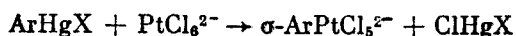


REACTION OF STERICALLY HINDERED ARYLMERCURY COMPOUNDS WITH Pt(IV),  
Pt(II), AND Pd(II) CHLORIDE COMPLEXES

G. V. Nizova and G. B. Shul'pin

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In our previous work [1-3], we showed that the reaction of the  $\text{PtCl}_6^{2-}$  ion with arylmercury compounds (AMC) leads to the formation of Pt(IV)  $\sigma$ -aryl complexes. Aqueous acetone or acetic acid served as the solvent.



Prolonged heating of a solution of the  $\text{PtCl}_6^{2-}$  ion and an arylmercury gives Pt(II) and a diaryl. Similar  $\sigma$ -complexes are also formed in the reaction of the  $\text{PtCl}_6^{2-}$  ion with arenes in organic acids upon heating [4] or upon the action of light [5]. We should stress that the platinumochloride fragment in reactions with arenes does not enter the ortho position even in the case of such small benzene ring substituents as F or  $\text{CH}_3$ . The reaction with naphthalene leads to the formation of  $\beta$ -platinated naphthalene [6]. If there are only aromatic protons adjacent to the substituents in the arene (p-dimethoxybenzene, mesitylene, pentafluorobenzene, and pentamethylbenzene), Pt(IV)  $\sigma$ -aryl complexes are not formed at all [7]. Apparently, such an orientation of the Pt fragment ( $\text{PtCl}_5^-$ ) is a consequence of steric factors since this fragment has considerable bulk.

In the present work, we studied the reaction of  $\text{PtCl}_6^{2-}$  with sterically hindered AMC containing the mercury atom in the ortho position to the substituent: di( $\alpha$ -naphthyl)mercury (I),  $\alpha$ -naphthylmercury acetate (II) and pentamethylphenylmercury acetate (III). Aqueous acetone was used as the solvent. As expected, Pt(IV)  $\sigma$ -aryl complexes were not formed in these reactions. Nevertheless, oxidation-reduction reactions proceed leading to the formation of a Pt(II) complex. A characteristic feature in the case of all these AMS is a significant induction period for the reaction, which is markedly diminished upon the addition of small amounts of  $\text{Na}_2\text{PtCl}_4$ . In the case of the reaction with (I), the products are  $\alpha$ , $\alpha$ -dinaphthyl (IV),  $\alpha$ -naphthylmercury chloride and a Pt(II) chloride complex. The reaction with (II) gives (IV) and small amount of naphthalene. We note that heating of a solution of (II) in aqueous acetone at reflux does not lead to the formation of naphthalene. We also found that the reaction between  $\text{PtCl}_6^{2-}$  and (II) in acetic acid may be induced by light radiation. In this case, (IV) and a very small amount of naphthalene are formed. The photoirradiation of (II) in the absence of  $\text{PtCl}_6^{2-}$  also gives a very small amount of naphthalene.

Pentamethylbenzene (V) and mesitylene were separated from the products of the thermal reaction of the  $\text{PtCl}_6^{2-}$  ion with (II) or with dimesitylmercury, respectively. The formation of diaryls was not noted in these reactions. Under these conditions, heating a solution of (III) in aqueous acetone at reflux in the absence of  $\text{Na}_2\text{PtCl}_4$  does not lead to the production of any significant amounts of (V).

Since the reaction of sterically hindered  $\alpha$ -naphthylmercury compounds with the  $\text{PtCl}_6^{2-}$  ion cannot give a Pt(IV)  $\sigma$ -( $\alpha$ -naphthyl) complex which might be an intermediate in the formation of (IV), the most likely mechanism for the coupling and formation of the free arene

