Aromatic Substitution of Olefins.[1] The Reaction of Ferrocene with Styrene in the Presence of Palladium(II) Acetate

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Summary Ferrocene reacts with styrene to produce *trans*-α-styrylferrocene in the presence of palladium(II) acetate, which exemplifies an extremely convenient method for the direct synthesis of alkenylferrocenes.

WE have reported a novel reaction of olefins with benzene derivatives to produce aryl-substituted olefins *via* direct substitution in the presence of palladium(II) salts.[2] It was of interest to determine whether nonbenzenoid aromatic compounds also react with olefins. Ferrocene has been found to react easily with styrene, to produce styrylferrocene, in the presence of palladium(II) acetate. This is the first example of such a substitution reaction between a nonbenzenoid aromatic compound and an olefin.

A solution of palladium(II) acetate, styrene (1 equiv), ferrocene (1 equiv), acetic acid, and dioxan was stirred at reflux for 8 hr. The resulting mixture was worked-up in the usual way, and the residue was chromatographed on a column of alumina. Besides the starting styrene and ferrocene, there was obtained an orange yellow crystalline material, m.p. 119—119·5° (lit.[3] 118°), *trans*-α-styrylferrocene† (20% yield based on palladium acetate); 100 MHz n.m.r. spectrum (CCl_4), τ 2·55—3·00 (m, phenyl, 5H), 3·27 (olefinic, 1H) and 3·40 (olefinic, 1H), 5·64 and 5·83 (mono-substituted cyclopentadienyl, 2H : 2H), and 5·95 (s, cyclopentadienyl, 5H). I.r. spectrum (Nujol), 701 and 760 (mono-substituted phenyl), 963 (*trans*-C–H), and 1002 and 1108 (ferrocenyl) cm^{-1}.

It is clear that the styrylferrocene was produced *via* substitution of a hydrogen of the cyclopentadienyl group with styrene by the catalysis of palladium(II) acetate. In general it is troublesome to introduce substituents, especially alkenyl groups, into ferrocene, but this reaction provides a very convenient method for the synthesis of ferrocene derivatives.

Further, the fact that ferrocene, a nonbenzenoid aromatic compound, undergoes the substitution reaction with olefins suggests that other compounds having aromaticity could react with olefins in the presence of palladium(II) acetate to give alkenyl-substituted products.

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† A good elemental analysis was obtained. The i.r. spectrum (peak at 963 cm^{-1}) clearly shows that this is a *trans*-isomer.

[1] Previous paper: S. Danno, I. Moritani, Y. Fujiwara, and S. Teranishi, *J. Chem. Soc.* (*B*), in the press.
[2] For example, Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Amer. Chem. Soc.*, 1969, **91**, 7166; *Chem. Comm.*, 1970, 610.
[3] G. Drefahl, G. Plötner, and I. Winnefeld, *Chem. Ber.*, 1962, **95**, 2788.