

Palladium bis(2,2,6,6-tetramethyl-3,5-heptanedionate) catalyzed Suzuki, Heck, Sonogashira, and cyanation reactions

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Abstract

Palladium bis(2,2,6,6-tetramethyl-3,5-heptanedionate): a structurally well-defined *O*-containing transition metal complex is reported as an efficient catalyst for Suzuki, Heck, and Sonogashira cross-coupling reactions. The protocol was also applied successfully for cyanation of aryl halides under milder operating conditions. The system tolerated the coupling of various aryl halides with alkenes, alkynes, and organoboronic acid along with the cyanation of aryl halides providing good to excellent yields of desired products.

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Keywords: Suzuki reaction; Heck reaction; Sonogashira reaction; Cyanation reaction; TMHD–palladium complex

1. Introduction

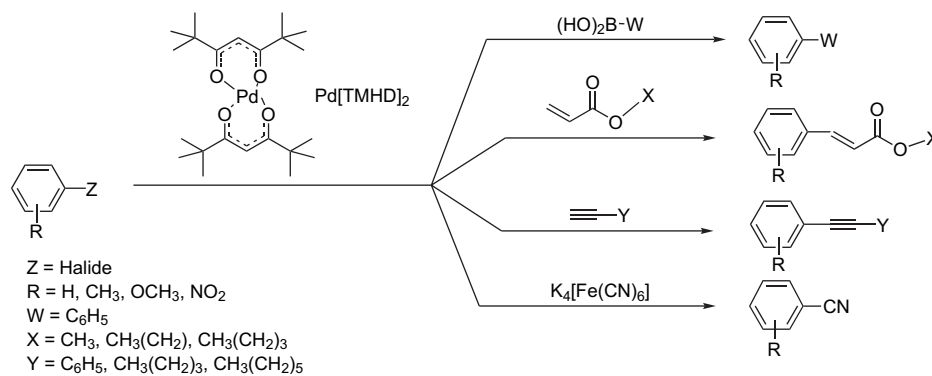
Homogenous catalysts offer some important advantages over their heterogeneous counterparts.^{1,2} Such catalysts can usually be dissolved in reaction media making all catalytic sites accessible to reactants in solution. In addition many homogenous catalysts demonstrate high selectivity and can be utilized to control the stereochemistry and regiochemistry of the reaction products. Because of these advantages the formation of carbon–carbon bonds via homogenous palladium catalyzed cross-coupling reactions has become an essential tool for synthetic organic chemists. In C–C bond formation reactions particular attention has been paid to the coupling of aryl halides with organoboronic acids (Suzuki cross-coupling reaction),³ alkenes (Heck reaction),⁴ and alkynes (Sonogashira cross-coupling reaction),⁵ respectively. These Pd-catalyzed cross-coupling reactions are ranked today among the most general transformations in organic synthesis, which have great industrial potential for the synthesis of chemicals, therapeutic drugs, and their intermediates. Several groups have extended these methodologies for coupling of aryl halides employing catalyst such as (a) (AdNC)₂PdCl₂,⁶ Pd(OAc)₂/TBAB,⁷

Pd-NHC,⁸ [C₃CNpy]₂[PdCl₄],⁹ etc. for Suzuki reaction; (b) Pd/DPPP [DPPP=1,3-bis(diphenyl phosphinopropane)],¹⁰ Pd-TXPTS [TXPTS=tris(4,6-dimethyl-3-sulfonatophenyl) phosphine],¹¹ Pd/C-Aliquot,¹² Pd(OAc)₂/[bmim]PF₆,¹³ etc. for Heck reaction; and (c) Pd(OAc)₂/DABCO,¹⁴ Cyclopalladated ferrocenyl imines,¹⁵ PdCl₂(PPh₃),¹⁶ PdCl₂/pyrrolidine,¹⁷ MCM-41-S-Pd(O),¹⁸ etc. for Sonogashira cross-coupling reaction. The reaction system mostly employs an in situ generated catalyst from a Pd source and highly efficient N/P containing ligand. In spite of the significant advances in this area, very few reports employ a structurally well-defined Pd complex as a catalyst.¹⁹ Thus, there is a need to develop a chemically well-defined, air stable single-component Pd complex as a versatile catalyst for Suzuki, Heck, Sonogashira, and cyanation reactions. Previously, we reported C- and N-arylation of heterocycles and carbonylative Sonogashira coupling reaction using a preformed Pd and Cu bis(2,2,6,6-tetramethyl-3,5-heptanedionate) as the catalyst.²⁰ The use of 2,2,6,6-tetramethyl-3,5-heptanedione (TMHD) as a ligand resulted in excellent yields of products and such reactivity could be attributed to the fact that a good balance exists between the steric and electronic properties of the complex.

