Synlett L.-Y. He Spotlight

Bis(tri-*tert*-butylphosphine)palladium(0) [Pd(*t*-$Bu_3P)_2$]

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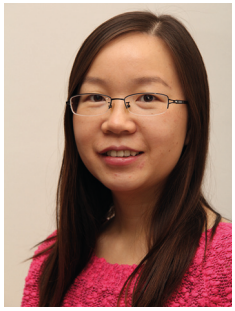
Lu-Ying He was born in Sichuan, China, in 1986. She obtained her B.Sc. from Southwest University in 2008, China and studied at South China University of Technology from 2008 to 2011. Currently, she is working towards her Ph. D. at the Otto-Diels-Institute for Organic Chemistry under supervision of Prof.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



Introduction

The catalyst bis(tri-*tert*-butylphosphine)palladium(0) [Pd(*t*-$Bu_3P)_2$, **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*-$Bu_3P)_2$] (**1**) contains bulky, electron-rich tertiary phosphine ligands [*t*-Bu_3P]. 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($Ph_3P)_4$] catalyst. [Pd(*t*-$Bu_3P)_2$] is not only efficient for typical cross-coupling reactions, such as Stille, Negishi, Suzuki, Heck, Sonogashira, or Buchwald–Hartwig aminations, with electrophiles R-X (X = Cl, Br, I, OTf, SO_2Cl and others), but also for cross-coupling of organolithium reagents,[1] alkenylgermanes,[2] alkali-metal silanolates,[3] triorgano-indium reagents[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 olefins[11] 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*-$Bu_3P)_2$] is commercially available and can also be prepared by treating [Pd(η^5-C_5H_5)(η^3-C_3H_5)] with the ligand [*t*-Bu_3P] 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.

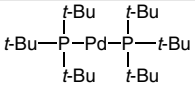


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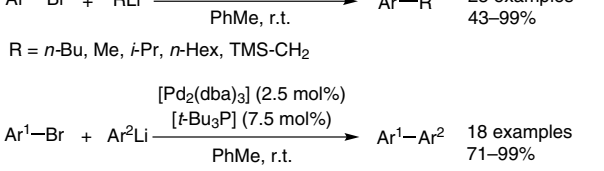
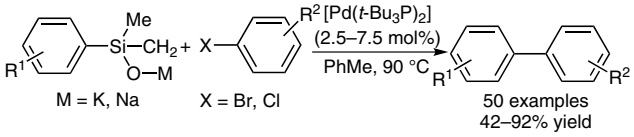
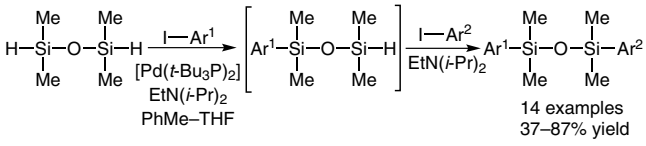
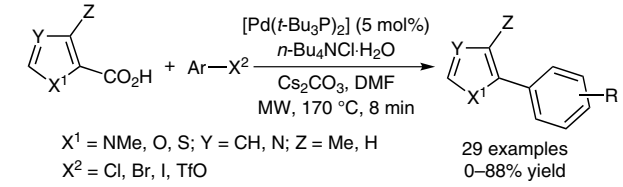
Figure 1 Bis(tri-*tert*-butylphosphine)palladium

Table 1 The Use of Bis(tri-*tert*-butylphosphine)palladium(0) [Pd(*t*-$Bu_3P)_2$]

[Pd(t-$Bu_3P)_2$]-Catalyzed Cross-Coupling of Organolithium Reagents Feringa and coworkers reported [Pd(*t*-$Bu_3P)_2$]-catalyzed cross-coupling reactions between alkyllithium reagents and a variety of aryl- and alkenylbromides under mild conditions.[1] 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 [$Pd_2(dba)_3$] and [*t*-Bu_3P] as ligand.	
[Pd(t-$Bu_3P)_2$]-Catalyzed Cross-Coupling of Alkali-Metal Silanolates A broadly applicable protocol for the [Pd(*t*-$Bu_3P)_2$]-catalyzed cross-coupling of a wide range of alkali metal arylsilanolates with various aryl halides was developed.[3] This method also applied to the cross-coupling of heteroarylsilanolates.	
[Pd(t-$Bu_3P)_2$]-Catalyzed Arylation of Hydrosiloxanes Symmetrical and unsymmetrical siloxanes were synthesized by [Pd(*t*-$Bu_3P)_2$]-catalyzed arylation of hydrosiloxanes.[5] This method was a one-pot process and showed high functional group tolerance. It was also exploited to perform triple arylations.	

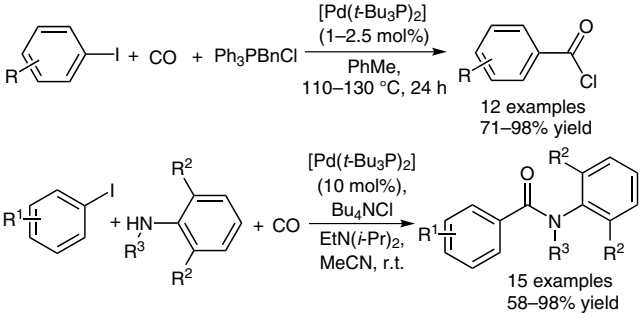
[Pd(t-Bu$_3$P)$_2$]-Catalyzed Decarboxylative Cross-Coupling Reaction

Forgione, and Biloudeau 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.[6] 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.



