Synthesis and spectroscopic characteristics of σ-vinyl derivatives of platinum(IV) chloride complexes

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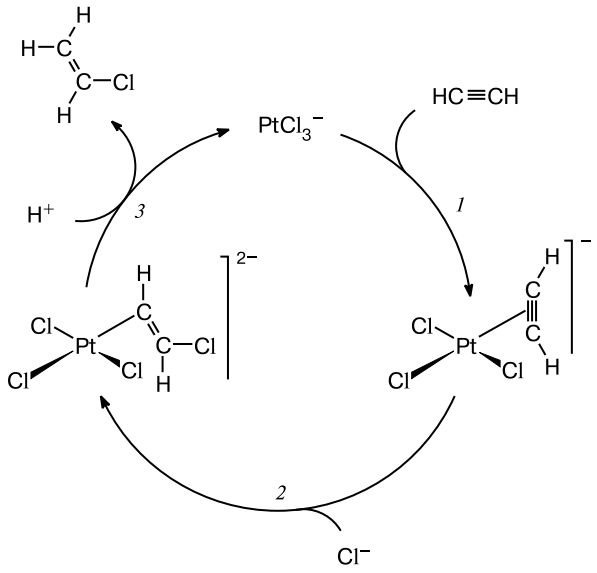
A procedure was developed for the synthesis of previously unknown β-chlorovinyl derivatives of Pt^{IV} chloride complexes by chloroplatination of terminal alkynes catalyzed by Pt^{II} chloride complexes. The reaction is highly stereoselective and gives only the products of *trans—anti*-addition of platinum and chlorine atoms. The regioselectivity of the catalytic reaction formally corresponds to Markovnikov's rule, *e.g.*, in alkynes containing electron-donating substituents, platinum attacks the terminal carbon atom. The σ-vinyl derivatives of Pt^{IV} chloride complexes were characterized by IR spectroscopy and ^1H and ^{13}C NMR spectroscopy.

Key words: alkynes, platinum chloride complexes, chloroplatination, homogeneous catalysis.

Earlier,[1—4] it has been demonstrated that bis-σ-vinyl derivatives of platinum(IV) iodide complexes can be synthesized by iodoplatination of acetylenes (HC≡CH, HC≡C—CH_2OH, HC≡C—CH_2OMe, and HC≡C—C(O)—OMe) with Pt^{IV} iodides in aqueous solutions. However, σ-vinyl derivatives of platinum(IV) chloride complexes cannot be synthesized in a similar way because platinum(IV) chloride complexes are inactive under analogous reaction conditions.[1—4] We found that these organoplatinum compounds can be prepared by catalytic chloroplatination of alkynes in the $PtCl_4^{2-}$—$PtCl_6^{2-}$—NaCl—H_2O system. Platinum(II) chloride complexes are known[5,6] to exhibit high catalytic activity in hydrochlorination of acetylene. The mechanism of the catalytic reaction (Scheme 1), which was proposed[5,6] based on the kinetic data, the stereochemistry of the product prepared by hydrochlorination of acetylene with DCl, and an analogy with other catalytic systems, includes π-coordination of acetylene (step *1*), the nucleophilic attack of the external chloride ion on the π-coordinated acetylene with the intermediate formation of the β-chlorovinyl derivative of Pt^{II} (step *2*), and protonolysis of the latter (step *3*). However, no direct evidence for the involvement of β-chlorovinyl organoplatinum derivatives as intermediates was presented. The aim of the present study was to synthesize such organoplatinum compounds.

Taking into account that σ-organic derivatives of platinum(II) can be subjected to complementary oxidation[7] with platinum(IV), we trapped σ-vinyl derivatives of Pt^{II}, which are generated in step *2*, with platinum(IV) complexes to obtain more stable σ-vinyl derivatives of platinum(IV) chloride complexes **1—3** with composition Pt^{IV}—RC=CR´Cl (Scheme 2).

Scheme 1



The stoichiometry of the reaction formally corresponds to Scheme 3.

