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# Reaction of Platinum Complexes with (+)-α-Pinene and (+)-Limonene. Synthesis, Molecular Structure, and Catalytic Activity of Dichloro($\eta^4$-[*p*-mentha-1,8{9}-diene])platinum(II)

**D. A. de Vekki[a], V. M. Uvarov[a], V. K. Bel'skii[b], and N. K. Skvortsov[a]**

[a] *St. Petersburg State Institute of Technology, Moskovskii pr. 26, St. Petersburg, 190013 Russia*

[b] *Karpov Research Physicochemical Institute, State Scientific Center of the Russian Federation, Moscow, Russia*

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**Abstract** — The transformations of platinum(II) and platinum(IV) complexes with inner- and outer-sphere ligands by the action of (+)-α-pinene and (+)-limonene were studied. Reduction of the metal complex is the main process whose rate increases in the following outer-sphere ligand series: $(Me_2SO)_2H^+ < Et_3NH^+ < K^+ < H^+$. The reaction of $K_2PtCl_4$ with α-pinene gave *cis*-terpine monohydrate and dichloro-$\eta^4$-[*p*-mentha-1,8(9)-diene]platinum(II), and their structure was proved by X-ray analysis. The complex belongs to monoclinic crystal system, the Pt–Cl and Pt–C bonds therein have different lengths, the ClPtCl angle is 85.88°, and the C=C bond plane is orthogonal to the square coordination core. Dichloro-$\eta^4$-[*p*-mentha-1,8(9)-diene]-platinum(II) was tested as catalyst in the hydrosilylation of acetophenone with diphenylsilane.
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Monoterpenes are accessible raw materials for the synthesis of metal complexes as promising catalysts in organic and organometallic chemistry. The main difficulty in the synthesis of such coordination compounds originates from the low stability of monoterpenes in the presence of metal complexes: they readily undergo isomerizations, polymerization [1–4], rearrangements, oxidation [5–8], etc. Nevertheless, we thought it to be interesting to study transformations of platinum coordination compounds in the presence of (+)-α-pinene and (+)-limonene.

Treatment of a solution of chloroplatinic acid in propan-2-ol with excess α-pinene at 20°C in 3 h led to change of the color from orange to red and then to black–brown, indicating fast reduction of Pt(IV) through Pt(II) to Pt(0). The $^1$H NMR spectrum ($CDCl_3$) of the reaction solution did not change; however, after 4 days, new signals appeared as δ 1.07, 1.11, 1.43, 1.47, 1.63, and 1.79 ppm, i.e., transformation of the pinene skeleton occurred just in the presence of platinum(0).

The presence of two outer-sphere dimethylsulfoxonium ligands $(Me_2SO)_2H^+$ considerably hinders reduction of the metal complex; even after 6 months ($CH_2Cl_2$, platinum–pinene ratio 1 : 50), no brown color was observed. According to the $^1$H NMR data [$(CD_3)_2CO$], after 6 days the reaction solution contained traces of $(Me_2SO)_2H^+$ (δ 2.63 ppm, t, $J_{Pt-H}$ = 28 Hz), geometric isomers of $[Pt(Me_2SO)_2Cl_2]$ (δ, ppm: 3.58 t, $J_{Pt-H}$ = 23 Hz; 3.31 t, $J_{Pt-H}$ = 21 Hz; *cis*–*trans* ratio 7 : 3), *trans*-$[Pt(Me_2S)_2Cl_4]$ (δ 2.59 ppm, t, $J_{Pt-H}$ = 30 Hz), uncoordinated dimethyl sulfoxide (δ 2.52 ppm, s), and trichloro(dimethyl sulfoxide)platinate(II) ion $[Pt(Me_2SO)Cl_3]^-$ (δ 3.53 ppm, t, $J_{Pt-H}$ = 26 Hz). The transformation of $[(Me_2SO)_2H]_2[PtCl_6]$ into *cis*-$[Pt(Me_2SO)_2Cl_2]$ was reported previously [9], but the reaction occurred in excess dimethyl sulfoxide. It is also known that *trans*-$[Pt(Me_2S)_2Cl_4]$ is formed in the solid-phase thermolysis of $[(Me_2SO)_2H]_2[PtCl_6]$ through $[(Me_2SO)_2H]\cdot[Pt(Me2SO)Cl5]$ [9]; however, the latter was not detected in our case. Taking into account the presence of species detected by NMR spectroscopy, *cis*-$[Pt(Me_2SO)_2Cl_2]$ is likely to be formed according to the following scheme:

