N)); 1017, 977 (v(C-C), δ (C-H)); 956 (v(C-C)); 926 (δ (C-H)); 872, 842, 766 (v(C-C), δ (C-H)).

(1R)-(+)-Bornylamine hydrochloride. A mixture of (+)-bornylamine (0.9 g) and 0.1 *M* hydrochloric acid (10 mL) was kept for 0.5 h and the solution was concentrated by the air flow to 1 mL. A precipitate formed was filtered off and dried in air to obtain a white substance (0.97 g, 87%), $[\alpha]_D^{20}$ +12.7 (c 0.15, EtOH), $[\alpha]_D^{20}$ +18.2 (c 0.1, DMSO). ¹³C NMR (CDCl₂), δ: 12.7 (CH₃); 17.7, 18.7 (CH₃C<u>C</u>H₃); 26.8 (CH₂); 33.5 (<u>C</u>H₂CHN); 43.8 (CH₂<u>C</u>HCH₂); 47.8 (CH₃<u>C</u>CH₃); 48.2 (CH₃<u>C</u>CH₂); 56.4 (NCH). IR, $v(\delta)/cm^{-1}$: 3190 sh, 2985, 2952 (v(N-H), v(C-H)); 1600 (δ_{as} (N-H)); 1525, 1512 (δ_c(N-H)); 1495, 1485, 1476, 1459 (δ(C-H) ring); 1410 (δ(NC-H)); 1392 (δ(C-H)); 1368 (δ(C-H) ring); 1310 (δ(C-H)); 1279, 1251, 1177, 1162, 1152 (v(C-C), δ(C-H)); 1084 (v(C-N)); 1043, 1024, 1004 (v(C-C), δ(C-H)); 942 (ν(C-C)); 927 (δ(C-H)); 875, 825, 762 (ν(C-C), δ(C-H)). Found (%): C, 63.31; H, 10.63; N, 7.38. C₁₀H₂₀ClN. Calculated (%): C, 63.30; H, 10.62; N, 7.39.

(1*R*)-(–)-Menthylammonium hexachloroplatinate(vi). Solutions of H₂PtCl₆•4H₂O (187 mg) in PrⁱOH (3 mL) and (-)-menthylammonium hydrochloride (244 mg) in PrⁱOH (2 mL) were mixed up, after 10 min, diethyl ether (10 mL) was added to the mixture. A precipitate formed was immediately filtered off, washed on the filter sequentially with PrⁱOH (5 mL) and diethyl ether to obtain an orange complex (220.6 mg, 67%), $[\alpha]_{D}^{20}$ –17.6 (c 0.05, DMSO), m.p. 206 °C (with decomp.). CD, λ/nm ($\Delta\epsilon/L$ mol⁻¹ cm⁻¹): 333 (-0.010), 327 (+0.022). ¹H NMR (($(CD_3)_2SO$), δ : 0.72, 0.85, 0.89 (all d, 3 H each, $CHC\underline{H}_3$, $C\underline{H}_3CHC\overline{H}_3$, $CH_3CHC\underline{H}_3$, J = 6.7 Hz); 1.05 (q, 2 H, CH_2 , J = 7.8 Hz, J = 6.4 Hz); 1.28 (t, 2 H, CH_2 , J = 11.3 Hz); 1.39 (m, 1 H, C<u>H</u>CH₃); 1.64 (t, 2 H, CHC<u>H₂</u>CH, J = 8.0 Hz); 1.93 (t, 1 H, $CH_{2}CHCH_{2}$, J = 11.2 Hz); 2.89 (m, 1 H, NCH); 7.85 (br.s, 3 H, $\tilde{N}H_3$). UV, λ/nm ($\epsilon/L mol^{-1} cm^{-1}$): 371 (371), 475 (43), 880 (5). IŘ, v(δ)/cm⁻¹: 3176 (v(N–H)); 3031, 2957, 2929 sh, 2871 sh (v(N-H), v(C-H)); 1604 (δ_{as} (N-H)); 1503, 1495 ($\delta_{c}(N-H)$); 1460, 1454 ($\delta(C-H)$ ring); 1389 ($\delta(NC-H)$); 1369 (δ(C–H)); 1352 (δ(C–H) ring); 1284, 1250 (δ(C–H)); 1123, 1109 (v(C–C), δ (C–H)); 953 (v(C–C)). IR, v/cm⁻¹: 330 (Pt-Cl); 265, 205. Found (%): C, 33.36; H, 6.18; N, 3.89. C₂₀H₄₄Cl₆N₂Pt. Calculated (%): C, 33.35; H, 6.16; N, 3.89.

