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 alkylalkenylgermanes,2 alkali-metal silanolates,3 triorgano-indium reagents4 and others. Moreover, it has been used for arylation of hydro-siloxanes,5 decarboxylative cross-coupling reactions,6 carboxylations and amino-carbonylations,7 carboxidinations,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(t-Bu3P)2] 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.

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 | Ar—Br + RL → [Pd(t-Bu3P)2] (6 mol%) PhMe, r.t. | Ar→R | 25 examples | 43–99% |
| [Pd(t-Bu3P)2]-Catalyzed Cross-Coupling of Alkali-Metal Silanolates | Ar1—Br + Ar2Li → [Pd(t-Bu3P)2] (7.5 mol%) PhMe, r.t. | Ar1→Ar2 | 18 examples | 71–99% |
| [Pd(t-Bu3P)2]-Catalyzed Arylation of Hydro-siloxanes | R2 [Pd(t-Bu3P)2] (2.5–7.5 mol%) PhMe, 90 °C | R1 | 50 examples | 42–92% yield |

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.1 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, thiophyl 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 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 alkanyl aryl iodides in the presence of an amine base Et3N.4 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.5

References