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Nickel-Catalyzed Reactions of Silacyclobutanes with Aldehydes: Ring Opening and Ring Expansion Reaction

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ABSTRACT

The nickel-catalyzed ring opening reaction of silacyclobutanes with aldehydes affords the corresponding alkoxyallylsilanes. In contrast, the ring expansion reaction of benzosilacyclobutene with aldehydes occurs under nickel catalysis to give oxasilacyclohexenes.

Silacyclobutanes are an interesting class of compounds that have unique reactivity due to their ring strain and Lewis acidity.[1] Therefore, our group[2] and others[3] have developed their synthetic utilities. Among them, palladium and platinum complexes are known to catalyze quite useful transformations including ring opening polymerization,[4] cycloaddition with alkynes and allenes,[5] and coupling reactions with aryl and acid halides.[6] However, nickel-catalyzed reactions of silacyclobutanes have not been explored, although nickel belongs to the same group, group 10. In this communication, we describe the transformations of silacyclobutanes under nickel catalysis.

Treatment of 1,1-dimethylsilacyclobutane (**1a**, 0.5 mmol) with benzaldehyde (**2a**, 0.6 mmol) in the presence of 5 mol % of Ni(cod)$_2$ and 10 mol % of P(c-C_6H_{11})$_3$ in toluene (5 mL) at 100 °C for 12 h afforded allylbenzyloxydimethylsilane (**3a**) in 20% yield (Table 1, entry 1).[7] Apparently, a carbon−silicon bond cleavage was involved in this transformation, albeit the yield was low. We then screened various ligands (Table 1). Although a number of phosphine ligands have poor to moderate activity for this reaction, PPh$_2$Me and P(n-Bu)$_3$ showed high efficiency (entries 3 and 7). Finally, we found that the desired product was obtained in 88% yield with 10 mol % of Ni(cod)$_2$ and 20 mol % of PPh$_2$Me in toluene (5 mL) at 100 °C (entry 10). This reaction is regarded as a hydrosilane-free reductive silylation of aldehydes.

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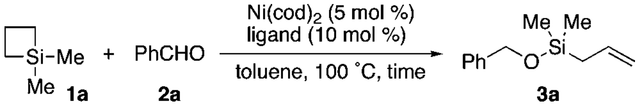
[6] (a) Tanaka, Y.; Yamashita, H.; Tanaka, M. *Organometallics* **1996**, *15*, 1524−1526. (b) Bhanu, P. S. C.; Tanaka, Y.; Yamashita, H.; Tanaka, M. *Chem. Commun.* **1996**, 1207−1208. (c) Tanaka, Y.; Nishigaki, A.; Kimura, Y.; Yamashita, M. *Appl. Organomet. Chem.* **2001**, *15*, 667−670.

[7] NiCl$_2$ and Ni(acac)$_2$ did not catalyze the reaction.

10.1021/ol0527577 CCC: $33.50

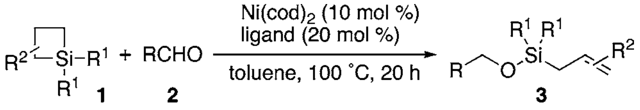
Table 1. Optimization of the Ring Opening Reaction of 1,1-Dimethylsilacyclobutane (**1a**) with Benzaldehyde (**2a**)



entry	ligand	time (h)	yield of **3a** (%)
1	$P(c\text{-}C_6H_{11})_3$	12	20
2	$P(t\text{-}Bu)_3$	12	0
3	$P(n\text{-}Bu)_3$	12	67
4	PMe_3	12	2
5	PPh_3	12	7
6	PPh_2Et	12	52
7	PPh_2Me	12	67
8[a]	$P(n\text{-}Bu)_3$	12	67
9[a]	PPh_2Me	12	76
10[a]	PPh_2Me	20	88

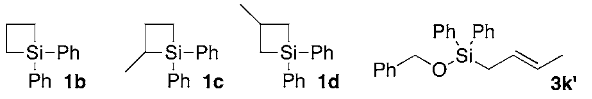
[a] With 10 mol % of $Ni(cod)_2$ and 20 mol % of ligand.

