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

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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 amination, but also for cross-coupling of organolithium reagents,1 alkynylgermanes,2 alkali-metal silanolates,3 triarylsilanes,4 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 next-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(nido-C₃H₅)][η₃-C₇H₅] 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](image)

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

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Conditions</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(t-Bu₃P)₂]-Catalyzed Cross-Coupling of Organolithium Reagents</td>
<td>PhMe, r.t.</td>
<td>43–99%</td>
</tr>
<tr>
<td>[Pd(t-Bu₃P)₂]-Catalyzed Cross-Coupling of Alkali-Metal Silanolates</td>
<td>PhMe, r.t.</td>
<td>71–99%</td>
</tr>
<tr>
<td>[Pd(t-Bu₃P)₂]-Catalyzed Arylation of Hydrosiloxanes</td>
<td>PhMe, 90 °C</td>
<td>42–92% yield</td>
</tr>
</tbody>
</table>

Lu-Ying He was born in Sichuan, China, in 1986. She obtained her B.Sc. from Southwest University in 2008, China and studied at South China University of Technology from 2008 to 2011. Currently, she is working towards her Ph. D. at the Otto-Diels-Institute for Organic Chemistry under supervision of Prof. Dr. Anne Staubitz. Her research focuses on transition-metal-catalyzed cross-coupling reactions and semiconducting polymers with alternating heterocycle units.
[Pd(t-Bu₃P)₂]-Catalyzed Carboiodination

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 carboiodination of aryl iodides under mild conditions. 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).

References