

FORMATION OF σ -ARYL COMPLEXES OF PLATINUM(IV) IN THE
REACTIONS OF H_2PtCl_6 WITH PHENYLBORONIC ACID AND WITH
THE TETRAPHENYLBORATE ION. ARYLATION OF OLEFINS WITH
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We showed recently that anionic σ -aryl complexes of platinum(IV) [1] are formed in the reactions of arylmercury compounds with H_2PtCl_6 [2]. In the present work we have found that heating a solution of a phenyl derivative of boron with H_2PtCl_6 in a mixture of CF_3COOH and H_2O also leads to the formation of anionic σ -aryl complexes of platinum(IV). A mixture of 0.1 g of $C_6H_5B(OH)_2$, 0.4 g of $H_2PtCl_6 \cdot 6H_2O$, 10 ml of CF_3COOH , and 2 ml of H_2O was heated at the boil for 6 h. Solvent was evaporated to give a dry residue, and the residue was dissolved in acetone and applied to a column of silica gel containing ammonia and treated with hexane. A 2 : 1 mixture of acetone and hexane eluted a yellowish-orange band of the complex, which was further purified chromatographically on plates of silica gel and was recrystallized from acetone. We obtained 0.05 g (yield 15% on the phenylboronic acid) of ammonium aminetetra-chlorophenylplatinate(IV) $[C_6H_5PtCl_4NH_3]NH_4 \cdot (CH_3)_2CO$. The performance of the reaction in an acetone-water mixture gave this complex in only 1-2% yield. In an analogous way, in the reaction of $(C_6H_5)_4BNa$ with H_2PtCl_6 in a $CF_3COOH-H_2O$ mixture (heating in a boiling water bath for 6.5 h) we obtained the σ -phenyl complex of platinum(IV) in 7% yield.

We also found that heating a solution of an aryl derivative of boron and H_2O in presence of an olefin leads to the product of the arylation of the olefin. Thus, a mixture of 1.0 g of $(C_6H_5)_4BNa$, 0.35 g of $H_2PtCl_6 \cdot 6H_2O$, 2 ml of $CH_2=CHCOOH$, 15 ml of CF_3COOH and 2 ml of H_2O was heated at the boil for 2 h. The solution was evaporated to dryness, the residue was dissolved in water, and the resulting solution was extracted with chloroform. The extract was dried over Na_2SO_4 , solvent was vacuum-evaporated, and the residue was chromatographed on a column of silica gel (eluent hexane-acetone 1 : 1). After recrystallization from hot water we obtained 0.019 g of $C_6H_5CH=CHCOOH$ (yield 19% on the Pt). In analogous reaction with $C_6H_5B(OH)_2$ cinnamic acid was obtained in 6.5% yield. All the compounds synthesized were characterized by comparison with previously prepared [1-3] samples (R_f , mp PMR spectra).

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