**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(PPh₃)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, with electrophiles R-X (X = Cl, Br, I, OTf, SO₂Cl and others), but also for cross-coupling of organolithium reagents, alkanylgermanes, alkali-metal silanolates, triorganometallic reagents, and others. Moreover, it has been used for arylation of hydro-siloxanes, decarboxylative cross-coupling reactions, carboxylations and amino-carboxylations, carboiodinations, C-H functionalizations, cyano-, methylation of olefins and annihilation reactions. 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(n³-C₅H₇)(η¹-C₅H₇)] with the ligand [t-Bu₃P] in n-hexane at room temperature to give pure colorless crystals.

![Figure 1](https://example.com/bis(tri-tert-butylphosphine)palladium.png)

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

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>Yield (%)</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(t-Bu₃P)₂]</td>
<td>43–99%</td>
<td>25</td>
</tr>
<tr>
<td>[Pd₂(dba)₃]</td>
<td>71–99%</td>
<td>18</td>
</tr>
<tr>
<td>[Pd(t-Bu₃P)₂]</td>
<td>42–92%</td>
<td>50</td>
</tr>
</tbody>
</table>

**References**

1. Feringa and coworkers reported [Pd(t-Bu₃P)₂]-catalyzed cross-coupling reactions between allyl lithium reagents and a variety of aryl- and alkenylboronates under mild conditions. 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)aryl lithium reagents by using the in situ prepared catalyst [Pd₂(dba)₃] and [t-Bu₃P] as ligand.

2. A broadly applicable protocol for the [Pd(t-Bu₃P)₂]-catalyzed cross-coupling of a wide range of alkali metal aryilsilanes with various aryl halides was developed. This method also applied to the cross-coupling of heteroarylsilanes.

3. Symmetrical and unsymmetrical siloxanes were synthesized by [Pd(t-Bu₃P)₂]-catalyzed arylation of hydro-siloxanes. 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. 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.

[\text{[Pd(t-Bu₃P)₂]-Catalyzed Decarboxylative Cross-Coupling Reaction}}\]

\begin{align*}
  \text{Y} & = \text{NMe, O, S; Y} = \text{CH, N; Z} = \text{Me, H} \\
  \text{X} & = \text{Cl, Br, I, TIO}
\end{align*}

References


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