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Highly Diastereo- and Regioselective Transition Metal-Catalyzed Additions of Metal Hydrides and Bimetallic Species to Cyclopropenes: Easy Access to Multisubstituted Cyclopropanes

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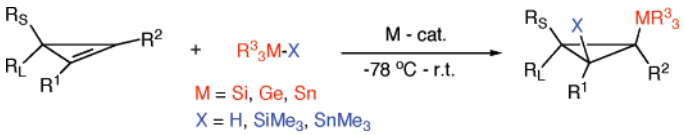
Received August 29, 2007



The first highly efficient, diastereo- and regioselective transition metal-catalyzed addition of metal hydrides (stannanes, silanes, and germanes) and bimetallic species (ditins and silyltins) to cyclopropenes has been developed. It was shown that the addition across the double bond of cyclopropenes is generally controlled by steric factors and proceeds from the least hindered face. This methodology represents a powerful and atom-economic approach toward a wide variety of highly substituted stereodefined cyclopropylmetals, useful building blocks unavailable by other methods.

Introduction

Cyclopropylmetals, such as cyclopropylstannanes,[1] boronates,[2] and silanes,[3] are highly versatile building blocks that have found numerous applications in organic synthesis.[4] In contrast to cyclopropyllithium and -magnesium reagents, tin, boron, and silicon analogues are much more stable, functional group tolerant, yet still reactive and thus more convenient synthons. They readily undergo a number of stereoselective transformations, involving exchange of the metal moiety with a broad range of functional groups, with or without ring expansions,[5] and are also used for installation of a three-membered carbocyclic unit into more advanced scaffolds via different cross-coupling protocols.[6]

Thus, not surprisingly, increasing attention is being paid to the development of efficient and selective methods toward these important building blocks. Generally, they are accessed via several different approaches (Scheme 1): substitution of cyclopropylanion equivalents with corresponding electrophiles,[7] [2 + 1]-cycloadditions,[8] and 1,3-cyclizations.[9]

Another emerging, very powerful approach that complements other methods and permits access to diverse multisubstituted cyclopropylmetals hardly accessible by the previously mentioned cyclization methodologies is the direct addition of metal species across the double bond of easily available[10] and highly reactive[10c,11−13] cyclopropenes (Scheme 1). Our group previously communicated a new finding of highly stereo- and regioselective transition metal-catalyzed hydro-, sila-, and stannastannation reactions of cyclopropenes.[14,15] In this paper, we provide a full account of the Pd-catalyzed diastereoselective hydrostannation of cyclopropenes, as well as the extension of this methodology to Pt-catalyzed hydrosilylation and hydrogermylation, for

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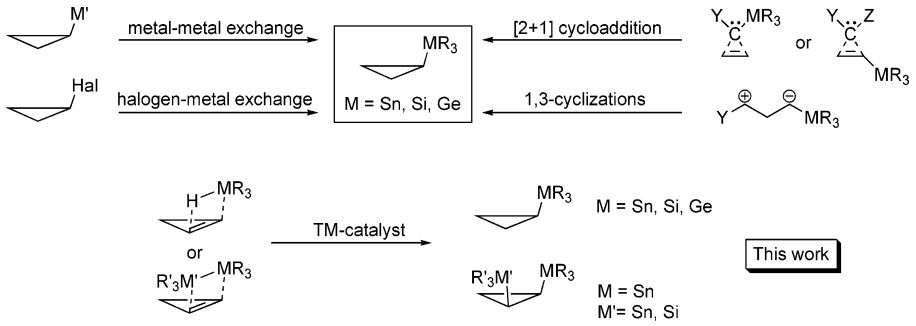
10.1021/jo701855c CCC: $37.00
Published on Web 10/13/2007

SCHEME 1. Synthetic Approaches toward Cyclopropylmetals



syntheses of cyclopropylsilanes and -germanes (Scheme 1). Herein, we also account for the expansion of the scope of previously reported sila- and stannastannation of cyclopropenes, as well as demonstrate the synthetic utility of cyclopropylstannanes through several highly selective transformations.

Results and Discussion

Hydrostannation of Cyclopropenes. Radical and transition metal-catalyzed hydrostannation of a multiple carbon−carbon bond represents one of the most efficient strategies for the introduction of a tin moiety in organyl substrates.[16] This approach has proven to be successful on a variety of alkenes, alkynes, and allenes providing functionally rich alkyl-, vinyl-, and allylstannanes amenable to further transformations. Strained monocyclic olefins have also been shown to undergo the hydrostannation reaction, however, with only moderate selectivities. Thus, activated cyclobutenes underwent radical hydrostannation, affording mixtures of regioisomers and cis- and trans-adducts.[17] Nakamura et al. demonstrated that radical-initiated hydrostannation of cyclopropenone acetals produced a variety of stannylcyclopropanone acetals in high yields and moderate degrees of regio- and diastereoselectivity.[18] In both reported radical-promoted reactions,[17,18] the addition of H−Sn entities to a strained double bond proceeded in the trans-fashion predominantly, albeit not cleanly, as a result of the configurational instability of the intermediate cyclic radical species.[19] We, therefore, were very surprised to find that exposure of the 3,3-disubstituted cyclopropene **1a** to tributyltin deuteride in the absence of any additive afforded a 1:1 mixture of isomeric cyclopropylstannanes **3aa-*d*** and **4aa-*d*** (eq 1). Most remarkably, syn-addition products were obtained exclusively even in the dark and in the presence of radical traps.

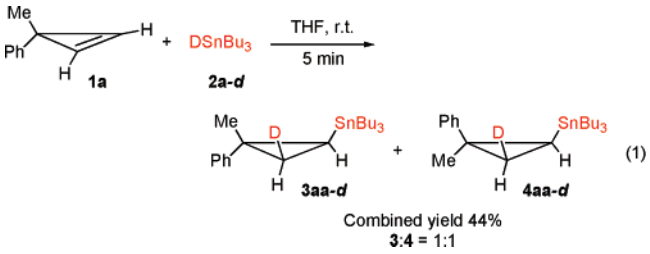


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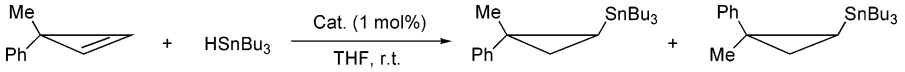
TABLE 1. Catalyst Optimization for Hydrostannation of 1a



1a **2a** **3aa** **4aa**

entry	catalyst	time	**3** (%)[a]	**4** (%)[a]	**3**/**4**[a]
1	$Ru(PPh_3)_3Cl_2$	20 h	67	3	96:4
2	$Pt(PPh_3)_4$	20 h	66	4	94:6
3	$Rh(PPh_3)_3Cl$	20 h	75	4	95:5
4	$Ni(dppp)Cl_2$	20 h	32	1	97:3
5	$Ni(dppe)_2$	5 h	2		
6	$Pd(PPh_3)_2Cl_2$	5 min	36	16	69:31
7	TCPC[b]	5 min	15	14	52:48
8	$Pd(OAc)_2$/TDMPP	5 min	19	15	56:44
9	Pd_2dba_3/*o*-Tol_3P	5 min		>1	
10	[π-allyl-PdCl]$_2$/MOP	5 min	29	6	83:17
11	[π-allyl-PdCl]$_2$/TCPC[b]	5 min	32	8	80:20
12	$Pd(PPh3)_4$	5 min	79	>1	98:2
13	$Pd(PPh_3)_4$[c]	5 min	86[d]	>1	>99:1

[a] GC data. [b] TCPC = [1,2,3,4-tetrakis(methoxycarbonyl)-1,3-butadiene-1,4-diyl]palladium. [c] Reaction was performed at −78 °C. [d] Isolated yield.

