

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

Christina McSweeney was born in Co.Cork, Ireland in 1986. She received a B.Sc. in Chemistry from the University College Cork in 2009, and is currently pursuing a Ph.D. under the supervision of Dr. Gerard P. McGlacken at University College Cork. Her current research is focused on the asymmetric α -alkylation of ketones.

Chemistry Department and Analytical and Biological Chemical Research Facility, University College Cork, Co.Cork, Ireland
E-mail: 105011272@umail.ucc.ie

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.

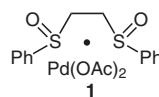
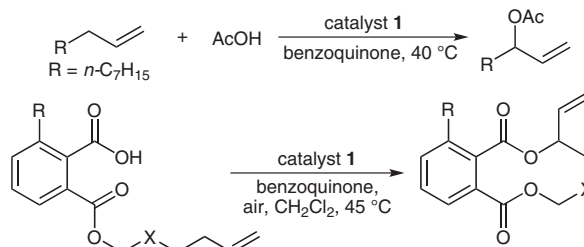


Figure 1 White catalyst

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

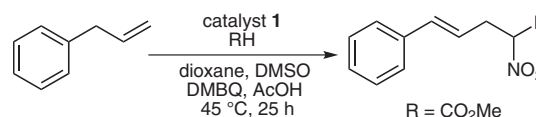
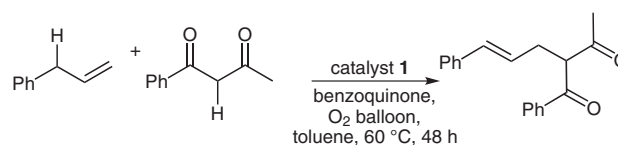
Abstracts

(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

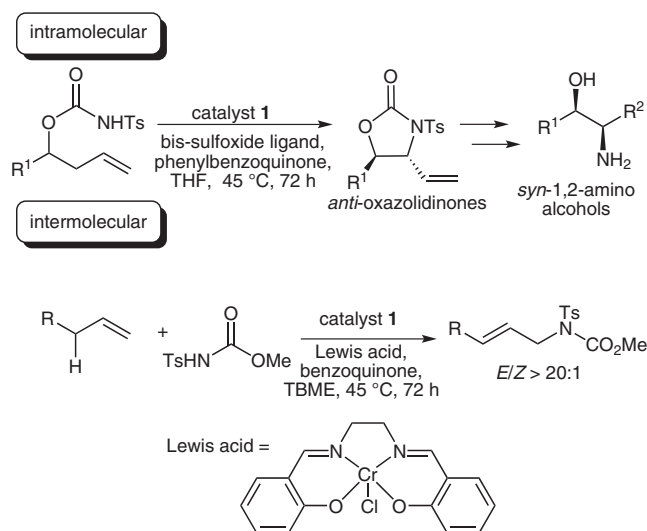
(B) The catalyst was also used in the first catalytic direct alkylation of allylic C–H bonds via Pd(II) catalysis in the absence of base.³ Shi and co-workers employed this methodology for the alkylation of 1,3-diketones.^{3a} White and colleagues applied this methodology to furnish a wide range of linear (*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.



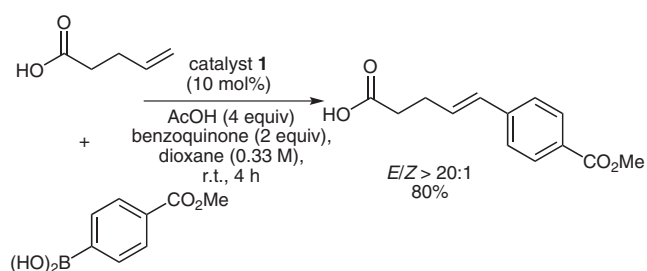
(C) Compound **1** has also been reported to be highly effective in one-pot sequential allylic oxidation/C–H arylation reactions to afford the *E*-arylated allylic ester from the corresponding olefin, carboxylic acid, and arylboronic acid.⁴



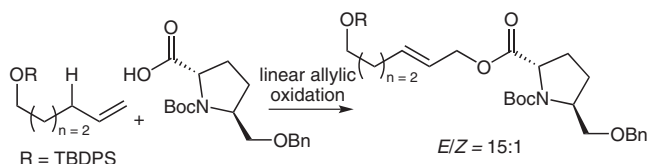
(D) The catalyst has also been employed in the first general and stereoselective Pd(II)-catalyzed allylic C–H aminations, yielding functionalized oxazolidinones from *N*-tosylcarbamate precursors.^{6a} This process is selective for the *anti*-oxazolidinone diastereomer, from which *syn*-1,2 amino alcohols 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 an oxygen functionality late in the synthetic sequence.



References

- (1) Jazzar, R.; Hitce, J.; Renaudat, A.; Sofack-Kreutzer, J.; Baudoin, O. *Chem. Eur. J.* **2010**, *16*, 2654.
- (2) (a) Chen, M. S.; White, M. C. *J. Am. Chem. Soc.* **2004**, *126*, 1346. (b) Chen, M. S.; Prabakaran, N.; Labenz, N. A.; White, M. C. *J. Am. Chem. Soc.* **2005**, *127*, 6970.
- (c) Vermeulen, N. A.; Delcamp, J. H.; White, M. C. *J. Am. Chem. Soc.* **2010**, *132*, 11323.
- (3) (a) Lin, S.; Song, C.-X.; Cai, G.-X.; Wang, W.-H.; Shi, Z.-J. *J. Am. Chem. Soc.* **2008**, *130*, 12901. (b) Young, A. J.; White, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 14090.
- (4) Delcamp, J. H.; White, M. C. *J. Am. Chem. Soc.* **2006**, *128*, 15076.
- (5) (a) Fraunhoffer, K. J.; Prabakaran, N.; Sirois, L. E.; White, M. C. *J. Am. Chem. Soc.* **2006**, *128*, 9032. (b) Stang, E. M.; Christina, W. M. *Nat. Chem.* **2009**, *1*, 547.
- (6) (a) Fraunhoffer, K. J.; White, M. C. *J. Am. Chem. Soc.* **2007**, *129*, 7274. (b) Rice, G. T.; White, M. C. *J. Am. Chem. Soc.* **2009**, *131*, 11707. (c) Reed, S. A.; Mazzotti, A. R.; White, M. C. *J. Am. Chem. Soc.* **2009**, *131*, 11701.
- (7) Delcamp, J. H.; Brucks, A. P.; White, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 11270.
- (8) Pettinari, C.; Pellei, M.; Cavicchio, G.; Crucianelli, M.; Panzeri, W.; Colapietro, M.; Cassetta, A. *Organometallics* **1999**, *18*, 555.
- (9) Nahra, F.; Liron, F.; Prestat, G.; Mealli, C.; Messaoudi, A.; Poli, G. *Chem. Eur. J.* **2009**, *15*, 11078.