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Metal-Catalyzed Di-*tert*-butylsilylene Transfer: Synthesis and Reactivity of Silacyclopropanes

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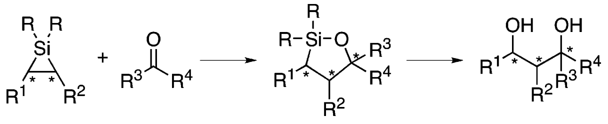
Metal-catalyzed di-*tert*-butylsilylene transfer was developed as a mild, operationally simple, functional-group-tolerant method for silacyclopropane formation. Di-*tert*-butylsilylene was transferred from cyclohexene silacyclopropane **1** to an alkene through the use of a metal salt. Silacyclopropanation occurred at temperatures as low as −27 °C when AgOTf or $AgOC(O)CF_3$ were used as catalysts. Complex silacyclopropanes were formed stereospecifically and diastereoselectively from functionalized alkenes. Silacyclopropanes reacted with various carbonyl compounds, including aldehydes, ketones, formate esters, and formamides, in an overall process that efficiently converts alkenes into oxasilacyclopentanes with defined stereochemistry.

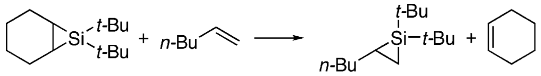
Introduction

Silacyclopropanes are strained[1] silanes that undergo carbon−carbon bond-forming reactions with various carbonyl compounds.[2,3] Carbonyl insertions proceed with high stereo-, regio-, and chemoselectivity to afford oxasilacyclopentane adducts under mild, metal-catalyzed conditions.[2] Upon oxidation of the carbon−silicon bond, oxasilacyclopentanes give 1,3-diols with up to three contiguous sterocenters, thus making silacyclopropanes useful intermediates for the synthesis of polyoxygenated organic compounds (Scheme 1).[4,5]

SCHEME 1



Silacyclopropanes are typically prepared by reaction of an alkene with a silylene or a silenoid species. Methods for generating silylenes, however, require forcing conditions, including photolysis, strongly reducing conditions, or elevated temperatures, which limit the alkene substrate compatibility.[6−8] Thermal methods for silacyclopropane formation involve thermolysis of cyclic silanes such as hexamethylsilacyclopropane,[11] cyclotrisilanes,[8,9,14,15] or cyclohexene silacyclopropane (**1**, eq 1)[6,7,16] in the



1 **2** (1)

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[1] (a) Naruse, Y.; Ma, J.; Inagaki, S. *J. Phys. Chem. A* **2003**, *107*, 2860−2864. (b) Sella, A.; Basch, H.; Hoz, S. *J. Am. Chem. Soc.* **1996**, *118*, 416−420. (c) Sella, A.; Basch, H.; Hoz, S. *Tetrahedron Lett.* **1996**, *37*, 5573−5576. (d) Gordon, M. S.; Boatz, J. A.; Walsh, R. *J. Phys. Chem.* **1989**, *93*, 1584−1585.

[2] Franz, A. K.; Woerpel, K. A. *Acc. Chem. Res.* **2000**, *33*, 813−820.

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[14] Belzner, J.; Dehnert, U.; Ihmels, H. *Tetrahedron* **2001**, *57*, 511−517.

[15] Weidenbruch, M. *Chem. Rev.* **1995**, *95*, 1479−1493.