$$[(Me_2SO)_2H]_2[PtCl_6] \xrightarrow[CH_2Cl_2]{\alpha\text{-pinene}} [(Me_2SO)_2H][Pt(Me_2SO)Cl_3] \xrightarrow[CH_2Cl_2]{} \textit{trans}\text{-}[Pt(Me_2SO)_2Cl_2] \xrightarrow[CH_2Cl_2]{Me_2SO} \textit{cis}\text{-}[Pt(Me_2SO)_2Cl_2].$$

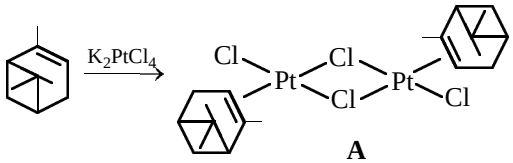
In the first step, dimethylsulfoxonium hexachloroplatinate(IV) is reduced to dimethylsulfoxonium trichloro(dimethyl sulfoxide)platinate(II) by the action of α-pinene, and the reduction product is gradually transformed into readily isomerizable *trans*-dichlorobis(dimethyl sulfoxide)platinum(II). The final step is isomerization of *trans*-$[Pt(Me_2SO)_2Cl_2]$ into the *cis* complex; this process is well known [10] to readily occur in the presence of a small amount of free dimethyl sulfoxide (which is liberated during the reaction).

The reaction of bis(triethylammonium) hexachloroplatinate(IV) with α-pinene at 20°C in 2 months leads to appearance in the $^1$H NMR spectrum ($CDCl_3$) of new signals belonging to triethylammonium chloride [δ, ppm: 1.37 t ($CH_3$, $J$ = 7.3 Hz), 3.08 q ($CH_2$, $J$ = 6.1, 7.4 Hz)] and bis(triethylammonium) tetrachloroplatinate(II) $(Et_3NH)_2[PtCl_4]$ [δ, ppm: 1.45 t ($CH_3$, $J$ = 7.3 Hz), 3.29 q ($CH_2$, $J$ = 7.0 Hz)]. In the reaction of α-pinene with bis(triethylammonium) tetrachloroplatinate(II) (3 months), the same products as in the reaction with the Pt(IV) complex were detected in the reaction mixture. The presence of free triethylammonium chloride indicates gradual decomposition of both bis(triethylammonium) tetrachloroplatinate(II) and bis(triethylammonium) hexachloroplatinate(IV).

$$(Et_3NH)_2[PtCl_6] \xrightarrow{\alpha\text{-pinene}} (Et_3NH)_2[PtCl_4]$$

$$\xrightarrow{\alpha\text{-pinene}} Pt + 2Et_3N\cdot HCl.$$

The reaction of α-pinene with $K_2PtCl_4$ in aqueous solution is sensitive to the reagent–substrate ratio. The optimal ratio α-pinene–$K_2PtCl_4$ is 10 : 1; raising the fraction of α-pinene leads to gradual reduction of Pt(II) to metallic platinum (the complete reduction requires 1 month); when the above ratio is decreased, no products are formed even after prolonged keeping of the reaction mixture (8 months). The $^1$H NMR spectrum of the reaction mixture after keeping for 5 months at 20°C coincided with that of the mixture heated for 5 h at 60°C: new signals at δ 0.89, 1.01, 1.34, and 1.36 ppm appeared; these signals are likely to belong to γ-terpinene and α- and β-fenchenes. When the reaction was carried out under argon, yellow crystals separated from the solution in 2 months; the product is insoluble in water and unstable: it quickly decomposes on exposure to air or on further keeping in the solution); presumably, the product is a short-lived platinum complex **A** with bridging chlorine atoms and coordinated α-pinene molecules.