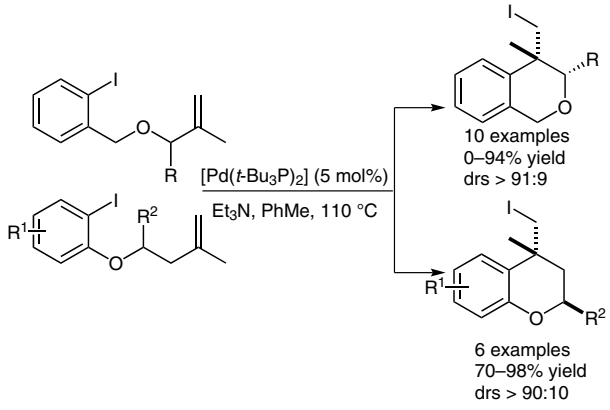
[Pd(t-Bu$_3$P)$_2$]-Catalyzed Carbonylation and Aminocarbonylation

Traditional methods to synthesize acid chloride involve toxic reagents, such as PCl_3, thionyl chloride and oxalyl chloride. Quesnel and Arndtsen described a new method to construct acid chlorides via the [Pd(*t*-Bu$_3$P)$_2$]-catalyzed carbonylation of aryl iodides under mild conditions.[7] The decisive step of the process was reductive elimination of [(*t*-Bu$_3$P)(CO)Pd(COAr)Cl], which was facilitated by the combination of the bulky, electron-rich [*t*-Bu$_3$P], 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).



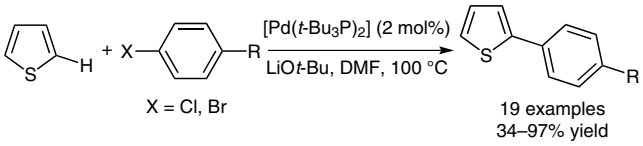
[Pd(t-Bu$_3$P)$_2$]-Catalyzed Carboiodination

Various functionalized chromans and isochromans were prepared via the intramolecular [Pd(*t*-Bu$_3$P)$_2$]-catalyzed carboiodination of alkenyl aryl iodides in the presence of an amine base Et_3N.[8] 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-Bu$_3$P)$_2$]-Catalyzed C-H Functionalization

Tamba and coworkers described a facile [Pd(*t*-Bu$_3$P)$_2$]-catalyzed C-H arylation of heteroarene compounds with aryl bromides and aryl chlorides in the presence of LiO*t*-Bu as a base.[9]



References

(1) Giannerini, M.; Fananas-Mastral, M.; Feringa, B. L. *Nature Chem.* **2013**, *5*, 667.
(2) Matsumoto, K.; Shindo, M. *Adv. Synth. Catal.* **2012**, *354*, 642.
(3) Denmark, S. E.; Smith, R. C.; Chang, W. T. T.; Muhuhi, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 3104.
(4) Riveiros, R.; Saya, L.; Sestelo, J. P.; Sarandeses, L. A. *Eur. J. Org. Chem.* **2008**, 1959.
(5) Kurihara, Y.; Yamanoi, Y.; Nishihara, H. *Chem. Commun.* **2013**, *49*, 11275.
(6) (a) Forgione, P.; Brochu, M. C.; St-Onge, M.; Thesen, K. H.; Bailey, M. D.; Bilodeau, F. *J. Am. Chem. Soc.* **2006**, *128*, 11350. (b) Bilodeau, F.; Brochu, M. C.; Guimond, N.; Thesen, K. H.; Forgione, P. *J. Org. Chem.* **2010**, *75*, 1550.
(7) Quesnel, J. S.; Arndtsen, B. A. *J. Am. Chem. Soc.* **2013**, *135*, 16841.
(8) Petrone, D. A.; Malik, H. A.; Clemenceau, A.; Lautens, M. *Org. Lett.* **2012**, *14*, 4806.
(9) Tamba, S.; Okubo, Y.; Tanaka, S.; Monguchi, D.; Mori, A. *J. Org. Chem.* **2010**, *75*, 6998.
(10) Littke, A.; Soumeillant, M.; Kaltenbach, R. F.; Cherney, R. J.; Tarby, C. M.; Kiau, S. *Org. Lett.* **2007**, *9*, 1711.
(11) den Hartog, T.; Toro, J. M. S.; Chen, P. *Org. Lett.* **2014**, *16*, 1100.
(12) Nazare, M.; Schneider, C.; Lindenschmidt, A.; Will, D. W. *Angew. Chem. Int. Ed.* **2004**, *43*, 4526.
(13) Otsuka, S.; Yoshida, T.; Matsumoto, M.; Nakatsu, K. *J. Am. Chem. Soc.* **1976**, *98*, 5850.