Although the exact mechanism of this reaction is unclear, these results indicate that it may proceed via a hydrometalation pathway typical for the hydrides of the III group elements (boron, aluminum, etc.). To the best of our knowledge, the highly syn-selective addition of a tin hydride species to a double bond has thus far been only known to occur in the presence of a transition metal catalyst. Despite the unprecedented syn-selectivity of addition, the overall efficiency and diastereoselectivity of the noncatalytic reaction was unsatisfactory.

Thus, aiming at the development of an efficient and diastereoselective hydrostannation methodology, we tested the hydrostannation of cyclopropene **1a** in the presence of various transition metal catalysts (Table 1). Surprisingly, in contrast to the very quick noncatalyzed reaction (eq 1), the hydrostannation of **1a** catalyzed by ruthenium, platinum, rhodium, and nickel complexes proceeded very sluggishly, affording moderate to good yields of products, albeit with good facial selectivity (Table 1, entries 1−4). Most Pd(0) and Pd(II) catalysts showed high reaction rates, although the yields and selectivity were disappointingly low (Table 1, entries 6−11), attributed to the poor stability of cyclopropenes in the presence of Pd complexes, which are well-known to cause ring-opening,[20] oligomerization,[21] or polymerization[22] of the strained substrates. In striking contrast to the previous examples, $Pd(PPh_3)_4$ allowed for both, a very good yield and a very high facial selectivity (Table 1, entry 12). Optimization of the reaction conditions showed that this reaction can be carried out at as low as −78 °C. Still, the reaction was complete in less than 5 min, and virtually a single facial isomer **3aa** was isolated in 86% yield (entry 13). The best conditions (Table 1, entry 13) were applied to the hydrostannation reaction of a series of 3,3-disubstituted cyclopropenes (Table 2). Hydrostannation of most of the 3,3-disubstituted cyclopropenes was governed by steric effects, regardless of the tin hydride source: addition across the cyclopropene double bond proceeded extremely rapidly at −78 °C from the least hindered face (Table 2, entries 1−7). Hydrostannation of the more sterically encumbered cyclopropene **1d** required, however, a higher temperature (0 °C) for the efficient formation of adduct **3da** (Table 2, entry 8). In all these examples (Table 2, entries 1−8), a drastically different steric environment of two cyclopropene faces ensured the high selectivity of the addition. On the other hand, hydrostannation of vinylcyclopropene **1g** and cyclopropenylmethanol **1h** produced nonselectively a mixture of two facial isomers in a nearly equimolar ratio (Table 2, entries 9 and 10). A lack of selectivity in these cases is explained by comparable sizes of the methyl group and the vinyl or hydroxymethyl substituent. Surprisingly, in contrast to **1h**, cyclopropenes **1e**,**f** revealed a notable directing effect.[23] Apparently, a coordination of oxygen to palladium affected the facial selectivity of hydrostannation, favoring addition from the more sterically hindered face (Table 2, entries 11 and 12).

After developing an efficient method for the hydrostannation of 3,3-disubstituted cyclopropenes, we next turned our attention to the hydrostannation of tri- and tetrasubstituted cyclopropenes en route to tetra- and pentasubstituted cyclopropylstannanes. It should be mentioned that in contrast to 3,3-disubstituted cyclopropenes, hydrostannation of most trisubstituted analogues proceeded very sluggishly in the presence of $Pd(PPh_3)_4$, producing mixtures of facial isomers accompanied by ring-opening products. However, employment of a [(π-allyl)PdCl]$_2$/MOP[24] catalyst system enabled a smooth reaction, providing tetrasubstituted cyclopropylstannanes with a high facial selectivity and good yields (Table 3, entries 1−3). Interestingly, the hydrostannation of 1-methoxycarbonyl-substituted cyclopropene **1m** produced notable amounts of the sterically less favorable product

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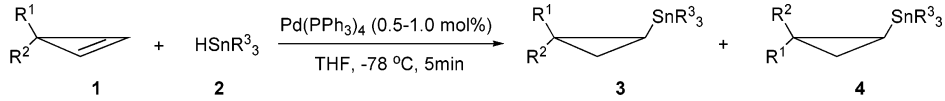
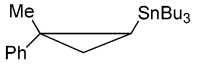
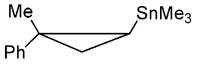
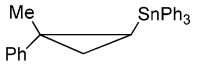
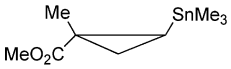
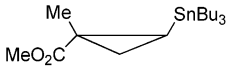
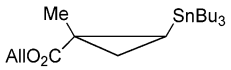
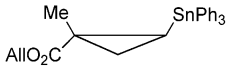
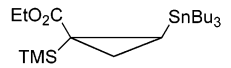
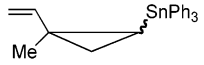
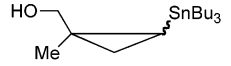
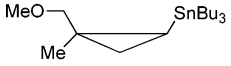
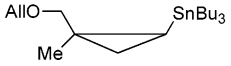
(24) MOP = (*RS*)-2-(diphenylphosphino)-2′-methoxy-1,1′-binaphtyl.

TABLE 2. Pd-Catalyzed Hydrostannation of 3,3-Disubstituted Cyclopropenes



1 2 3 4

Entry	Cyclopropene 1		Tin hydride 2	Cyclopropane 3		Yield (%)[a]
	R^1	R^2	R^3			
1	Me	Ph (**a**)	Bu (**a**)		**3aa**	92
2	Me	Ph (**a**)	Me (**b**)		**3ab**	91[b]
3	Me	Ph (**a**)	Ph (**c**)		**3ac**	92
4	Me	CO_2Me (**b**)	Me (**b**)		**3bb**	83
5	Me	CO_2Me (**b**)	Bu (**a**)		**3ba**	85
6	Me	CO_2All (**c**)	Bu (**a**)		**3ca**	87
7	Me	CO_2All (**c**)	Ph (**c**)		**3cc**	78
8	CO_2Et	TMS (**d**)	Bu (**a**)		**3da**	82[c]
9	$CH{=}CH_2$	Me (**g**)	Ph (**c**)		80 (**3gc**/**4gc** 1:1)	
10	CH_2OH	Me (**h**)	Bu (**a**)		68 (**3ha**/**4ha** 1:1)	
11	CH_2OMe	Me (**e**)	Bu (**a**)		**3ea**	67[d]
12	CH_2OAll	Me (**f**)	Bu (**a**)		**3fa**	80[e]

[a] Isolated yield. [b] Formation of 5% **4ab** was detected. [c] Reaction was performed at 0 °C. [d] Combined yield of a 4:1 mixture of **3ea**/**4ea**. [e] Combined NMR yield of a 4:1 mixture of **3fa**/**4fa**.