**A**

The reaction of $K_2PtCl_4$ with α-pinene in a hydrochloric acid solution in 6 months at 20°C leads to platinum(II) complex with $\eta^4$-coordinated limonene [*p*-mentha-1,8(9)-diene]; the structure of that complex was proved by X-ray analysis (Fig. 1). We presumed that the isomerization of α-pinene into *dl*-limonene is directly related to its coordination, for the main process in the presence of hydrochloric acid is thermal isomerization into alloocimene [1] which was not detected in the reaction mixture.

Apart from dichloro-$\eta^4$-[*p*-mentha-1,8(9)-diene]-platinum(II), 10% of terpine hydrate crystallized from the reaction solution; its structure as *cis*-terpine monohydrate was also proved by X-ray analysis (Fig. 2; its structural parameters coincided with those reported in [11]). In order to rule out the possibility

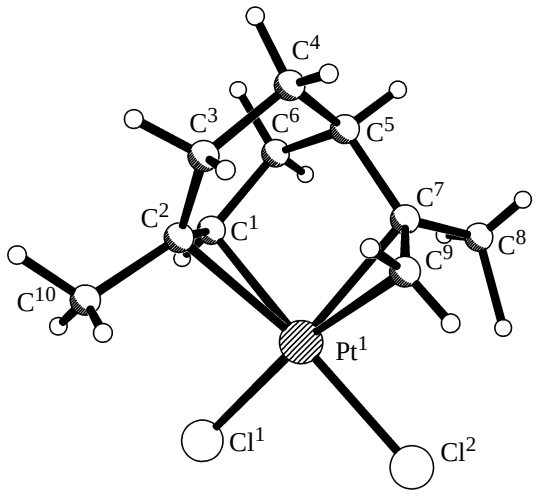



**Fig. 1.** Structure of the molecule of dichloro[$\eta^4$-*p*-mentha-1,8(9)-diene]platinum(II) according to the X-ray diffraction data.

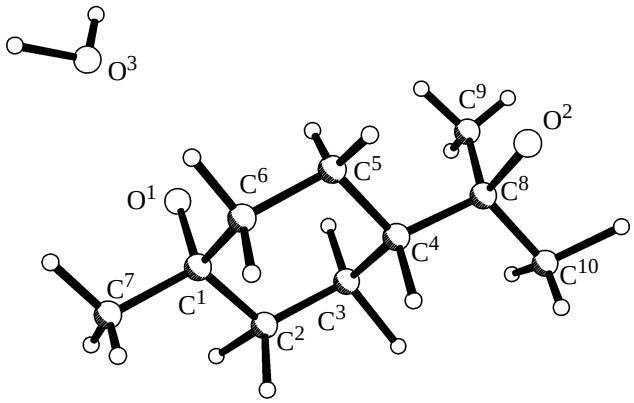
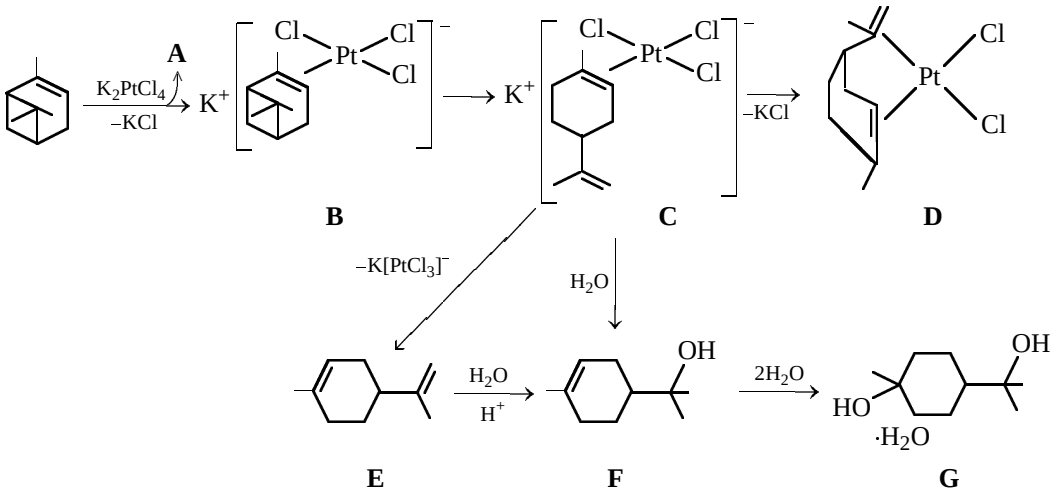



