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Intramolecular σ-Bond Metathesis Between Carbon–Carbon and Silicon–Silicon Bonds

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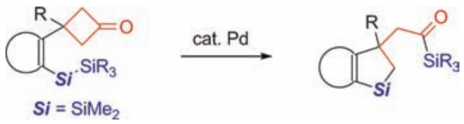
ABSTRACT



An intramolecular σ-bond metathesis between carbon–carbon and silicon–silicon bonds took place on treatment of a disilane tethered to a cyclobutanone with a palladium(0) catalyst, furnishing a silaindane skeleton as well as an acylsilane functionality at once.

The reactivities inherent in most organic compounds reside in their π-bonds or polar σ-bonds. On the other hand, in the past decade, organic chemists have devoted keen and ever-increasing attention to reactions involving direct cleavage of nonpolar σ-bonds[1] such as a carbon–hydrogen bond from a synthetic perspective.[2] Such reactions are not only of scientific novelty but also of considerable potential to improve the efficiency of synthesis. We describe herein the palladium-catalyzed intramolecular σ-bond metathesis[3] between carbon–carbon[4–6] and silicon–silicon single bonds.[7] The unique swapping of the group of 14 elements takes place on treatment of a disilane tethered to a cyclobutanone[8] with a palladium(0)

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(1) *Activation of Unreactive Bonds and Organic Synthesis*; Murai, S., Ed.; Springer: Berlin, 1999.

(2) (a) *Handbook of C–H Transformations*; Dyker, G., Ed.; Wiley-VCH: Weinheim, 2005. (b) Kakiuchi, F.; Kochi, T. *Synthesis* **2008**, 3013. (c) Daugulis, O.; Do, H.-Q.; Shabashov, D. *Acc. Chem. Res.* **2009**, *42*, 1074. (d) Giri, R.; Shi, B.-F.; Engle, K. M.; Maugel, N.; Yu, J.-Q. *Chem. Soc. Rev.* **2009**, *38*, 3242. (e) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (f) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890. (g) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (h) Xu, L.-M.; Li, B.-J.; Yang, Z.; Shi, Z.-J. *Chem. Soc. Rev.* **2010**, *39*, 712. (i) Ackermann, L. *Chem. Commun.* **2010**, *46*, 4866. (j) Rauf, W.; Hazari, A.; Gouverneur, V.; Brown, J. M. *Pure Appl. Chem.* **2010**, *82*, 1415. (k) Nakao, Y. *Chem. Rec.* **2011**, *11*, 242.

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(7) For σ-bond metathesis of silicon–silicon bonds, see: (a) Sakurai, H.; Hosomi, A. *J. Organomet. Chem.* **1972**, *36*, C15. (b) Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *124*, C19. (c) Ishikawa, M.; Okazaki, S.; Naka, A.; Sakamoto, H. *Organometallics* **1992**, *11*, 4135. (d) Kusukawa, T.; Kabe, Y.; Nestler, B.; Ando, W. *Organometallics* **1995**, *14*, 2556. (e) Suginome, M.; Oike, H.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 1665. (f) Sun, H.; Pan, Y.; Huang, X.; Guo, Z.; Zhang, Z.; Zhang, H.; Li, J.; Wang, F. *Organometallics* **2006**, *25*, 133 and references cited therein.

(8) For transition-metal-catalyzed reaction involving cleavage of a carbon–carbon bond of cyclobutanones, see: (a) Murakami, M.; Amii, H.; Shigeto, K.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 8285. (b) Murakami, M; Itahashi, T.; Ito, Y. *J. Am. Chem. Soc.* **2002**, *124*, 13976. (c) Liu, L.; Ishida, N.; Murakami, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 2485 and references cited therein.

