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THE REACTION OF $PtCl_6^{2-}$ WITH AROMATIC COMPOUNDS TO AFFORD ANIONIC σ-ARYL COMPLEXES OF PLATINUM(IV)

VII *. CLEAVAGE OF ARYL–ELEMENT BONDS (ELEMENT = Hg, Sn, Pb OR B). ARYLATION REACTIONS OF ARENES AND OLEFINS WITH σ-ARYL COMPLEXES OF PLATINUM(IV)

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Summary

The transmetallation reaction between the $PtCl_6^{2-}$ ion and aryl derivatives of non-transition metals (Hg, Sn, Pb or B) affords the anionic σ-aryl complexes previously prepared by the reaction of $PtCl_6^{2-}$ with arenes. When treated with olefins, the complexes give arylated olefins. Heating a solution of the complex $[ArPtCl_4NH_3]^-$ with an other arene (Ar'H) leads to the formation of the complex $[Ar'PtCl_4NH_3]^-$ (transarylation reaction).

Introduction

Stoichiometric and catalytic oxidation reactions of organic compounds (arenes, olefins, acetylenes, etc.) with transition metal complexes are novel important methods for the preparation of valuable products. Palladium(II) compounds are the most commonly used reagents for these purposes. The reactions discovered by Van Helden [2] and Fujiwara and co-workers [3,4] afford biaryls and arylated olefins, respectively, under the action of palladium(II) salts:

$$ArH + Ar'H + Pd^{II} \rightarrow ArAr' + Pd^0 \quad (1)$$

$$ArH + RHC{=}CHR' + Pd^{II} \rightarrow Ar(R)C{=}CHR' + Pd^0 \quad (2)$$

It is proposed that both reactions proceed via an unstable σ-aryl complex of palladium(II) [5,6]. These complexes may also be obtained as transient intermediates in the transmetallation reaction:

$$M\text{–}Ar + Pd^{II} \rightarrow \sigma\text{-}Ar\text{–}Pd^{II} \xrightarrow{RHC=CHR'} Ar(R)C{=}CHR' + Pd^0 \quad (3)$$

(M = Hg, Sn, Pb, etc.)

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* For part VI see ref. 1.

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Such reactions, discovered by Heck [7], are convenient methods for the syntheses of arylated olefins.

Recently, we have found that the thermal reaction of $PtCl_6^{2-}$ ion with arenes affords anionic σ-aryl complexes of platinum(IV) [8,9], which decompose on prolonged heating to produce biaryls and chlorinated aryls [9,10]:

$$ArH + Pt^{IV} \rightarrow \underset{(I)}{\sigma\text{-Ar-}Pt^{IV}} \rightarrow ArAr + Pt^{II} \tag{4}$$

In the present work, we studied the formation of biaryls in this reaction, as well as the arylation reaction of olefins with the anionic σ-aryl complexes (I) of platinum(IV). We have also found that the reaction of aryl derivatives of non-transition metals (e.g. mercury, tin, lead and boron) with $PtCl_6^{2-}$ ion gives σ-aryl complexes of platinum(IV) which may be isolated and so the reaction is a convenient method for the preparation of such complexes. The complexes prepared in situ starting from $PtCl_6^{2-}$ and Ar–M compounds (M = Hg, Sn, Pb, B) react with olefins to afford arylated olefins in moderate to excellent yields. Due to the product yields obtained, the reaction with $PtCl_6^{2-}$ is not only a rather close model for palladium(II)-induced reactions (eq. 3) but is also a convenient method for olefin arylation.

Initially, we will discuss the formation of the σ-aryl complexes in the reaction of aryl derivatives of mercury, tin, lead and boron with $PtCl_6^{2-}$ ion. The arylation reactions of arenes and olefins with the σ-aryl complexes of platinum(IV) prepared in the reactions of $PtCl_6^{2-}$ with both Ar–M compounds and arenes will then be described. Some parts of this work have been published previously as preliminary communications [11–14].

