

SHORT
COMMUNICATIONS

Catalytic Chloroplatination of a Triple C–C Bond as an Easy Way to σ -Vinyl Derivative of Platinum(IV) Chloride Complexes

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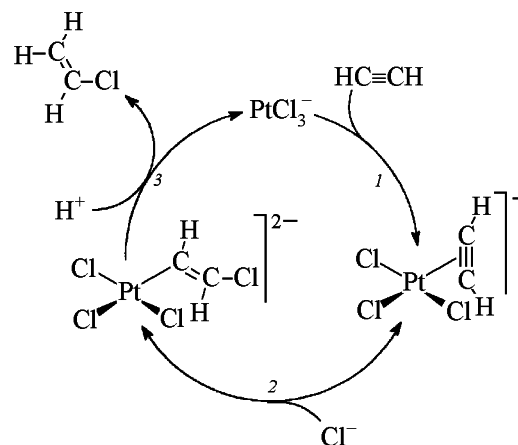
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Catalytic processing of raw hydrocarbons is among the most important targets of the modern organic chemistry. These processes as a rule proceed through intermediate formation of organometallic compounds containing a σ -bond metal–carbon [1]. The proper selectivity and efficiency of catalytic systems originate from the ease of formation of these intermediates and of their subsequent transformations. In this sense studies on preparation and decomposition pattern of σ -organometallic derivatives participating as intermediates in catalytic processes, or of relatively stable compounds simulating the characteristics of such intermediates underlie in many respects the progress in theory and practical application of catalysis with metal complexes. This research is also important for understanding of specific features of chemical processes in the biological systems.

It was formerly observed that platinum(II) chloride complexes are active catalysts of acetylene hydrochlorination in water solutions [2, 3]. Relying on kinetic data, on stereochemistry of acetylene hydrochlorination with DCl, and on analogy to the other catalytic systems a suggestion was advanced that the mechanism of the catalytic reaction (Scheme 1) includes stages of the π -coordination of acetylene (stage 1), the nucleophilic attack of an “alien” chloride ion on the π -coordinated acetylene with intermediate formation of a β -chlorovinyl platinum(II) complex (stage 2), and protolysis of the latter species (stage 3). However no direct proofs of participation in the process of β -chlorovinyl organoplatinum intermediates was obtained. The search for these proofs is the goal of the present study.

We utilized the known reaction of complementary oxidation of platinum σ -organic derivatives by

Scheme 1.



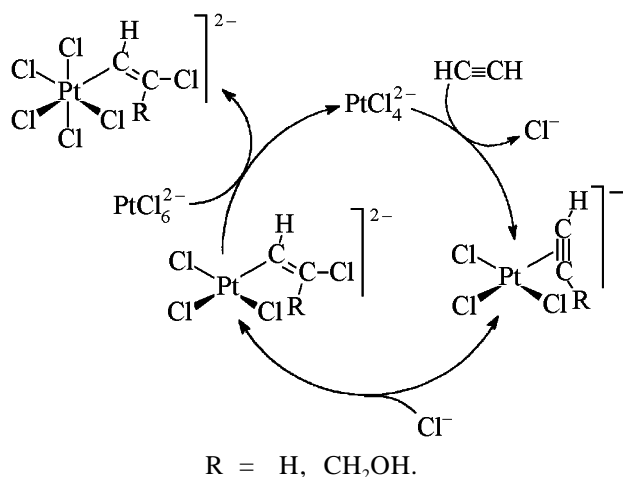
platinum(IV) [4] to perform “trapping” of platinum(II) σ -vinyl derivatives generated in the second stage of the reaction under consideration. Therewith formed previously unknown more stable σ -vinyl derivatives of platinum(IV) chloride complexes [Pt^{IV}-HC=CRCl, R = H (I) or CH₂OH (II) (Scheme 2) and Pt^{IV}-C(COOCH₃)=CHCl (III)].

The reactions were carried out in water solutions of NaCl (5M) in the presence of PtCl₆²⁻ and catalytic amounts of PtCl₄²⁻ at 25–40°C and in a neutral medium to prevent protolysis of the platinum(II) σ -vinyl derivatives.

Propargyl alcohol or methyl propiolate (40 μ l) by portions of 10 μ l once in 24 h was added to 2 ml of 5 M NaCl solution containing 0.082 g of Na₂PtCl₄ and 0.262 g of Na₂PtCl₆, and the reaction mixture was kept in the dark at room temperature for 5 days. The reaction with acetylene was performed under

similar conditions but at 40°C within 48 h in a closed reactor filled with acetylene at constant shaking. Then to the reaction mixture was added in excess saturated solution of KOH for precipitation of unreacted platinum(IV) compound, and the reaction mixture was dried in an air stream without heating. The organoplatinum compounds were extracted with acetone or methanol from the dry residue, and on repeated evaporation of the extract yellow crystalline reaction products were obtained.