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TABLE 1. Catalyst Screening for the Silylene Transfer (Eq 1)

entry	catalyst (10 mol %)	temp, °C	time	% transfer[a,b]
1	none	130	36 h	100
2	$Zn(OTf)_2$	55	12 h	95
3	$CeCl_3$	25	15 h	69
4	CuF_2	25	18 h	70
5	AgI	25	30 min	80
6	$Cu(OTf)_2$	25	17 min	100
7	$Cu(OTf)_2$	0	2 h	100
8	$Cu(OTf)_2 \cdot PhH$	0	2 h	100
9	AgOTf	−27	2 h	100
10	$AgOC(O)CF_3$	−27	2 h	100

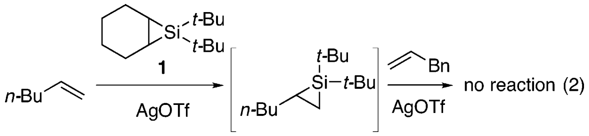
[a] As determined by ^{1}H MMR spectroscopic analysis of the reaction mixture. [b] Reaction took place in a sealed NMR tube with C_6D_6 as a solvent.

presence of an alkene.[6−15] The catalytic silacyclopropanation of alkenes would be a mild alternative to the more stringent conditions normally required to form silacyclopropanes. While metal-catalyzed reactions are commonly employed in three-membered-ring syntheses from alkenes,[17−20] catalytic alkene silacyclopropanation was unknown.

We recently reported metal-catalyzed silylene transfer as a mild method for silacyclopropane synthesis,[21] and we report here our improvements in this methodology. By using silver salts as catalysts, alkene silacyclopropanation proceeds stereospecifically, and with high diastereoselectivity. The mild reaction conditions allow for a broad alkene substrate scope. By using low silver catalyst loading, in situ formed silacyclopropanes undergo insertions with a wide variety of carbonyl compounds, affording oxasilacyclopentane products with diverse structures and high regioselectivities.

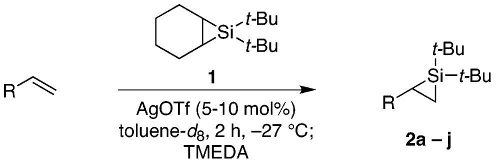
Results and Discussion

Since di-*tert*-butylsilylene can be generated thermally from cyclohexene silacyclopropane **1** (eq 1, Table 1, entry 1), we initiated a search for conditions that would allow the silylene transfer process at reduced temperatures. We investigated various metal salts to catalyze the transfer of di-*tert*-butylsilylene to 1-hexene (eq 1).[22] Of the large number of metal salts screened, several were shown to reduce the temperature of the silylene transfer (Table 1). Catalytic amounts (10 mol %) of $Zn(OTf)_2$ reduced the temperature for the transfer to 55 °C (entry 2). Room temperature (25 °C) silylene transfer was possible with use of substoichiometric amounts of $CeCl_3$ (entry 3), CuF_2 (entry 4), and AgI (entry 5). Catalytic amounts of CuOTf$\cdot$PhH and $Cu(OTf)_2$ further decreased the reaction temperature to 0 °C (entries 7 and 8), though with increased reaction times (compare entries 6 and 7).[23] The most efficient catalysts, AgOTf and $AgOC(O)CF_3$, reduced the transfer temperature to −27 °C (entries 9 and 10).[23] Control experiments suggest that the silylene transfer is not reversible. Exposing the in situ formed *n*-butyl silacyclopropane to allylbenzene and AgOTf did not furnish any benzyl-substituted silacyclopropane (eq 2).



(2)

The generality of the metal-catalyzed silylene transfer methodology was explored utilizing AgOTf and AgOC(O)CF_3, the most efficient catalysts. A variety of monosubtituted alkenes undergo metal-catalyzed silacyclopropanation in high yield (eq 3, Table 2). Increasing the



(3)

steric bulk of the vinyl substituent did not affect the yield of the reaction (entries 1−3). The mild reaction conditions allowed for a broad substrate scope, including aryl, benzyl, and silyl ethers (entries 4−6 and 8−10), as well as primary and aryl pivaloate esters (entries 7 and 10).