**Fig. 2.** Structure of the molecule of *cis*-terpine hydrate according to the X-ray diffraction data.

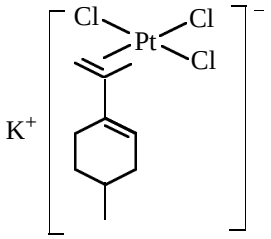
for formation of terpine by the action of hydrochloric acid, we performed special experiments. When α-pinene was treated with dilute hydrochloric acid, no terpine signals were detected in the $^1$H NMR spectrum of the reaction mixture after 3 months at 20°C, while terpine hydrate was formed on keeping a solution of α-pinene and $K_2PtCl_4$ in aqueous HCl. Presumably, potassium tetrachloroplatinite promotes the transformation of α-pinene into *dl*-limonene and *cis*-terpine hydrate according to the following scheme.




In the first step potassium trichloro($\eta^2$-pinene)-platinate(II) (**B**) and already noted bis[chloro(μ-chloro)($\eta^2$-pinene)platinum] (**A**) are formed. However, taking into account stronger *trans*-effect of the alkene as compared to chlorine [12, 13], dimer **A** should give rise to *trans*-complex instead of dichloro-[$\eta^4$-*p*-mentha-1,8(9)-diene]platinum(II) (**D**) (*cis*). Therefore, the formation of complex **B** seems to be more probable. Opening of the smaller ring in $\eta^2$-coordinated α-pinene leads to more energetically favorable potassium trichloro[$\eta^2$-*p*-mentha-1,8(9)-diene]platinate(II). The latter is converted into either complex **D** or limonene (**E**); the presence of limonene in the reaction mixture is confirmed by the $^{13}$C NMR spectrum ($CDCl_3$), $\delta_C$, ppm: 20.57, 23.24, 27.72, 30.37, 30.59, 40.89, 108.17, 120.47, 133.47, 149.98.

It is known [14] that terpine hydrate (**G**) is formed by acid hydrolysis of pinene or limonene, which involves intermediate formation of α-terpineol (**F**). On the other hand, hydration of the uncoordinated double bond in the limonene molecule can occur directly in complex **C** with subsequent elimination of alcohol **F**. This reaction pathway follows from the results of studies on catalytic oxidation of limonene with molecular oxygen in the presence of palladium complexes: α-terpineol was detected among the oxidation products [15, 16].

The reaction of (+)-limonene with $K_2PtCl_4$ (5 months at 20°C) gave no products **D** and **G**, and the NMR spectra of the reaction solution coincided almost completely with those of the reaction mixture obtained from α-pinene and $K_2PtCl_4$ under analogous conditions. Presumably, limonene coordinates to platinum at the more reactive exocyclic double bond (complex **H**) [14–16], while the endocyclic double bond is not involved in coordination for conformational reasons (according to the X-ray diffraction data, $\eta^4$-coordination of limonene strongly distorts its *boat* conformation). Insofar as the NMR spectra of both reaction solutions (obtained from limonene and α-pinene) are almost identical, we presume that the isomerization of α-pinene into *dl*-limonene is the main process occurring in the presence of $K_2PtCl_4$.




**H**

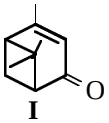
Thus, the ability of outer-sphere complexes to react with α-pinene depends on the nature of the outer-sphere cation. The rate of decomposition of metal

complexes decreases in the following series of cations: $(Me_2SO)_2H^+ > Et_3NH^+ > K^+ > H^+$.