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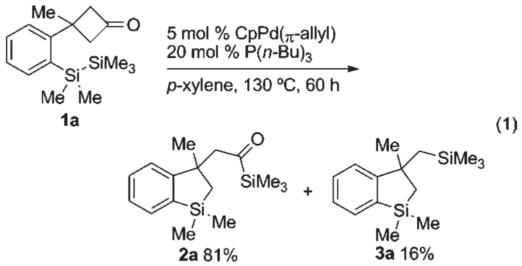
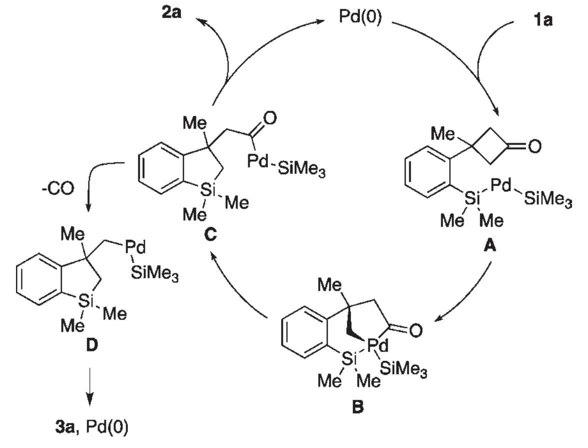
catalyst, simultaneously giving rise to a silaindane skeleton as well as an acylsilane functionality.

Disilane **1a**, which was tethered to a cyclobutanone unit through an *o*-phenylene linker, was prepared from *o*-bromo-α-methylstyrene through introduction of a disilanyl group followed by a standard [2 + 2]-cycloaddition reaction with dichloroketene.[9] The disilane **1a** thus obtained was treated with 5 mol % of CpPd(π-allyl) and 20 mol % of $\mathrm{P}(n\text{-Bu})_3$[10] in *p*-xylene at 130 °C (eq 1). After 60 h, the acylsilane **2a** was isolated in 81% yield together with the decarbonylated alkylsilane **3a** (16%). The structure of **2a** was elucidated by a comprehensive set of NMR spectra (^{1}H, ^{13}C, DEPT, COSY, HMQC, HMBC, and NOESY) and finally verified by derivatization to the known nitrile.[9]

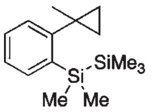


Thus, both the silicon−silicon σ-bond of the disilanyl group and the carbon−carbon σ-bond of the cyclobutanone unit were cleaved, and the originally bonded group of 14 elements were swapped to result in σ-bond metathesis. It necessitates cleavage of both the carbon−carbon and silicon−silicon linkages. Depicted in Scheme 1 is a possible mechanistic scenario. Oxidative addition of the silicon−silicon bond onto palladium(0) generates bissilylpalladium(II) **A**,[7,11] in which the palladium(II) center is located in close proximity to the cyclobutanone unit. The σ-bond between the carbonyl carbon and the α-carbon undergoes oxidative addition onto the palladium(II) center to give rise to bicyclic palladium(IV) intermediate **B**.[12,13] Reductive elimination of the sp^3 carbon−silicon bond furnishes the (α-silaindan-3-ylacetyl)silylpalladium(II) **C**,[14] which then follows two pathways. One is direct reductive elimination to afford acylsilane **2a** with regeneration of palladium(0).[15,16] The other is a decarbonylation/reductive elimination pathway which leads to the formation of alkylsilane **3a**.[17]

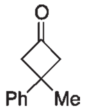
Scheme 1. Proposed Mechanism



Cyclopropane **4**, which was produced through direct decarbonylation of the cyclobutanone unit under the rhodium-catalyzed reaction conditions,[8a,18] was not observed in the reaction mixture. Furthermore, the simple cyclobutanone lacking a disilanyl group **5** remained intact under the present palladium-catalyzed reaction conditions. These experimental results suggested that initial activation of the cyclobutanone prior to the disilane activation was unlikely. Instead, we assume that the silicon−silicon bond is initially activated to locate the palladium(II) center in close proximity to the carbon−carbon bond next to the carbonyl, inducing its oxidative addition.



4



5

Various disilanes having phenylene-type linkers successfully underwent the σ-bond metathesis to afford the corresponding silaindanes in good yields (Table 1). Both electron-donating and -withdrawing substituents were allowed on the phenylene linker (entries 1 and 2). A thiophene linker also worked to give **2e** (entry 4). For the substituents at the 3-positions of the cyclobutanones, functionalized alkyl as

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[9] See the Supporting Information for details.