Disubstituted alkenes underwent silacyclopropanation stereospecifically and diastereoselectively. Transformations of *cis*- and *trans*-2-butene yielded the corresponding products **3**[7] and **4**[7] with complete transfer of stereochemical information (Table 3, entries 1 and 2).[24] Metal-catalyzed silylene transfer was also diastereoselective (Table 3, entries 3−5): cyclopentene derivative **5** and β-pinene **7**[25] (entries 3 and 4) afforded single isomers of the silacyclopropane products **6** and **8**, respectively.[24] Norbornene **9** afforded only the *exo* isomer of the corresponding silacyclopropane (entry 5).[26] Acyclic alkene **11** provided the corresponding silacyclopropane **12** as an 89:11 ratio of isomers.[24,27] The diastereoselectivity observed

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[17] For recent examples of metal-catalyzed cyclopropanation, refer to: (a) Miki, K.; Nishino, F.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 5260−5261. (b) Wurz, R. P.; Charette, A. B. *Org. Lett.* **2002**, *4*, 4531−4533. (c) Li, Y.; Huang, J.-S.; Zhong, Z.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2001**, *123*, 4843−4844. (d) For a review on metal-catalyzed cyclopropanation see: Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A. B. *Chem. Rev.* **2003**, *103*, 977−1050.

[18] For recent examples of metal-catalyzed aziridination, refer to: (a) Chanda, B. M.; Vyas, R.; Bedekar, A. V. *J. Org. Chem.* **2001**, *66*, 30−34. (b) Dauban, P.; Saniere, L.; Tarrade, A.; Dodd, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 7707−7708. (c) Evans, D. A.; Bilodeau, M. T.; Faul, M. M. *J. Am. Chem. Soc.* **1994**, *116*, 2742−2753.

[19] For recent examples of metal-catalyzed epoxidation, refer to: (a) Daly, A. M.; Renehan, M. F.; Gilheany, D. G. *Org. Lett.* **2001**, *3*, 663−666. (b) Adam, W.; Stegmann, V. R.; Saha-Moller, C. R. *J. Am. Chem. Soc.* **1999**, *121*, 1879−1882.

[20] For metal-catalyzed silacyclopropene synthesis, refer to: (a) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 4824−4827. (b) Ishikawa has reported tungsten-catalyzed silylene transfer for silacyclopropene synthesis: Ohshita, J.; Ishikawa, M. *J. Organomet. Chem.* **1991**, *407*, 157−165.

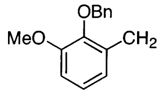
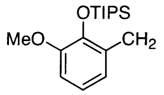
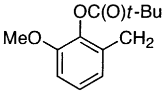
[21] Ćiraković, J.; Driver, T. G.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 9370−9371.

[22] For recent examples of metal−silylene complexes, refer to: (a) Mork, B. V.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 357−360. (b) Evans, W. J.; Perotti, J. M.; Ziller, J. W.; Moser, D. F.; West, R. *Organometallics* **2003**, *22*, 1160−1163. (c) Okazaki, M.; Tobita, H.; Ogino, H. *Dalton Trans.* **2003**, 493−506. (d) Cai, X.; Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F.; Slootweg, J. C. *J. Organomet. Chem.* **2002**, *643*−*644*, 272−277. (e) Papkov, V. S.; Gerasimov, M. V.; Dubovik, I. I.; Sharma, S.; Dementiev, V. V.; Pannell, K. H. *Macromolecules* **2000**, *33*, 7107−7115.

[23] To examine reactions performed below room temperature, TMEDA was added to quench the metal catalyst so that ^{1}H NMR spectroscopic analysis could be performed at room temperature.

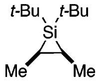
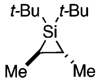
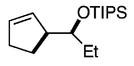
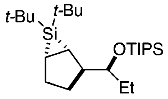
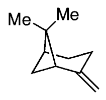
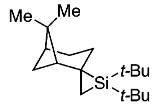
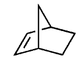
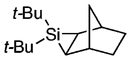
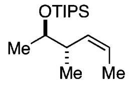
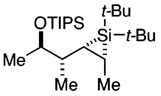
[24] Based on ^{1}H and ^{29}Si NMR spectroscopic analysis of the unpurified product mixture.