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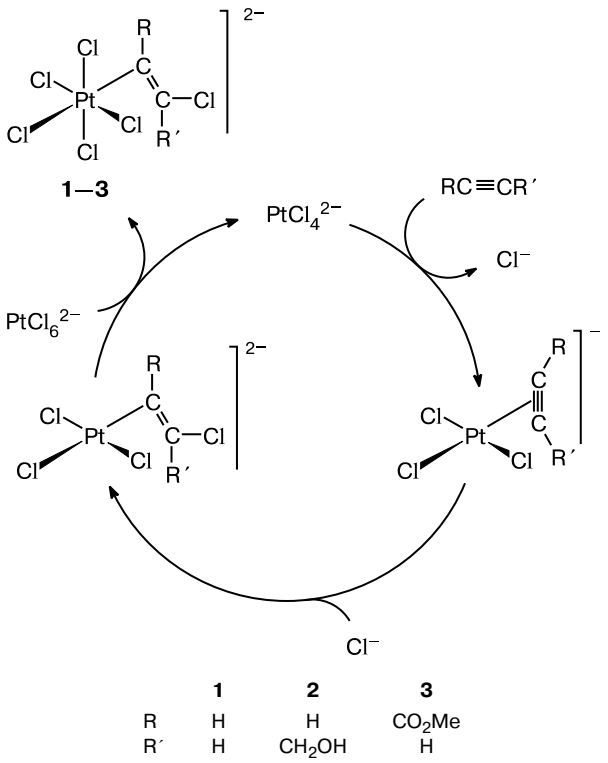
Scheme 2



	1	2	3
R	H	H	CO_2Me
R′	H	CH_2OH	H

Scheme 3

$$Na_2PtCl_6 + RC{\equiv}CR' \xrightarrow{PtCl_4^{2-}} Na_2Pt(RC{=}CR'Cl)Cl_5$$

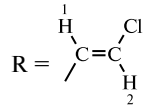
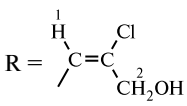
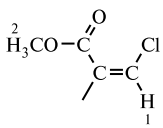
The reactions were carried out in aqueous 5 *M* NaCl solutions in the presence of $PtCl_6^{2-}$ and catalytic amounts of $PtCl_4^{2-}$ at 25—40 °C in a neutral medium (to prevent protonolysis of σ-vinyl derivatives of platinum(II)). When Pt^{II} compounds were absent, σ-vinyl derivatives of platinum were not produced in detectable amounts. Platinum(II) (see Scheme 3) serves as a catalyst. The reaction of propargyl alcohol was monitored by NMR. In the ^1H NMR spectrum of an aqueous solution (D_2O, 2 mL) containing NaCl (0.588 g), $Na_2PtCl_4 \cdot nH_2O$ (0.00975 g, ≤25 μmol of Pt^{II}), and Na_2PtCl_6 (0.21875 g, 482 μmol), the intensity of the signal at δ 2.97 corresponding to the protons of ≡CH of propargyl alcohol decreases with time, and a signal assigned to the vinyl protons (—CH=) of complex **2** (δ 6.92, $^2J_{Pt,H}$ = 81 Hz) appears and its intensity gradually increases. According to the results of ^1H NMR spectroscopy, the reaction performed at room temperature for 5 weeks afforded complex **2** in a yield of ~360 μmol, *i.e.*, >1400% with respect to the initial amount of platinum(II).

The parameters of the NMR spectra confirm the structures of compounds **1—3** (Table 1). The spin-spin coupling constants $J_{^{195}Pt,^1H}$ and $J_{^{195}Pt,^{13}C}$ for complex **1** are indicative of the σ character of the Pt—C bond. The rather large constant $^3J_{H,H}$ is indicative of the *trans—anti* addition of the Pt and Cl atoms to the intermediate acetylene π-complex. Taking into account the large constant $J_{^{195}Pt,^1H}$ for compound **2**, a structure with the Pt—terminal C atom σ-bond can be assigned to this compound (*cf.* compound **1**). To the contrary, the small constant $J_{^{195}Pt,^1H}$ for complex **3** is evidence for the presence of a Pt—internal C atom σ-bond in accordance with that expected for alkynes containing an electron-withdrawing substituent. This regioselectivity of the reaction formally corresponds to the addition at the triple bond according to Markovnikov's rule (*cf.* Ref. 4).