5ma. We rationalized that the formation of **5ma** arose from strong polarization of the cyclopropene double bond in the Michael acceptor-type substrate. Accordingly, the pronounced electronic effect competed with the steric effect and caused an addition of palladium to the electronically enriched, yet more sterically hindered, α-carbon atom during the hydropalladation step. Additional steric bulk created by the introduction of the methyl substituent at the *β*-carbon atom in **1n** shifted the regioselectivity further toward formation of the α-adduct. Thus, hydrostannation of tetrasubstituted cyclopropene **3n** produced a mixture of regioisomers, with the α-substituted adduct being a major product (Table 3, entry 5). Finally, tetrasubstituted cyclopropene **1o** underwent smooth hydrostannation to produce the corresponding pentasubstituted cyclopropylstannane **3oa**, in 82% isolated yield, as a single reaction product (Table 3, entry 6).

It is important to emphasize that the extremely mild conditions of the Pd-catalyzed hydrostannation allowed for remarkable functional group compatibility: a wide variety of substituents ranging from esters, ethers, and unprotected alcohols to vinyl and allyl groups was completely tolerated in this reaction.

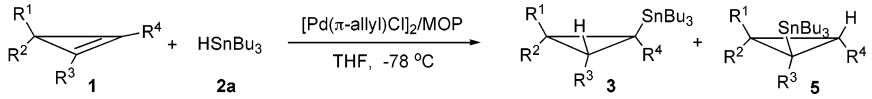
Hydrosilylation of Cyclopropenes. Next, we aimed at expanding this methodology to another as yet unknown hydrometalation reaction on cyclopropenes: hydrosilylation[25] toward cyclopropylsilanes. While cyclopropylsilanes share some reactivity with cyclopropylstannanes,[26,27] they also undergo a number of transformations characteristic of organosilanes, including

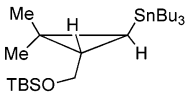
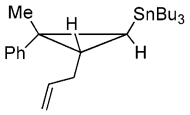
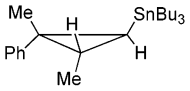
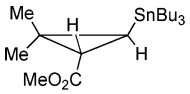
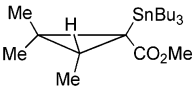
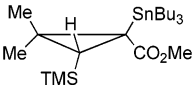
(25) Marciniec, B. *Hydrosilylation and Related Reactions of Silicon Compounds: Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; 2002; Vol. 1, p 491.

(26) For an example of Lewis acid mediated reactions of cyclopropylsilanes with electrophiles, see: Schaumann, E.; Mergardt, B. *J. Chem. Soc., Perkin Trans. 1* **1989**, *7*, 1361.

(27) For reactions of cyclopropylsilanes involving generation of cyclopropylanions, see: (a) Blankenship, C.; Wells, G. J.; Paquette, L. A. *Tetrahedron* **1988**, *44*, 4023. (b) Ohno, M.; Tanaka, H.; Komatsu, M.; Ohshiro, Y. *Synlett* **1991**, *12*, 919. (c) Shibuya, A.; Pietz, S.; Taguchi, T. *Tetrahedron Lett.* **1997**, *38*, 5537. (d) Adams, D. J.; Blake, A. J.; Cooke, P. A.; Gill, C. D.; Simpkins, N. S. *Tetrahedron* **2002**, *58*, 4603. (e) Wang, Z.; Silverman, R. B. *J. Enzyme Inhibit. Med. Chem.* **2004**, *19*, 293.

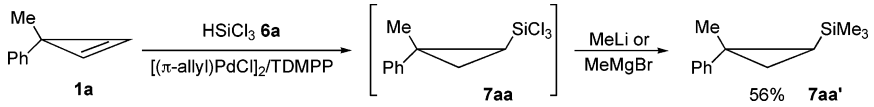
TABLE 3. Pd-Catalyzed Hydrostannation of Tri- and Tetrasubstituted Cyclopropenes



Entry	Cyclopropene 1				Cyclopropane 3		Yield (%)[a]
	R^1	R^2	R^3	R^4			
1	Me	Me	CH_2OTBS	H (**i**)		**3ia**	68[b,c]
2	Me	Ph	All	H (**j**)		**3ja**	63
3	Me	Ph	Me	H (**l**)		**3la**	83[d]
4	Me	Me	CO_2Me	H (**m**)		**3ma**	91[e]
5	Me	Me	Me	CO_2Me (**n**)		**3na**	93[f]
6	Me	Me	TMS	CO_2Me (**o**)		**3oa**	82[g]

[a] Isolated yield. [b] NMR yield. [c] $Pd(PPh_3)_4$ was used as catalyst. [d] Formation of 5% **4la** was observed. [e] Combined yield of a 3:1 mixture of **3ma**/**5ma**. [f] Combined yield of a 3.5:1 mixture of **3na**/**5na**. [g] Performed at −40 °C using hexane as solvent.

SCHEME 2. Palladium-Catalyzed Hydrosilylation of 1a



Tamao−Flemming oxidation[28] and the Peterson olefination reaction,[29] which makes them very attractive synthons in their own right.

Initially, we tested the hydrosilylaton of disubstituted cyclopropene **1a** in the presence of various transition metal catalysts. Our experiments indicated that the employment of nickel, rhodium, and iridium complexes, known to catalyze the addition of H−Si species to unsaturated carbon−carbon bonds,[25,30] did not result in the hydrosilylation of cyclopropenes. However, it was found that the hydrosilylation of **1a** in the presence of [(π-allyl)PdCl]$_2$ and a bulky electron-rich TDMPP ligand with trichlorosilane **6a** proceeded very selectively from the less hindered face. Subsequent exhaustive methylation of product **7aa** produced the corresponding cyclopropyltrimethylsilane **7aa′** in good yield as a single diastereomer (Scheme 2). Unfortunately, all other silicon hydrides tested did not undergo this transformation in the presence of a Pd catalyst.

In contrast, several Pt complexes[31] allowed for the smooth hydrosilylation of **1a** with a variety of triorganyl-, chlorodiorganyl-, and trialkoxysilanes, albeit affording diastereomeric mixtures of cyclopropylsilanes **7** and **8** (Table 4). Platinum halide complexes, particularly $PtCl_2$, appeared to be the most efficient catalysts for this transformation (Table 4, entries 4−11). Further optimization revealed that the diastereoselectivity of addition was practically independent of the size and electronic

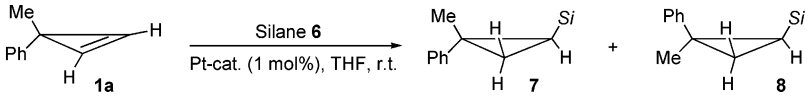
(28) See, for example: (a) Angelaud, R.; Landais, Y.; Maignan, C. *Tetrahedron Lett.* **1995**, *36*, 3861. (b) Yamamura, Y.; Toriyama, F.; Kondo, T.; Mori, A. *Tetrahedron: Asymmetry* **2002**, *13*, 13. (c) Begis, G.; Sheppard, T. D.; Cladingboel, D. E.; Motherwell, W. B.; Tocher, D. A. *Synthesis* **2005**, *19*, 3186.

(29) See, for example: (a) Mizojiri, R.; Urabe, H.; Sato, F. *J. Org. Chem.* **2000**, *65*, 6217. (b) Honda, M.; Mita, T.; Nishizawa, T.; Sano, T.; Segi, M.; Nakajima, T. *Tetrahedron Lett.* **2006**, *47*, 5751.

