

A Novel Palladium(0) Complex; Bis(dibenzylideneacetone)palladium(0)

By Y. TAKAHASHI,* Ts. ITO, S. SAKAI, and Y. ISHII

(Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya, Japan)

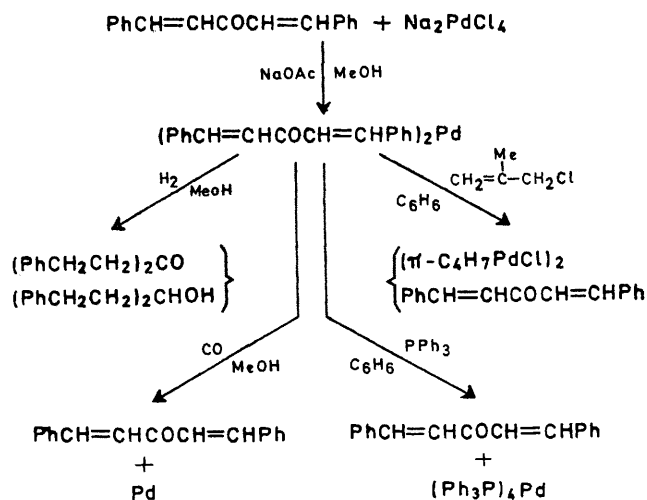
Summary A convenient preparative method of a novel palladium(0) complex, bis(dibenzylideneacetone)palladium(0), is reported.

LIGANDS used for the preparation of palladium(0) complexes have been limited to phosphines,¹⁻³ phosphite,¹ arsines,¹ isocyanides,² and carbon monoxide.⁴ We have prepared a novel type of palladium(0) complex with dibenzylideneacetone as ligand.

Sodium acetate was added to a hot methanolic solution (*ca.* 60°) of sodium chloropalladite and an excess of dibenzylideneacetone ($\text{PhCH}=\text{CHCOCH}=\text{CHPh}/\text{Pd} \geq 3$), and the mixture was allowed to cool, with stirring. A brownish crystalline complex, $(\text{PhCH}=\text{CHCOCH}=\text{CHPh})_2\text{Pd}$, was precipitated, removed by filtration, and washed with water and acetone, successively. The complex [m.p. 135° (decomp.)] was obtained quantitatively.

Bis(dibenzylideneacetone)palladium(0) is fairly stable in air in the solid state, but slowly decomposes in solution to metallic palladium and dibenzylideneacetone. The complex is slightly soluble in CH_2Cl_2 , CHCl_3 , and benzene to give deep wine-coloured solutions.

Elemental analysis was consistent with the structure $(\text{PhCH}=\text{CHCOCH}=\text{CHPh})_2\text{Pd}$. In the i.r. spectrum of the complex, absorption bands similar to those of dibenzylideneacetone were observed, but with the disappearance of



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absorption bands at 1627 and 983 cm^{-1} ($\text{C}=\text{C}$) and a shift of $\nu(\text{C}=\text{O})$ from 1651 (free dibenzylideneacetone) to 1620 cm^{-1} (co-ordinated dibenzylideneacetone). No $\text{Pd}-\text{Cl}$ stretching band was observed. These facts suggest that dibenzylideneacetone is co-ordinated to Pd^0 mainly by $\text{C}=\text{C}$ bonds.

The complex reacted with hydrogen or carbon monoxide in methanol to give a mixture of 1,5-diphenylpentan-3-one and 1,5-diphenylpentan-3-ol or dibenzylideneacetone, respectively, indicating the absence of a Pd-C σ -bond. Evidence for the existence of the palladium(0) complex is obtained from the fact that the reaction of the complex with

triphenylphosphine or methylallyl chloride gave the known complexes $(\text{Ph}_3\text{P})_4\text{Pd}$ or bis- $(\pi$ -methylallyl)palladium chloride), respectively.

These results are summarized in the Scheme.

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