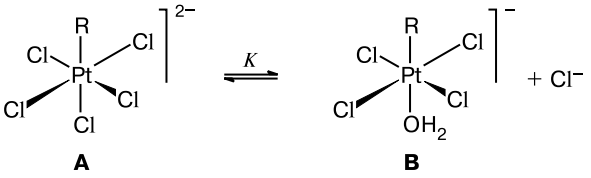
The ^1H NMR spectra of the reaction products in more dilute NaCl solutions in D_2O show groups of signals in the vinyl region, which are accompanied by Pt satellites and are shifted upfield (see Table 1). The integrated intensity ratio of these signals linearly depends on the concentration of chloride ions (Fig. 1). These effects can be due to the existence of an equilibrium described[7,8] for σ-alkyl derivatives of Pt^{IV} (Scheme 4).

In this case, lower-field signals are attributed to the vinyl protons of complexes **A** containing the chloride ion in the *trans* position with respect to the vinyl ligand, and

Table 1. ^1H NMR spectra of β-chlorovinyl derivatives of platinum(IV) chloride complexes in D_2O

Complex	δ (*J*/Hz)					
	R = 		R = 		R = 	
	H(1)	H(2)	H(1)	H(2)	H(1)	H(2)
A	6.74 ($J_{Pt,H(1)}$ = 66.3)	5.87 ($J_{Pt,H(2)}$ = 26.7)	6.92 ($J_{Pt,H(1)}$ = 81.0)	4.60	6.21 ($J_{Pt,H(1)}$ = 34.9)	3.74
B	6.54 ($J_{Pt,H(1)}$ = 74.3)	5.82 ($J_{Pt,H(2)}$ = 26.7)	6.77 ($J_{Pt,H(1)}$ = 89.2)	4.60	6.14 ($J_{Pt,H(1)}$ = 35.4)	3.74

Scheme 4



A **B**

higher-field signals are assigned to the vinyl protons of complexes **B** containing the aqua ligand in the *trans* position. The equilibrium constants K for compounds **1—3**, which were determined from the plots presented in Fig. 1, are 0.64±0.01, 0.63±0.03, and 0.45±0.05 mol L^{-1}, respectively, and are similar to the constant $K = 0.8$ mol L^{-1} for the platinum(IV) methyl complex[7] (see Scheme 4 for R = Me).

