Aromatic Substitution of Olefins. XIV. Reaction of σ-Bonded Olefin-Palladium(II) Complexes with Benzene: Evidence for the Mechanism of the Aromatic Substitution of Olefins

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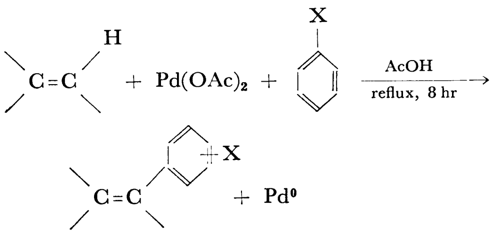
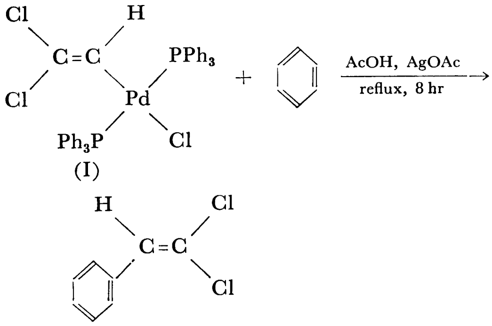
The substitution reaction of olefins is as follows:[1]



(1)

We have demonstrated that this is the general reaction occurring between common olefins and aromatics to produce aromatic-substituted olefins and that the reaction proceeds through a different mechanism from that of the Wacker process.[2]

The mechanism proposed involves σ-bonded olefin-palladium(II) intermediate.[3] In order to prove this mechanism, we have performed the reaction of a σ-bonded 2,2-dichlorovinyl-palladium(II) complex (I) with benzene. If the proposed mechanism is reasonable, the σ-bonded complex bearing a C=C double bond would react with benzene to produce an aryl-substituted olefin. The starting complex (I) was prepared by Fitton,[4] and the reaction was carried out using complex(I), benzene, acetic acid, and silver acetate under reflux for 8 hr. The silver acetate was introduced to abstract a chloride ligand from (I) to enable benzene to coordinate to palladium(II) metal.*1 From the reaction mixture, β,β-dichlorostyrene was obtained in a 7.4% yield based on complex(I) (equation 2).*2*3



(2)

Moreover, σ-bonded *cis*- and *trans*-2-chlorovinyl-palladium(II) complexes reacted with benzene to produce corresponding β-chlorostyrenes.

These results clearly show that the aromatic substitution of olefins proceeds *via* formation of a σ-bond between olefin and palladium(II) metal, and support the proposed mechanism.[3]

1) Y. Fujiwara, I. Moritani, S. Danno and S. Teranishi, *J. Amer. Chem. Soc.*, **91**, 7166 (1969).

2) S. Danno, I. Moritani and Y. Fujiwara, *Chem. Commun.*, **1970**, 610; S. Danno, I. Moritani, Y. Fujiwara and S. Teranishi, *J. Chem. Soc.*, *B*, in press.

3) S. Danno, I. Moritani and Y. Fujiwara, *Tetrahedron*, **25**, 4819 (1969).

4) P. Fitton and J. E. McKeon, *Chem. Commun.*, **1968**, 4.

*1 As silver acetate alone cannot bring about the reaction, it is apparent that the reaction takes place by the action of palladium(II) of complex (I).

*2 That the σ-complex(I) is stable under the reaction condition without benzene was confirmed by a separate experiment.

*3 Note added in Proof. When the reaction time was 1.5 hr to present the polymerization of the styrene formed, the yield increased up to 80%.