

# 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

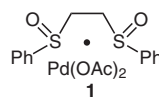
Christina McSweeney was born in Co.Cork, Ireland in 1986. She received a B.Sc. in Chemistry from the University College Cork in 2009, and is currently pursuing a Ph.D. under the supervision of Dr. Gerard P. McGlacken at University College Cork. Her current research is focused on the asymmetric  $\alpha$ -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.<sup>1</sup> The bis-sulfoxide palladium(II) catalyst participates in a number of important reactions including allylic C–H oxidation,<sup>2</sup> inter- and intramolecular alkylations,<sup>3</sup> sequential hydrocarbon functionalization,<sup>4</sup> macrolactonizations,<sup>5</sup> allylic C–H amination<sup>6</sup> and intermolecular oxidative Mizoroki–Heck reactions.<sup>7</sup> These useful transformations allow for

rapid access to an array of synthetically useful moieties, such as allylic carboxylates, macrocycles, and amino alcohol derivatives.

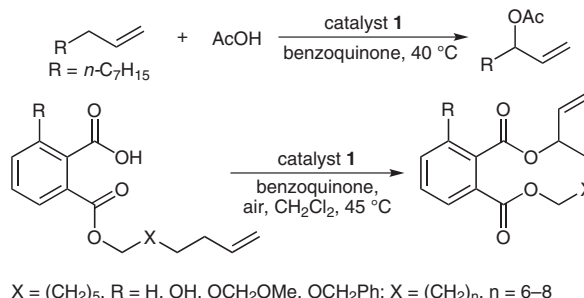


**Figure 1** White catalyst

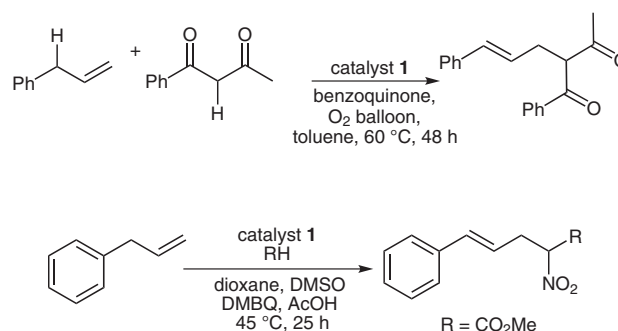
Bis-sulfoxide palladium(II) acetate complex **1** is commercially available and can also be prepared via routine metal complexation with 1,2-bis(phenylmethanesulfinyl)ethane in dichloromethane at 40 °C.<sup>8</sup>

### Abstracts

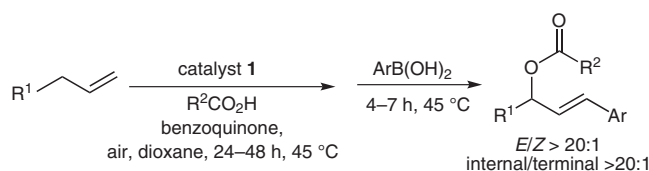
(A) The first documented use of this catalyst described an allylic C–H oxidation reaction for the preparation of allylic carboxylate compounds from substituted or unsubstituted alkenes and carboxylic acids.<sup>2</sup> These reactions can be performed in both an inter- or intramolecular fashion, the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



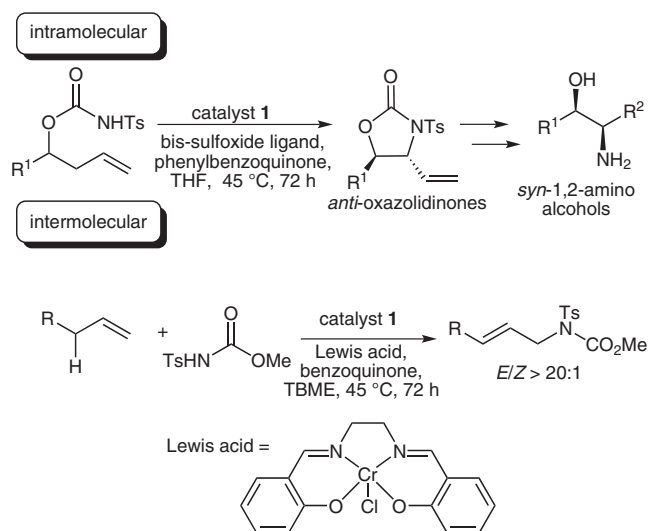
(B) The catalyst was also used in the first catalytic direct alkylation of allylic C–H bonds via Pd(II) catalysis in the absence of base.<sup>3</sup> Shi and co-workers employed this methodology for the alkylation of 1,3-diketones.<sup>3a</sup> White and colleagues applied this methodology to furnish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



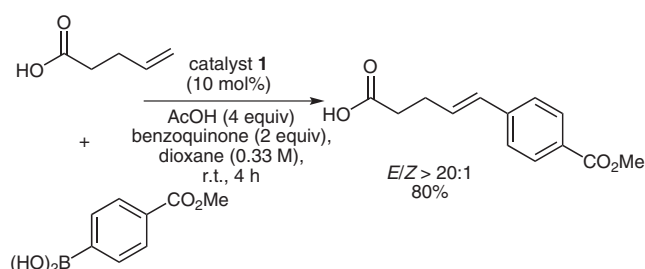
(C) Compound **1** has also been reported to be highly effective in one-pot sequential allylic oxidation/C–H arylation reactions to afford the *E*-arylated allylic ester from the corresponding olefin, carboxylic acid, and arylboronic acid.<sup>4</sup>



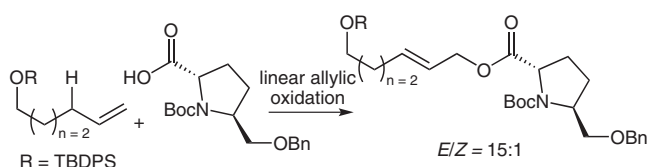
(D) The catalyst has also been employed in the first general and stereoselective Pd(II)-catalyzed allylic C–H aminations, yielding functionalized oxazolidinones from *N*-tosylcarbamate precursors.<sup>6a</sup> This process is selective for the *anti*-oxazolidinone diastereomer, from which *syn*-1,2 amino alcohols are easily obtained. White also demonstrated the use of a more electron-deficient *N*-nosyl carbamate nucleophile, which furnishes vinyl *syn*-1,3-amino alcohol precursors from terminal olefins.<sup>6b</sup> 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.<sup>9</sup> Catalyst **1** has also been used in intermolecular allylic aminations using *O*-methyl-*N*-tosylcarbamate as the amination reagent.<sup>6c</sup> Here the Pd(II)–bis(sulfoxide) operated in combination with a [Cr<sup>III</sup>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.<sup>7</sup> These reactions proceed with a wide range of non-resonance stabilized  $\alpha$ -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.<sup>2c</sup> 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

- (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.