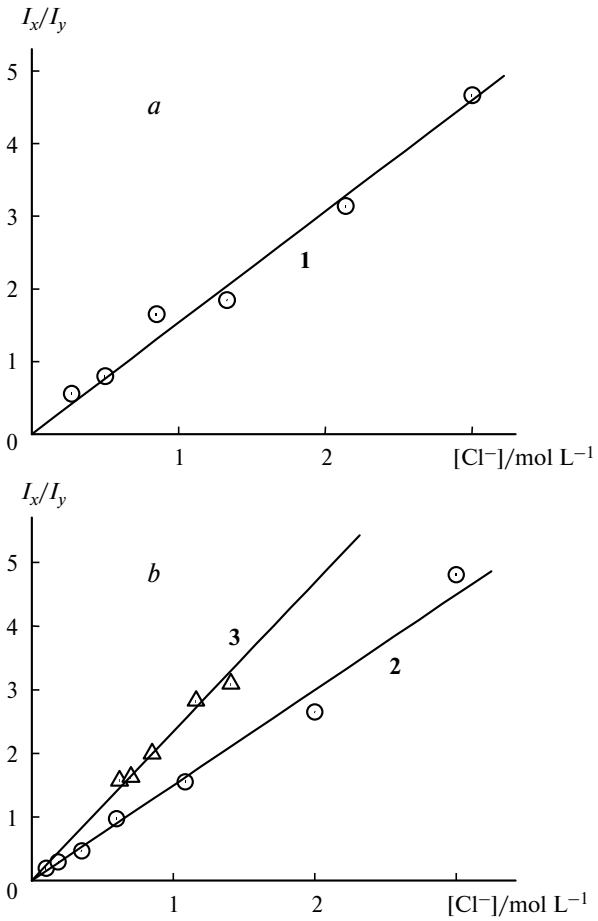


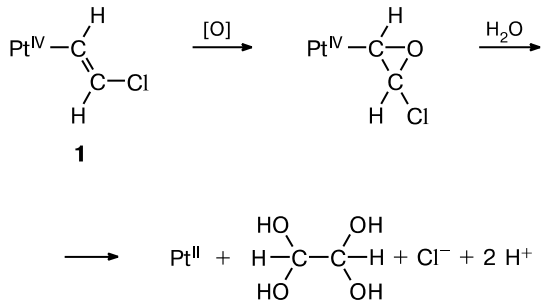
Fig. 1. Plots of the intensity ratio of the signals for the vinyl protons (I_x/I_y) in the ^{1}H NMR spectra of compounds **1** (*a*), **2**, and **3** (*b*) *vs.* the concentration of chloride ions (the starting concentration of the complexes was 0.03 mol L^{-1}; x and y are the chemical shifts of the vinyl protons).

Complex	x, ppm	y, ppm
1	6.74	6.54
2	6.92	6.77
3	6.21	6.14

The upfield shifts of the signals for the vinyl protons upon dissociation of the Cl^- *trans*-ligand according to Scheme 4 can be attributed to deshielding of these nuclei as a result of a change in the total charge of the complex from −2 to −1. It should be noted that dissociation of the Cl^- *trans*-ligand from platinum(IV) alkyl complexes is not accompanied by changes in the parameters of the ^{1}H NMR spectra of the complexes; however, changes in the parameters of the ^{195}Pt NMR spectra were observed.[7,8] These differences in the spectral behavior of σ-vinyl and alkyl derivatives of platinum(IV) chloride complexes can be attributed, first, to the better conductivity of the stronger and shorter Pt—C(sp^2) bond compared to the Pt—C(sp^3) bond and, second, to the higher polarizability of the C—C bond.

Unlike monoalkyl derivatives,[7—9] monovinyl derivatives of platinum(IV) chloride complexes are not subjected to reductive elimination in the presence of nucleophilic agents. A decrease in the reactivity of vinyl derivatives compared to the corresponding alkyl derivatives is consistent with that expected for the nucleophilic substitution at the sp^3- and sp^2-hybridized carbon atoms. However, complex **1** in aqueous solutions decomposes in air at room temperature within a few days to form hydrated glyoxal, which is the only product detected by NMR methods. The possible reaction mechanism includes epoxidation of the double bond followed by the opening of the oxirane ring under the action of water and hydrolytic cleavage of the Pt—C and Cl—C bonds (Scheme 5).

Scheme 5



To summarize, we proposed a procedure for the synthesis of previously unknown β-chlorovinyl derivatives of Pt^{IV} chloride complexes by chloroplatination of terminal alkynes catalyzed by Pt^{II} chloride complexes. This reaction is highly stereoselective and gives only the products of *trans—anti* addition of the platinum and chlorine atoms. The regioselectivity of the catalytic reaction formally corresponds to Markovnikov's rule, *e.g.*, in alkynes contain-

ing electron-donating substituents, the attack of platinum occurs on the terminal carbon atom.

Experimental

The NMR spectra were recorded on Varian GEMINI 200 (200 MHz for ^1H and 50.3 MHz for ^{13}C) and Bruker DRX 500 (500 MHz for ^1H and 125.75 MHz for ^{13}C) instruments. The ^1H NMR monitoring of the reaction of propargyl alcohol in D_2O was performed with the use of *tert*-butanol as the internal standard. The IR spectra were recorded on a FTIR Perkin—Elmer Spectrum BX instrument in KBr pellets.

The salts Na_2PtCl_6 (anhydr.) and Na_2PtCl_4 were synthesized according to standard procedures.[10] Commercial propargyl alcohol was purified by distillation. Acetylene was prepared according to a known procedure.[11]

Synthesis of σ-vinyl derivatives of platinum(IV) chloride complexes (general procedure). Propargyl alcohol or methyl propiolate (40 μL) was added portionwise (10 μL) at 1 day intervals (in the reaction with methyl propiolate, at 4 day intervals) to a 5 *M* NaCl solution (2 mL) containing Na_2PtCl_4 (0.082 g) and Na_2PtCl_6 (0.262 g). After the addition of the last portion of the substrate, the reaction mixture was kept in the dark at room temperature for 5 days. The reaction with acetylene was carried out under analogous conditions, but the mixture was kept at 40 °C for 2 days in a closed shaking reactor filled with acetylene. Then an excess of a saturated KCl solution was added to the reaction mixture to precipitate unconsumed Pt^{IV}, and the reaction mixture was concentrated to dryness without heating under a stream of air. Organoplatinum compounds were extracted from the dry residue with an acetone—methanol mixture (2 : 3 v/v), and the extract was concentrated. The extraction—evaporation process was repeated two times, after which yellow crystalline products were obtained. Elemental analysis data, IR spectra, and NMR spectra confirm the structures of complexes **1—3**.

