SYNLETT
Spotlight 365

[1,2-Bis(phenylsulfinyl)ethane]-palladium Acetate

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Introduction

[1,2-Bis(phenylsulfinyl)ethane]-palladium acetate 1, the ‘White catalyst’, was developed by M. Christina White and co-workers at the University of Illinois–Urbana. It has been shown to be an excellent, air-stable catalyst for the functionalization of allylic carbon centers.¹ The bis-sulfoxide palladium(II) catalyst participates in a number of important reactions including allylic C–H oxidation,² inter- and intramolecular alkylations,³ sequential hydrocarbon functionalization,⁴ macrolactonizations,⁵ allylic C–H amination⁶ and intermolecular oxidative Mizoroki–Heck reactions.⁷ These useful transformations allow for rapid access to an array of synthetically useful moieties, such as allylic carboxylates, macrocycles, and amino alcohol derivatives.

Abstracts

(A) The first documented use of this catalyst described an allylic C–H oxidation reaction for the preparation of allylic carboxylate compounds from substituted or unsubstituted alkenes and carboxylic acids.² These reactions can be performed in both an inter- or intramolecular fashion, the latter allowing access to highly functionalized, large-ring macrolactone products.⁵

(B) The catalyst was also used in the first catalytic direct alkylation of allylic C–H bonds via Pd(II) catalysis in the absence of base.³ Shi and co-workers employed this methodology for the alkylation of 1,3-diketones.² White and colleagues applied this methodology to furnish a wide range of linear (E),(R)-nitroarylpentenoates from aromatic and heteroaromatic allyl compounds alkylated with methyl nitroacetate.³ These products can serve as nuclophiles in asymmetric conjugate additions to generate enantiomerically enriched, unnatural R,R-disubstituted amino acid precursors.
(C) Compound 1 has also been reported to be highly effective in one-pot sequential allylic oxidation/C–H arylation reactions to afford the E-arylated allylic ester from the corresponding olefin, carboxylic acid, and aryloboronic acid.

(D) The catalyst has also been employed in the first general and stereoselective Pd(II)-catalyzed allylic C–H aminations, yielding functionalized oxazolidinones from N-tosylcarbamate precursors. This process is selective for the anti-oxazolidinone diastereomer, from which syn-1,3-amino alcohol precursors are easily obtained. White also demonstrated the use of a more electron-deficient N-aryl carbamate nucleophile, which furnishes vinyl syn-1,3-amino alcohol precursors from terminal olefins. Nahra et al. has demonstrated that when ace-}

(E) The White catalyst has been utilized in novel chelate-controlled intermolecular oxidative Heck reactions. These reactions proceed with a wide range of non-resonance stabilized α-olefin substrates and organoboron reagents. The catalyst is sensitive to chelation effects from proximal oxygen and nitrogen moieties resulting in excellent regioselectivities for olefin insertion.

(F) Catalyst 1 has also been used by White to forge complex allylic esters by combining carboxylic acids and terminal olefins. This method employs mild conditions, such as low loadings of carboxylic acid and catalytic base, which enables broadening of the substrate scope. The method also facilitates the introduction of a oxygen functionality late in the synthetic sequence.

References