Apart from platinum complexes with outer-sphere ligands, it was also interesting to examine the behavior of platinum(II) complexes with inner-sphere ligands in the presence of α-pinene and limonene, i.e., under reductive conditions. We found that *cis*-$[Pt(Me_2SO)_2Cl_2]$ failed to react with α-pinene in methylene chloride at 20°C (3 months) and that heating of the reaction mixture (60°C, 3 h) induced fast decomposition of the complex with liberation of metallic platinum. Unlike α-pinene, limonene promoted decomposition of *cis*-$[Pt(Me_2SO)_2Cl_2]$ in 26 h at 20°C: In the $^1$H NMR spectrum ($CDCl_3$) we observed signals belonging to limonene, initial complex, and free dimethyl sulfoxide (δ 2.62 ppm, s), as well as new signals indicating transformation of the terpene skeleton (δ, ppm: 1.24 s, 1.36 s, 2.19 m, and 2.33 s) and a signal at δ 3.48 ppm, t ($J_{Pt-H}$ = 21 Hz); presumably, the latter corresponds to *trans*-$[Pt(Me_2SO)\cdot(\eta^2\text{-limonene})Cl_2]$.

The complex *cis*-$[Pt(MeCN)_2Cl_2]$ (δ 2.66 ppm, t, $J_{Pt-H}$ = 14 Hz) in methylene chloride turned out to be the most stable toward reduction with α-pinene. The $^1$H NMR spectrum ($CDCl_3$) of the reaction mixture (60°C, 27 h) contained signals from *cis*-$[Pt(MeCN)_2Cl_2]$ and its *trans* isomer (δ 2.75 ppm, t, $J_{Pt-H}$ = 14 Hz) at a ratio of 76 : 34 and a number of signals at δ (ppm) 0.82 s, 0.86 s, 0.95 s, 0.99 s, 1.32 s, 1.48 s, 1.71 s, and 2.03 s due to transformation products of α-pinene.

The $^1$H NMR spectrum ($CDCl_3$) of the organic component changed even more strongly when $[Pt(MeCOD)Cl_2]$ was used as substrate (in methylene chloride); presumably, the reason is high lability of 1-methylcycloocta-1,5-diene (MeCOD) as ligand. After 17 h at 60°C, the spectrum contained numerous signals, the most intense of which were located at δ 0.82, 0.96, 1.28, 1.45, 1.63, 1.97, and 2.15 ppm. In the $^{13}$C NMR spectrum ($CDCl_3$) of the same mixture we observed signals belonging to products of both isomerization and rearrangement of α-pinene and its oxidation. For example, signals at $\delta_C$ 203.82, 155.19, 120.72, and 57.1 ppm were assigned to 4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-one (**I**) which is formed in the catalytic oxidation of α-pinene [4, 8]. Thus $[Pt(MeCOD)Cl_2]$ cannot be used for the preparative synthesis of new monoterpene complexes, but it can be regarded as a potential catalyst for oxidation of monoterpenes.




**I**

Crystals of dichloro-[$\eta^4$-*p*-mentha-1,8(9)-diene]-platinum(II) belong to the monoclinic system; the ClPtCl angle is 85.88°, which is typical of other platinum(II) complexes with chelating ligands [17–21]. For example, the ClPtCl angle in dichloro[$\eta^4$-5-methylidenecycloheptene]platinum(II) is 86.6°, and in dichloro[$\eta^4$-cycloocta-1,5-diene]platinum(II) $[Pt(COD)Cl_2]$, 89.78°. The Pt–Cl bond lengths in complex **D** are similar to those found in $[Pt(COD)Cl_2]$ (2.310, 2.317 Å and 2.309, 2.315 Å [17, 18], respectively; Table 1; cf. standard Pt–Cl bond length 2.303 Å [19]). The distances from platinum to the olefinic fragments are also different: the Pt–C distances to the endocyclic double bond are 2.156 and 2.269 Å, and to the exocyclic, 2.155 and 2.232 Å; therefore, these bonds should differ in their strength. As follows from the Pt–C bond lengths, coordination to metal does not change the order of the double bonds to an appreciable extent (the C=C bond lengths in complex **D** are 1.355 and 1.366 Å for the endocyclic and exocyclic double bonds, respectively). Both C=C bonds are almost orthogonal to the coordination square plane, though the exocyclic double bond should be expected to lie in that plane, as was reported in [19]. The torsion angles between the square plane and double C=C bond planes are similar (93.61°), the $Cl^1Pt^1C^1C^2$ angle is 101.35°, and the $Cl^2Pt^1C^9C^7$ angle is 110.28°; the latter values somewhat exceed those found in $[Pt(COD)Cl_2]$ [20, 21]. The two double bonds are turned apart with respect to each other through an angle of 27.31°. As a result of coordination, the cyclohexene skeleton of the organic ligand adopts a distorted *boat* conformation, the single C–C bond lengths range from 1.510 to 1.526 Å, and the bond angles range from 107.70° to 116.02°.