TABLE 2. Silacyclopropanation of Monosubstituted Alkenes (Eq 3)

entry	R[a]	product	% yield[b]
1	*n*-Bu	**2a**	90
2[c]	*i*-Pr	**2b**	99
3	*t*-Bu	**2c**	96
4	Bn	**2d**	90
5	TIPSO−(CH$_2$)$_2$	**2e**	82
6	BnO−(CH$_2$)$_2$	**2f**	71
7	*t*-Bu(O)CO−(CH$_2$)$_2$	**2g**	67
8		**2h**	61
9		**2i**	72
10		**2j**	83

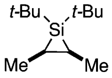
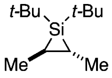
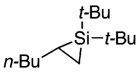
[a] 1.3 equiv of alkene was used. [b] As determined by ^{1}H NMR spectroscopic analysis of the product mixture relative to an internal PhSi(CH$_3$)$_3$ standard. [c] An excess of alkene was used (ca. 10 equiv).

TABLE 3. Silacyclopropanation of Disubstituted Alkenes

entry	alkene[a]	product	% yield[b]
1	*cis*-2-butene[c]	 **3**	99
2	*trans*-2-butene[c]	 **4**	92
3	 **5**	 **6**	85[d]
4	 **7**	 **8**	72[d]
5	 **9**	 **10**	90[d]
6	 **11**	 **12**	79[e]

[a] 1.3 equiv of alkene were used. [b] As determined by ^{1}H NMR spectroscopic analysis of the product mixture relative to an internal PhSi(CH$_3$)$_3$ or 1,3-dimethoxybenzene standard. [c] An excess of alkene was used (ca. 10 equiv). [d] One diastereomer was visible by ^{1}H NMR and ^{29}Si NMR spectroscopy (dr ≥ 95:5). [e] dr = 89:11, as determined by ^{29}Si NMR spectroscopy.

TABLE 4. Isolation of Silacyclopropanes

entry	alkene	product	% yield[a]
1	*cis*-2-butene	 **3**	67
2	*trans*-2-butene	 **4**	85
3	1-hexene	 **13**	90

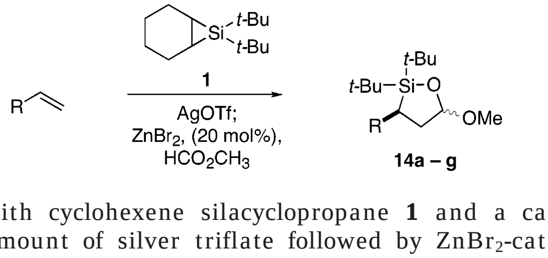
[a] Isolated yield after bulb-to-bulb distillation.

in these reactions represents an improvement over that obtained with thermal silylene transfer from **1** or silacyclopropanation by reduction of *t*-Bu$_2$SiCl$_2$ with lithium.[16]

By using the catalyst loadings initially developed (10 mol %), attempts to isolate silacyclopropanes resulted only in decomposition products.[28] While stable in solution, silacyclopropanes generated in the presence of metal salts decomposed upon concentration. We propose that the decomposition of silacyclopropanes is likely catalyzed by silver salts, so upon removal of the solvent, the concentration of both the silacyclopropane and the silver salt increase, leading to faster decomposition.

The isolation procedure was optimized by reducing the amount of silver catalyst from about 5 mol % to ≤1 mol %. Schlenk filtration of the unpurified reaction mixture, followed by bulb-to-bulb distillation, afforded pure silacyclopropanes (Table 4). The decrease in the catalyst loading had no effect on the yield of the silylene transfer.