(30) See, for example: (a) Ir: Cipot, J.; Ferguson, M. J.; Stradiotto, M. *Inorg. Chim. Acta* **2006**, *359*, 2780. (b) Ni: Boucher, S.; Zargarian, D. *Can. J. Chem.* **2006**, *84*, 233. (c) Rh: Rivera, G.; Crabtree, R. H. *J. Mol. Catal. A: Chem.* **2004**, *222*, 59. (d) Goikhman, R.; Milstein, D. *Chem.—Eur. J.* **2005**, *11*, 2983. (e) Imlinger, N.; Wurst, K.; Buchmeiser, M. R. *J. Organomet. Chem.* **2005**, *690*, 4433. (f) Muraoka, T.; Matsuda, I.; Itoh, K.; Ueno, K. *Organometallics* **2007**, *26*, 387. (g) Pd: Sui-Seng, C.; Groux, L. F.; Zargarian, D. *Organometallics* **2006**, *25*, 571.

(31) For Pt-catalyzed hydrosilylation, see for example: (a) Marko, I. E.; Sterin, S.; Buisine, O.; Berthon, G.; Michaud, G.; Tinant, B.; Declercq, J.-P. *Adv. Synth. Catal.* **2004**, *346*, 1429. (b) Berthon-Gelloz, G.; Buisine, O.; Briere, J. F.; Michaud, G.; Sterin, S.; Mignani, G.; Tinant, B.; Declercq, J.-P.; Chapon, D.; Marko, I. E. *J. Organomet. Chem.* **2005**, *690*, 6156. (c) Jankowiak, M.; Maciejewski, H.; Gulinski, J. *J. Organomet. Chem.* **2005**, *690*, 4478. (d) Oyamada, H.; Akiyama, R.; Hagio, H.; Naito, T.; Kobayashi, S. *Chem. Commun.* **2006**, *41*, 4297. (e) Poyatos, M.; Maisse-Francois, A.; Bellemin-Lapponaz, S.; Gade, L. H. *Organometallics* **2006**, *25*, 2634. (f) Zhao, L.; Loy, D. A.; Shea, K. J. *J. Am. Chem. Soc.* **2006**, *128*, 14250.

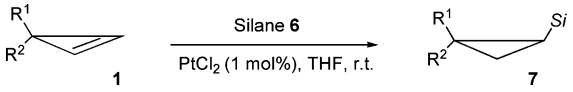
TABLE 4. Selected Data on Catalyst and Silane Optimization for Hydrosilylation of 1a

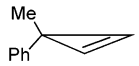
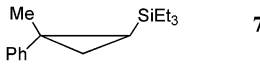
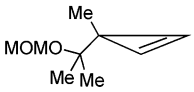
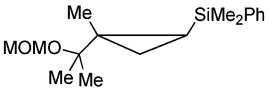
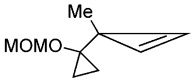
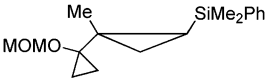
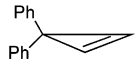
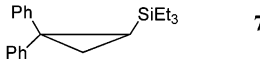
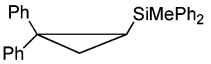
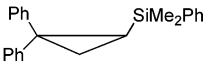
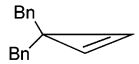
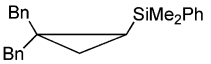
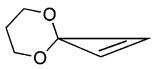
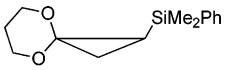
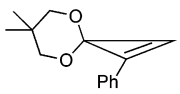
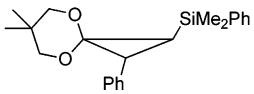


entry	catalyst	silane **6**		**7**/**8** (yield, %)[a]
1	$O[(CH_3)_2SiCH{=}CH_2\text{-}\eta^2]_2Pt$	$HSiEt_3$	**6b**	NR
2		$HSiPh_2Me$	**6c**	NR
3		$HSiPhMe_2$	**6d**	65:35[b,c]
4	$PtBr_2$		**6b**	60:40[b]
5	PtI_2		**6d**	64:36[b]
6	$PtCl_2$		**6b**	83:17 (61%)
7			**6c**	73:27 (60%)
8			**6d**	64:36 (75%)
9		$HSiPh_3$	**6e**	73:27 (71%)
10		$HSi(OEt)_3$	**6f**	77:23[b]
11		$HSiMe_2Cl$	**6g**	73:27[b]

[a] NMR data. [b] GC data. [c] Complex reaction mixture and sluggish reaction.

TABLE 5. Pt-Catalyzed Hydrosilylation of Cyclopropenes



Entry	Cyclopropene 1		Silane 6		Cyclopropane 7		Yield (%)[a]
1		**1a**	$HSiEt_3$	**6b**		**7ab**	61[b]
2		**1p**	$HSiMe_2Ph$	**6d**		**7pd**	79
3		**1q**		**6d**		**7qd**	100
4		**1r**		**6b**		**7rb**	72
5		**1r**	$HSiMePh_2$	**6c**		**7rc**	73
6		**1r**		**6d**		**7rd**	82
7		**1s**		**6d**		**7sd**	78
8		**1t**		**6d**		**7td**	75
9		**1u**		**6d**		**7ud**	0[c]

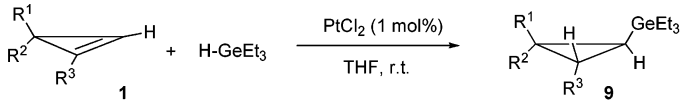
[a] Isolated yield. [b] Combined yield of a 4:1 mixture of facial isomers. [c] Opening of cyclopropenone acetal occurred.

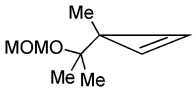
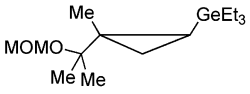
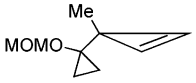
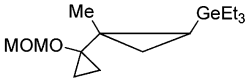
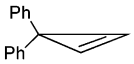
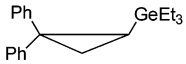
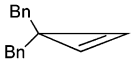
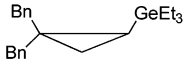
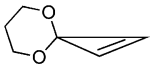
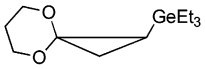
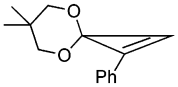
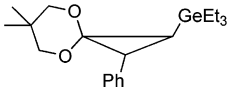
nature of the silane (Table 4, entries 6−11). Employment of different solvents and additives (phosphines and amines), as well as altering the reaction temperature, did not allow for a notable improvement of the selectivity.

Screening other substrates under these conditions (Table 5) demonstrated that, in contrast to **1a** (Table 5, entry 1), hydrosilylation of cyclopropenes **1p** and **1q**, having a drastically different steric environment on the two faces, efficiently afforded cyclopropylsilanes **7pd** and **7qd** as single facial isomers (Table 5, entries 2 and 3). Symmetrically substituted 3,3-diphenyl- and 3,3-dibenzylsubstituted cyclopropenes **1r** and **1s**, as well as cyclopropenone acetal **1t**, also underwent facile hydrosilylation with various silanes, providing good yields of the corresponding products (Table 5, entries 4−8). In contrast, attempts on the hydrosilylation of trisubstituted cyclopropene **1u** resulted in no reaction (Table 5, entry 9).