(1*R*)-(+)-Bornylammonium hexachloroplatinate(vi). Solutions of H₂PtCl₆•4H₂O (212 mg) in PrⁱOH (5 mL) and (+)-bornylammonium hydrochloride (220 mg) in PrⁱOH (5 mL) were mixed up. A precipitate immediately formed was filtered off, washed on the filter sequentially with PrⁱOH (5 mL) and diethyl ether to obtain a yellow complex (280 mg, 74%), $[\alpha]_D^{20}$ +9.9 (*c* 0.05, DMSO), $[\alpha]_D^{20}$ +12.7 (*c* 0.05, DMF), m.p. 240 °C (decomp.). CD, λ/nm ($\Delta\epsilon/\text{L}$ mol⁻¹ cm⁻¹): 388 (+0.020), 343 (+0.034). ¹H NMR ((CD₃)₂SO), δ : 0.83 (s, 6 H, CH₃CCH₃); 0.83 (s, 3 H, CH₃); 1.02 (dd, 1 H, CH₂, J = 4.0 Hz, J = 14.0 Hz); 1.28 (d, 1 H, CH₂, J = 7.3 Hz); 1.44 (m, 2 H, CH₂); 1.66 (m, 2 H, CH₂); 2.15 (dt, 1 H, CH, J = 7.2 Hz, J = 11.4 Hz); 3.27 (m, 1 H, CHN); 7.74 (br.s, 3 H, NH₃). UV, λ/nm (ϵ/L mol⁻¹ cm⁻¹): 272 (26060), 370 (505), 470 (56), 880 (5). IR, v(δ)/cm⁻¹: 3185 (v(N-H)); 3137, 3103 sh, 2988 sh, 2954, 2888 sh (v(N-H), v(C-H)); 1591 (δ_{as} (N-H)); 1496 (δ_{s} (N-H)); 1481, 1473, 1460 (δ (C-H) ring); 1391 (δ (NC-H)); 1368 (δ (C-H)); 1315 (δ (C-H) ring); 1300, 1282, 1208, 1197, 1162, 1137 (δ (C-H)); 1082 (v(C-N)); 1067, 1032, 1017, 998 (v(C-C), δ (C-H)); 942 (v(C-C)); 874, 822, 757 (v(C-C), δ (C-H)). IR, v/cm⁻¹: 333 (Pt-Cl); 240, 195. Found (%): C, 33.53; H, 5.65; N, 3.90. C₂₀H₄₀Cl₆N₂Pt. Calculated (%): C, 33.53; H, 5.63; N, 3.91.

(1R)-(+)-Bornylammonium tetrachloroplatinate(II). A mixture of (+)-(bornylNH₂)₂[PtCl₆] (145.35 mg) in H₂O (50 mL) and $N_2H_4 \cdot 2HCl (10.65 \text{ mg}) \text{ in } H_2O (5 \text{ mL}) \text{ was heated in a boiling}$ water bath and the solvent was evaporated by the air flow to obtain a reddish orange complex (130.96 mg, 88%), $[\alpha]_D^{20}$ +14.5 (c 0.05, DMSO), m.p. 268–269 °C (decomp.). CD, λ/nm $(\Delta \varepsilon / L \text{ mol}^{-1} \text{ cm}^{-1})$: 388 (+0.016), 286 (-0.032). ¹H NMR $((CD_3)_2SO), \delta: 0.82 (s, 3 H, CH_3CCH_3); 0.83 (s, 3 H, CH_3CCH_3);$ 0.87 (s, 3 H, CCH₂); 1.03 (dd, 1 H, CH₂, J = 4.0 Hz, J = 14.0 Hz); 1.31 (m, 1 H, CH_2); 1.53 (t, 2 H, CH_2 , J = 10.1 Hz); 1.65 (br.d, 1 H each, CH_2 , $\tilde{J} = 4.2$ Hz); 2.15 (dt, 1 H, CH, J = 3.2 Hz, J = 10.8 Hz); 3.23 (m, 1 H, CHN); 7.93 (m, 3 H, NH₃). UV, λ/nm (ϵ/L mol⁻¹ cm⁻¹): 272 (2270), 396 (486), 490 (22), 880 (8). IR, v/cm^{-1} : 3166 sh (v(N-H)); 3122, 2985 sh, 2953, 2893 sh (v(N-H), v(C-H)); 1584 (δ_{ac} (N-H)); 1504, 1501 $(\delta_{c}(N-H)); 1460 \ (\delta(C-H) \ ring); 1390 \ (\delta(NC-H)); 1369$ (δ(C–H)); 1315 (δ(C–H) ring); 1299, 1162, 1136 (δ(C–H)); 1083 (v(C-N)); 1067, 1037, 1020, 998, 883, 760, 516(v(C-C), δ(C-H)). Found (%): C, 37.23; H, 6.28; N, 4.33. C₂₀H₄₀Cl₄N₂Pt. Calculated (%): C, 37.22; H, 6.25; N, 4.34.

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