Bis(tri-tert-butylphosphine)palladium(0) [Pd(t-Bu$_3$P)$_2$]

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Introduction

The catalyst bis(tri-tert-butylphosphine)palladium(0) [Pd(t-Bu$_3$P)$_2$] is a colorless, air-sensitive solid. It must be manipulated in a glove box or under inert gas. [Pd(t-Bu$_3$P)$_2$] (1) contains bulky, electron-rich tertiary phosphine ligands [t-Bu$_3$P]. In a palladium-catalyzed cross-coupling reaction, they promote the oxidative addition as they can stabilize higher oxidation states. Reductive elimination is also facilitated because of the bulky ligands. Thus 1 has been shown to be superior in transition-metal-catalyzed cross-coupling reactions compared to the classical [Pd(PPh$_3$)$_4$] catalyst. [Pd(t-Bu$_3$P)$_2$] is not only efficient for typical cross-coupling reactions, such as Stille, Negishi, Suzuki, Heck, Sonogashira, or Buchwald–Hartwig amination, with electrophiles R-X (X = Cl, Br, I, OTf, SO$_2$Cl and others), but also for cross-coupling of organolithium reagents, alkynylgermanes, alkali-metal silanolates, triarylindium reagents and others. Moreover, it has been used for arylation of hydro-siloxanes, decarboxylative cross-coupling reactions, carbonylations and amino-carbonylations, carbodioxidations, C-H functionalizations, cyanations, methylolation of olefins and annulation reactions. In recent years, 1 has become one of the best new-generation catalysts and plays an important role in organic synthesis.

[Pd(t-Bu$_3$P)$_2$] is commercially available and can also be prepared by treating [Pd(η$_3$-C$_6$H$_5$)(η$_1$-C$_5$H$_5$)] with the ligand [t-Bu$_3$P] in n-hexane at room temperature for 3 h. The pale red crude product can be recrystallized from n-hexane at −20 °C to give pure colorless crystals.

Table 1 The Use of Bis(tri-tert-butylphosphine)palladium(0) [Pd(t-Bu$_3$P)$_2$]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>42–92% yield</th>
<th>71–99% yield</th>
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</table>

Figure 1 Bis(tri-tert-butylphosphine)palladium
**[Pd(t-Bu₃P)₂]-Catalyzed Decarbonylative Cross-Coupling Reaction**

Forgione, and Bilodeau and coworkers developed a procedure for highly selective Pd-catalyzed decarbonylative cross-coupling reactions between heteroaromatic carboxylic acids and various aryl halides in the presence of a reactive C-H group.² This process provides a valuable alternative for other cross-coupling reactions, in cases where appropriate cross-coupling partners are not commercially available and hard to be synthesized.

**[Pd(t-Bu₃P)₂]-Catalyzed Carbonylation and Aminocarbonylation**

Traditional methods to synthesize acid chloride involve toxic reagents, such as PCl₃, thionyl chloride and oxalyl chloride. Quesnel and Arndtsen described a new method to construct acid chlorides via the [Pd(t-Bu₃P)₂]-catalyzed carbonylation of aryl iodides under mild conditions.⁷ The decisive step of the process was reductive elimination of [Pd(t-Bu₃P)₂(CO)Pd(COAr)Cl], which was facilitated by the combination of the bulky, electron-rich [t-Bu₃P], the phosphine chloride and CO coordination. This method was exploited to perform traditional aminocarbonylation of aryl iodides under exceptionally mild conditions (ambient temperature and pressure).

**[Pd(t-Bu₃P)₂]-Catalyzed Carboiodination**

Various functionalized chromans and isochromans were prepared via the intramolecular [Pd(t-Bu₃P)₂]-catalyzed carboiodination of alkenyl aryl iodides in the presence of an amine base Et₃N.⁸ Those cyclizations had a broad functional group tolerance and showed high diastereoselectivities, which was thought to originate from the minimization of axial–axial interactions in the carboiodination step.

**[Pd(t-Bu₃P)₂]-Catalyzed C–H Functionalization**

Tamba and coworkers described a facile [Pd(t-Bu₃P)₂]-catalyzed C–H arylation of heteroarene compounds with aryl bromides and aryl chlorides in the presence of LiOt-Bu as a base.⁹

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**References**