

# Mechanistic Study of Palladium-Catalyzed Direct Arylation of Benzene: Evidence for the Intermediacy of “Ligandless” Arylpalladium(II) Species in the C-H Cleavage Step

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Direct arylations are catalytic reactions in which aryl halides react with arenes to form biaryl products. These reactions are a type of C-H bond functionalization that is beginning to be utilized for the synthesis of medicinally active compounds. It has been proposed that in these reactions, arylpalladium carboxylate complexes  $\text{LPd}(\text{Ar})(\text{OC}(\text{O})\text{R})$  react with arenes to cleave the aryl C-H bonds.

We have prepared the proposed arylpalladium carboxylate intermediate  $\text{LPd}(\text{Ar})(\text{OC}(\text{O})\text{R})$  ( $\text{L} = \text{P}(t\text{-Bu})_3$ ,  $\text{R} = t\text{-Bu}$ ) and studied the reactions with benzene. No biaryl product from reaction with benzene was formed. Instead, biaryl from disproportionation of the  $\text{LPd}(\text{Ar})(\text{OC}(\text{O})\text{R})$  complex was formed. However, reaction with added  $\text{Br}^-$  led to the cross-coupled product in good yield. Moreover, reactions with added air or  $\text{Ag}^+$  to consume the phosphine ligand also led to the cross-coupled products. Thus, we propose that the species that reacts with arene is the arylpalladium carboxylate complex that lacks phosphine ligand. Furthermore, reactions catalyzed by  $\text{Pd}(\text{OAc})_2$  without ligand occur faster than, and with comparable selectivities to reactions catalyzed by  $\text{Pd}(\text{OAc})_2$  and  $\text{P}(t\text{Bu})_3$  or  $\text{P}(\text{Cy})_2(2\text{-biaryl})$ . These observations further support the intermediacy of “ligandless” arylpalladium species in the C-H cleavage step.

