

# An Improved Catalyst for the Cyclization/Hydrosilylation of Functionalized 1,6-Dienes Employing Dimethylphenylsilane

Ross A. Widenhoefer\* and Anand Vadehra

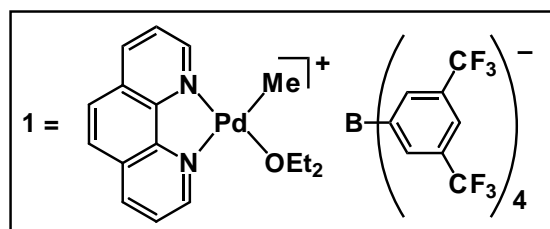
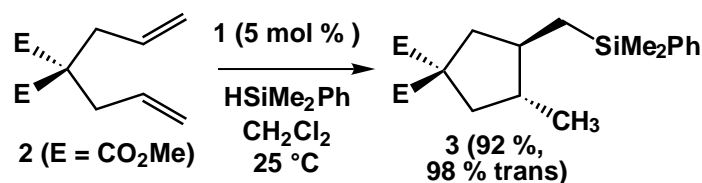
P. M. Gross Chemical Laboratory, Duke University, Durham, NC 27708-0346

**Abstract:** A 1:1 mixture of (Me<sub>4</sub>-phen)Pd(Me)Cl [Me<sub>4</sub>-phen = 3,4,7,8-tetramethyl-1,10-phenanthroline] and NaBAR<sub>4</sub> [Ar = 3,5-C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>] catalyzed the cyclization/hydrosilylation of functionalized 1,6-dienes with dimethylphenylsilane within minutes at room temperature to form silylated cyclopentanes in good yield with high trans-selectivity.

*Keywords:* catalysis, cyclization, dienes, palladium

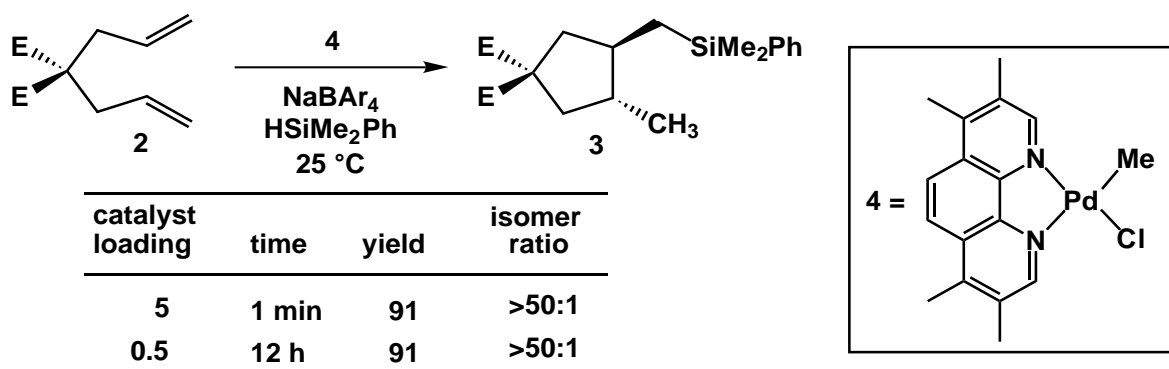
## Introduction

We recently reported several related protocols for the cyclization/hydrosilylation of functionalized dienes catalyzed by cationic palladium complexes such as [(phen)Pd(OEt<sub>2</sub>)Me]<sup>+</sup> [BAR<sub>4</sub>]<sup>-</sup> [phen = 1,10-phenanthroline; Ar = C<sub>6</sub>H<sub>3</sub>(CF<sub>3</sub>)<sub>2</sub>] (**1**).<sup>1,2</sup> Unfortunately, these protocols were considerably more efficient with triethylsilane than with dimethylphenylsilane. Specifically, although **1** catalyzed the reaction of dimethyl diallylmalonate (**2**) and HSiMe<sub>2</sub>Ph to form the silylated cyclopentane **3** with good yield and selectivity (Scheme 1), dienes which did not possess the homoallylic gem(dicarbomethoxy) groups typically failed to undergo efficient cyclization/hydrosilylation with dimethylphenylsilane.<sup>1d</sup> Because a phenyl group or a heteroatom on the silane is required for oxidation to form the corresponding alcohol,<sup>3</sup> the failure of many substrates to undergo cyclization/hydrosilylation with HSiMe<sub>2</sub>Ph represented a serious limitation to the protocol. As a result, we sought to identify a more general catalyst for the cyclization/hydrosilylation of functionalized dienes employing dimethylphenylsilane and we report the preliminary results of this study herein.



