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21. Phosphine-Free Hydrazone-Pd Complex as the Catalyst Precursor for a Suzuki-Miyaura Reaction under Mild Aerobic Conditions

By Mino, Takashi; Shirae, Yoshiaki; Sakamoto, Masami; Fujita, Tsutomu
From Journal of Organic Chemistry (2005), 70(6), 2191-2194. | Language: English, Database: CAPLUS

Glyoxal bis(N-methyl-N-phenylhydrazone) and its related compds., such as 2-pyridinecarboxaldehyde N-methyl-N-phenylhydrazone, were prep. and examd. as ligands for the Suzuki-Miyaura cross-coupling reaction of aryl halides and arylboronic acids. Phosphine-free catalysts, such as Pd(OAc)₂ combined with the hydrazone ligands are efficient catalysts for a variety of substrates to produce the coupling products in good yields.

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1. Simple Amino-Pd(OAc)₂-Catalyzed Suzuki Coupling Reactions

By Tao, Bin; Bocelli, David W.
From Journal of Organic Chemistry (2004), 69(13), 4330-4335. | Language: English, Database: CAPLUS

A new palladium catalyst, trans-Pd(OAc)₂(Cy₂NH), is available, using Suzuki coupling coupling products in good to high yields. The air-stable catalyst was characterized and well-defined by X-ray crystallog. A catalytic system involving DAPCy in dioxane demonstrates a temp.-dependent reactivity toward aryl bromides with different electronic substituents, and selectively couples electron-deficient aryl bromides with boronic acids over electron-rich ones at room temp. Another catalytic system employing DAPCy in EtOH provides a general and convenient method to prep. biaryls from aryl bromides and boronic acids with a broad range of functional groups at room temp. and under aerobic conditions.

2. Trans-Pd(OAc)₂(Cy₂NH)₂ catalyzed Suzuki coupling reactions and its temperature-dependent activities toward aryl bromides

By Tao, Bin; Bocelli, David W.
From Tetrahedron Letters (2003), 44(43), 7993-7996. | Language: English, Database: CAPLUS

A new catalytic system based on complexes of Pd(OAc)₂ with simple amines was developed for Suzuki coupling reactions of aryl bromides. A well-defined air-stable complex, trans-Pd(OAc)₂(Cy₂NH) (Cy = cyclohexyl) effectively promotes Suzuki couplings of aryl bromides R¹Br (R¹ = 4-O₂NC₆H₄, 4-OMeC₆H₄, 4-MeOC₆H₄, etc.) with a range of arylboronic acids R²B(OH)₂ (R² = Ph, 4-PhC₆H₄, 2-MeC₆H₄, 3-O₂NC₆H₄) to give diaryl products R¹R² in high yields. This complex also exhibits temp.-dependent activity toward aryl bromides bearing different electronic substituents under reaction conditions.

3. Phosphine free Suzuki Miyaura reactions catalyzed by bihydrazone-Pd complex

By Mino, Takashi; Shirae, Yoshiaki; Sakamoto, Masami; Fujita, Tsutomu
From Synlett (2003), (8), 802-804. | Language: English, Database: CAPLUS

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1. Modified (NHC)Pd(allyl)Cl (NHC = N-Heterocyclic Carbene) Complexes for Buchwald-Hartwig Reactions

By Marion, Nicolas; Navaro, Oscar; Mei, Zhenqun; Stevens, Edwin D.; Scott, Natalie H.; Bulan, Soren
From Journal of the American Chemical Society (2006), 128(32), 4103-4111. | Language: English, Database: CAPLUS

A series of heterocyclic carbene (NHC = N,N-bis(2,6-diisopropyl-3,5-dimethylphenyl)-4,5-dihydroimidazol-2-ylidene; R = H, Me, gem-Me₂, Ph) have been synthesized and fully characterized. When compared to (NHC)Pd(allyl)Cl, substitution at the terminal position of the allyl scaffold favors a more facile activation step. This translates into higher catalytic activity in the Suzuki-Miyaura and Buchwald-Hartwig reactions, allowing for the coupling of unactivated aryl chlorides at room temp. in minutes. In the Suzuki-Miyaura reaction, aryl triflates, bromides, and chlorides react with boronic acids using very low catalyst loading. In the N-arylation reaction, a wide range of substrates has been coupled efficiently: primary and secondary alkyl- or aryl-amines react in high yields with unactivated, neutral, and activated aryl chlorides and bromides. In both reactions, extremely hindered substrates such as tri-ortho-substituted biaryls and tetra-ortho-substituted diarylamines can be produced without loss of activity. Finally, the present catalytic system has proven to be efficient with as low as 10 parts-per-million (ppm) of precatalyst in the Buchwald-Hartwig reaction and 50 ppm in the Suzuki-Miyaura reaction.

2. Palladium-Catalyzed Benzene Arylation: Incorporation of Catalytic Pivalic Acid as a Proton Shuttle and a Key Element in Catalyst Design

By Lefranc, Marc; Fujino, Kazuhiro
From Journal of the American Chemical Society (2006), 128(31), 16496-16497. | Language: English, Database: CAPLUS

A palladium-pivalic acid cocatalyst system that exhibits unprecedented reactivity in direct arylation has been developed. This reactivity is illustrated with the first examples of high yielding direct metalation-arylation reactions of a completely unactivated arene, benzene. Exptl. and computational evidence indicates that the pivalate anion is a key component in the palladation/C-H bond breaking event, that it lowers the

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