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Tandem Cyclization/Hydrosilylation of Functionalized 1,6-Dienes Catalyzed by a Cationic Palladium Complex

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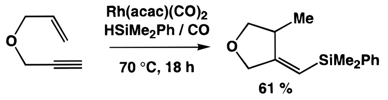
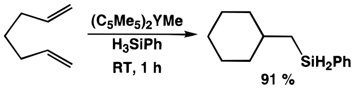
The Pd(0)- or Rh(I)-catalyzed cyclization/addition of diynes,[1] enynes,[2] and tetraenes[3] employing H−X or X−X′ [X, X′ = SiR$_3$, SnR$_3$, BR$_2$] as the stoichiometric reductant is a synthetically useful transformation which forms both a C−C bond and one or more C−X bond (eq 1). In contrast, Pd- or Rh-catalyzed cyclization/addition of dienes has not been demonstrated and instead requires a group 3,[4] 4,[5] or lanthanide[6] catalyst (eq 2). The high activity of these d^0-early-transition-metal complexes relative to the Pd and Rh catalysts stems from the electropositivity of the metal and the presence of an open coordination site. These features facilitate both olefin β-migratory insertion and σ-bond metathesis, the latter in preference to oxidative addition/reductive elimination processes. Unfortunately, the synthetic utility of these protocols is restricted by the extreme air- and moisture-sensitivity and oxophilicity of the catalyst. Therefore, we began a program directed toward the development of a facile and selective catalyst for the cyclization/addition of functionalized dienes.



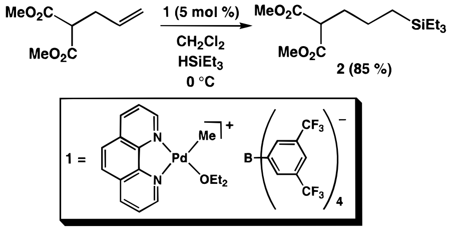
(1)



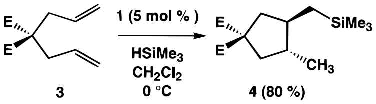
(2)

A growing body of evidence suggests that a cationic, electrophilic group 9 or 10 transition-metal complex employed in conjunction with a noncoordinating counterion can display reactivity analogous to a d^0-metallocene complex (olefin insertion, σ-bond metathesis) while maintaining good functional group compatibility.[7−10] Specifically, we targeted the cationic palladium methyl complex (phen)Pd(Me)(OEt$_2$)$^+$ BAr$_4$$^-$ [phen = 1,1-phenanthroline, Ar = 3,5-C$_6$H$_3$(CF$_3$)$_2$] (**1**) as a potential cyclization/addition catalyst due to its high reactivity with respect to olefin β-migratory insertion.[11,12] Organosilanes were initially employed as the stoichiometric reductant due to their availability, their low inherent reactivity toward olefins,[13] and the ease of C−Si oxidation.[14] Although hydrosilylation of functionalized olefins employing **1** as a catalyst had not previously been demonstrated, we found that **1**[15] catalyzed the addition of triethylsilane to dimethyl allylmalonate at 0 °C to form the terminal alkyl silane **2** in 85% isolated yield (Scheme 1).

Scheme 1

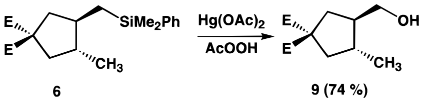


With both the migratory insertion and hydrosilylation reactivity of **1** established, we explored cyclization/hydrosilylation of functionalized dienes catalyzed by **1**. When trimethylsilane was bubbled through a solution of dimethyl diallylmalonate (**3**) (0.05 M) and **1** (5 mol %) at 0 °C for 5 min, the pale yellow solution turned dark with complete consumption of the starting material as determined by GC analysis. Evaporation of the solvent and flash chromatography of the residue gave the *trans*-silylated cyclopentane **4** in 80% yield (eq 3, Table 1).[16] In addition to **4**, GC-MS analysis of the crude reaction mixture revealed the presence of a small quantity of an isomeric silylated cyclopentane **4a** (**4**:**4a** = 54:1)[17] and traces (~5%) of hexamethyldisiloxane.[18]