Scheme 1

The efficiency and selectivity of transition metal catalyzed processes can be strongly effected by the nature of the ancillary ligands on the metal complex. As a result, we reasoned that the proper choice of ligand might produce a cyclization/hydrosilylation catalyst suitable for use in conjunction with HSiMe<sub>2</sub>Ph. However, because palladium complexes ligated with bidentate phosphine ligands such as dimethylphosphinoethane or amine ligands such as *N,N,N',N'*-tetramethylenediamine were ineffective as cyclization/hydrosilylation catalysts, it became apparent that a less drastic perturbation in the ligand was required. To this end, a range of substituted 1,10-phenanthroline ligands were screened for activity in the palladium-catalyzed conversion of **2** to **3**. From this group of ligands, 3,4,7,8-tetramethyl-1,10-phenanthroline (Me<sub>4</sub>-phen) displayed particularly high reactivity. For example, a 1:1 mixture of the palladium methyl chloride complex (Me<sub>4</sub>-phen)Pd(Me)Cl (**4**) and NaBAR<sub>4</sub> (5 mol %)<sup>4</sup> converted **2** to **3** in 91 % yield as a single diastereomer within 1 min at room temperature and up to 200 turnovers were achieved employing this catalyst system (Scheme 2).<sup>5</sup>



**Scheme 2**

In addition to serving as an active catalyst for the conversion of **2** to **3**, **4** also served as a general precatalyst for the cyclization/hydrosilylation of 1,6-dienes employing HSiMe<sub>2</sub>Ph. For example, a 1:1 mixture of **4** and NaBAR<sub>4</sub> catalyzed the cyclization/hydrosilylation of 1,6-dienes possessing a homoallylic acetyl, phenyl, sulfonyl, cyano, carbamoyl, benzoyl, or acetoxy group to form the corresponding carbocycles in  $\geq 74$  % yield, typically within 5 min at room temperature (Table 1, entries 1-8). In contrast, cyclization/hydrosilylation of these substrates catalyzed by **1** required  $\geq 12$  h at room temperature and formed  $\leq 40$  % of the desired carbocycle.<sup>1d</sup> Dienes which possessed homoallylic ether or acetoxy groups also underwent facile cyclization/hydrosilylation to form carbocycles with excellent trans-selectivity (Table 1, entries 9-12). Likewise, the protocol tolerated substitution at an allylic carbon atom or at a terminal olefinic carbon atom without loss of reactivity (Table 1, entries 13-15). Although cyclization/hydrosilylation of these latter substrates with HSiMe<sub>2</sub>Ph was also catalyzed by **1**,<sup>1d</sup> reactions employing the catalyst generated from **4** were  $>25$  times faster.

In summary, a 1:1 mixture of the palladium methyl chloride complex (Me<sub>4</sub>-phen)Pd(Me)Cl (**4**) and NaBAR<sub>4</sub> catalyzed the cyclization/hydrosilylation of functionalized 1,6-dienes employing dimethylphenylsilane. The catalyst generated from **4** was both considerably more active and more general than the palladium phenanthroline catalyst **1** in cyclization/hydrosilylation reactions employing HSiMe<sub>2</sub>Ph.

**Table 1.** Cyclization/Hydrosilylation of functionalized dienes employing HSiMe<sub>2</sub>Ph catalyzed by (Me<sub>4</sub>-phen)Pd(Me)Cl (**4**) and NaBAR<sub>4</sub> (≤ 5 mol %) in DCE at 25 °C for 3-5 min.

entry	diene	carbocycle	yield (%) <sup>a</sup>	isomer ratio <sup>b</sup>	yield and time employing <b>1</b> <sup>c</sup>
1	E = COMe		74	2.1:1	40 %, 24 h
2	E = Ph		86	2.0:1	32 %, 12 h
3	E = SO <sub>2</sub> Me		77	1.7:1	NR, 12 h
4	E = CN		86	2.2:1	NR, 12 h
5	E = CONMe <sub>2</sub>		62	4.8:1	NR, 12 h
6			77	1:1	NR, 12 h
7 <sup>d</sup>	R = Me		90	2.3:1	42 %, 12 h
8 <sup>d</sup>	R = Ph		67	2.3:1	—
9	R = COMe		69	>50:1	41 %, 2 h
10	R = CO <sup>t</sup> Bu		94	>50:1	—
11	R = Bn		77	>50:1	—
12	R = Me		91	>50:1	72 %, 24 h
13	R = Me		75	20:1	78 %, 3 h
14	R = <i>n</i> -Bu		86	7:1	—
15			85	1:1	—

<sup>a</sup>Yield refers to isolated material of >95 % purity. <sup>b</sup>Isomer ratio determined by capillary GC. <sup>c</sup>Results employing catalyst **1** taken from reference 1d. <sup>d</sup>Reaction run for 30 min.

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5) Representative Procedure: Dimethylphenylsilane (250 mg, 3.01 mmol) was added to a solution of **2** (100 mg, 0.47 mmol), **4** (9 mg, 0.023 mmol), NaBAR<sub>4</sub> (24 mg, 0.023 mmol) in DCE (10 mL) at 0° C and then stirred for 5 minutes at room temperature. The resulting brown solution was concentrated under vacuum and the residue was chromatographed (SiO<sub>2</sub>, 24:1 hexane:EtOAc) to give **3** (149 mg, 91 %) as a colorless oil.