Table 2. Scope and Limitation



entry	**1**[b]	**2**	ligand	yield of **3** (%)
1	**1a**	$2\text{-}MeC_6H_4CHO$ (**2b**)	PPh_2Me	85 (**3b**)
2	**1a**	$4\text{-}MeOC_6H_4CHO$ (**2c**)	PPh_2Me	47 (**3c**)
3	**1a**	$4\text{-}CF_3C_6H_4CHO$ (**2d**)	PPh_2Me	48 (**3d**)
4[a]	**1a**	**2c**	$P(n\text{-}Bu)_3$	53 (**3c**)
5	**1a**	**2d**	$P(n\text{-}Bu)_3$	77 (**3d**)
6	**1a**	$4\text{-}MeOCOC_6H_4CHO$ (**2e**)	$P(n\text{-}Bu)_3$	53 (**3e**)
7	**1a**	$Ph(CH_2)_2CHO$ (**2f**)	$P(n\text{-}Bu)_3$	73 (**3f**)
8[a]	**1a**	$c\text{-}C_6H_{11}CHO$ (**2g**)	$P(n\text{-}Bu)_3$	69 (**3g**)
9	**1a**	*trans*-PhCH═CHCHO (**2h**)	PPh_2Me	51 (**3h**)
10	**1b**	**2a**	PPh_2Me	87 (**3i**)
11	**1b**	**2f**	$P(n\text{-}Bu)_3$	80 (**3j**)
12	**1c**	**2a**	PPh_2Me	63 (**3k**)[c]
13	**1d**	**2a**	PPh_2Me	0 (**3l**)

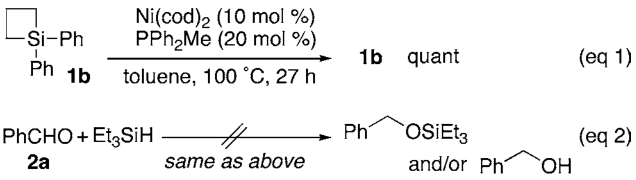
[a] Reaction time was 12 h. [b] Structures of silacyclobutanes **1b**−**1d** are shown below. [c] Crotylsilane **3k′** was obtained in 24% yield as a byproduct.



By using the optimal conditions, we surveyed the scope and limitation of this reaction (Table 2). Reaction of sterically hindered 2-methylbenzaldehyde (**2b**) proceeded smoothly to afford the corresponding alkoxyallylsilane (**3b**) in high yield (entry 1). Although reductive silylations of 4-methoxybenzaldehyde (**2c**) and 4-trifluoromethylbenzaldehyde (**2d**) resulted in low conversions (entries 2 and 3), the use of $P(n\text{-}Bu)_3$ as a ligand instead of PPh_2Me improved yields to 53% and 77%, respectively (entries 4 and 5). Ester functionality was compatible under the reaction conditions (entry 6). Aliphatic aldehydes as well as aromatic aldehydes were converted to alkoxyallylsilanes. The reductive silylations of dihydrocinnamaldehyde (**2f**) and cyclohexanecarbaldehyde (**2g**) furnished **3f** and **3g** in 73% and 69% yields, respectively (entries 7 and 8). In the case of *trans*-cinnamaldehyde (**2h**), 1,2-reduction occurred preferentially to give allylcinnamyloxysilane **3h** as a sole product (entry 9). Other silacyclobutanes could be employed for this reaction. 1,1-Diphenylsilacyclobutane (**1b**) reduced aromatic and aliphatic aldehydes without any difficulties despite its increased steric hindrance (entries 10 and 11). With 1,1-diphenyl-2-methylsilacyclobutane (**1c**), cleavage of the primary carbon−silicon bond predominated over that of the secondary carbon−silicon bond to produce benzyloxydiphenyl(1-methyl-2-propenyl)silane (**3k**) as a major product (entry 12). The transfer of the primary alkyl carbon to the nickel center is preferable to that of the secondary one in the transmetalation step (vide infra).[8] However, 1,1-diphenyl-3-methylsilacyclobutane (**1d**) did not react with benzaldehyde (**2a**) to recover the starting materials (entry 13). The reason for the unsuccessful conversion is not clear.

