Bis(tri-*tert*-butylphosphine)palladium(0) [Pd(*t*-Bu₃P)₂]

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Published online: 26.02.2015

DOI: 10.1055/s-0034-1380286; Art ID: st-2015-v0511-v

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Introduction

The catalyst bis(tri-*tert*-butylphosphine)palladium(0) [Pd(*t*-Bu₃P)₂, **1**, CAS: 53199-31-8] is a colorless, air-sensitive solid. It must be manipulated in a glove box or under inert gas. [Pd(*t*-Bu₃P)₂] (**1**) contains bulky, electron-rich tertiary phosphine ligands [*t*-Bu₃P]. 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(Ph₃P)₄] catalyst. [Pd(*t*-Bu₃P)₂] is not only efficient for typical cross-coupling reactions, such as Stille, Negishi, Suzuki, Heck, Sonogashira, or Buchwald–Hartwig aminations, with electrophiles R-X (X = Cl, Br, I, OTf, SO₂Cl and others), but also for cross-coupling of organolithium reagents,¹ alkenylgermanes,² alkali-metal silanolates,³ trior-

gano-indium reagents⁴ and others. Moreover, it has been used for arylations of hydro-siloxanes,⁵ decarboxylative cross-coupling reactions,⁶ carbonylations and amino-carbonylations,⁷ carboiodinations,⁸ C-H functionalizations,⁹ cyanations,¹⁰ methylenation of olefins¹¹ and annulation reactions.¹² In recent years, **1** has become one of the best new-generation catalysts and plays an important role in organic synthesis.

[Pd(*t*-Bu₃P)₂] is commercially available and can also be prepared by treating [Pd(η⁵-C₅H₅)(η³-C₃H₅)] with the ligand [*t*-Bu₃P] in *n*-hexane at room temperature for 3 h.¹³ The pale red crude product can be recrystallized from *n*-hexane at –20 °C to give pure colorless crystals.

Figure 1 Bis(tri-*tert*-butylphosphine)palladium

Table 1 The Use of Bis(tri-*tert*-butylphosphine)palladium(0) [Pd(*t*-Bu₃P)₂]

[Pd(*t*-Bu₃P)₂]-Catalyzed Cross-Coupling of Organolithium Reagents
Feringa and coworkers reported [Pd(*t*-Bu₃P)₂]-catalyzed cross-coupling reactions between alkyllithium reagents and a variety of aryl- and alkenylbromides under mild conditions.¹ Those cross-coupling reactions are highly selective, avoiding lithium–halogen exchange and homocoupling side reactions. The authors also extended the cross-coupling reactions to (hetero)aryllithium reagents by using the in situ prepared catalyst [Pd₂(dba)₃] and [*t*-Bu₃P] as ligand.

[Pd(*t*-Bu₃P)₂]-Catalyzed Cross-Coupling of Alkali-Metal Silanolates
A broadly applicable protocol for the [Pd(*t*-Bu₃P)₂]-catalyzed cross-coupling of a wide range of alkali metal arylsilanolates with various aryl halides was developed.³ This method also applied to the cross-coupling of heteroarylsilanolates.

[Pd(*t*-Bu₃P)₂]-Catalyzed Arylation of Hydrosiloxanes
Symmetrical and unsymmetrical siloxanes were synthesized by [Pd(*t*-Bu₃P)₂]-catalyzed arylation of hydrosiloxanes.⁵ This method was a one-pot process and showed high functional group tolerance. It was also exploited to perform triple arylations.

[Pd(*t*-Bu₃P)₂]-Catalyzed Decarboxylative Cross-Coupling Reaction

Forgione, and Bilodeau and coworkers developed a procedure for highly selective Pd-catalyzed decarboxylative cross-coupling reactions between heteroaromatic carboxylic acids and various aryl halides in the presence of a reactive C-H group.⁶ 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 [(*t*-Bu₃P)(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 diastereo-selectivities, which was thought to originate from the minimization of axial–axial interactions in the carbopalladation 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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