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An improved catalyst for the cyclization/hydrosilylation of functionalized 1,6-dienes employing dimethylphenylsilane

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Abstract

A 1:1 mixture of (Me_4-phen)Pd(Me)Cl [Me_4-phen=3,4,7,8-tetramethyl-1,10-phenanthroline] and $NaBAr_4$ [Ar=3,5-$C_6H_3(CF_3)_2$] 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.

We recently reported several related protocols for the cyclization/hydrosilylation of functionalized dienes catalyzed by cationic palladium complexes such as $[(phen)Pd(OEt_2)Me]^+$ $[BAr_4]^-$ [phen=1,10-phenanthroline; Ar=$C_6H_3(CF_3)_2$] (**1**).[1,2] Unfortunately, these protocols were considerably more efficient with triethylsilane than with dimethylphenylsilane. Specifically, although **1** catalyzed the reaction of dimethyl diallylmalonate (**2**) and $HSiMe_2Ph$ 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.[1d] Because a phenyl group or a heteroatom on the silane is required for oxidation to form the corresponding alcohol,[3] the failure of many substrates to undergo cyclization/hydrosilylation with $HSiMe_2Ph$ 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.

The efficiency and selectivity of transition metal catalyzed processes can be strongly affected 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 $HSiMe_2Ph$. However, because palladium complexes ligated with bidentate phosphine ligands such as bis(dimethylphosphino)ethane or amine ligands such as *N,N,N′N′*-tetramethylethylenediamine were ineffective as cyclization/hydrosilylation catalysts, it became apparent that a less drastic perturbation of

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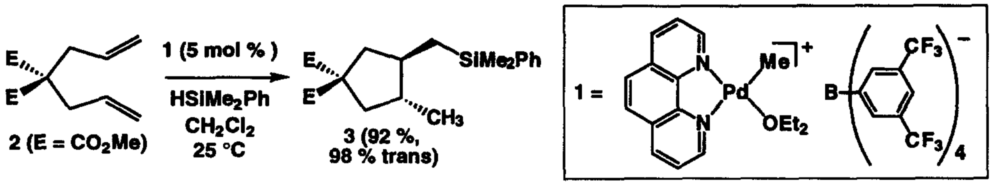
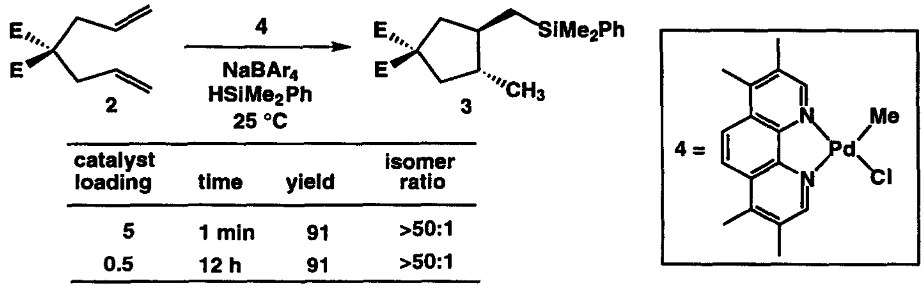


Scheme 1.

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$_4$-phen) displayed particularly high reactivity. For example, a 1:1 mixture of the palladium methyl chloride complex (Me$_4$-phen)Pd(Me)Cl (**4**) and NaBAr$_4$ (5 mol%)[4] 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).[5]



catalyst loading	time	yield	isomer ratio
5	1 min	91	>50:1
0.5	12 h	91	>50:1

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$_2$Ph. For example, a 1:1 mixture of **4** and NaBAr$_4$ 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 ≥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 ≥12 h at room temperature and formed ≤40% of the desired carbocycle.[1d] 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$_2$Ph was also catalyzed by **1**,[1d] reactions employing the catalyst generated from **4** were >25 times faster.

In summary, a 1:1 mixture of the palladium methyl chloride complex (Me$_4$-phen)Pd(Me)Cl (**4**) and NaBAr$_4$ 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$_2$Ph.

Acknowledgements

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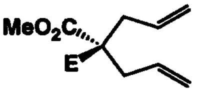
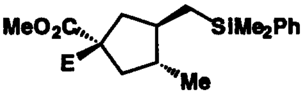
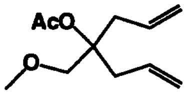
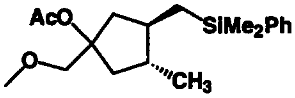
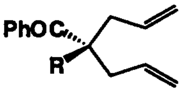
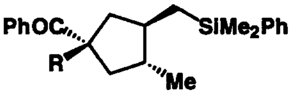
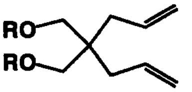
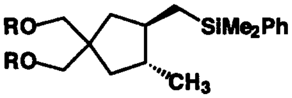
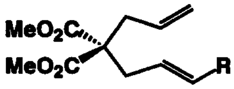
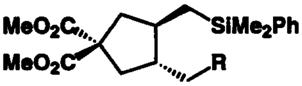
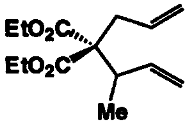
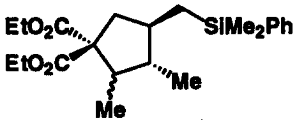
Table 1

Cyclization/hydrosilylation of functionalized dienes employing $HSiMe_2Ph$ catalyzed by $(Me_4\text{-phen})Pd(Me)Cl$ (4) and $NaBAr_4$ (≤5 mol%) in DCE at 25°C for 3–5 min

entry	diene	carbocycle	yield (%)[a]	isomer ratio[b]	yield and time employing 1[c]
					
1	E = COMe		74	2.1:1	40 %, 24 h
2	E = Ph		86	2.0:1	32 %, 12 h
3	E = SO_2Me		77	1.7:1	NR, 12 h
4	E = CN		86	2.2:1	NR, 12 h
5	E = $CONMe_2$		62	4.8:1	NR, 12 h
6			77	1:1	NR, 12 h
					
7[d]	R = Me		90	2.3:1	42 %, 12 h
8[d]	R = Ph		67	2.3:1	—
					
9	R = COMe		69	>50:1	41 %, 2 h
10	R = CO*t*-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 = *n*-Bu		86	7:1	—
15			85	1:1	—

[a] Yield refers to isolated material of >95 % purity. [b] Isomer ratio determined by capillary GC. [c] Results employing catalyst 1 taken from reference 1d. [d] 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), $NaBAr_4$ (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_2, 24:1 hexane:EtOAc) to give **3** (149 mg, 91%) as a colorless oil.