(3)

A range of tertiary silanes possessing both alkyl and aryl groups reacted with **3** to give carbocycles **5**−**8** in good yield and with excellent diastereoselectivity (>25:1) (Table 1).[19] The dimethylphenylsilyl derivative **6** was converted to the corresponding alcohol **9** in 74% yield by treatment with mercuric acetate and peracetic acid (eq 4).[20] The cyclization/hydrosilylation procedure also tolerated both allylic and terminal olefinic substitution. For



(4)

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[15] Complex **1** was generated in situ at 0 °C from a 1:1 mixture of HBAr$_4$·(OEt$_2$)$_2$ and (phen)Pd(Me)$_2$; control experiments revealed that both components were required for catalysis.

[16] The ^{1}H and ^{13}C NMR spectra of **4** were identical to published NMR data: Miura, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2348. The trans stereochemistry of the remaining compounds was inferred by analogy to **4**.

[17] The minor isomer may correspond to either a diastereomer or a regioisomer of **4**.

[18] Confirmed by GC-MS analysis and comparison to authentic sample.

[19] Limitations include primary and secondary silanes, dienes which possessed internal or diterminal olefinic substitution, 1,6-enynes, and 1,6-diynes.

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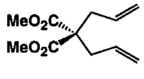
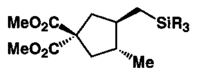
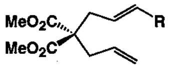
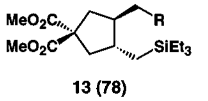
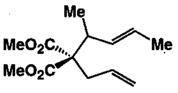
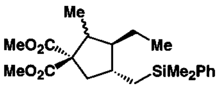
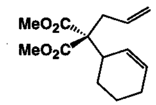
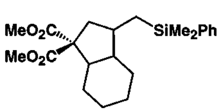
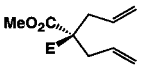
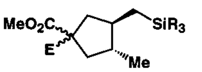
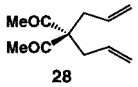
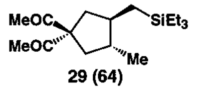
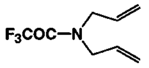
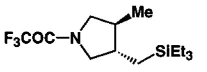
S0002-7863(98)00242-X CCC: $15.00

Table 1. Cyclization/Hydrosilylation of Functionalized Dienes Catalyzed by **1**

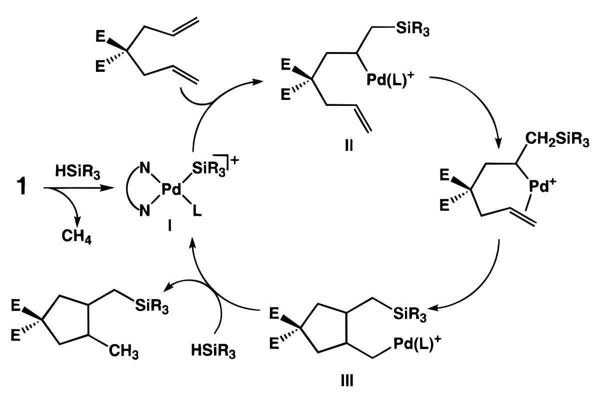
Diene	Silane	Cyclopentane (Isolated yield[a])	isomer ratio[b]
			
3	$HSiMe_3$	**4** (80)	55:1
	$HSiEt_3$	**5** (92)	55:1
	$HSiMe_2Ph$	**6** (93)	53:1
	$HSiMe_2t\text{-}Bu$	**7** (67)	44:1
	$HSiPh_3$	**8** (84)	>25:1[c]
			
10 (R = Me)[d]	$HSiEt_3$	**13** (78)	90:4:1
11 (R = Ph)		**14** (76)	12:1
12 (R = CH_2OPh)		**15** (71)	>25:1[c]
			
