# The Reaction of Acetylacetonato-(π-allylic)palladium(II) Complexes with Carbon Monoxide and Conjugated Dienes

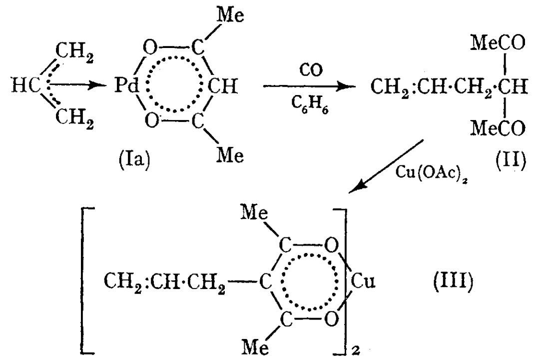
By YASUTAKA TAKAHASHI,* SHIZUYOSHI SAKAI, and YOSHIO ISHII
(*Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Fuoro-cho, Chikusa-ku, Nagoya, Japan*)

IN our previous Paper[1] concerning the n.m.r. spectra of acetylacetonato-(substituted cinnamyl)-palladium(II) complexes, we suggested that π-allylic ligands were unexpectedly labile in the presence of π-donor additives such as styrene. We now report a ligand–ligand coupling reaction of a π-allylic palladium complex with carbon monoxide and an insertion reaction of butadiene at the allyl–palladium bond of the complex.

When carbon monoxide was bubbled into a benzene solution of acetylacetonato-(π-allyl)palladium (Ia) at ordinary pressure and temperature, palladium black separated immediately. The solution was kept overnight, and analysed by gas chromatography. Allylacetylacetone (II) was the sole product, b.p. 94°/12 mm., having i.r. bands at 920 and 995 cm.$^{-1}$ due to the presence of a vinyl group, and at 1700 and 1730 cm.$^{-1}$ due to the carbonyl group. The copper complex (III), m.p. 200·5—202°, prepared from (II) and cupric acetate, was identical with an authentic sample (i.r. spectrum and mixed melting point).

A similar coupling reaction was reported by Wilke,[2] in the reaction of bis(π-allyl)nickel to give biallyl.

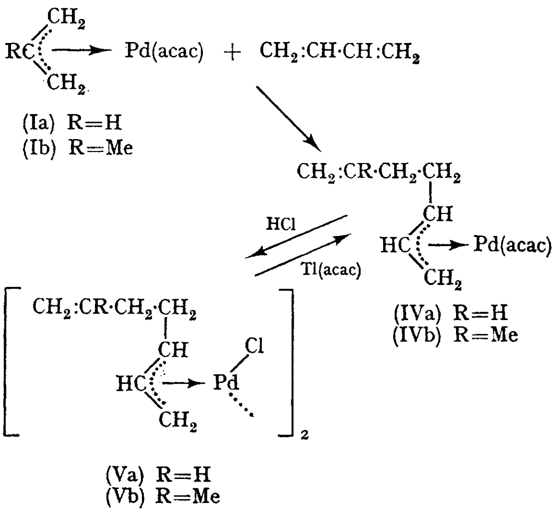
Tsuji *et al.* found ethyl allylacetoacetate as a product of the reaction between bis-(π-allylpalladium chloride) and ethyl acetoacetate in basic



methanol–dimethyl sulphoxide solution. They suggested two possible mechanisms; (1) a direct attack of acetoacetate carbanion on the ligand carbon atom, and (2) a replacement of the chloro-ligand by a carbanion and subsequent ligand–ligand coupling.[3,4] Our result supports the latter mechanism, where donor molecules such as carbon monoxide and dimethyl sulphoxide cause an anomalous accelerating effect.

On the other hand, the reaction of butadiene with (Ia) resulted in the insertion of diene at the allyl-palladium bond instead of coupling. A benzene solution of (Ia) was saturated with butadiene at room temperature and left overnight. The small quantity of palladium metal which precipitated was filtered off, the solvent was removed at reduced pressure, and the residual viscous yellow oil was analysed. The i.r. spectrum of the resultant complex (IVa) resembled closely that of complex (Ia) but had additional bands, due to a terminal vinyl group at 1640, 995, and 910 cm.$^{-1}$. When (IVa) was converted into the halogen-bridged dimeric complex (Va) by reaction with hydrogen chloride, the vinyl group remained in the complex. The complex (Va) could be re-converted into (IVa) by reaction with thallous acetylacetonate [Tl(acac)]. Furthermore, the reaction of 2-methylallylpalladium complex (Ib) with butadiene gave (IVb), having an i.r. band at 890 cm.$^{-1}$ due to the presence of the terminal methylene group. The n.m.r. spectra of the dimers were consistent with structures (Va) and (Vb), respectively.

Hence the following reaction sequence is suggested:



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