The metal-catalyzed silacyclopropanation of alkenes allows the reactive silacyclopropanes to be generated in situ and then carried on in subsequent reactions without isolation (eq 4). Treatment of a monosubstituted alkene with cyclohexene silacyclopropane **1** and a catalytic amount of silver triflate followed by ZnBr$_2$-catalyzed



(4)

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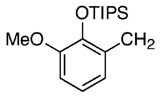
(25) Silver-catalyzed silylene transfer to β-pinene provided the opposite isomer of silacyclopropane product to the one that was obtained by reduction of *t*-Bu$_2$SiCl$_2$ by lithium in the presence of β-pinene.[16] Studies to determine the origin of the reversal of selectivity are underway.

(26) Norbornenes normally exhibit *exo*-selective reactions. See for example: (a) Brown, H. C.; Kawakami, J. H.; Liu, K. T. *J. Am. Chem. Soc.* **1973**, *95*, 2209−2216. (b) Houk, K. N.; Rondan, N. G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmayer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980−5988.

(27) The configuration of the major product was assigned based on 1,3-allylic strain considerations: Hoffmann, R. W. *Chem. Rev.* **1989**, *89*, 1841−1860.

(28) Schlenk filtration of the unpurified product mixture through Celite, silica, or alumina followed by concentration of the filtrate resulted in the decomposition of the silacyclopropane product.

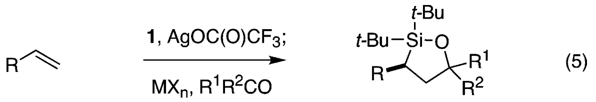
TABLE 5. One-Flask Silylene Transfer and Methyl Formate Insertion (Eq 4)

entry	R	regioselectivity[a]	d.r.[a]	product	% yield[b]
1	*n*-Bu	>99:1	76:24	**14a**	87
2	*i*-Pr	>99:1	70:30	**14b**	92
3	*t*-Bu	74:26	major, 70:30 minor, 91:9	**14c**	75
4	Bn	97:3	major, 70:30	**14d**	80
5	BnO(CH$_2$)$_2$	>99:1	64:36	**14e**	61
6	TIPSO(CH$_2$)$_2$	96:4	70:30	**14f**	61
7		>99:1	70:30	**14g**	82

[a] As determined by ^{1}H NMR spectroscopic analysis of the unpurified product mixture. [b] Isolated yield over two steps after purification by flash chromatography.

insertion of methyl formate provided the oxasilacyclopentane acetals **14a**–**g** (Table 5, eq 4).[21] The formate insertion is regioselective, favoring the 1,3-regioisomer.[29] *n*-Butyl-, isopropyl-, and benzyl-substituted ethenes gave high yields of the corresponding five-membered-ring products (entries 1, 2, and 4). The regioselectivity of the formate insertion decreased with increased steric bulk of the alkene substituent (entry 3). A high yield of the oxasilacyclopentane product was also obtained for the TIPS-protected eugenol (entry 7). Benzyl and silyl ethers were also tolerated in this reaction sequence, albeit with lower yield for the overall reaction (entries 5 and 6).

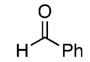
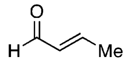
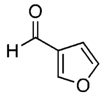
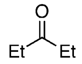
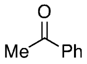
The two-step, one-flask reaction sequence described above was utilized for addition of other carbonyl electrophiles into silacyclopropanes (eq 5, Table 6). Aromatic and α,β-unsaturated aldehydes inserted readily into the carbon–silicon bond of the intermediate silacyclopropane (entries 1–3). Both aliphatic and aromatic ketones (entries 4 and 5) afforded five-membered-ring products **15d** and **15e** in 57% and 71% yield over two steps, respectively. While the zinc-catalyzed insertion reaction was completely regioselective, giving only the 1,3-regioisomer shown,[30] the diastereoselectivity of the 1,3-product formation was low. Both ZnBr$_2$ and ZnI$_2$ catalyzed the carbonyl insertions with equal efficiency.