Herein, we report a facile Suzuki, Heck, Sonogashira, and cyanation reactions catalyzed by a well-defined *O*-containing transition metal complex, via Pd bis(2,2,6,6-tetramethyl-3,5-

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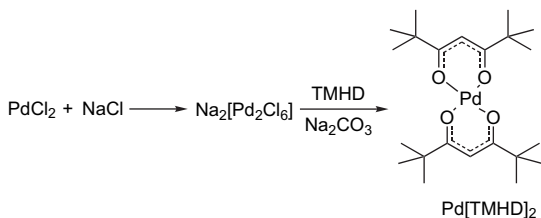
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Scheme 1. Pd(TMHD)₂ catalyzed Suzuki, Heck, Sonogashira, and cyanation reactions.

heptanedionate) [Pd(TMHD)₂] in an efficient manner (Scheme 1). The ease of preparation of the complex, its high solubility in organic solvents, indefinite shelf life, stability toward air, and compatibility with a wide variety of aryl halides, phenylboronic acid, alkenes, and alkynes, make it an ideal complex for the above transformations.

2. Result and discussion

Diketonates of Pd have been prepared by treating PdCl₂ with NaCl to form Na₂[Pd₂Cl₆] [sodium hexa chlorodipalladate(II)]. Further adding a methanol solution of Na₂[Pd₂Cl₆] to more than 2 equiv of free TMHD ligand followed by an appropriate amount of sodium carbonate results in the formation of the corresponding Pd(TMHD)₂ complex (Scheme 2).

Scheme 2. Synthesis of Pd(TMHD)₂ from palladium chloride and TMHD.

In order to explore its catalytic activity, we examined Pd(TMHD)₂ (A) along with Pd(acac)₂ (B), Cu(TMHD)₂ (C), and Ni(TMHD)₂ (D) as catalyst for (a) Suzuki, (b) Heck, (c) Sonogashira, and (d) cyanation reactions (Table 1). Cu and Ni(TMHD)₂ catalysts were found to be completely ineffective under the present conditions. Pd(acac)₂ was found to provide good yield. However, Pd(TMHD)₂ was found to be highly active catalyst providing excellent yield of desired product for all the above transformations and was used for further studies.

2.1. Suzuki reactions

Initially the reaction of iodobenzene with phenylboronic acid was studied as a model reaction and the role of various bases like Na₂CO₃ (98%), K₂CO₃ (98%), and piperidine (25%), and solvents like toluene (75%), *N,N*-dimethylformamide [DMF] (97%), 1,4-dioxane (69%), and water (98%)

Table 1

Effect of catalysts on Suzuki, Heck, Sonogashira, and cyanation reactions

Entry	Catalyst	Yield ^a (%)			
		Suzuki ^a	Heck ^b	Sonogashira ^c	Cyanation ^d
1	A	98	98	97	96
2	B	87	85	79	83
3	C	15	—	12	5
4	D	—	—	10	3

^a Reaction conditions: iodobenzene (1 mmol), phenylboronic acid (1.2 mmol), catalyst (5 mol %), K₂CO₃ (2 mmol), water (5 ml), 16 h at 80 °C.

^b Iodobenzene (1 mmol), methylacrylate (1.2 mmol), catalyst (5 mol %), K₂CO₃ (2 mmol), DMF (5 ml), 12 h at 80 °C.

^c Iodobenzene (1 mmol), phenylacetylene (1.2 mmol), catalyst (5 mol %), triethylamine (2 mmol), water (5 ml), 4 h at rt.

^d K₄Fe(CN)₆ (1 mmol), iodobenzene (1.3 mmol), catalyst (5 mol %), triethylamine (2 mmol), DMF (5 ml), 5 h at 90 °C.

^e GC yields.

was screened using Pd(TMHD)₂ as catalyst. It was observed that the reaction was more favorable using K₂CO₃ as base and environmentally benign water as solvent. The efficiency of this system was further extended for coupling of various aryl halides having different steric and electronic properties with phenylboronic acid. The results are summarized in Table 2. Phenylboronic acid was found to couple smoothly with iodobenzene providing an excellent yield (96%) of desired product. The reaction also worked well with less reactive bromobenzene providing 92% yield. Electron donating groups such as methyl and methoxy, and withdrawing group such as nitro were well tolerated under the present catalytic system (entries 3–5). Heterocyclic aryl halide like iodothiophene was also found to react smoothly under the present conditions (entry 6). Sterically hindered iodonaphthalene also reacted efficiently providing 83% yield of the desired product (entry 7).

2.2. Heck reactions

The scope of this methodology was further extended for Heck reaction. Using Pd(TMHD)₂ as catalyst bases like Na₂CO₃ (89%), K₂CO₃ (98%), and Cs₂CO₃ (60%) and solvents like toluene (87%), DMF (98%), and NMP (90%) were screened for the standard reaction. It was observed that the reaction was more favorable using K₂CO₃ as base and DMF as solvent and the protocol was applied for coupling

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