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# ARYL SUBSTITUTION OF OLEFINS. REACTION OF σ-VINYL PALLADIUM(II) WITH BENZENE OR TOLUENE: EVIDENCE FOR THE REACTION MECHANISM

ICHIRO MORITANI AND YUZO FUJIWARA
*Faculty of Engineering Science, Osaka University, Machkaneyama, Toyonaka, Osaka (Japan)*
AND SADAO DANNO
*Polymer Research Laboratory, Ube Industries Ltd., Goi, Ichihara, Chiba (Japan)*

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## SUMMARY

The reactions of σ-olefin–palladium(II) complexes with an aromatic compound such as benzene or toluene have been found to produce aryl-substituted olefins. This result provides support for a mechanism for the aromatic substitution of olefins in the presence of palladium acetate which involves a σ-bonded olefin–palladium(II) intermediate.

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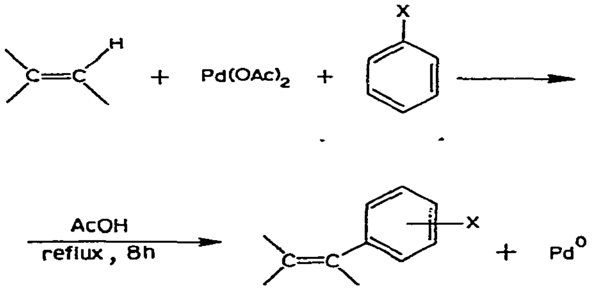
## INTRODUCTION

Attachment of aryl groups to olefins is known to be brought about by the following process[1]:



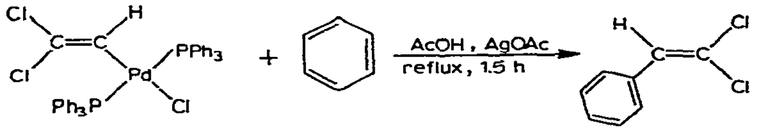
(1)

We have demonstrated that this general reaction occurs between common olefins and aromatic compounds to produce aryl-substituted olefins, and that the reaction proceeds through a different mechanism from that of the Wacker process[2] and involves retention of configuration of the olefin[3].

The mechanism proposed involves an olefin–palladium(II) σ-bonded intermediate[4]. In order to confirm this mechanism, it was important to ascertain whether an olefin–palladium(II) σ-bonded complex reacts with aromatic compounds to produce an aryl-substituted olefin.

## RESULTS AND DISCUSSION

If the proposed mechanism is reasonable, the σ-bonded complex bearing a C=C double bond would react with benzene to produce a phenyl-substituted olefin. The starting complex (I), chloro-σ-(β,β-dichlorovinyl)-*trans*-bis(triphenylphosphine)-palladium(II) was prepared by the method of Fitton and McKeon[5], and the reaction was carried out between the complex (I), benzene, acetic acid, and silver acetate under reflux for 1.5 h. The silver acetate was introduced to abstract a chloride ligand from the complex (I) so that benzene would be able to coordinate to the palladium(II) ion*. β,β-Dichlorostyrene was obtained in 80% yield based on the complex (I) [eqn. (2)].



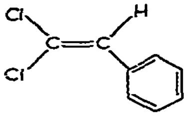
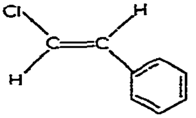
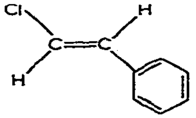
(I)

(2)

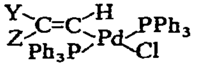
The results for β-substituted vinylpalladium complexes, involving *cis*- and *trans*-(β-chlorovinyl)palladium compounds, are summarized in Table 1.

TABLE 1

THE REACTION OF σ-VINYL–PALLADIUM COMPLEXES[a] WITH BENZENE

| Complex[a] | Phenyl-substituted product | Yield[b] (%) |
|---|---|---|
| (I) |  | 80 |
| (II) |  | 85 |
| (III) |  | 82 |

[a] These complexes are as follows:



(I) ; Y=Z=Cl
(II) ; Y=Cl, Z=H
(III); Y=H, Z=Cl

[a] Based on palladium complex.

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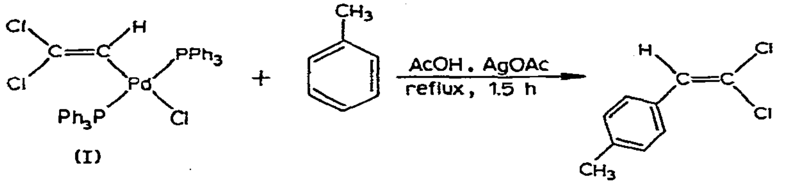
* As silver acetate alone can not cause the reaction, it is apparent that the reaction takes place by the action of the palladium(II) of the complex (I).

In the case of the *trans*-($\beta$-chlorovinyl)palladium(II) complex (II), the $\sigma$-bonded *trans*-$\beta$-chlorovinyl ligand was phenylated to produce *trans*-$\beta$-chlorostyrene. The *cis*-isomer (III) also treated with benzene produced *trans*-$\beta$-chlorostyrene. In the latter case, *cis*-$\beta$-chlorostyrene may be formed initially and then isomerize to the *trans*-isomer under the reaction conditions.