15a-e

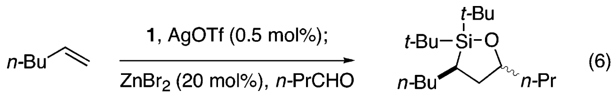
15a, R^1 = Ph, R^2 = H
15b, R^1 = CH=CHMe, R^2 = H
15c, R^1 = 3-furanyl, R^2 = H
15d, R^1 = R^2 = Et
15e, R^1 = Me, R^2 = Ph

TABLE 6. One-Flask Silylene Transfer, Carbonyl Insertion (Eq 5)[a]

entry	R	MX$_n$	R^{1}R^{2}CO	d.r.	% yield[b]
1	*n*-Bu	ZnBr$_2$		65:35	73
2	PhCH$_2$	ZnI$_2$		64:36	78
3	PhCH$_2$	ZnI$_2$		65:35	80
4	PhCH$_2$	ZnI$_2$		--	57
5	PhCH$_2$	ZnI$_2$		55:45	71

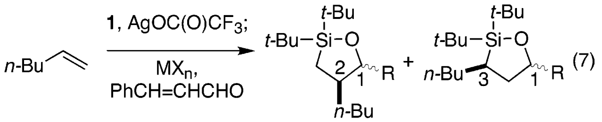
[a] 20 mol % of MX$_n$ used. [b] Isolated yield over two steps after purification by flash chromatography.

Decreasing the silver catalyst loading from 5 mol % to ≤1 mol % proved to be critical for the insertion of saturated aldehydes. When 5 mol % of silver catalyst was used, in situ formed silacyclopropanes did not react with saturated aldehydes. With 0.5 mol % of AgOTf used in the transfer step, the zinc bromide-catalyzed insertion of butyraldehyde proceeded to give the corresponding oxasilacyclopentane **16** in good yield over two steps (eq 6). Optimization of solvent, temperature, and use of additives did not improve the diastereoselectivity of the reaction.



16
79%
d.r. = 39:61

Variation of the catalyst for the insertion step controlled the regioselectivity of the oxasilacyclopentane product.[29,31] Treatment of the in situ formed butyl silacyclopropane with cinnamaldehyde and CuI as the catalyst resulted in formation of the 1,2-regioisomer, **17a** (eq 7, Table 7, entry 1). ZnI$_2$-catalyzed insertion of cinnamaldehyde afforded the 1,3-product, **17b** (Table 7, entry 2).



17a **17b**

R = CH=CHPh

Low silver catalyst loading enabled the insertions of formamides to disubstituted silacyclopropanes.[32] *cis*-2-Butene was converted to oxasilacyclopentane acetate **18** through the use of 0.5 mol % of AgOC(O)CF$_3$ for silylene transfer followed by CuI-catalyzed formamide inser-

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(29) Franz, A. K.; Woerpel. K. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 4295–4299.

(30) Based on GC analysis of the unpurified product mixture.

(31) Franz, A. K.; Woerpel, K. A. *J. Am. Chem. Soc.* **1999**, *121*, 949–957.

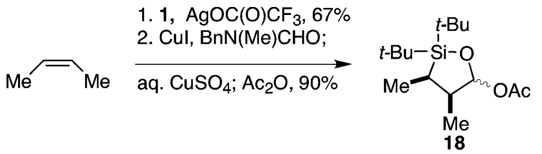
(32) With high silver catalyst loading (5 mol %), 2,3-disubstituted silacyclopropanes did not form oxasilacyclopentane products with any carbonyl compounds. Instead, decomposition products were formed.