Results and discussion

Reaction of $PtCl_6^{2-}$ with aryl derivatives of non-transition metals to yield the σ-aryl complexes of platinum(IV)

The ion $PtCl_6^{2-}$ reacts with arylmercury compounds in aqueous acetone, aqueous trifluoroacetic acid or acetic acid. The σ-aryl complexes formed may be isolated in the form of ammonia salts during chromatography on silica gel containing ammonia (1–2 mg of NH_3 per 1 g of silica gel).

$$PtCl_6^{2-} + ArHgX \xrightarrow[2\ SiO_2\cdot NH_3]{1.acetone/water} [\sigma\text{-}ArPtCl_4NH_3]^- \tag{5}$$

This method is convenient for the preparation of pure *para*- or *meta*-platinated isomers of monosubstituted benzenes, in contrast to the thermal reaction of $PtCl_6^{2-}$ with arenes in organic acids which affords mixtures of isomers [9,15,16]. The photoinduced reaction with arenes [17,18] leads to the formation of *para*-platinated anisole, phenol or toluene, and the reaction does not proceed with arenes bearing electron-withdrawing substituents. However, it is not easy to separate the product of reaction 5 and the mercury compounds. Such a separation may only be carried out by repeated chromatography on a column and then on silica gel plates.

Tetraphenyltin and tetraphenyllead also react with $PtCl_6^{2-}$ to afford the σ-phenyl complex of platinum(IV). Aqueous acetone may be used as the solvent.

$$PtCl_6^{2-} + Ph_4M \xrightarrow[2\ SiO_2\ NH_3]{1.acetone/water} [\sigma\text{-}PhPtCl_4NH_3]^- \tag{6}$$

(M = Sn, Pb)

Finally, $PtCl_6^{2-}$ ion cleaves the Ph–B bond in $PhB(OH)_2$ or Ph_4BNa in CF_3COOH/H_2O solution.

$$PtCl_6^{2-} + Ph_4BNa \xrightarrow[2.SiO_2 \cdot NH_3]{1.CF_3COOH/H_2O} [\sigma\text{-}PhPtCl_4NH_3]^- \tag{7}$$

The reaction conditions and the yields of complexes I in the reactions described are summarized in Table 1.

The mechanism of the reaction of $PtCl_6^{2-}$ with aryl derivatives of non-transition metals is apparently electrophilic substitution and appears to involve an electron-transfer stage. Indeed, if the very large steric hindrance for the reaction with tetraaryl derivatives of tin and lead is taken into account, then the concerted mechanism S_Ei in these cases seems to be less probable. The kinetics and a discussion of the mechanism of the reaction under investigation will be published in a subsequent paper [18].

Reactions of the σ-aryl complexes of platinum(IV) with arenes

The yield of the σ-tolyl complex of platinum(IV) after a solution of $PtCl_6^{2-}$ and toluene in CF_3COOH/H_2O is heated at 94.5 °C for 1 h is about 95% (Fig. 1). In the presence of an excess of toluene, very rapid decomposition of the complex then occurs to produce bitolyl, $PtCl_4^{2-}$ and other substances. If toluene is extracted from the reaction mixture with hexane 1 h after the start of the reaction, the rate of complex decomposition is much lower (Fig. 1). However, if anisole is added to the reaction mixture instead of toluene, the rate of the decomposition is approximately equal to that of the reaction in the presence of toluene. The mechanism of the decomposition of the σ-aryl complex is not clear. One may tentatively assume that the formation of biaryls proceeds by two routes. The first route is platination of the arene by the σ-aryl complex, followed by reductive elimination:

$$(\sigma\text{-Ar})\text{–}Pt^{IV} + Ar'H \rightarrow (\sigma\text{-Ar})\text{–}Pt^{IV}\text{–}(\sigma\text{-Ar}') \tag{8}$$

$$(\sigma\text{-Ar})\text{–}Pt^{IV}\text{-}(\sigma\text{-Ar}') \rightarrow Ar\text{–}Ar' + Pt^{II} \tag{9}$$

The second route is the attack of a Wheland-type complex of platinum(IV), which

TABLE 1

REACTIONS OF $PtCl_6^{2-}$ WITH ARYL DERIVATIVES OF NON-TRANSITION METALS (HEATING UNDER REFLUX) TO AFFORD THE σ-ARYL COMPLEXES OF PLATINUM(IV) [a]