It is known that $\sigma$-bonded olefin–palladium complexes react with benzene to produce phenyl-substituted olefins*.



(I)

(3)

Furthermore $\beta$,$\beta$-dichloro-4-methylstyrene was produced in 64% yield from the reaction between the complex (I) and toluene [eqn. (3)] and it is clear in this case that the phenyl group does not come from the triphenylphosphine ligand.

The results demonstrate that the $\sigma$-olefin–palladium complex proposed as an intermediate in the course of the aryl substitution of olefins[4] reacts with benzene and produces the phenyl-substituted olefin.

## EXPERIMENTAL

All boiling points and melting points are uncorrected. Infrared spectra were recorded on a Hitachi EPI-S2 IR spectrophotometer and the NMR spectra were recorded on a Japan Electron Optics JNM-4H-100 or JNM-C-60HL spectrometer with tetra-methylsilane as an internal standard unless otherwise noted. Chemical shifts are given in $\tau$ units together with splitting patterns and relative integrated area.

### *General procedure for arylation of $\sigma$-substituted vinylpalladium complexes with aromatic compounds*

Mixtures of the palladium complex, silver acetate (5 moles proportions), acetic acid, and the aromatic compound were stirred for 1.5 h at reflux. The reactions were carried out in an excess of the aromatic compound which behaved as both reactant and a solvent. The resulting mixture was filtered to remove palladium metal, the filtrate was poured into water, and the organic layer was separated. The organic layer was treated with aqueous sodium bicarbonate solution, washed with water to remove acetic acid, and dried over anhydrous sodium sulfate. After evaporation of the solvent, the products were isolated by column or gas chromatography. Analyses of products were carried out on a Yanagimoto GCH-3 gas chromatograph using an Apiezon L or Carbowax 20M column. The identities of the products were confirmed by comparison of GLC retention times and IR or NMR spectra with those of authentic samples.

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* A separate experiment confirmed complex (I) is stable under the reaction conditions in the absence of benzene.

### *Preparation of the palladium complexes* (I), (II), *and* (III)

These complexes were prepared by the method of Fitton and McKeon[5]: a suspension in benzene of the olefin and tetrakis(triphenylphosphine)palladium(0) (*cf.* ref. 6) was agitated at reflux for 2 h under nitrogen. The solvent was evaporated and the stable complex produced was recrystallized from benzene. Complex (I) had m.p. 310–312° (decompn.): IR spectrum (Nujol); 1670 $cm^{-1}$ (C=C): NMR spectrum (in $CDCl_3$); $\tau$ 5.03 ppm (s). Complex (II) had m.p. 275~277° (decompn.): IR spectrum (Nujol); 1660 $cm^{-1}$ (C=C): NMR spectrum (in $CDCl_3$); $\tau$ 4.37 ppm (m). Complex (III) had m.p. 274–282° (decompn.): IR spectrum (Nujol); 1670 $cm^{-1}$ (C=C): NMR spectrum (in $CDCl_3$); $\tau$ 4.93 ppm (m).

### *Preparation of β,β-dichlorostyrene*

This compound was prepared by the method of Rabinowitz and Ruth[7]: a solution of triphenylphosphine 72 g (0.274 mole) and freshly distilled benzaldehyde 29 g (0.274 mole) in tetrachloromethane (150 ml) was heated at 60° and stirred for 2 h. Petroleum ether (200 ml) was then added, and cause precipitation of triphenylphosphine oxide. The latter was filtered off and the solvent was evaporated. The residual oil was distilled *in vacuo* to give a mixture of *β,β*-dichlorostyrene and *α,α*-dichlorotoluene (31 g, 122–127°/47 mm). The distillate was separated by GLC(SE-30 column). IR spectrum (direct); 690 and 750 $cm^{-1}$ (monosub. benzene): NMR spectrum (in $CCl_4$); $\tau$ 2.63 (m, 5H) and 3.22 ppm (s, 1H). *β,β*-Dichloro-*p*-methylstyrene was prepared by the similar method; b.p. 110°/15 mm: m.p. 40.0–40.5° (lit.[8] 40–41°); IR spectrum (direct): 1640 $cm^{-1}$ (C=C); NMR spectrum (in $CCl_4$): $\tau$ 2.78 (q, 4H), 3.27 (s, 1H), and 7.68 ppm (s, 3H).

### *Preparation of trans-β-chlorostyrene*

*trans-β*-Chlorostyrene[10] was made in 11% yield by Biltz's procedure[9], from cinnamic acid and chlorine gas. It had b.p. 80–82°/11 mm (lit.[9] 89°/17.5 mm). (Found: C, 69.51; H, 5.11; Cl, 25.70. $C_8H_7Cl$ calcd.: C, 69.33; H, 5.09; Cl, 25.58%.) IR spectrum (direct): 690, 740 (monosub. benzene), 940 $\left({}^{\mathrm{H}}\!\!>\mathrm{C{=}C}\!<_{\mathrm{H}}\right)$, and 1675 $cm^{-1}$ (C=C); NMR spectrum (in $CCl_4$): $\tau$ 2.86 (m, 5H) and 3.45 ppm (m, 2H).

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