

FORMATION OF METHYL PLATINUM COMPLEX IN THE REACTION OF METHANE WITH CHLOROPLATINIC ACID

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The ^1H NMR method and chemical analysis indicate that a complex of Pt(IV) containing a $\text{CH}_3\text{-Pt}$ fragment is formed in the reaction of $\text{H}_2\text{PtCl}_6 + \text{H}_2\text{PtCl}_4$ with methane at 120°C in aqueous $\text{CF}_3\text{CO}_2\text{H}$. The complex was isolated from the solution as an adduct of Ph_3P .

Методом ПМР и химическим анализом показано, что при нагревании метана с раствором H_2PtCl_6 в присутствии H_2PtCl_4 в водной CF_3COOH при 120°C в течение двух часов образуется комплекс платины (IV), содержащий фрагмент Pt-CH_3 . Комплекс был выделен из раствора после добавления Ph_3P в виде производного, включающего трифенилфосфин.

C-H bonds in alkanes can be activated to H-D exchange with the solvent /1/ and to oxidation by Pt(IV) complexes, the products being mainly alkyl chlorides and arenes /2/.

According to the mechanism suggested for primary alkane reaction with Pt(II), the reaction proceeds via σ -alkyl platinum compounds /3/. Recently σ -aryl complexes of Pt(IV) have been obtained in a similar reaction of aromatic hydrocarbons and their derivatives with H_2PtCl_6 in aqueous trifluoroacetic acid /4/. For naphthalene the X-ray analysis confirmed the formation of a σ -bonded β -naphthyl platinum (IV) complex /5/. This result, showing the stability of Pt(IV)-C bonds in acidic media at elevated temperatures, has prompted us to try to isolate a σ -methyl derivative of Pt(IV) in the reaction of methane with H_2PtCl_6 in the presence of H_2PtCl_4 .

The reaction was performed in an autoclave (methane pressure 100 atm), the reaction mixture was water and trifluoroacetic acid (volume ratio 1:5). The concentration of $H_2PtCl_6 \cdot 6H_2O$ was 0,1 M. To determine the optimal conditions (temperature, time), the reaction mixture after heating was cooled and evaporated to complete dryness in a rotary evaporator and decomposed by hydrazine hydrate with subsequent chromatographic analysis of the methane formed. The greatest yields of Pt- CH_3 complex (1-2% with respect to the initial Pt(IV)) were obtained for 2 h at 120 °C after adding 5-7% K_2PtCl_4 as a catalyst.

To isolate a methylplatinum complex, the reaction mixture was evaporated to dryness, the residue was dissolved in acetone and a solution of Ph_3P in acetone (20% excess phosphine with respect to the ratio $Ph_3P : P = 2:1$) was added. After staying overnight, the insoluble precipitate (Pt complexes free of CH_3 groups) was filtered, washed with acetone and chloroform, then the united acetone and chloroform solutions were evaporated and the remaining solution was separated on Silufol UV-254 plates, the eluent being acetone-ether (1:1 ratio). The band with $R_f = 0.2$ was separated. The substance obtained was a fine yellow powder. The NMR spectrum of its solution in $CDCl_3$ (Fig. 1) exhibits two signals with $\sigma_H = 1.08$ ppm (broad singlet) and $\sigma_H = 7-8$ ppm (complex multiplet). Decomposition of the complex by hydrazine hydrate (150-200 °C) produces methane, ethane and ethylene (57%, 10% and 33%, respectively). Mass-spectrometric measurements indicate that CH_3D is practically the only product in the case of DCl decomposition in D_2O (mass 17). If all three gases (CH_4 , C_2H_6 , C_2H_4) in the case of $N_2H_4 \cdot xH_2O$ are formed from CH_3 bound to platinum, then the $CH_3:Pt$ ratio in the complex is 0,85, (chromatographic analysis for gaseous products, spectrophotometric analysis for platinum after dissolving in HCl and HNO_3).

In a standard experiment the amount of methylplatinum complex isolated from the reaction mixture is $(1 - 1.2) \times 10^{-6}$ mol per 1.3×10^{-3} mol of $H_2PtCl_6 \cdot 6H_2O$.

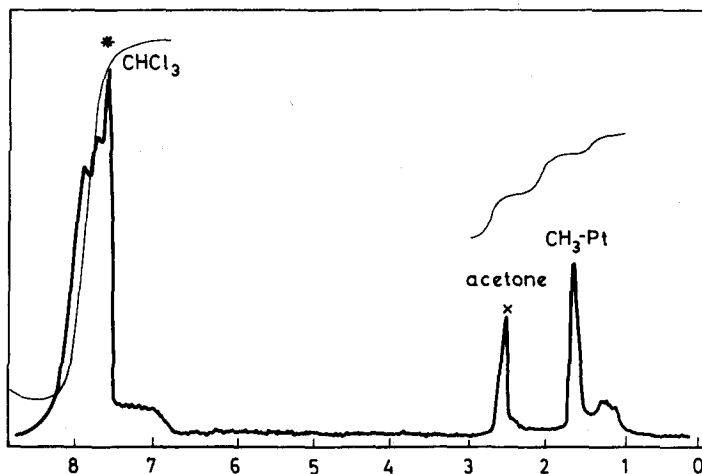


Fig. 1. ^1H NMR spectrum of the σ -methylplatinum compound (Bruker HFX-90, 90 MHz)

The results confirm that the complex is a methyl derivative of platinum stabilized by triphenylphosphine. This is direct evidence for the existence of alkyl-platinum intermediates in alkane activation and, to our knowledge, the first example of the synthesis of organometallic σ -alkyl derivatives directly from alkanes.

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REFERENCES

1. N. F. Goldshleger, M. B. Tyabin, A. E. Shilov, A. A. Shteinman: Zh. Fiz. Khim., 43, 2174 (1969).
2. N. F. Goldshleger, V. V. Eskova, A. E. Shilov, A. A. Shteinman: Zh. Fiz. Khim., 46, 1353 (1972).

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3. A.A. Shreinman, A.E. Shilov: Kinet. Katal., 18, 1129 (1977).
4. G.B. Shulpin, A.E. Shilov, D.V. Zeele-Krevor, A.N. Kitaigorodskii: J. Organomet. Chem., 1980 (in press).
5. G.B. Shulpin, L.P. Rozenberg, R.P. Shibaeva, A.E. Shilov: Kinet. Katal., 20, 1570 (1979).