Hydrogermylation of Cyclopropenes. Remarkably, it was found that the hydrosilylation conditions could be successfully

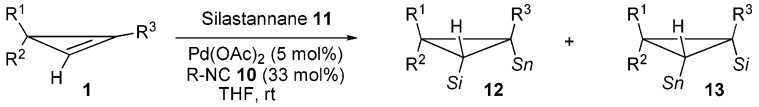
TABLE 6. Pt-Catalyzed Hydrogermylation of Cyclopropenes

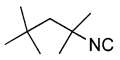
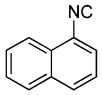
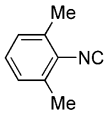


Entry	Cyclopropene 1		Cyclopropane 9		Yield (%)[a]
1		**1p**		**9p**	42
2		**1q**		**9q**	68
3		**1r**		**9r**	93
4		**1s**		**9s**	98
5		**1t**		**9t**	56
6		**1u**		**9u**	62

[a] Isolated yield.

TABLE 7. Optimization of Regioselectivity in Silastannation of Cyclopropenes

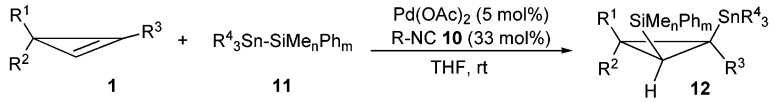


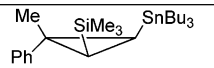
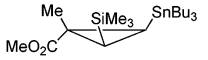
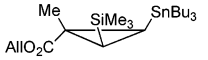
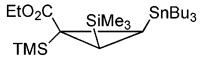
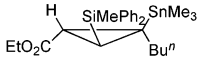
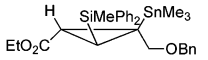
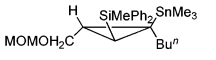
Entry	Cyclopropene 1				Isocyanide 10		Silastannane 11		12:13[a]
	R^1	R^2	R^3						
1	Ph	Me	H	**1a**		**10a**	Bu_3Sn-$SiMe_3$	**11a**	94%[b]
2	CO_2Et	H	*n*-Bu	**1v**		**10a**		**11a**	64:36
3				**1v**		**10a**	Me_3Sn-$SiMe_2Ph$	**11b**	87:13
4				**1v**	*t*-BuNC	**10b**		**11b**	85:15
5				**1v**	*c*-HexNC	**10c**		**11b**	73:27
6				**1v**		**10d**		**11b**	100:0[c]
7				**1v**		**10e**		**11b**	100:0
8	CO_2Et	H	CH_2OBn	**1w**		**10e**		**11b**	67:33
9				**1w**		**10e**	Me_3Sn-$SiMePh_2$	**11c**	92:8
10	Ph	Me	Me	**1l**		**10e**		**11c**	80:20

[a] NMR data. [b] Isolated yield of a single diastereomer. [c] Complex reaction mixture.

applied to the hydrogermylation of cyclopropenes (Table 6). Analogously to hydrosilylation, hydrogermylation was also governed by steric factors, resulting in the addition of the H−Ge moiety from the least hindered face (Table 6, entries 1 and 2). Symmetrically 3,3-disubstituted cyclopropenes **1r** and **1s** underwent addition of triethylgermane to produce cyclopropylgermanes **9r** and **9s** in excellent yields (Table 6, entries 3 and 4). Cyclopropenone acetal **1t** was also hydrogermylated in 56%

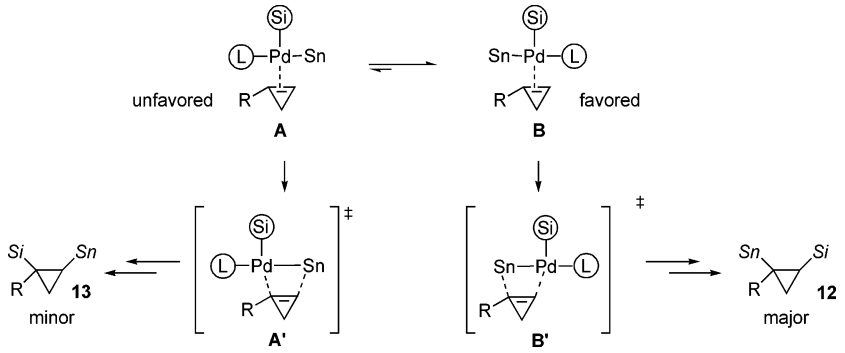
TABLE 8. Pd-Catalyzed Silastannation of Cyclopropenes



Entry	Cyclopropene 1				R^4_3Sn-$SiMe_nPh_m$ 11		R-NC 10		Cyclopropane 12		Yield (%)[a]
	R^1	R^2	R^3								
1	Me	Ph	H	**1a**	$Bu_3SnSiMe_3$	**11a**	**10a**		**12aa**	94	
2	Me	CO_2Me	H	**1b**		**11a**	**10a**		**12ba**	84	
3	Me	CO_2All	H	**1c**		**11a**	**10a**		**12ca**	69	
4	CO_2Et	TMS	H	**1d**		**11a**	**10a**		**12da**	85	
5	H	CO_2Et	*n*-Bu	**1v**	$Me_3SnSiMePh_2$	**11c**	**10e**		**12vc**	78	
6	H	CO_2Et	CH_2OBn	**1w**		**11c**	**10e**		**12wc**	64[b]	
7	H	CH_2OMOM	*n*-Bu	**1x**		**11c**	**10e**		**12xc**	70	

[a] Isolated yields. [b] 8% **13we** was detected.

SCHEME 3



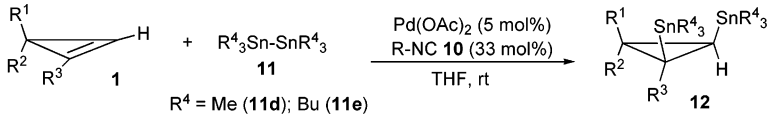
yield (Table 6, entry 5). Interestingly, 1-phenyl-cyclopropenone acetal **1u**, which failed to afford a hydrosilylation product (Table 5, entry 10), underwent regioselective hydrogermylation, producing adduct **9u** exclusively, with a triethylgermyl group attached to the least hindered carbon atom (Table 6, entry 6).

