

OXIDATIVE COUPLING OF ARENES OR ARYL DERIVATIVES WITH OLEFINS UNDER THE ACTION OF PLATINUM(IV) COMPOUNDS[†]

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Refluxing the $\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ or CH_3COOH solutions of non-transition metal (Hg, Sn, Sb, B) aryl derivatives and olefins (acrylic acid, styrene) in the presence of Pt(IV) salts results in substituted styrenes (cinnamic acid, 1,2-diphenylethylene). The reaction proceeds via an σ -aryl complex of Pt(IV).

Aims

Isolation and characterization of intermediate complexes is important for understanding of mechanisms of catalytic processes. One can carry out a model reaction frequently, using a derivative of heavier metal instead of transition metal catalyst, the intermediates in this case being more stable. In the present work we describe the oxidative coupling of hydrocarbons under the action of platinum(IV) derivatives which can be appropriate models for the well-known palladium(II) catalysts.

Background

The oxidative coupling reactions of organic molecules are of great interest in chemistry. These reactions include the van Helden oxidative coupling of arenes,¹ the Fujiwara arylation of olefins by arenes,² the Heck arylation of olefins by aryl derivatives of mercury and other non-transition metals,³ the Heck arylation of olefins by aryl halogen compounds.⁴ All these reactions proceed in the presence of palladium(II) salts. The formation of unstable σ -aryl complex of palladium(II) was proposed as an intermediate for these arylation processes.

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It is known that heating a solution of benzene and hexachloroplatinic acid in acetic acid leads to a mixture of chlorobenzene and diphenyl.⁵ Recently we have found that anionic σ -aryl complexes of platinum(IV) could be isolated from this reaction mixture.^{6,7} Thus, the chlorination and oxidative coupling of arenes under the action of H_2PtCl_6 proceed via σ -aryl complex of platinum(IV) formation.

Experimental

All the reactions were carried out in open vessels in air. The results are summarized in Table 1.

Oxidative coupling of benzene with acrylic acid

A mixture of 0.82 g of H_2PtCl_6 , 1 ml of benzene, 2 ml of acrylic acid, 18 ml of CF_3COOH , and 4 ml of H_2O was refluxed for 6 hours. The solvent was removed under reduced pressure. The residue was chromatographed on a silica gel (eluent: 3:4 mixture of acetone and hexane) giving cinnamic acid.

Olefination of σ -aryl complex of Pt(IV) with styrene

A solution of 0.41 g of H_2PtCl_6 , 2 ml of benzene in 8 ml acetic acid and 2 ml of H_2O was refluxed for 1 hour (corresponding to maximum of the σ -complex concentration). Styrene (0.5 ml) was added to the solution and the mixture was refluxed for 3.5 hours. *Trans*-1,2-diphenylethylene was isolated by chromatography on silica gel.

Arylation of acrylic acid with tetraphenyltin

A solution of 0.2 g of H_2PtCl_6 , 0.3 g of Ph_4Sn , 2 ml of acrylic acid in 10 ml of CH_3COOH was refluxed for 3 hours. The reaction mixture was developed as described above, yielding cinnamic acid.

Other reactions were carried out analogously.

Results

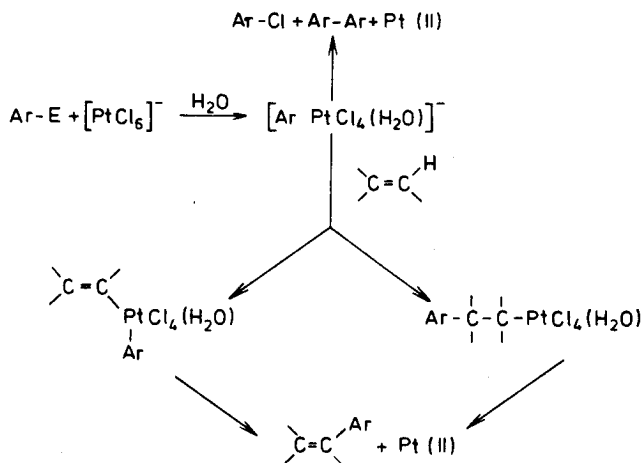
Continuing our investigation, we carried out the arylation reaction of olefins by σ -aryl complexes of platinum(IV). The σ -aryl complex (which could be isolated in a form stabilized with ammonia [$\text{ArPtCl}_4\text{NH}_3$] NH_4) was prepared in situ. Arenes or aryl derivatives of non-transition metals (Hg, Sn, Pb, Bi, B) could be used as sources of aryl group. Aqueous trifluoroacetic acid or acetic acid are appropriate solvents for the arylation reaction. Acrylic acid and styrene were used as olefins. Data on arylation of olefins are summarized in Table 1.

Table 1
 Arylation of olefins by arenes or aryl derivatives in the presence of H_2PtCl_6
 (Heating under reflux)

Aryl derivative	Olefin	Solvent	Time, h	Product	Yield, %
$[PhPtCl_4(H_2O)]^-$	$CH_2=CHCOOH$	$CF_3COOH-H_2O$	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	$CH_2=CHCOOH$	$CH_3COCH_3-H_2O$	18	$PhCH=CHCOOH$	traces
Ph_2Hg	$CH_2=CHCOOH$	CH_3COOH	8	$PhCH=CHCOOH$	5
Ph_2Hg	$CH_2=CHCOOH$	$CF_3COOH-H_2O$	6	$PhCH=CHCOOH$	10
Ph_3BiCl_2	$CH_2=CHCOOH$	CH_3COOH	3	$PhCH=CHCOOH$	traces
Ph_2SbCl_3	$CH_2=CHCOOH$	CH_3COOH	3	$PhCH=CHCOOH$	traces

Discussion

The first stage of the arylation reaction is undoubtedly the formation of the σ -aryl complex of Pt(IV). This complex was produced by the cleavage of the Ar—H or Ar-Element bond with Pt(IV) compound. The accumulation rate of the complex is sufficient in acidic media and very low in water or aqueous acetone. Arylated compounds of non-transition metals form more easily arylplatinum complexes when reacted with H_2PtCl_6 in comparison with arenes.



Chlorination, dimerization, and olefination of arenes and aryl derivatives via σ -aryl complex of Pt(IV) formation. Ar-aryl; E=H, Hg, Sn, Pb, Sb, B

The formation of arylated olefin could proceed via olefin insertion into the Ar—Pt-bond followed by reductive elimination of the hydride Pt(IV)—H or via formation of an intermediate σ -aryl- σ -vinyl complex of platinum(IV) (see Scheme). The platinum(IV) compound is reduced to platinum(II) derivative during this reaction.

The overall yield of arylated olefin appears to depend on the ratio of the rates of the two stages. In some cases (e.g. aryl derivatives of Bi and Sb) side reactions become predominant and yield of styrene derivative decreases.

Conclusions

Arylation of olefins with arenes or aryl derivatives of non-transition metals in the presence of H_2PtCl_6 is a convenient method for preparing arylated olefins and a model of oxidation reaction which proceeds under the action of palladium(II) salts.

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