[10] No reaction occurred, and the starting disilane **1a** was recovered when other palladium(0) precursors (e.g., $\mathrm{Pd(dba)_2}$ and $\mathrm{Pd(OAc)_2}$) and/or ligands (e.g., $\mathrm{P}(t\text{-Bu})_3$, IPr, and 1,1,3,3-tetramethylbutyl isocyanide) were employed. Better reproducibility was observed with the use of 20 mol % of $\mathrm{P(n\text{-}Bu)_3}$, although 10 mol % was generally enough.

[11] For direct observation of oxidative addition of a silicon−silicon bond onto palladium(0), see: (a) Eaborn, C.; Griffiths, R. W.; Pidcock, A. *J. Organomet. Chem.* **1982**, *225*, 331. (b) Biershenk, T. R.; Guerra, M. A.; Juhlke, T. J.; Larson, S. B.; Lagow, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 4855. (c) Murakami, M.; Yoshida, Y.; Ito, Y. *Organometallics* **1994**, *13*, 2900. (d) Ozawa, F.; Sugawara, M.; Hayashi, T. *Organometallics* **1994**, *13*, 3237. (e) Suginome, M.; Oike, H.; Shuff, P. H.; Ito, Y. *Organometallics* **1996**, *15*, 2170.

[12] For palladium(IV) complexes with silyl ligands, see: (a) Shimada, S.; Tanaka, M.; Shiro, M. *Angew. Chem., Int. Ed.* **1996**, *35*, 1856. (b) Suginome, M.; Kato, Y.; Takeda, N.; Oike, H.; Ito, Y. *Organometallics* **1988**, *17*, 495.

[13] For a general review on palladium(IV) complexes, see: Sehnal, P.; Taylor, R. J. K.; Fairlamb, I. J. S. *Chem. Rev.* **2010**, *110*, 824.

[14] An another conceivable mechanism from intermediate **A** to **C** is a direct σ-bond exchange between carbon−carbon and silicon−palladium bonds.

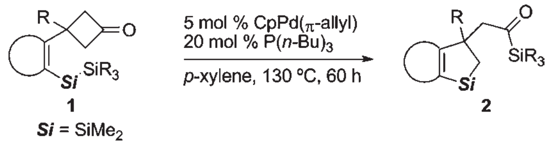
[15] For reactions of acyl chlorides with disilanes giving acylsilanes and/or decarbonylated products, see: (a) Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J. *Organometallics* **1987**, *6*, 974. (b) Rich, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5886. (c) Kashiwabara, T.; Tanaka, M. *Organometallics* **2006**, *25*, 4648.

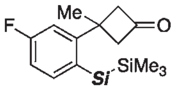
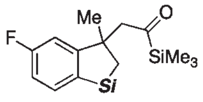
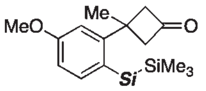
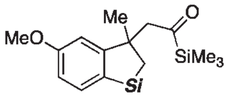
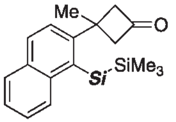
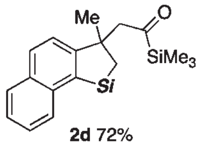
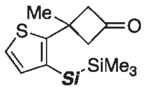
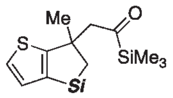
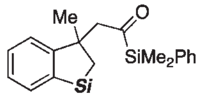
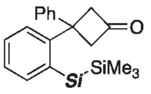
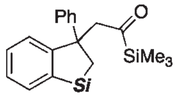
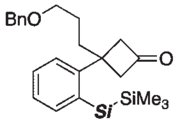
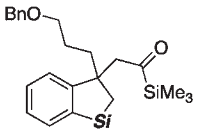
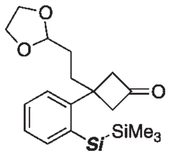
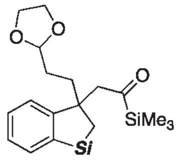
[16] A pathway involving initial reductive elimination of the acyl carbon−trimethylsilyl bond and subsequent reductive elimination of the sp^2 carbon−silicon bond is also conceivable for production of **2a**.

[17] No decarbonylation was observed when isolated acylsilane **3a** was subjected to the palladium-catalyzed reaction conditions. For palladium-catalyzed decarbonylation of bis(organosilyl) ketones, see: Sakurai, H.; Yamane, M.; Iwata, M.; Saito, N.; Narasaka, K. *Chem. Lett.* **1996**, *25*, 841.