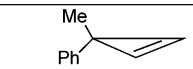
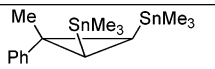
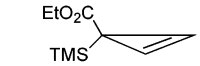
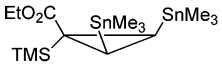
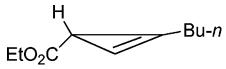
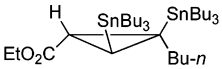
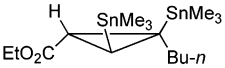
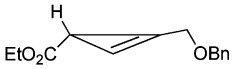
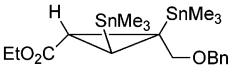
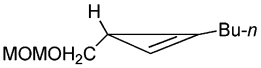
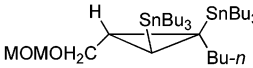
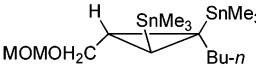
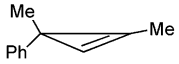
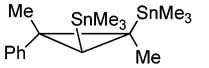
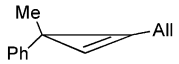
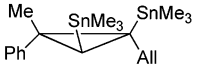
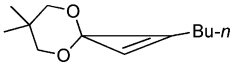
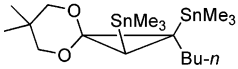
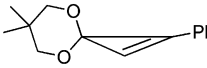
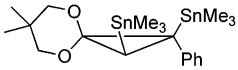
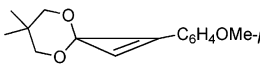
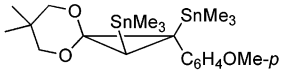
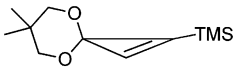
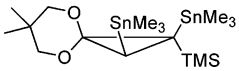
Sila- and Stannastannation of Cyclopropenes. We also envisioned another attractive possibility for the efficient functionalization of three-membered carbocycles via the transition metal-catalyzed dimetalation of cyclopropenes, which would allow for simultaneous diastereoselective introduction of two modifiable groups in a single step. Our initial experiments indicated that the $Pd(OAc)_2$/*t*-octyl isocyanide (**10a**: −Walborsky's ligand) combination[32,33] readily catalyzed addition of the Si−Sn species to 3,3-disubstituted cyclopropenes with perfect facial selectivity (Table 7, entry 1). However, only moderate regioselectivity was achieved in the silastannation of 1,3-disubstituted cyclopropene **1v** using this catalyst system (Table 7, entry 2). Screening various isocyanide ligands (Table 7, entries 3−7) revealed that employment of arylisocyanide **10d** produced single regioisomer **12vb** (entry 6); however, the reaction mixture was complicated by a number of unidentified side products. Gratifyingly, the use of 2,6-dimethylphenylisocyanide **10e** not only allowed for the exclusive formation of **12vb** but also ensured a clean and efficient conversion (Table 7, entry 7). Notably, improvement of regioselectivity was also observed upon employment of silastannanes with a more sterically demanding Si moiety (Table 7, entries 2 vs 3 and 8 vs 9). The new conditions also allowed for silastannation of 1,3,3-trisubstituted cyclopropenes, which failed to produce any reaction in the presence of the *t*-octyl isocyanide ligand **10a** (entry 10).

With the optimized conditions in hand, we investigated the scope of this transformation (Table 8). Thus, silastannation of all 3,3-disubstituted cyclopropenes proceeded uneventfully, affording the corresponding tetrasubstituted cyclopropanes as sole reaction products in good to very high yields (Table 8, entries 1−4). Furthermore, 1,3-disubstituted cyclopropenes **1v**−**x**, possessing an unsymmetrically substituted double bond, underwent an efficient and highly regioselective silastannation producing tetrasubstituted cyclopropanes **12vc**−**xc**, in which the silyl group was attached to the least hindered site (Table 8, entries 5−7).

(32) Oshima, K. VII.5 Metallopalladation. In *Handbook on Organopalladium Chemistry*; Negishi, E., Ed.; Wiley: New York, 2002; p 2825.
(33) Pohlmann, T.; de Meijere, A. *Org. Lett.* **2000**, *2*, 3877.

TABLE 9. Pd-Catalyzed Distannation of Cyclopropenes



Entry	Cyclopropene 1		Ditin 11	R-NC 10	Cyclopropane 12		Yield (%)[a]
1		**1a**	**11d**	**10a**		**12ad**	83
2		**1d**	**11d**	**10a**		**12dd**	89
3		**1v**	**11e**	**10e**		**12ve**	79
4		**1v**	**11d**	**10e**		**12vd**	88
5		**1w**	**11d**	**10e**		**12wd**	61
6		**1x**	**11e**	**10e**		**12xe**	55
7		**1x**	**11d**	**10e**		**12xd**	72
8		**1l**	**11d**	**10e**		**12ld**	78
9		**1j**	**11d**	**10e**		**12jd**	86
10		**1y**	**11d**	**10e**		**12yd**	96
11		**1u**	**11d**	**10e**		**12ud**	90
12		**1z**	**11d**	**10e**		**12zd**	100
13		**1aa**	**11d**	**10e**		**12aad**	100[b]

[a] Isolated yield. [b] NMR yield.

The origins of the very high regioselectivity observed in the latter examples could be rationalized in terms of steric and electronic control during the migratory insertion step. It is well-documented that the palladametalation step can occur with insertion of the olefin into either Pd−Si or Pd−Sn bond. While the insertion into a more electrophilic Pd−Sn bond is usually preferred,[34,35] there is a number of literature examples of selective transformations proceeding via the palladasilylation pathway.[36] Furthermore, theoretical computations on the silastannation of alkynes suggest that, in the absence of strong steric effects, addition of the palladium moiety to a more substituted carbon atom is electronically more favorable[34]—the effect also is observed in numerous other reactions involving olefin insertion into various Pd−X bonds.[32,37] However, increasing the steric bulk on Pd can reverse the addition aptitude, resulting in the addition of palladium to the least hindered site (Scheme 3).[32,35,37] In view of that, the observed regioselectivity trend in the silastannation of cyclopropenes (Table 7), with regards to the size of the isocyanide ligand and the relative sizes of the Sn and Si moieties in the silastannane reagents, is in better agreement with the palladastannation rather than the palladasilylation pathway for the following reasons.

First, increasing the bulk on the Pd moiety upon switching to a more sterically demanding isocyanide ligand significantly improves the selectivity of the addition (Table 7, entries 6 and 7 vs 3 and 5). Furthermore, improvement of the selectivity was also observed when silastannanes with a bulkier Si moiety were used (Table 7, entries 2 vs 3 and 8 vs 9). A synergistic steric effect of the large isocyanide and a bulky silyl group at the Pd ligands causes the equilibrium A ↔ B (Scheme 3) to shift right, thus improving the regioselectivity of the reaction toward the

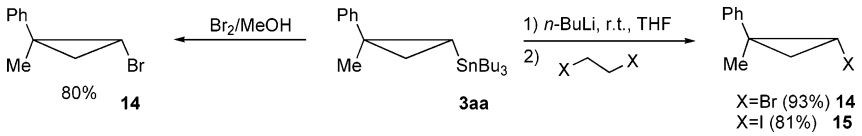
(34) (a) Sagawa, T.; Sakamoto, Y.; Tanaka, R.; Katayama, H.; Ozawa, F. *Organometallics* **2003**, *22*, 4433. (b) Hemeon, I.; Singer, R. D. *J. Mol. Catal. A: Chem.* **2004**, *214*, 33.

(35) Hada, M.; Tanaka, Y.; Ito, M.; Murakami, M.; Amii, H.; Ito, Y.; Nakatsuji, H. *J. Am. Chem. Soc.* **1994**, *116*, 8754.