To determine the reaction mechanism, we performed two experiments shown below (Scheme 1). Heating a solution of 1,1-diphenylsilacyclobutane (**1b**), $Ni(cod)_2$, and PPh_2Me in toluene at 100 °C for 27 h resulted in quantitative recovery of **1b** (eq 1).[9] In addition, treatment of benzaldehyde (**2a**) with triethylsilane in the presence of $Ni(cod)_2$ and PPh_2Me in toluene at 100 °C did not afford the reduced products, that is, benzyloxytriethylsilane and/or benzyl alcohol, at all (eq 2).[10] These facts excluded the possibility that isomerization of silacyclobutanes to allylhydrosilanes followed by hydrosilylation of aldehydes gives the products under nickel catalysis.

Scheme 1



On the basis of the above results, we are tempted to assume the mechanism for the reductive silylation of aldehydes is as follows (Scheme 2). A nickel(0) species **4** initially reacts with **2a** to generate η^2-coordinated complex **5** or its resonance

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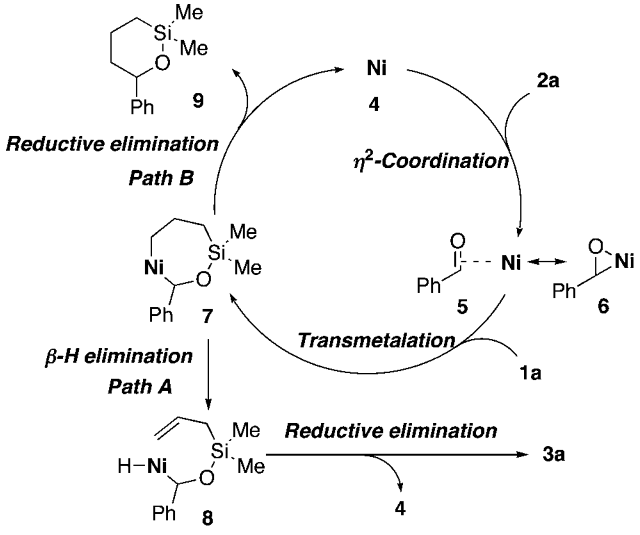
(8) In the Suzuki−Miyaura cross-coupling reactions, the same tendency was observed. See: Netherton, M. R.; Dai, C.; Neuschütz, K.; Fu, G. C. *J. Am. Chem.* Soc. **2001**, *123*, 10099−10100.

(9) Silacyclobutanes were found to undergo oxidative addition to platinum and palladium complexes. (a) Yamashita, H.; Tanaka, M.; Honda, K. *J. Am. Chem. Soc*. **1995**, *117*, 8873−8874. (b) Tanaka, Y.; Yamashita, H.; Shimada, S.; Tanaka, M. *Organometallics* **1997**, *16*, 3246−3248.

(10) Nickel-catalyzed hydrosilylations of aldehydes and imines are quite rare. See: (a) Lappert, M. F.; Nile, T. A. *J. Organomet. Chem.* **1975**, *102*, 543−550. (b) Frainnet, E.; Bourhis, R.; Simonin, F.; Moulines, F. *J Organomet. Chem.* **1976**, *105*, 17−31. (c) Vetter, A. H.; Berkessel, A. *Synthesis* **1995**, 419−422.