The catalytic activity of complex **D** was studied in the reaction of acetophenone with diphenylsilane by comparing with the catalytic activity of structurally related dichloro($\eta^4$-1-methylcycloocta-1,5-diene)platinum(II) $[Pt(MeCOD)Cl_2]$. Taking into account that both these complexes are achiral (but asymmetric induction was desirable), the reactions were performed according to the standard procedure (see Experimental). Excess (+)-limonene (4 mol %) was added, and $AgBF_4$ was used as Lewis acid to enhance the solubility and catalytic activity of the complexes.

Dichloro[$\eta^4$-*p*-mentha-1,8(9)-diene]platinum(II) turned out to be less active but more selective catalyst than $[Pt(MeCOD)Cl_2]$. According to the $^1$H NMR data, the yield of the corresponding silyl ether (δ 1.38 ppm, d, $CH_3$, $J$ = 6.0 Hz; $CDCl_3$) at 5°C was 98% in 10 days in the presence of complex **D** and 100% in 5 days in the presence of $[Pt(MeCOD)Cl_2]$, and the

**Table 1.** Bond angles (*d*) and bond angles (ω) in the molecule of dichloro[$\eta^4$-*p*-mentha-1,8(9)-diene]platinum(II)

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| Pt–$C^1$ | 2.156(7) | $C^2$–$C^3$ | 1.510(12) |
| Pt–$C^9$ | 2.155(9) | $C^2$–$C^{10}$ | 1.535(12) |
| Pt–$C^7$ | 2.232(8) | $C^3$–$C^4$ | 1.526(13) |
| Pt–$C^2$ | 2.269(8) | $C^4$–$C^5$ | 1.511(12) |
| Pt–$Cl^1$ | 2.310(2) | $C^5$–$C^6$ | 1.516(11) |
| Pt–$Cl^2$ | 2.317(2) | $C^5$–$C^7$ | 1.525(11) |
| $C^1$–$C^2$ | 1.355(11) | $C^7$–$C^9$ | 1.366(12) |
| $C^1$–$C^6$ | 1.525(11) | $C^7$–$C^8$ | 1.513(12) |
| **Angle** | **ω, deg** | **Angle** | **ω, deg** |
| $C^9PtC^1$ | 104.6(3) | $C^1C^2C^{10}$ | 122.1(8) |
| $C^9PtC^7$ | 36.2(3) | $C^3C^2C^{10}$ | 113.1(8) |
| $C^1PtC^7$ | 81.8(3) | $C^1C^2Pt$ | 67.6(4) |
| $C^9PtC^2$ | 90.4(3) | $C^3C^2Pt$ | 114.9(5) |
| $C^1PtC^2$ | 35.6(3) | $C^{10}C^2Pt$ | 107.5(6) |
| $C^7PtC^2$ | 87.7(3) | $C^2C^3C^4$ | 116.0(7) |
| $C^9PtCl^1$ | 165.2(3) | $C^5C^4C^3$ | 112.7(7) |
| $C^1PtCl^1$ | 87.0(2) | $C^4C^5C^6$ | 109.0(7) |
| $C^7PtCl^1$ | 157.9(2) | $C^4C^5C^7$ | 114.6(7) |
| $C^2PtCl^1$ | 94.1(2) | $C^6C^5C^7$ | 108.5(6) |
| $C^9PtCl^2$ | 85.9(2) | $C^5C^6C^1$ | 107.7(7) |
| $C^1PtCl^2$ | 160.2(2) | $C^9C^7C^8$ | 121.3(8) |
| $C^7PtCl^2$ | 98.4(2) | $C^9C^7C^5$ | 121.9(7) |
| $C^2PtCl^2$ | 163.6(2) | $C^8C^7C^5$ | 115.4(8) |
| $Cl^1PtCl^2$ | 85.88(9) | $C^9C^7Pt$ | 68.8(5) |
| $C^2C^1C^6$ | 120.4(8) | $C^8C^7Pt$ | 107.7(5) |
| $C^2C^1Pt$ | 76.8(4) | $C^5C^7Pt$ | 105.9(5) |
| $C^6C^1Pt$ | 106.2(5) | $C^7C^9Pt$ | 75.0(5) |
| $C^1C^2C^3$ | 120.9(8) | | |