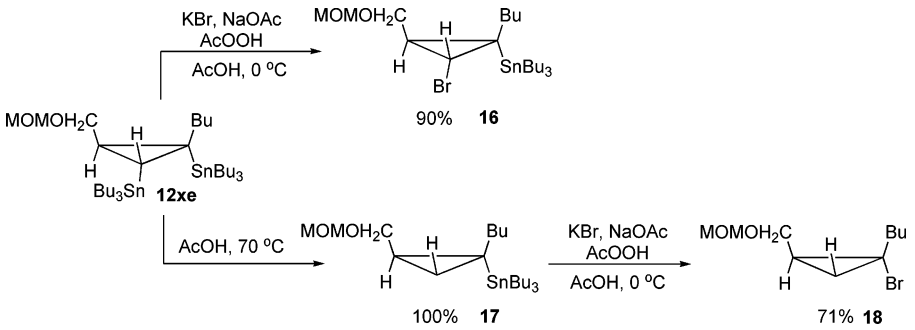
(36) (a) Mori, M.; Hirose, T.; Wakamatsu, H.; Imakuni, N.; Sato, Y. *Organometallics* **2001**, *20*, 1907. (b) Shin, S.; RajanBabu, T. V. *J. Am. Chem. Soc.* **2001**, *123*, 8416. (c) Sato, Y.; Imakuni, N.; Hirose, T.; Wakamatsu, H.; Mori, M. *J. Organomet. Chem.* **2003**, *687*, 392. (d) Kumareswaran, R.; Shin, S.; Gallou, I.; RajanBabu, T. V. *J. Org. Chem.* **2004**, *69*, 7157.

(37) Larhed, M.; Hallberg, A. IV.2.1.1 Scope, mechanism, and other fundamental aspects of the intermolecular Heck reaction. In *Handbook on Organopalladium Chemistry*; Negishi, E., Ed.; Wiley: New York, 2002; p 1133.

SCHEME 4. Transformations of Cyclopropylstannanes



SCHEME 5. Transformations of Cyclopropyldistannanes



formation of the major product **12** via the transition state B′. Conversely, the palladasilylation pathway appears as a less likely route, as increasing the size of the isocyanide ligand in this case would have resulted in deterioration of the regioselectivity.

Next, a variety of di- and trisubstituted cyclopropenes was subjected to the distannation reaction (Table 9). Analogously to all transition metal-catalyzed additions discussed previously, distannation proceeded selectively from the least hindered face to produce tetrasubstituted cyclopropanes in good to high yields (Table 9, entries 1−9). Trisubstituted cyclopropenes **1l** and **1j** produced pentasubstituted cyclopropanes **12ld** and **12jd**, respectively, in excellent yields (Table 9, entries 8 and 9). Importantly, the allyl group can be tolerated under these reaction conditions (Table 9, entry 9): no addition to the external double bond was observed. Furthermore, differently substituted cyclopropenone acetals appeared to be excellent substrates for the distannation reaction, affording very high yields of the corresponding adducts (Table 9, entries 10−13).

Selected Transformations of Cyclopropylstannanes. To demonstrate the synthetic utility of the novel cyclopropylstannanes and to compare the reactivity aptitude of the two stannyl groups in the cyclopropyldistannanes, we tested several destannylative transformations with the obtained adducts. Thus, it was found that the tributyltin moiety of cyclopropylstannane **3aa** can readily be converted into the corresponding bromide **14** with a retention of configuration (Scheme 4).[38] Alternatively, the tributyltin group can also undergo a Sn−Li exchange to produce a cyclopropyllithium species, which upon trapping with halogen electrophiles[39] affords the corresponding cyclopropylbromide **14** and -iodide **15** in high yield (Scheme 4).

Remarkably, it was also found that two tributyltin moieties can display dramatically different reactivities depending on the substitution pattern at the corresponding cyclopropyl carbon atoms (Scheme 5). Thus, a tin group attached to a tertiary carbon atom in cyclopropyldistannane **12xe** can chemoselectively be substituted with a halogen to give bromocyclopropylstannane **16** in excellent yield (Scheme 5).[39] Alternatively, the same tin moiety can selectively undergo protiodestannylation with acetic acid to quantatively afford the hardly available product of a formal Markovnikov addition of tin hydride to cyclopropene **17**.[39] Subsequent modification of the remaining tributyltin group produced the corresponding bromide **18** in 71% yield (Scheme 5).[39]

(38) (a) Baekelmans, P.; Gielen, M.; Nasielski, J. *Tetrahedron Lett.* **1967**, *8*, 1149. (b) Gielen, M.; Baekelmans, P.; Nasielski, J. *J. Organomet. Chem.* **1972**, *34*, 329.

Conclusion

In conclusion, the first transition metal-catalyzed hydrosilylation and -germylation of cyclopropenes have been demonstrated. Additionally, the scope of the previously reported hydro-, sila-, and distannation reactions was significantly broadened. This novel methodology allows for efficient preparation of up to pentasubstituted cyclopropanes possessing an easily modifiable metal substituent. Generally, the stereoselectivity of addition is controlled by steric factors, which result in a metallic species being added from the least hindered site of the cyclopropene. The observed regioselectivity of the Pd-catalyzed silastannation of cyclopropenes is in accordance with the palladastannation pathway and depends on the relative sizes of the silyl group and the isocyanide ligand used. The synthetic utility of the obtained cyclopropylstannanes was demonstrated through several stereospecific transformations. Different reactivities of the two tin groups toward electrophiles permits efficient chemoselective transformation of cyclopropyldistannanes into the synthetically valuable cyclopropylhalides.

Experimental Section

General Information. NMR spectra were measured on Bruker Avance DRX-500 (500 MHz) and DPX-400 (400 MHz) instruments. (+) and (−) represent positive and negative intensities of signals in ^{13}C DEPT-135 experiments. ^{119}Sn NMR spectra were recorded using an inverse-gated decoupling technique, and chemical shifts were assigned relative to Me_3SnPh (δ −30.0). Values of selected X−Sn coupling constants are given for the ^{117}Sn and ^{119}Sn nuclei, respectively. If only one value is listed, it represents an average constant observed in cases where the difference between constant values for these isotopes was smaller than the digital resolution of the recorded spectrum. ^{1}H−^{13}C HMBC experiments were tuned for a long-range coupling constant of ∼10 Hz, typical $^3J_{CH}$ values. GC-MS analysis was performed on a Hewlett-Packard Model 6890 gas chromatograph interfaced to a Hewlett-Packard Model 5973 mass selective detector (15 mm × 0.25 mm capillary

(39) See Supporting Information for details.

column, HP-5MS). Column chromatography was carried out employing Merck silica gel (Kieselgel 60, 63−200 μm). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography. HRMS (EI) analysis was performed on a JEOL GC mate II instrument.

All manipulations with cyclopropenes and cyclopropylstannanes, -silanes, and -germanes were conducted under argon atmosphere using a combination of glovebox and standard Schlenk techniques. Anhydrous dichloromethane, DMSO, diethyl ether, and THF were purchased from Aldrich and stored over calcium hydride. All other chemicals were purchased from Aldrich or Acros Organics and used without additional purification.