Ar–M compound	Solvent	Time, (min)	Product	Yield (%)
$(C_6H_5)_2Hg$	CH_3COCH_3/H_2O (20/1)	30	$[PhPtCl_4NH_3]^-$	40
$(p\text{-}CH_3C_6H_4)_2Hg$	CH_3COCH_3/H_2O (20/1)	45 [b]	$[p\text{-}CH_3C_6H_4PtCl_4NH_3]^-$	90
$(C_6H_5)_4Sn$	CH_3COCH_3/H_2O (30/1)	270	$[PhPtCl_4NH_3]^-$	7
$(C_6H_5)_4Pb$	CH_3COCH_3/H_2O (30/1)	270	$[PhPtCl_4NH_3]^-$	20
$C_6H_5B(OH)_2$	CF_3COOH/H_2O (5/1)	360	$[PhPtCl_4NH_3]^-$	15
$(C_6H_5)_4BNa$	CF_3COOH/H_2O (5/1)	420	$[PhPtCl_4NH_3]^-$	7

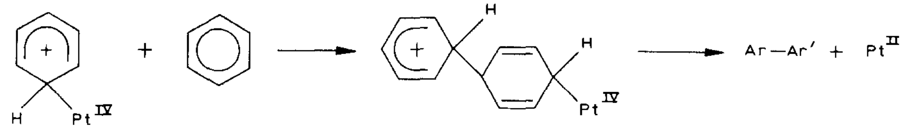
[a] $Na_2PtCl_6 \cdot 6H_2O$ was used in reactions carried out in aqueous acetone; $H_2PtCl_6 \cdot 6H_2O$ was used in reactions in aqueous trifluoroacetic acid. [b] At 42 °C.

TABLE 2

REACTIONS OF THE σ-ARYL COMPLEXES OF PLATINUM(IV) (OR ArM (M = Hg, Sn, Pb, B) COMPOUNDS IN THE PRESENCE OF $PtCl_6^{2-}$) WITH ARENES AND OLEFINS (HEATING UNDER REFLUX)

Reagent	Substrate	Solvent	Time (h)	Product	Yield (%)
$[MeC_6H_4PtCl_4NH_3]^-$	PhOMe	CF_3COOH/H_2O	0.25	$[MeOC_6H_4PtCl_4NH_3]^-$	ca. 2
$[MeC_6H_4PtCl_4(H_2O)]^-$	PhOMe	CF_3COOH/H_2O	5	$MeOC_6H_4$-C_6H_4OMe	ca. 5
$[MeC_6H_4PtCl_4NH_3]^-$	PhEt	CF_3COOH/H_2O	0.25	$[EtC_6H_4PtCl_4NH_3]^-$	4
$[PhPtCl_4(H_2O)]^-$	CH_2=CHCOOH	CF_3COOH/H_2O	8	PhCH=CHCOOH	35
$[PhPtCl_4(H_2O)]^-$	PhCH=CH_2	CH_3COOH	4.5	PhCH=CHPh	30
PhH	CH_2=CHCOOH	CH_3COOH	6	PhCH=CHCOOH	15
$PhHgOCOCF_3$	CH_2=CHCOOH	CH_3COOH	6	PhCH=CHCOOH	15
Ph_4Sn	CH_2=CHCOOH	CH_3COOH	3	PhCH=CHCOOH	86
Ph_4Pb	CH_2=CHCOOH	CH_3COOH	0.5	PhCH=CHCOOH	30
Ph_4BNa	CH_2=CHCOOH	CF_3COOH/H_2O	2	PhCH=CHCOOH	19
$PhB(OH)_2$	CH_2=CHCOOH	CF_3COOH/H_2O	6	PhCH=CHCOOH	6.5
Ph_2Hg	CH_2=CHCOOH	CH_3COOH	8	PhCH=CHCOOH	5
Ph_2Hg	CH_2=CHCOOH	CF_3COOH/H_2O	6	PhCH=CHCOOH	10

may be in equilibrium with the σ-aryl complex in acidic solutions, on a free arene molecule:



(10)