[18] When cyclobutanone **1a** was treated with 5 mol % of $\mathrm{[Rh(cod)dppp]PF_6}$ in *p*-xylene at 130 °C for 60 h, cyclopropane **4** was obtained in 34% yield.

Table 1. Palladium-Catalyzed σ-Bond Metathesis between Carbon−Carbon and Silicon−Silicon Linkages[a]

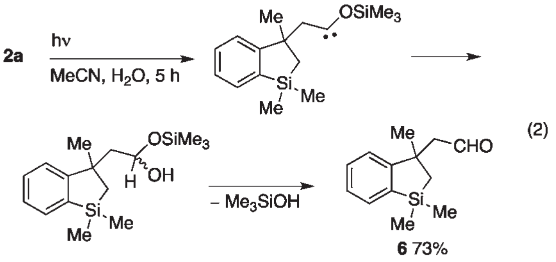


entry	1	2[b]
1	 **1b**	 **2b** 71%
2[c]	 **1c**	 **2c** 80%
3	 **1d**	 **2d** 72%
4	 **1e**	 **2e** 72%
5	 **1f**	 **2f** 80%
6[c]	 **1g**	 **2g** 70%
7	 **1h**	 **2h** 76%
8	 **1i**	 **2i** 80%

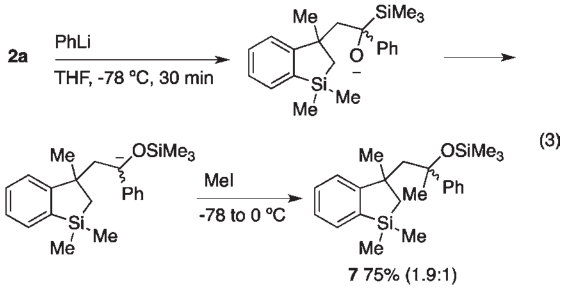
[a] Reaction conditions: 5 mol % of CpPd(π-allyl), 20 mol % of P(n-Bu)$_3$, p-xylene (0.1 M), 130 °C, 60 h unless otherwise noted. [b] Isolated yields. [c] 10 mol % of CpPd(π-allyl) and 40 mol % of P(n-Bu)$_3$ were used.

well as phenyl groups were suitable (entries 6−8). The disilane having a hydrogen atom there, however, gave the corresponding silaindane in only 20% yield.[19]

Reactivities peculiar to acylsilanes were briefly examined using the product **2a**. For example, irradiation with UV light (λ = 360 nm) generated a siloxycarbene species with the aryl−Si linkage remaining intact (eq 2). The resulting carbene underwent insertion into water and the following elimination of trimethylsilanol afforded aldehyde **6** in 73% isolated yield based upon **2a**.[20] Addition of phenyllithium to **2a** prompted the Brook rearrangement to give a carbanion (eq 3).[21] Subsequent methylation with methyl iodide afforded *tert*-alkyl silyl ether **7** as a mixture of diastereomer (1.9:1). These transformations demonstrated that the acylsilanes produced by the present σ-bond metathesis serve as versatile platforms for the synthesis of functionalized silaindane derivatives.



(2)



(3)

In summary, we have presented a unique example of the σ-bond metathesis reaction between carbon−carbon and silicon−silicon bonds. The process involves activation of carbon−carbon and silicon−silicon σ-bonds, which are both far less reactive than π-bonds or polar σ-bonds. Whereas the full potential awaits further exploration, the present reaction provides a prototype of a highly atom-economical method, which dispenses with a substitution process, for the synthesis of organosilicon compounds.

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Note Added after ASAP Publication. Equation 3 contained an error in the version published ASAP May 31, 2012. The correct version reposted June 4, 2012.

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

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(19) Most of the starting material remained. The contrast in reactivity may indicate that the Thorpe−Ingold effect reinforces the proximity effect.

(20) Wegert, A.; Behr, J.-B.; Hoffmann, N.; Miethchen, R.; Portella, C.; Plantier-Royon, R. *Synthesis* **2006**, 2343 and references cited therein.

(21) Reich, H. J.; Olson, R. E.; Clark, M. C. *J. Am. Chem. Soc.* **1980**, *102*, 1423.

The authors declare no competing financial interest.