16	$HSiMe_2Ph$	**18** (74)	1:1
			
17		**19** (73)	33:11:3:1
			
20 (E = COMe)	$HSiMe_2t\text{-}Bu$	**24** (78)	1.5:1
21 (E = $CONMe_2$)	$HSiEt_3$	**25** (99)	5:1
22 (E = SO_2Me)		**26** (88)	2:1
23 (E = CN)		**27** (60)	2:1
			
28		**29** (64)	≥ 98:1
			
30		**31** (43)	33:1

[a] Yields refer to isolated material which was >95% pure as determined by ^1H NMR, GC, and/or elemental analysis. [b] Determined by capillary GC analysis of the crude reaction mixture. [c] GC not obtained, a single isomer detected by ^1H NMR spectroscopy. [d] 3:1 mixture of trans:cis isomers.

example, reaction of triethylsilane with dienes possessing a methyl (**10**), phenyl (**11**), or methylphenoxy (**12**) group at a terminal olefinic carbon atom gave the corresponding carbocycles (**13**–**15**) in >70% yield with good regio- and diastereoselectivity (Table 1). The disubstituted diene **16** and cyclohexenyl derivative **17** also underwent facile cyclization/hydrosilylation to form carbocycles **18** and **19**, respectively, in >70% yield as mixtures of diastereomers.

The protocol required *gem*-bis(carbomethoxy) or related groups at the 4,4′-position of the diene for greatest efficiency.[21] For example, dienes which possessed both a carbomethoxy and an acetyl (**20**), acetamide (**21**), sulfonyl (**22**), or cyano (**23**) group at the 4,4′-position underwent cyclization/hydrosilylation to form the corresponding carbocycles **24**–**27** in good yield as mixtures of diastereomers. Likewise, 1,3-diketone **28** cyclized to form **29** in 64% yield while *N*,*N*-diallyltrifluroroacetamide (**30**) reacted with triethylsilane to form pyrrolidine **31** in 43% yield (Table 1).[19]

Scheme 2



We propose a plausible mechanism for diene cyclization/hydrosilylation initiated by reaction of **1** with silane to generate the palladium-silyl intermediate **I** (Scheme 2). β-Migratory insertion of an olefin into the Pd–Si bond of **I** followed by β-migratory insertion of the pendant olefin into the resulting Pd–C bond of **II** would generate palladium alkyl intermediate **III**. Reaction of **III** with silane could then release the carbocycle and regenerate the palladium silyl complex **I**. Reaction of a late-transition-metal alkyl complex with a silane is known to generate a metal–silyl complex,[8,22] and ample precedence exists for β-migratory insertion of an olefin into a M–Si bond.[22] In addition, the resistance of palladium(II) toward oxidative addition strongly suggests that Si–H bond cleavage occurs via a σ-bond metathesis pathway. σ-Bond metathesis has been invoked in a range of transformations involving late-transition-metal alkyl complexes with H–X bonds [X = C, Si, B].[7,23]

In summary, the electrophilic palladium complex **1** served as an effective catalyst for the cyclization/hydrosilylation of suitably functionalized 1,6-dienes. Despite a limited substrate scope, the protocol displayed impressive reaction rates and high regio- and diastereoselectivity and was tolerant to a range of functionality and terminal olefin substitution. This combination of reactivity and selectivity establishes the potential of cationic late-transition-metal complexes as catalysts for use in organic synthesis.

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Supporting Information Available: Experimental procedures, spectroscopic and analytical data for relevant compounds (11 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

Note Added in Proof. The hydrosilylation of unfunctionalized olefins catalyzed by **1** has been reported: LaPoint, A. M.; Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1997**, *119*, 906.

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[21] For an example of analogous substrate dependence, see: Grigg, R.; Malone, J. F.; Mitchell, T. R. B.; Ramasubbu, A.; Scott, R. M. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1745.

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