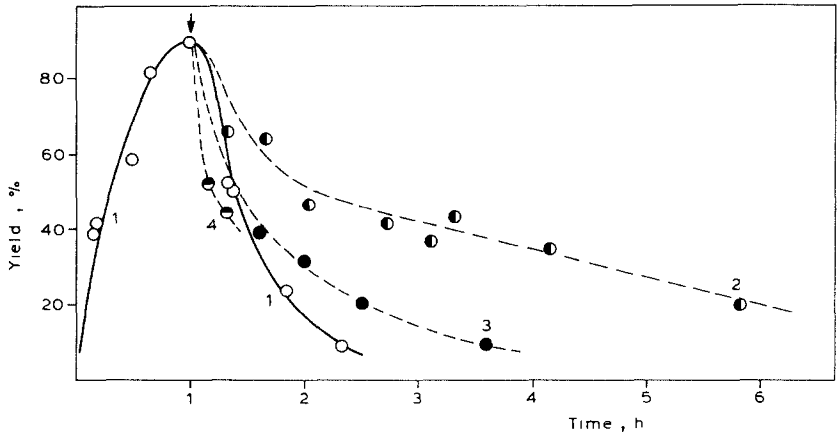


Fig. 1. Reaction of H_2PtCl_6 (0.17 *M*) with toluene (1.58 *M*) in CF_3COOH/H_2O (4/1, v/v) solution at 94.5 °C. (1) Formation and decomposition of the σ-tolyl complex of platinum(IV); (2) decomposition of the complex when toluene was extracted with hexane 1 h after the start of the reaction (arrow); (3) decomposition of the complex when toluene was replaced by anisole (1.5 *M*); (4) decomposition of the complex when toluene was replaced by acrylic acid (2.3 *M*).

We have also found the transarylation reaction, i.e. platinum(IV)-containing moiety transfer from one arene to another (see Table 2):

$$\sigma\text{-Ar-Pt}^{IV} + \text{Ar}'\text{-H} \overset{(H^+)}{\rightleftharpoons} \text{Ar}'\text{-Pt}^{IV} + \text{Ar-H} \qquad (11)$$

This reaction may proceed via stage 8, followed by elimination of Ar-H:

$$(\sigma\text{-Ar})\text{-Pt}^{IV}\text{-}(\sigma\text{-Ar}') + H^+ \rightleftharpoons (\sigma\text{-Ar}')\text{-Pt}^{IV} + \text{Ar-H} \qquad (12)$$

Alternatively, the transarylation may be due to the reversibility, to some extent, of the reaction of platinum(IV) halogen complex with the arene:

$$\text{Pt}^{IV} + \text{ArH} \rightleftharpoons \sigma\text{-Ar-Pt}^{IV} + H^+ \qquad (13)$$

When a solution of the σ-complex $\sigma\text{-Ar-Pt}^{IV}$ in a CF_3COOH/H_2O mixture is heated for a long time with other more nucleophilic arenes, the transarylated complex $(\sigma\text{-Ar}')\text{-Pt}^{IV}$ decomposes and the reaction mixture contains predominantly Ar′-Ar′ (see Experimental).

It should be noted that transarylation reactions in acidic media are known for aryl derivatives of mercury(II) [19] and thallium(III) [20].

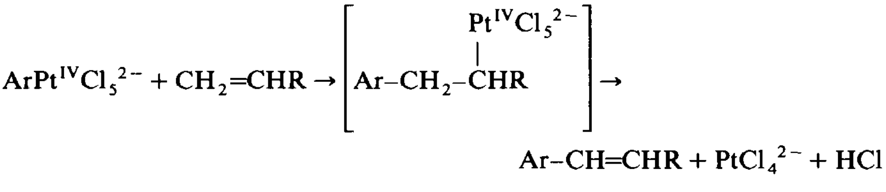
Reactions of the σ-aryl complexes of platinum(IV) with olefins

