

SYNLETT Spotlight 365

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

Compiled by Christina McSweeney



This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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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.

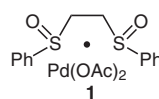
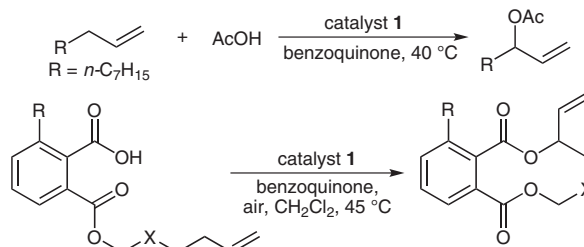


Figure 1 White catalyst

Bis-sulfoxide palladium(II) acetate complex **1** is commercially available and can also be prepared via routine metal complexation with 1,2-bis(phenylmethanesulfinyl)ethane in dichloromethane at 40 °C.⁸

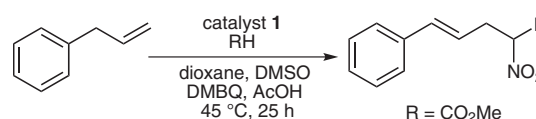
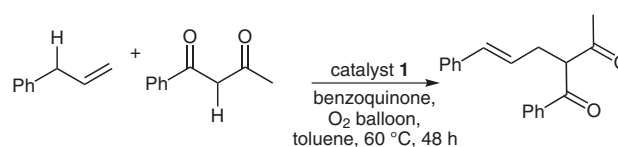
Abstracts

(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

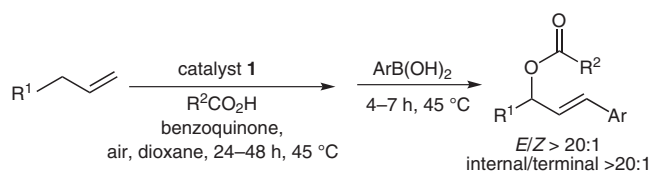


X = (CH₂)₅, R = H, OH, OCH₂OMe, OCH₂Ph; X = (CH₂)_n, n = 6–8

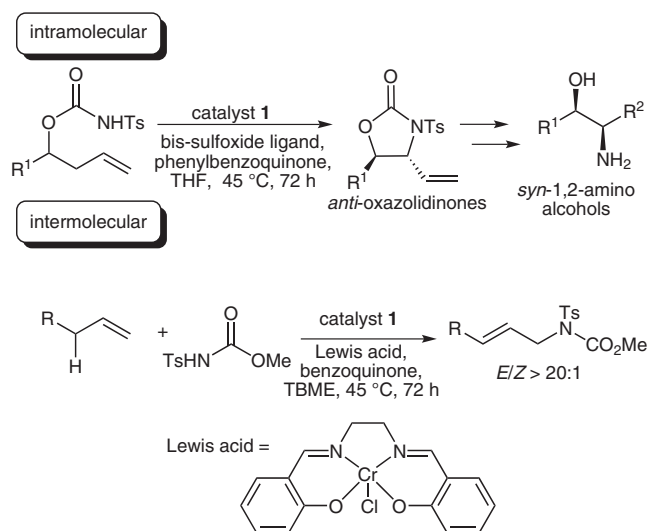
(B) The catalyst was also used in the first catalytic direct alkylation of allylic C–H bonds via Pd(II) catalysis in the absence of base.³ Shi and co-workers employed this methodology for the alkylation of 1,3-diketones.^{3a} White and colleagues applied this methodology to furnish a wide range of linear (*E*),(*R*)-nitroaryl pentenoates from aromatic and heteroaromatic allyl compounds alkylated with methyl nitroacetate.^{3b} These products can serve as nucleophiles in asymmetric conjugate additions to generate enantiomerically enriched, unnatural *R,R*-disubstituted amino acid precursors.



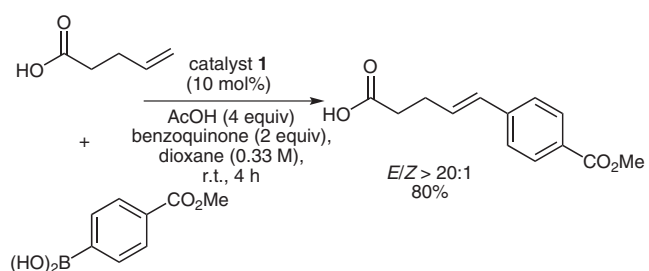
(C) Compound **1** has also been reported to be highly effective in one-pot sequential allylic oxidation/C–H arylation reactions to afford the *E*-arylated allylic ester from the corresponding olefin, carboxylic acid, and arylboronic acid.⁴



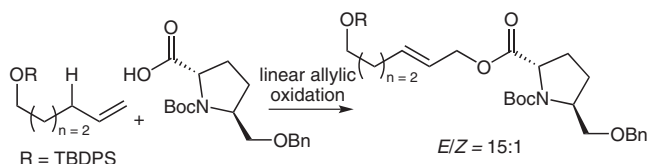
(D) The catalyst has also been employed in the first general and stereoselective Pd(II)-catalyzed allylic C–H aminations, yielding functionalized oxazolidinones from *N*-tosylcarbamate precursors.^{6a} This process is selective for the *anti*-oxazolidinone diastereomer, from which *syn*-1,2 amino alcohols are easily obtained. White also demonstrated the use of a more electron-deficient *N*-tosyl carbamate nucleophile, which furnishes vinyl *syn*-1,3-amino alcohol precursors from terminal olefins.^{6b} Nahra et al. has demonstrated that when acetic acid instead of THF was used as solvent, under White's conditions, a significant increase in the reaction rate is observed.⁹ Catalyst **1** has also been used in intermolecular allylic aminations using *O*-methyl-*N*-tosylcarbamate as the amination reagent.^{6c} Here the Pd(II)-bis(sulfoxide) operated in combination with a [Cr^{III}Cl(salen)] Lewis acid catalyst to obtain the linear allylic *N*-tosylcarbamate in good yield, regio- and diastereoselectivity.



(E) The White catalyst has been utilized in novel chelate-controlled intermolecular oxidative Heck reactions.⁷ 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.^{2c} 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

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