Bis(tri-tert-butylphosphine)palladium(0) \([\text{Pd}(t\text{-Bu}_3\text{P})_2]\)

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Introduction

The catalyst bis(tri-tert-butylphosphine)palladium(0) \([\text{Pd}(t\text{-Bu}_3\text{P})_2]\), 1, CAS: 53199-31-8 is a colorless, air-sensitive solid. It must be manipulated in a glove box or under inert gas. \([\text{Pd}(t\text{-Bu}_3\text{P})_2]\) (1) contains bulky, electron-rich tertiary phosphine ligands \([t\text{-Bu}_3\text{P}]\). 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 \([\text{Pd}(\text{Ph}_3\text{P})_2]\) catalyst. \([\text{Pd}(t\text{-Bu}_3\text{P})_2]\) is not only efficient for typical cross-coupling reactions, such as Stille, Negishi, Suzuki, Heck, Sonogashira, or Buchwald–Hartwig amination, with electrophiles \(R-X\) (\(X = \text{Cl, Br, I, OTf, SO}_2\text{Cl}\) and others), but also for cross-coupling of organolithium reagents, \(^1\) alkynylgermanes, \(^2\) alkali-metal silanolates, \(^3\) triorganometallic compounds, \(^4\) and others. Moreover, it has been used for arylation of hydro-siloxanes, \(^5\) decarboxylative cross-coupling reactions, \(^6\) carboiodinations, \(^7\) carbonylations and amino-carbonylations, \(^8\) carboxyldinations, \(^9\) C–H functionalizations, \(^9\) cyanations, \(^10\) methylation of olefins \(^11\) and annihilation reactions. \(^12\) In recent years, 1 has become one of the best new-generation catalysts and plays an important role in organic synthesis.

\([\text{Pd}(t\text{-Bu}_3\text{P})_2]\) is commercially available and can also be prepared by treating \([\text{Pd}(\text{η}^3\text{-C}_8\text{H}_3)(\text{η}^3\text{-C}_6\text{H}_3)]\) with the ligand \([t\text{-Bu}_3\text{P}]\) 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.

![Image](https://example.com/figure1.png)

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

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The Use of Bis(tri-tert-butylphosphine)palladium(0) ([\text{Pd}(t\text{-Bu}_3\text{P})_2])</th>
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</table>
| \([\text{Pd}(t\text{-Bu}_3\text{P})_2]\)-Catalyzed Cross-Coupling of Organolithium Reagents | \[\text{Ar}^1\text{Br} + \text{RL} \rightarrow [\text{Pd}(t\text{-Bu}_3\text{P})_2] \text{(6 mol%) \rightarrow Ar-R, PhMe, r.t.}] \]
| R = n-Bu, Me, t-Pr, n-Hex, TMS-CH\(_2\) | 25 examples 43–99% |
| \([\text{Pd}_2(\text{dba})_3]\) (2.5 mol%) | \([t\text{-Bu}_3\text{P}]\) (7.5 mol%) PhMe, r.t. 18 examples 71–99% |
| \([\text{Pd}(t\text{-Bu}_3\text{P})_2]\)-Catalyzed Cross-Coupling of Alkali-Metal Silanolates | A broadly applicable protocol for the \([\text{Pd}(t\text{-Bu}_3\text{P})_2]\)-catalyzed cross-coupling of a wide range of alkali metal arylsilanolates with various aryl halides was developed. \(^1\) This method also applied to the cross-coupling of heteroarylsilanolates. |
| \([\text{Pd}(t\text{-Bu}_3\text{P})_2]\)-Catalyzed Aarylation of Hydro-siloxanes | Symmetrical and unsymmetrical siloxanes were synthesized by \([\text{Pd}(t\text{-Bu}_3\text{P})_2]\)-catalyzed arylation of hydro-siloxanes. \(^5\) This method was a one-pot process and showed high functional group tolerance. It was also exploited to perform triple arylation. |
**References**