TABLE 7. One-Flask Silylene Transfer and Cinnamaldehyde Insertion (Eq 7)[a]

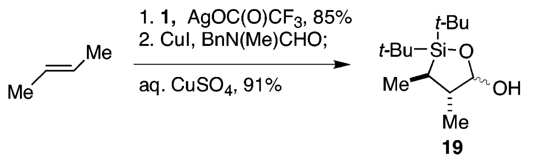
entry	MX_n	**17a**:**17b**	1,2 dr	1,3 dr	% yield[b]
1	CuI	96:4	82:18		85
2	ZnI_2	1:99		76:24	92

[a] 20 mol% of MXn used. [b] Isolated yield over two steps after purification by flash chromatography.

tion,[31,33] and hydrolysis of the intermediate *N*,*O*-acetal.[34] The hemiacetal product (not shown) was acetylated to afford **18** in 90% yield over three steps (eq 8). *trans*-2-Butene was elaborated in a similar fashion to provide hemiacetal **19** in 91% yield over two steps (eq 9).[34]

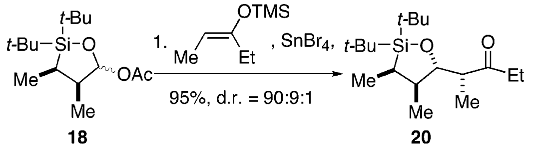


(8)

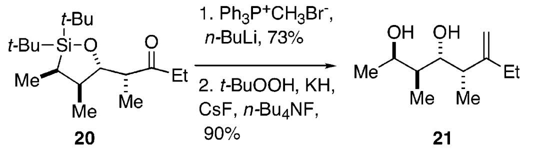


(9)

The synthetic utility of the one-flask silacyclopropanation/insertion methodology was demonstrated by the functionalization of acetate **18** (eq 10). Under Lewis acidic conditions, oxasilacyclopentane acetals undergo highly stereoselective carbon–carbon bond-forming reactions with various nucleophiles.[2,35] Treatment of acetate **18** with the silyl enol ether of diethyl ketone[36] in the presence of $SnBr_4$ afforded ketone **20** in high yield and selectivity (eq 10). Wittig methylenation followed by carbon–silicon bond oxidation afforded diol **21** in high overall yield (eq 11).



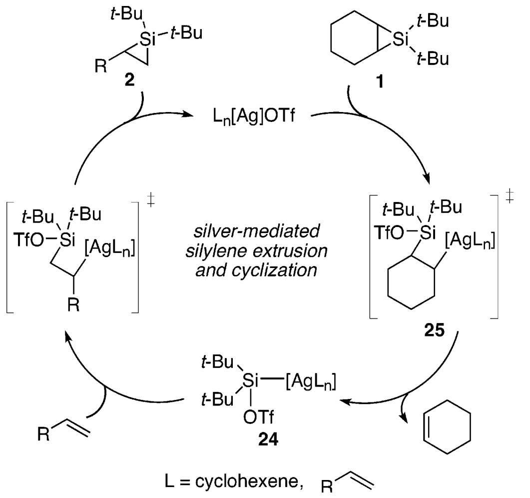
(10)

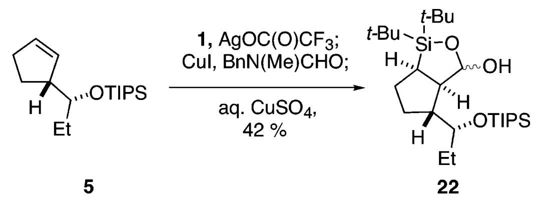


(11)

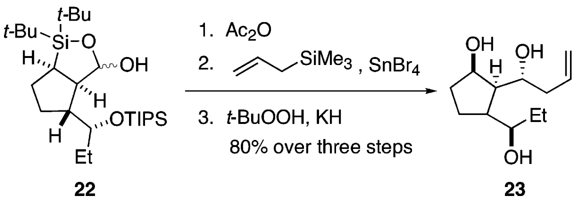
To demonstrate the level of complexity that can be achieved utilizing silacyclopropane chemistry, cyclopentene **5** was elaborated with use of the silacyclopropanation/insertion protocol. Silacyclopropanation of cyclopentene **5** afforded silacyclopropane **6** as a single diastereomer (Table 2). Treatment of in situ formed **6** with *N*-benzyl-*N*-methylformamide and CuI, followed by hydrolysis of the intermediate *N*,*O*-acetal, afforded **22** as a mixture of epimers at the hemiacetal position (eq 12). Hemiacetal **22** can be converted to triol **23** with five stereocenters in three steps and in excellent yield (eq 13).[16]