Scheme 2.



The structure of complexes **I–III** is confirmed by IR and NMR data.

Compound I. In the ¹H NMR spectrum recorded in CD₃OD appear two doublets at δ 6.50 and 5.68 ppm and intensity ratio 1:1, *J*(HH) 12.1 Hz, with the corresponding platinum satellites, ²*J*(¹⁹⁵Pt–¹H) 72.5 and ³*J*(¹⁹⁵Pt–¹H) 28.2 Hz respectively. Relatively large value of *J*(HH) showed the *trans*-anti addition of the platinum and chlorine atoms to the π-complex of acetylene. ¹³C{¹H} NMR spectrum (CD₃OD), δ, ppm: two singlets at 114.5 and 96.6 with platinum satellites ²*J*(¹⁹⁵Pt–¹³C) 45.7 and ¹*J*(¹⁹⁵Pt–¹³C) 749.6 Hz respectively. The appearance of platinum satellites in the ¹H and ¹³C NMR spectra of compound **I** confirms the σ-character of the Pt–C bond. IR spectrum (KBr pellet), cm⁻¹: 3014 (ν_{HC=}), 1639 (ν_{C=C}), 914 (γ_{HC=}), 676 (ν_{CCl}).

Compound II. ¹H NMR spectrum (CD₃OD), δ, ppm: 6.88 [singlet with platinum satellites, *J*(¹⁹⁵Pt–¹H) 81 Hz, –CH=], 4.59 s (–CH₂–). High value of coupling constant *J*(¹⁹⁵Pt–¹H) permits assignment to the complex a structure with σ-bond platinum–terminal carbon atom (cf. with compound **I**). ¹³C{¹H} NMR spectrum (CD₃OD), δ, ppm: 92.5

[singlet with ¹⁹⁵Pt satellites, ¹*J*(¹⁹⁵Pt–¹³C) 775.2, –CH=], 131.3 s (=CCl–), 65.1 s (–CH₂–). IR spectrum (KBr pellet), cm⁻¹: 3547 (ν_{HO}), 3016 (ν_{HC=}), 2928 (ν_{H-C-}), 1690 (δ_{OH}), 1615 (ν_{C=C}), 1378, 1345 (δ_{H₂C}), 1040 (ν_{OC}), 946 (γ_{HC=}), 677 (ν_{CCl}).

Compound III. ¹H NMR spectrum (CD₃OD), δ, ppm: 6.04 [singlet with ¹⁹⁵Pt satellites, ³*J*(¹⁹⁵Pt–¹H) 38.4 Hz, –CH=], 3.74 s (–CH₃). Small value of the coupling constant ¹⁹⁵Pt–¹H suggests that in compound **III** unlike complex **II** exists a σ-bond platinum–internal carbon atom in agreement with the structure expected for an alkyne with an electron-acceptor substituent. This formally corresponds to addition to the triple bond following the Marcownikoff rule (cf. with [5]).

In the absence of platinum(II) the σ-vinyl platinum derivatives were not found. In reaction of propargyl alcohol in the ¹H NMR spectrum of a water solution (D₂O, 2 ml) containing 0.0588 g of NaCl, 0.00975 g of Na₂PtCl₄·nH₂O [≤25 μmol of Pt(II)] and 0.21875 g of Na₂PtCl₆ (482 μmol), the signal at δ 2.97 ppm corresponding to HC≡ protons of propargyl alcohol decreased with time. Therewith appeared and grew with time the signal belonging to vinyl protons (–CH=) of complex **II** [δ 6.90 ppm, ²*J*(Pt–¹H) 88 Hz]. According to the ¹H NMR data within 5 weeks at room temperature formed about 360 μmol of complex **II**, i.e., over 1400% with respect to the initial amount of platinum(II). This fact proves that the reaction is catalytic relative to platinum(II).

The study of reactivity of the new organoplatinum compounds will be the subject of our further research.

NMR spectra were registered on spectrometers Varian GEMINI at operating frequency 200 MHz (¹H) and Bruker DRX-500 (operating frequencies 500 and 125 MHz for ¹H and ¹³C respectively). The reaction of propargyl alcohol in D₂O was monitored by ¹H NMR spectrum with *tert*-butanol as internal reference. IR spectra were recorded on spectrometer FTIR Perkin Elmer Spectrum BX from samples pelletized with KBr.

Salts Na₂PtCl₆ (anhydrous) and K₂PtCl₄·nH₂O were prepared by standard procedure [6]. Propargyl alcohol was purified by distillation, acetylene was prepared by known method [7].

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