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, but also for cross-coupling of organolithium reagents, alkynylgermanes, alkali-metal silanolates, triarylsilanes, and alkenylbromides 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)aryllithium reagents by using the in situ prepared catalyst [Pd2(dba)3] and [t-Bu3P] as ligand.

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

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pd(t-Bu3P)2] + Ar1-Br + Ar2Li</td>
<td>Ar1-Ar2</td>
<td>43–99%</td>
</tr>
<tr>
<td>[Pd(t-Bu3P)2] + RLi</td>
<td>PhMe, r.t.</td>
<td>71–99%</td>
</tr>
<tr>
<td>[Pd(t-Bu3P)2] + RLi</td>
<td>PhMe, 90 °C</td>
<td>42–92%</td>
</tr>
</tbody>
</table>

Figure 1 Bis(tri-tert-butylphosphine)palladium
[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.

[Pd(t-Bu₃P)₂]-Catalyzed Carboxylation 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. 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. 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.

References