Typical Procedures for Hydrostannation of Cyclopropenes. Method A. An oven-dried 3 mL Wheaton microreactor was loaded with $Pd(PPh_3)_4$ (5 mg, 0.5 mol %). Anhydrous THF (1 mL) was added, and the mixture was stirred at room temperature until all the catalyst dissolved. The solution was cooled to −78 °C, and tributyltin hydride (300 μL, 1.1 mmol) was added. The reaction mixture was stirred at −78 °C for 1 min, after which 3-methyl-3-phenylcyclopropene (**1a**) (130 mg, 1 mmol) was added, and the mixture was stirred at −78 °C for 5 min. The mixture was warmed to room temperature and transferred into a flask (ca. 5 mL of CH_2Cl_2 was used). Solvents were evaporated, and the product was purified by column chromatography (eluent: hexane) to obtain 387 mg (92%) of *trans*-tributyl-(2-methyl-2-phenylcyclopropyl)stannane (**3aa**).[14]

Method B. An oven-dried 3 mL Wheaton microreactor was loaded with $[(\pi\text{-allyl})PdCl]_2$ (2 mg, 0.5 mol %) and (−)-MOP (9 mg, 2 mol %). Anhydrous THF (1 mL) was added, and the mixture was stirred at room temperature until all catalyst dissolved. The solution was then cooled down to −100 °C, and 1,3-dimethyl-3-phenylcyclopropene (**1l**) (144 mg, 1 mmol) was added. To the resulting mixture was added a solution of Bu_3SnH (400 μL, 1.4 equiv) in THF (∼50%) via a syringe pump over 1 h. After the addition was complete, the reaction mixture was warmed up to room temperature, and the solvent was removed in vacuum. Column chromatography (eluent: hexane) gave 363 mg (83%) of tributyl-(2,3-dimethyl-2-phenylcyclopropyl)stannane (**3la**).[14]

Representative Procedure for Hydrosilylation of 7r. An oven-dried 3 mL Wheaton microreactor was charged with $PtCl_2$ (1.3 mg, 5 μmol, 1 mol %) and anhydrous THF (500 μL) in a nitrogen-filled glovebox. The reaction was allowed to stir for 10 min, and 3,3-diphenylcylopropene (**1r**) (96 mg, 0.5 mmol, 1 equiv) was added via a syringe, followed by addition of dimethylphenylsilane (**6d**) (0.077 mL, 0.5 mmol, 1 equiv). The reaction progress was monitored by TLC. After complete consumption of cyclopropene, the reaction mixture was concentrated in vacuum and purified by column chromatography to give **7rd** as a colorless oil (135 mg, 0.41 mmol, 82%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.65−7.57 (m, 2H), 7.50−7.38 (m, 5H), 7.38−7.26 (m, 7H), 7.22 (m, 1H), 1.71 (dd, J = 7.8 Hz, 3.8 Hz, 1H), 1.50 (dd, J = 10.6 Hz, 3.8 Hz, 1H), 1.12 (dd, J = 10.6 Hz, 7.8 Hz, 1H), 0.16 (s, 3H), −0.05 (s, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 148.0, 143.1, 139.8, 133.8 (+), 130.8 (+), 128.9 (+), 128.3 (+), 128.2 (+), 127.8 (+), 127.6 (+), 126.6 (+), 125.8 (+), 35.8, 18.2 (−), 14.5 (+) −2.8 (+) −3.4 (+); HRMS (EI) Calcd for $C_{23}H_{24}Si$ (M^+) 328.1647. Found 328.1637.

Representative Procedure for Hydrogermylation of 7r. An oven-dried 3 mL Wheaton microreactor was charged with $PtCl_2$ (1.3 mg, 5 μmol, 1 mol %) and anhydrous THF (500 μL) in a nitrogen-filled glovebox. The reaction was allowed to stir for 10 min, and 3,3-diphenylcylopropene (**1r**) (96 mg, 0.5 mmol, 1 equiv) was added via a syringe, followed by addition of triethylgermane (0.08 mL, 0.5 mmol, 1 equiv). The reaction progress was monitored by TLC. After complete consumption of cyclopropene, the reaction mixture was concentrated in vacuum and purified by column chromatography to give **9r** as a colorless oil (164 mg, 0.47 mmol, 93%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.44−7.40 (m, 2H), 7.34−7.20 (m, 7H), 7.19−7.14 (m, 1H), 1.54 (dd, J = 7.8 Hz, 3.9 Hz, 1H), 1.36 (dd, J = 10.6 Hz, 3.9 Hz, 1H), 1.06 (dd, J = 10.5 Hz, 7.7 Hz, 1H), 1.00 (t, J = 8.0 Hz, 9H), 0.62−0.52 (m, 3H), 0.49−0.40 (m, 3H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 148.3, 144.2, 130.4 (+), 128.2 (+), 128.1 (+), 127.7 (+), 126.4 (+), 125.6 (+), 34.0, 17.9 (−), 14.0 (+) 9.1 (+, 3C) 4.2 (−, 3C); HRMS (EI) Calcd for $C_{21}H_{28}{}^{74}Ge$ (M^+) 354.1403. Found 354.1415.

Representative Procedure for Silastannation of 1v. An oven-dried 3 mL Weaton microreactor was charged with $Pd(OAc)_2$ (5.6 mg, 25 μmol, 5 mol %), 2,6-dimethylphenylisocyanide (**10e**) (22 mg, 0.17 mmol, 33 mol %), and anhydrous THF (500 μL) in a nitrogen-filled glovebox. The reaction was stirred for 5 min, and cyclopropene **1v** (84 mg, 0.5 mmol, 1 equiv) was added via a syringe, followed by addition of trimethylstannylmethyldiphenylsilane (**11c**) (0.18 mL, 0.5 mmol, 1 equiv). The reaction progress was monitored by TLC. After complete consumption of cyclopropene, the reaction mixture was concentrated in vacuum and purified by column chromatography to give **12vc** as a colorless oil (206 mg, 0.39 mmol, 78%). ^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.49−7.69 (m, 4H), 7.47−7.28 (m, 6H), 4.30−4.15 (m, 2H), 1.91 (d, J = 7.2 Hz, $^3J_{Sn-H}$ = 54.3 Hz, 1H), 1.82−1.61 (m, 2H), 1.51−1.23 (m, 7H), 1.11 (d, J = 7.2 Hz, $^3J_{Sn-H}$ = 64.6 Hz, 1H), 0.93 (t, J = 6.9 Hz, 3H), 0.58 (s, 3H), −0.06 (s, $^2J_{Sn-H}$ = 26 Hz, 9H); ^{13}C NMR (125.76 MHz, $CDCl_3$) δ 173.1, 137.1, 136.7, 135.0 (+, 2C), 135.0 (+, 2C), 129.5 (+), 129.4 (+), 127. 9 (+, 2C), 60.5 (−), 35.6 (−), 33.0 (−), 28.2 (+), 26.7, 23.0 (+), 19.8 (+), 14.6 (+), 14.2 (+), −3.7 (+), −7.7 (+, 3C); ^{119}Sn NMR (186.50 MHz, $CDCl_3$) δ 18.1; ^{1}H−^{13}C HMBC ($CDCl_3$, 500.13 MHz, 125.76 MHz), selected cross-peaks: δ_H/δ_C −0.06/−7.3, −0.06/26.7, 0.58/19.8, 0.58/137.1, 0.58/137.7; HRMS (EI) Calcd for $C_{26}H_{38}O_2Si^{120}Sn$ (M^+) 530.1663. Found 530.1654.

Acknowledgment. Support from the National Science Foundation (CHE-0710749) is gratefully acknowledged.

Supporting Information Available: Experimental details and complete analytical data for unknown compound. This material is available free of charge via the Internet at http://pubs.acs.org.

JO701855C