The σ-aryl complexes of platinum(IV) prepared in situ in the form $\sigma\text{-Ar-PtCl}_5^{2-}$ or $\sigma\text{-Ar-PtCl}_4(H_2O)^-$ by the thermal reaction of arenes with H_2PtCl_6 in CH_3COOH or CF_3COOH/H_2O react readily with olefins to afford arylated olefins (Fig. 1, Table 2):

$$\sigma\text{-Ar-Pt}^{IV} + CH_2\text{=CHR} \rightarrow \text{ArCH=CHR} + \text{Pt}^{II} \qquad (14)$$

The σ-aryl complexes used in this reaction may also be prepared in situ by the reaction of aryl derivatives of non-transition metals (mercury, tin, lead and boron). The highest yield (86%) of arylated olefin (cinnamic acid) was obtained when a solution of tetraphenyltin, H_2PtCl_6 and acrylic acid in acetic acid was refluxed for 3 h. Only trace amounts of cinnamic acid were isolated when the reaction with diphenyl mercury was carried out in aqueous acetone. It should also be noted that refluxing a solution of $(C_6H_5)_3BiCl_2$ or $(C_6H_5)_2SbCl_3$ with H_2PtCl_6 and acrylic acid in acetic acid gave only trace amounts of cinnamic acid.

The mechanism of olefin arylation by the σ-aryl complexes of platinum(IV) appears to be similar to that of arylation in the presence of palladium(II) salts. This mechanism involves the addition of the σ-aryl complex to the olefin double bond, followed by the elimination of hydride ion:



$$\text{ArPt}^{IV}\text{Cl}_5^{2-} + CH_2\text{=CHR} \rightarrow \left[\begin{array}{l} \qquad\quad \text{Pt}^{IV}\text{Cl}_5^{2-} \\ \qquad\quad | \\ \text{Ar-CH}_2\text{-CHR} \end{array}\right] \rightarrow \text{Ar-CH=CHR} + \text{PtCl}_4^{2-} + \text{HCl} \qquad (15)$$

Experimental

All the reactions were carried out in air. The kinetic experiments described in refs. 15, 16 and 18 were followed. Examples of the syntheses are described below. Other reactions summarized in Tables 1 and 2 were carried out analogously.

Reaction of (p-$CH_3C_6H_4$)$_2$Hg with Na_2PtCl_6

A solution of 0.96 g of (p-$CH_3C_6H_4$)$_2$Hg and 0.28 g of $Na_2PtCl_6 \cdot 6H_2O$ and 1 ml of H_2O in 19 ml of acetone was heated at 42°C for 50 min. Acetone was removed under reduced pressure at room temperature and the residue was chromatographed on silica gel containing ammonia (eluent: acetone/hexane, 2/1). The amount of σ-tolyl complex of platinum(IV) obtained (yield ca. 100%) was determined spectrophotometrically. The complex, however, contained an admixture of a mercury derivative and was purified by repeated chromatography.

Reaction of $C_6H_5B(OH)_2$ with H_2PtCl_6

A solution of 0.1 g of $C_6H_5B(OH)_2$ and 0.4 g of $H_2PtCl_6 \cdot 6H_2O$ in 12 ml of CF_3COOH/H_2O (5/1, v/v) was heated under reflux for 6 h. The solvent was removed under reduced pressure and the residue was developed as described above. The yield of complex [σ-$PhPtCl_4NH_3$]NH_4 was 15%.

Reaction of the σ-tolyl complex of platinum(IV) with ethylbenzene

A solution of 0.8 g of [$CH_3C_6H_5PtCl_4NH_3$]NH_4, 2 ml of ethylbenzene and 4 ml H_2O in 18 ml of CF_3COOH was heated under reflux for 15 min. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel. The mixture of complexes (0.15 g) thus obtained contained, according to the ^1H NMR spectrum, 20% of the σ-ethylbenzene complex of platinum(IV).

Arylation of acrylic acid by $(C_6H_5)_4Sn$ in the presence of H_2PtCl_6

A mixture of 0.3 g of $(C_6H_5)_4Sn$, 2 ml of acrylic acid and 0.2 g of $H_2PtCl_6 \cdot 6H_2O$ in 10 ml of CH_3COOH was heated under reflux for 3 h. The solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel column (eluent: acetone/hexane, 3/4). The yield of cinnamic acid was 66 mg (86%).

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