**Table 2.** Coordinates of non-hydrogen atoms ($\times 10^4$) in the molecule of dichloro[$\eta^4$-*p*-mentha-1,8(9)-diene]platinum(II)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pt | 5522(1) | 2527(1) | 5340(1) |
| $Cl^1$ | 2996(3) | 5464(2) | 982(3) |
| $Cl^2$ | 4742(4) | 3878(2) | 2711(3) |
| $C^1$ | 6409(12) | 6544(5) | 1655(9) |
| $C^2$ | 5807(10) | 6808(5) | 2860(8) |
| $C^3$ | 7084(12) | 7075(5) | 4091(9) |
| $C^4$ | 9015(13) | 6799(5) | 4042(10) |
| $C^5$ | 9230(11) | 6107(5) | 2953(9) |
| $C^6$ | 8396(12) | 6435(5) | 1557(8) |
| $C^7$ | 8411(11) | 5220(5) | 3244(9) |
| $C^8$ | 9131(12) | 4447(7) | 2497(10) |
| $C^9$ | 7395(13) | 5102(6) | 4319(8) |
| $C^{10}$ | 3935(15) | 7187(6) | 2910(14) |

selectivity was 67 and 59%, respectively. In both cases, the subsequent hydrolysis of 1-diphenylsiloxy-1-phenylethane gave racemic 1-phenylethanol, i.e., no asymmetric induction was observed. Presumably, the reason is that coordination of the silicon hydride ($\eta^2$-coordination of silicon hydride is the key stage in the formation of true hydrosilylation catalyst [22]) predominates over coordination of (+)-limonene. As a result, $\eta^4$-coordinated achiral ligand is not replaced by the optically active analog, and the true catalyst is achiral dichloroplatinum(II) complex with $\eta^2$-coordinated diphenylsilane and *dl*-limonene.

## EXPERIMENTAL

The $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker AC-200 instrument at 200 ($^1H$) and 50 MHz ($^{13}C$) from solutions in $CDCl_3$, $(CD_3)_2SO$, and $(CD_3)_2CO$; no additional reference was added, and the chemical shifts were measured relative to the corresponding solvent signals. The IR spectra were obtained in KBr on a Shimadzu FTIR-8400S spectrometer in the range from 4000 to 500 $cm^{-1}$. Hydrosilylation of acetophenone with diphenylsilane was performed according to the procedure reported in [23]. Asymmetric induction was determined on a Perkin–Elmer 241MC polarimeter in 10-cm temperature-controlled quartz cells.