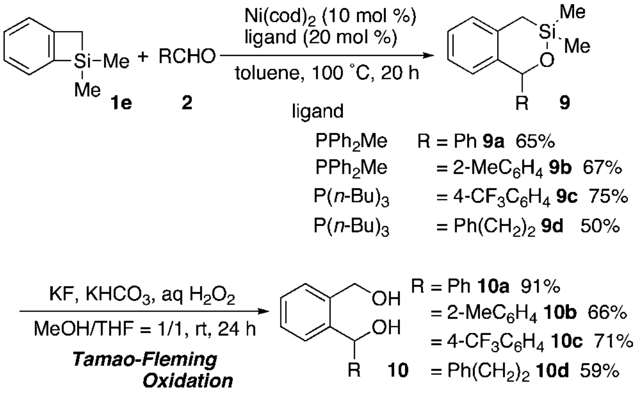
Scheme 2



form **6**.[11] Subsequent transmetalation of **6** with silacyclobutane **1a** gives the intermediate **7**.[12] Subsequent β-H elimination and reductive elimination furnish **3a** and regenerate **4** (path A).

If the intermediate **7** had no hydrogens at the β-position, reductive elimination would proceed to afford the ring expanded product **9** (path B). According to this assumption, benzosilacyclobutene **1e** was treated with benzaldehyde (**2a**) under the same conditions as those for the ring opening (Scheme 3). To our delight, the desired oxasilacyclohexene **9a** was obtained in 65% yield. Interestingly, regioselective cleavage of the sp^2 carbon−silicon bond occurred, which was completely opposite to the cases of base-induced[13] and photochemical[14] ring expansion reactions of **1e** with aldehydes. This is probably because transmetalation of arylsilane is more favored than that of benzylsilane.[15] Reactions with other aromatic and aliphatic aldehydes gave the corresponding ring expanded products **9b**−**9d** in good yields. Tamao−Fleming oxidation could transform **9** to diols. The conversions in Scheme 3 represent 2-(hydroxymethyl)phenylation of aldehydes.

Scheme 3



In summary, we have found two new transformations of silacyclobutanes with aldehydes by nickel catalysis. Ring opening allows silacyclobutanes to be reagents for hydrosilane-free reductive silylation of aldehydes. Ring expansion reactions can provide a facile access to 1,2-bis(hydroxymethyl)benzenes from aldehydes.

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Supporting Information Available: Detailed experimental procedures and characterization data of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] η^2-Coordinated nickel complexes with aldehydes have been reported. (a) Ogoshi, S.; Oka, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2004**, *126*, 11802−11803. The intermediate **5** or **6** was suggested in other nickel-catalyzed reactions. (b) Biswas, K.; Prieto, O.; Goldsmith, P. J.; Woodward, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 2232−2234. (c) Hirano, K.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2005**, *7*, 4689−4691. Nevertheless, oxidative addition of silacyclobutanes to palladium complexes is found to be an equilibrium reaction. Hence, it is also probable that initial oxidative addition of **1a** to **4** followed by subsequent direct insertion of **2a** generates **7**. See ref 9b.

[12] The reaction of **5** with TMSOTf can promote the formation of the covalent bond between nickel and carbonyl carbon with the aid of the Lewis acidity of silicon. See ref 11a. Thus, it seems quite possible that this transmetalation would include a similar intermediate.

[13] Takeyama, Y.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1990**, *31*, 6059−6062.

[14] Okazaki, R.; Kang, K. T.; Inamoto, N. *Tetrahedron Lett.* **1981**, *22*, 235−238.

[15] In the Hiyama cross-coupling reactions, to our knowledge, there are only two examples of benzyl group transfer from silicon. See: (a) Hatanaka, Y.; Hiyama, T. *J. Am. Chem. Soc.* **1990**, *112*, 7793−7794. (b) Itami, K.; Mineno, M.; Kamei, T.; Yoshida, J. *Org. Lett.* **2002**, *4*, 3635−3638.