

ISOLATION OF PLATINUM(II) π -OLEFIN COMPLEXES
FORMED BY THE REACTION OF SATURATED HYDROCARBONS
WITH H_2PtCl_6 IN $CF_3COOH - H_2O$ SOLUTION

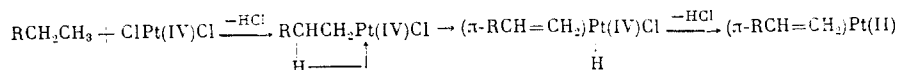
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The oxidation of aromatic and saturated hydrocarbons by H_2PtCl_6 in $CF_3COOH - H_2O$ solution proceeds via the formation of organometallic complexes with a C-Pt σ bond [1-3]. Platinum(IV) σ -aryl derivatives [4-7], whose structure was determined by x-ray structure analysis [8], were isolated from the reaction products of H_2PtCl_6 with various aromatic compounds. The oxidation of saturated hydrocarbons by H_2PtCl_6 in $CF_3COOH - H_2O$ leads to a complex mixture of products: For example, in the case of hexane a mixture of isomeric chlorohexanes, dichlorohexanes, hexanols, hexyl trifluoroacetates, carboxylic acids, dodecane, and other compounds is obtained [9]. Here the H_2PtCl_6 is reduced to a Pt(II) derivative. It was postulated that divalent platinum π complexes are also formed as reaction products [1-3, 9]. The isolation of such complexes is reported in the present paper.

When a solution of H_2PtCl_6 and n-hexane in aqueous CF_3COOH is heated under reflux for 20 h, a small amount of the π -hexane derivative of Pt(II) is formed, which, after evaporation of the reaction solution, can be isolated by extraction with $CHCl_3$ and, after adding Py, chromatography on silica gel. Since the reaction with hexane gives only a small amount of the π complex, we obtained this substance in several ways by a separate synthesis: by reacting H_2PtCl_6 in acetic acid with either 1-hexene, 1-hexanol, or n-hexyl acetate. The prepared samples were compared with each other and with the sample that was obtained in the reaction with n-hexane, on the basis of their PMR and IR spectra, and also by comparing the R_f values by the TLC method (Silufol, eluant = $CHCl_3$). The PMR spectrum of the obtained complex (Fig. 1) has the signals of the olefinic protons of the π -hexene ligand in the δ -4.2-6.0 ppm region (from TMS); the proton in the 2 position of the hexene chain appears as a multiplet with a center at δ 5.8 ppm. The olefine protons of the Pt π -propene complex (obtained

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The Pt(II) π -olefine complexes are stable toward H_2PtCl_6 in aqueous CF_3COOH . Thus, after heating (2 h) a solution of the $[(\text{C}_6\text{H}_5=\text{CH}_2)\text{PtCl}_2]_2$ dimer in a $\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ mixture we isolated the starting π complex, while the oxidation product, with a simultaneous rearrangement to the σ derivative [12], could not be detected. The dimeric complex with a π -ethylene ligand was obtained by heating a solution of ethyl acetate with H_2PtCl_6 in CH_3COOH , followed by evaporation of the solvent and extraction with CHCl_3 .

EXPERIMENTAL

The PMR spectra of the complexes in CDCl_3 solution were taken on a Bruker SXP-4-100 instrument (90 MHz).

Reaction of n-Hexane with H_2PtCl_6 . The hexane was purified by long refluxing with conc. H_2SO_4 and subsequent distillation. The absence of unsaturated compounds was checked via UV spectroscopy. A mixture of 1.0 g of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 5 ml of n-hexane, 15 ml of CF_3COOH , and 4 ml of H_2O was heated to reflux for 20 h. The solution was evaporated under reduced pressure, the residue was extracted with CHCl_3 (4×10 ml), and the CHCl_3 extracts were shaken with an aqueous solution of 0.3 ml of pyridine in 20 ml of H_2O , washed with water, and dried over Na_2SO_4 . The solvent was evaporated in vacuo, after which the residue was chromatographed twice on silica gel plates, using CHCl_3 as the eluant, and the yellow band with $R_f \sim 0.8$ was isolated. We obtained 10 mg (1.2%) of the complex. IR spectrum: 2960 (w), 2930 (s), 2875 (m), 2860 (m), 1610 (m), 1515 (w), 1490 (w), 1453 (x), 1382 (w), 1244 (w), 1220 (m), 1170 (m), 1070 (m), 1020 (w), 1000 (w), 760 (s), 740 (s), 690 (s), 655 (w).

Reaction of 1-Hexene with H_2PtCl_6 . A mixture of 1.0 g of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 2 ml of 1-hexene, and 10 ml of AcOH was heated to reflux for 0.5 h. The solvent was evaporated in vacuo, and the residue was worked up as in the preceding experiment. We obtained 73 mg (9%) of the complex $[(\text{C}_6\text{H}_{12})\text{PtCl}_2(\text{C}_5\text{H}_5\text{N})]$, as yellow-green crystals with mp $35-37^\circ\text{C}$. Found: C 30.80; H 4.28; N 3.32%. $\text{C}_{11}\text{H}_{17}\text{Cl}_2\text{N}$ Pt. Calculated: C 30.78; H 4.00; N 3.26%.

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CONCLUSIONS

1. The heating of a solution of n-hexane and H_2PtCl_6 in a $\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ mixture leads to the formation of the Pt(II) π -hexene complex, which, after treatment with pyridine, was isolated by chromatography on silica gel as $[(\text{C}_6\text{H}_{12})\text{PtCl}_2(\text{C}_5\text{H}_5\text{N})]$.
2. The reaction of 1-hexene, 1-hexanol, or n-hexyl acetate with H_2PtCl_6 in AcOH gives the same Pt(II) π -hexene complex.

LITERATURE CITED

1. A. F. Shilov, and A. A. Shteinman, *Kinet. Katal.*, **18**, 1129 (1977).
2. A. E. Shilov and A. A. Shteinman, *Coord. Chem. Rev.*, **24**, 97 (1977).
3. D. E. Webster, *Adv. Organomet. Chem.*, **15**, 147 (1977).
4. G. B. Shul'pin, L. P. Rozenberg, R. P. Shibaeva, and A. E. Shilov, *Kinet. Katal.*, **20**, 1570 (1979).
5. G. B. Shul'pin, A. E. Shilov, A. N. Kitaigorodskii, and J. V. Z. Krevor, *J. Organomet. Chem.*, **201**, 319 (1980).
6. G. B. Shul'pin, *J. Organomet. Chem.*, **212**, 267 (1981).
7. G. B. Shul'pin and A. N. Kitaigorodskii, *J. Organomet. Chem.*, **212**, 275 (1981).
8. R. P. Shibaeva, L. P. Rozenberg, R. M. Lobkovskaya, A. E. Shilov, and G. B. Shul'pin, *J. Organomet. Chem.*, **220**, 271 (1981).
9. J. R. Sanders, D. E. Webster, and P. B. Wells, *J. Chem. Soc. Dalton Trans.*, 1191 (1975).
10. P. D. Kaplan and M. Orchin, *Inorg. Chem.*, **6**, 1096 (1967).
11. H. P. Fritz, K. E. Schwarzahns, and D. Sellmann, *J. Organomet. Chem.*, **6**, 551 (1966).
12. J. Halpern and R. A. Jewsbury, *J. Organomet. Chem.*, **181**, 223 (1979).