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is as follows. The reduction of Pt(IV) to Pt(II) occurs upon prolonged heating of the solution of  $\text{PtCl}_6^{2-}$  in acetone. The Pt(II) complex reacts with the AMC. In this case, we may find formation of a Pt(II)  $\sigma$ -aryl complex, which decomposes to give a diaryl or arene and Pt(0) which is reoxidized to Pt(II) by the Pt(IV) complex. It is not excluded that the reaction of AMC with Pt(II) leads to electron transfer [8] from the mercury derivative with the formation of aryl radicals, which abstract hydrogen from the solvent. Another pathway involves homolysis of the Ar-Pt(II) bond. However, this pathway should give the same products. Indeed, heating a solution of (III) and  $\text{Na}_2\text{PtCl}_6$  in acetone leads to the formation of (V). In this case, we find the precipitation of metallic mercury, possibly as a result of the oxidation of Pt(I) by Hg(II) derivatives. An analogous result was obtained for the reaction of (III) with  $\text{Na}_2\text{PdCl}_4$ . We note that the coupling of mercury derivatives of sterically unhindered arenes by the action of Pd(II) complexes proceeds with the formation of a diaryl, Pd(0) and Hg(II) [9]. In a special experiment, we showed that a Pt(II) complex in  $\sim 0.01$  M concentration appears upon heating a solution of  $\text{NaPtCl}_6$  (0.036 M) in acetone at reflux for 4 h.

#### EXPERIMENTAL

Thermal Reaction of  $\text{Na}_2\text{PtCl}_6$  with di( $\alpha$ -naphthyl)mercury (I). A mixture of 410 mg (0.9 mmole) (I), 320 mg (0.6 mmole)  $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and 15 ml acetone was heated at reflux for 2.3 h. Acetone was evaporated at reduced pressure. The residue was subjected to chromatography on silica gel initially on a column and then on plates with hexane eluant to yield 20 mg (35% relative to Hg)  $\alpha, \alpha'$ -dinaphthyl (IV) and 100 mg (79%)  $\alpha$ -naphthylmercury chloride.

Thermal Reaction of  $\text{Na}_2\text{PtCl}_6$  with  $\alpha$ -Naphthylmercury Acetate (II). A solution of 190 mg (0.5 mmole) (II) 280 g (0.5 mmole)  $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and 1 ml water in 9 ml acetone was heated at reflux for 4 h. The solvent was evaporated at reduced pressure. The residue was extracted with  $\text{CHCl}_3$ , and evaporated at reduced pressure. The residue was separated on silica gel plates using hexane as eluant to give 16 mg (25% relative to Hg) (IV) and 3 mg (5%) naphthalene.

Photochemical Reaction of  $\text{Na}_2\text{PtCl}_6$  with (II). A suspension of 97 mg (0.25 mmole) (II) and 140 mg (0.25 mmole)  $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  in a mixture of 13 ml acetic acid and 7 ml water was irradiated for 4.5 h by the full light of a high pressure 1000-W mercury lamp in a glass vessel with a water jacket cooled by a water stream (15°C). Water was added to the solution and the mixture was extracted with  $\text{CHCl}_3$ . The chloroform extracts were washed with water and dried over  $\text{Na}_2\text{SO}_4$ . Analogous work-up gave 10 mg (32% relative to Hg) (IV) and 0.7 mg naphthalene.

Thermal Reaction of  $\text{Na}_2\text{PtCl}_6$  with Pentamethylphenylmercury Acetate (III). A solution of 220 mg (0.5 mmole) (III), 280 g (0.5 mmole)  $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and 2 ml water in 10 ml acetone was heated at reflux for 5.3 h. The solvent was evaporated at reduced pressure. The residue was extracted with chloroform. Chromatography on silica gel with hexane eluant gave 16 mg (22% relative to Hg) pentamethylbenzene and 65 mg unreacted mercury compound.

Thermal Reaction of  $\text{Na}_2\text{PtCl}_6$  with (III). A solution of 436 mg (1 mmole) (III), 455 mg (1 mmole)  $\text{Na}_2\text{PtCl}_6 \cdot 4\text{H}_2\text{O}$  and 2 ml water in 15 ml acetone was heated at reflux for 2 h. The solvent was evaporated at reduced pressure and the residue was extracted with chloroform. The work-up described above gave 91 mg (16.5%) (V).

Heating a solution of 436 mg (III), 300 mg (1.1 mmole)  $\text{Na}_2\text{PdCl}_4$  in 15 ml acetone at reflux for 2 h gave 89 mg (60%) (V).

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#### CONCLUSION

Heating of a solution of the  $\text{PtCl}_6^{2-}$  ion and an arylmercury compound containing a substituent in the ortho position to mercury leads to the formation of a diaryl (in the case of  $\alpha$ -naphthylmercury) or arene (in the case of the mesityl or pentamethylphenyl mercury derivatives).

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