Potassium [2(*E*)-chloroethenyl]pentachloroplatinate(IV) (1). The yield was 32% (with respect to Pt^{IV}). Found (%): C, 4.60; H, 0.50; Pt, 38.40. $C_2H_2Cl_6K_2Pt$. Calculated (%): C, 4.69; H, 0.39; Pt, 38.10. IR, ν/cm^{-1}: 3014 (ν(HC=)); 1639 (ν(C=C)); 914 (γ(HC=)); 676 (ν(CCl)). $^{13}C\{^1H\}$ NMR (CD_3OD), δ: 114.5 and 96.6 (both s, with Pt satellites, $^2J_{^{195}Pt,^{13}C}$ = 45.7 Hz and $^1J_{^{195}Pt,^{13}C}$ = 749.6 Hz, respectively).

Potassium [2(*E*)-chloropropen-1-yl]pentachloroplatinate(IV) (2). The yield was 77% (with respect to Pt^{IV}). Found (%): C, 6.70; H, 0.80; Pt, 35.60. $C_3H_4Cl_6K_2OPt$. Calculated (%): C, 6.64; H, 0.74; Pt, 36.00. IR, ν/cm^{-1}: 3547 (ν(HO)); 3016 (ν(HC=)); 2928 (ν(H—C)); 1690 (δ(OH)); 1615 (ν(C=C)); 1378, 1345 (δ(H_2C)); 1040 (ν(OC)); 946 (γ(HC=)); 677 (ν(CCl)). $^{13}C\{^1H\}$ NMR (5 *M* NaCl solution in D_2O), δ: 64.2 (s, CH_2); 105.0 (s, with Pt satellites, CH=, $^1J_{^{195}Pt,^{13}C}$ = 703.9 Hz); 132.2 (s, with Pt satellites, =CCl, $^2J_{^{195}Pt,^{13}C}$ = 48.4 Hz).

Potassium [1-carbomethoxy-2(*E*)-chloroethen-1-yl]pentachloroplatinate(IV) (3). The yield was 90% (with respect to Pt^{IV}). Found (%): C, 7.90; H, 1.30; Pt, 34.00. $C_4H_4Cl_6K_2O_2Pt$. Calculated (%): C, 8.42; H, 0.70; Pt, 34.20. IR, ν/cm^{-1}: 3101, 3010 (ν(HC=)); 2951, 2923 (ν(H—C)); 1704 (ν(C=O)); 1618 (ν(C=C)); 1433 (δ(H_3C)); 1295, 1218, 1007 (ν(OC)); 912 (γ(HC=)); 692 (ν(CCl)). $^{13}C\{^1H\}$ NMR (5 *M* NaCl solution in D_2O), δ: 53.2 (s, CH_3); 107.2 (s, with Pt satellites, $\underline{C}$(C)=, $^1J_{^{195}Pt,^{13}C}$ = 771.6 Hz); 116.6 (s, with Pt satellites, =C(H)Cl, $^2J_{^{195}Pt,^{13}C}$ = 27.6 Hz); 171.3 (s, C(O)O).

The equilibrium constants (see Scheme 4) were measured in aqueous D_2O solutions at a constant ionic strength maintained by adding sodium perchlorate: [NaCl] + [$NaClO_4$] = 3.0 mol L^{-1}.

The NMR spectra of the decomposition products of complex **1** in aqueous solutions (^1H NMR (D_2O), δ: 4.86 (s); ^{13}C NMR (D_2O), δ: 89.6 (d, $J_{^{13}C,^1H}$ = 164.8 Hz)) are identical to the spectra of dilute aqueous solutions of glyoxal.

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