X-ray analysis was performed on an Enraf–Nonius CAD-4 automatic four-circle diffractometer (Mo$K_\alpha$ radiation, β-filter, θ/2θ scanning). Single crystals for crystallographic studies were obtained from the reaction solution by slow evaporation. Dichloro[$\eta^4$-*p*-mentha-1,8(9)-diene]platinum(II): crystal size $0.38 \times 0.14 \times 0.14$ mm, yellow prisms; monoclinic crystal system; unit cell parameters: $a$ = 7.566(2), $b$ = 15.245(3), $c$ = 9.670(2) Å; $V$ = 1109.5(4) Å$^3$; $Z$ = 2; $\rho_{calc}$ = 2.408 g cm$^{-3}$; 1340 reflections with $I > 2\sigma(I)$; correction for absorption of X-rays by the sample $\mu$ = 13.080 mm$^{-1}$; $R$ = 0.0271. The structure was solved by the heavy-atom procedure in anisotropic approximation. *cis*-Terpine hydrate: crystal size $0.25 \times 0.12 \times 0.08$ mm, colorless prisms; orthorhombic crystal system; unit cell parameters: $a$ = 18.435(4), $b$ = 22.817(5), $c$ = 10.940(2) Å; $V$ = 4601.7(16) Å$^3$; $Z$ = 16; $\rho_{calc}$ = 1.099 g cm$^{-3}$; 1696 reflections with $I > 2\sigma(I)$; correction for absorption of X-rays by the sample $\mu$ = 0.079 mm$^{-1}$; $R$ = 0.0267.

Methylene chloride (Merck), diphenylsilane (Acros), $AgBF_4$ (Aldrich), and chemically pure grade aceto-

phenone, (+)-α-pinene, (+)-limonene, $K_2PtCl_4$, and $RhCl_3 \cdot 4H_2O$ were used.

The complexes *cis*-$[Pt(Me_2SO)_2Cl_2]$, *cis*-$[Pt(MeCN)_2Cl_2]$, $[Rh(CO)_2Cl]_2$ [24], $(Et_3NH)_2[PtCl_4]$, $(Et_3NH)_2[PtCl_6]$ [25], $[(Me_2SO)_2H]_2[PtCl_6]$ [26], and $[Pt(MeCOD)Cl_2]$ [27] were synthesized by known methods.

**Dichloro[$\eta^4$-*p*-mentha-1,8(9)-diene]platinum(II).** Potassium tetrachloroplatinate(II), 35.9 mg, and (+)-α-pinene, 0.1 ml, were dissolved in 50 ml of 0.001 N hydrochloric acid at room temperature. After 6 months (the solution was allowed to slowly evaporate), 12.7 mg of the brown complex was filtered off. Yield 36.5%. The X-ray diffraction data (bond lengths and angles and coordinates of non-hydrogen atoms) are given in Tables 1 and 2. IR spectrum, $cm^{-1}$: 2962 ($\nu_{C-H}$); 2278, 2257, 2249, 2123; 1643 ($\nu_{C=C}$); 1518 ($\delta_{C-H}$, ring); 1450 ($\delta_{C-H}$, ring, $CH_3$); 1157, 1132, 1020, 1008 ($\delta_{C-H}$); 841, 823 ($\nu_{C-C}$ and $\delta_{C-H}$); 789, 774 ($\nu_{C-C}$, ring); 636.

***cis*-Terpine hydrate** was isolated from the same reaction solution. Yield 54.0%. The bond lengths and bond angles determined by X-ray analysis coincided with those reported in [11]. $^1H$ NMR spectrum [$(CD_3)_2SO$], δ, ppm: 1.00 s (6H, $CH_3$), 1.05 s (3H, $CH_3$), 1.21 m (4H, $CH_2$), 1.50 t (4H, $CH_2$, $J$ = 14 Hz). IR spectrum, $cm^{-1}$: 3480, 3250 ($\nu_{O-H}$); 2966, 2830 ($\nu_{C-H}$); 1639 ($\delta_{O-H}$); 1385, 1312, 1255 ($\delta_{C-O}$ and $\delta_{C-H}$); 1242, 1222, 1178, 1135 ($\nu_{C-O}$ and $\delta_{C-H}$); 1118, 1016, 990, 954, 933, 904, 839 ($\delta_{O-H}$ and $\delta_{C-H}$); 772, 724, 655, 604, 462, 457, 451, 441, 436, 426, 400 ($\delta_{C-C}$ and $\delta_{C-H}$).

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