

Efficiently Catalytic C-H Activation. Direct and Mild Carbonylation
of Benzene and Cyclohexane by $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ under Irradiation

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A high turnover number was achieved in the photo-assisted carbonylation of C-H bonds of benzene catalyzed by $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$ under mild conditions (1 atm, 37 °C) to give mainly benzaldehyde. Cyclohexane could also be carbonylated under the same conditions.

Although great efforts have been made to activate and to functionalize C-H bonds of alkanes or arenes under mild conditions assisted by transition metal complexes,¹⁾ there have been few catalytic reactions attained. Several groups reported the intermolecular oxidative addition of C-H bonds to iridium or rhodium complexes under irradiation,²⁻⁴⁾ but the reactions were not catalytic. Although catalytic carboxylations of benzene under oxidative conditions to produce benzoic acid by $\text{Pd}(\text{OAc})_2$ -*t*-BuOOH system was reported, the turnover numbers were not so high.⁵⁾ Photo-assisted carbonylation of benzene to afford benzaldehyde by $\text{IrH}_3(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ was reported by Eisenberg et al.⁶⁾ The reactivity, however, was low and it is not clear whether the reaction proceeds catalytically. Very recently, they reported another system using $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, but the yields were still very poor.⁷⁾ They ascribed this to the equilibrium between benzene and benzaldehyde (Eq. 1).⁸⁾



In search for efficient complex catalysts, we have also examined the carbonylation of benzene using rhodium carbonyl complexes under irradiation. The mixture (Rh 0.21 mg-atom, benzene 30 cm³) in a Pyrex flask was irradiated by a 100 W high pressure mercury lamp under an atmospheric pressure of CO (balloon)

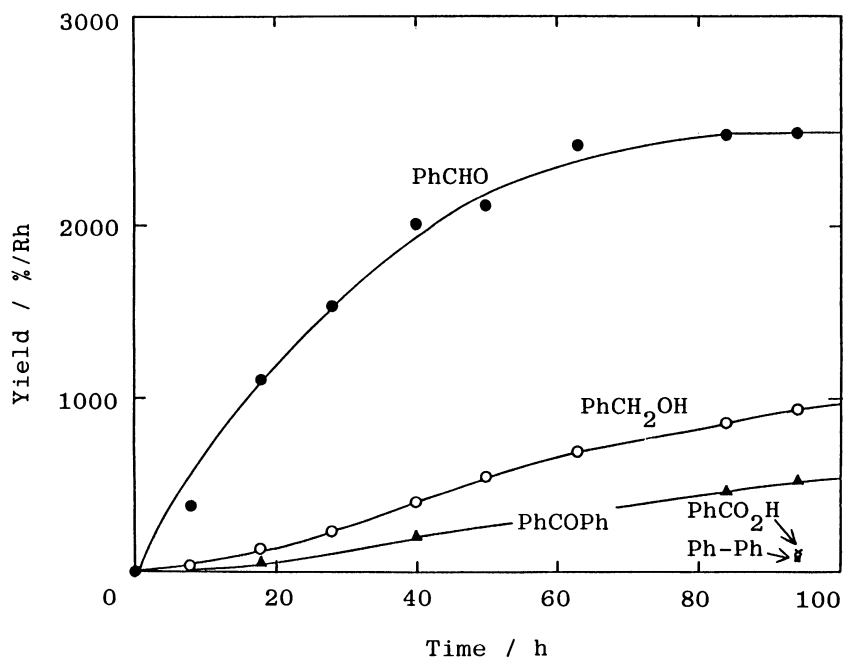


Fig. 1. Time dependence of the reaction catalyzed by $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$. Reaction conditions; Rh 0.21 mg-atom, benzene 30 cm^3 , CO 1 atm, 37°C .