SCHEME 2





(12)



(13)

A preliminary mechanism for silver-promoted silylene transfer, involving silver silylenoid **24**[37] (Scheme 2), can be proposed based on qualitative observations. Since silver salts form complexes with alkenes,[38] we propose that the silver catalyst is complexed by one or more alkene ligands. Because silylene transfer is dramatically accelerated relative to thermal transfer,[10b,39] silver must be involved in the silylene extrusion step. This condition can be satisfied by transmetalation with cyclohexene silacyclopropane **1** to give **25**.[40] To obey the principle of microscopic reversibility, the subsequent cyclization must also be mediated by silver to afford product silacyclopro-

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(33) (a) Shaw, J. T.; Woerpel, K. A. *Tetrahedron* **1997**, *53*, 16597–16606. (b) Shaw, J. T.; Woerpel, K. A. *J. Org. Chem.* **1997**, *62*, 442–443.

(34) Higher yields of the overall reaction were observed when silacyclopropanes were isolated after the first step.

(35) (a) Bear, T. J.; Shaw, J. T.; Woerpel, K. A. *J. Org. Chem.* **2002**, *67*, 2056–2064. (b) Shaw, J. T.; Woerpel, K. A. *J. Org. Chem.* **1997**, *62*, 6706–6707.

(36) Cazeau, P.; Duboudin, F.; Moulines, F.; Babot, O.; Dunogues, J. *Tetrahedron* **1987**, *43*, 2075–2088.

(37) Lewis base stabilized metal silylenoids have been reported: (a) Theil, M.; Jutzi, P.; Neumann, B.; Stammler, A.; Stammler, H.-G. *J. Organomet. Chem.* **2002**, *662*, 34–42. (b) Mitchell, G. P.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 7635–7636. (c) Ueno, K.; Sakai, M.; Ogino, H. *Organometallics* **1998**, *17*, 2138–2140.

(38) Kim, J. H.; Min, B. R.; Won, J.; Kang, Y. S. *Chem. Eur. J.* **2002**, *8*, 650–654.

(39) Driver, T. G.; Woerpel, K. A. *J. Am. Chem. Soc.* **2003**, *125*, 10659–10663.

(40) (a) Castillo, I.; Tilley, T. D. *J. Am. Chem. Soc.* **2001**, *123*, 10526–10534. (b) Mintcheva, N.; Nishihara, Y.; Mori, A.; Osakada, K. *J. Organomet. Chem.* **2001**, *629*, 61–67.

pane **2** and regenerate the active catalyst. If both extrusion and cyclization require silver, the silylene is probably shuttled between alkenes as silver silenoid **24**.

Conclusion

Silver-catalyzed silylene transfer is a mild, efficient method for silacyclopropane synthesis. The low temperature of the transfer resulted in improved diastereoselectivity and substrate compatibility compared to other methods for silacyclopropane formation. The silacyclopropanes formed react readily with a wide range of carbonyl compounds in a process that efficiently converts alkenes to oxasilacyclopentanes. Limiting the amount of silver catalyst used proved to be important in the two-step synthesis of oxasilacyclopentanes from alkenes. Reducing the amount of silver catalyst also resulted in a wider range of carbonyl compounds that underwent insertion into the in situ formed silacyclopropanes, without diminishing the efficiency of the silylene transfer step. This methodology provides efficient access to diverse oxasilacyclopentanes from alkenes and expands the utility of silacyclopropanes as intermediates in organic synthesis.

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Supporting Information Available: Experimental procedures and spectroscopic and analytical data for the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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