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Cleavage of C–C and C–Si σ-Bonds and Their Intramolecular Exchange

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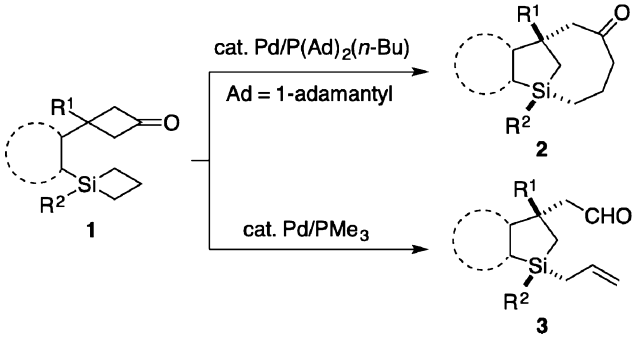
Supporting Information

ABSTRACT: C–C and C–Si σ-bonds are cleaved to undergo bond exchange when substrates equipped with cyclobutanone and silacyclobutane moieties are treated with a palladium(0) catalyst. The skeletal exchange results in construction of silabicyclo[5.2.1]decanes in a diastereoselective manner.

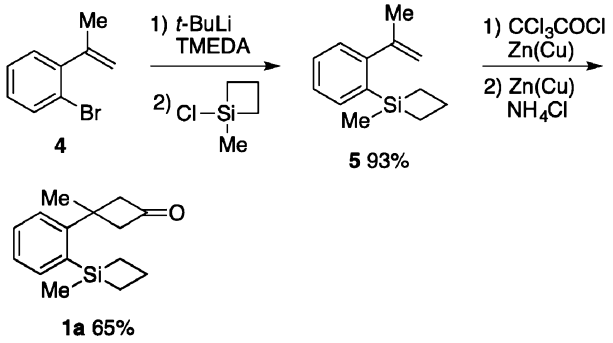
Most reactivities inherent to organic compounds are ascribed to their π-bonds and/or polar σ-bonds. These bonds have frontier orbitals which are far more accessible in energy as well as in space for interaction with the orbitals of reagents or catalysts than nonpolar σ-bonds such as C–C and C–H single bonds. Nonetheless, it would significantly streamline a pathway to construct organic skeletons if nonpolar σ-bonds are cleaved and directly subjected to new bond formation and/or functionalization.[1,2] For example, a synthetic pathway is substantially shortened by reactions in which unsaturated functionalities such as alkenes and alkynes are directly inserted into a C–C single bond.[3] In the case of intramolecular insertion of alkenes, the π-bond acts also as the directing group to facilitate the insertion of a metal into a C–C single bond.[4] The π-bond, once inserted, changes into two more stable σ-bonds to provide a thermodynamic driving force. Thus, participation of π-bonds promotes the transformation of C–C single bonds both kinetically and thermodynamically. On the other hand, it is considerably more difficult to transform nonpolar σ-bonds without participation of π-bonds. Therefore, σ-bond metathesis (exchange) reactions that involve cleavage of nonpolar σ-bonds and their subsequent exchange have been limited to biphenylenes[5] and alkylidenecyclopropane substrates.[6] We have recently reported a palladium-catalyzed intramolecular σ-bond exchange reaction between C–C and Si–Si bonds.[7] Herein, we report an intramolecular σ-bond exchange reaction in which a C–C single bond of a cyclobutanone[8] and a C–Si single bond[9] of a silacyclobutane[10] are cleaved and exchanged to construct a silabicyclo[5.2.1]-decane skeleton in a diastereoselective fashion (Scheme 1, top). Of additional note is a remarkable ligand-based product dichotomy; when sterically bulky $P(Ad)_2(n\text{-}Bu)$ (Ad = 1-adamantyl) is used as the ligand, a silabicyclo[5.2.1]decane skeleton is constructed. On the other hand, the use of sterically less bulky PMe_3 furnishes the ring-opened aldehydes **3** selectively (Scheme 1, bottom).

The benzene substrate *ortho*-disubstituted by cyclobutanone and silacyclobutane moieties **1a** was prepared from *o*-bromo(propen-2-yl)benzene **4** in two batches, as shown in Scheme 2. A silacyclobutane moiety was first introduced onto the benzene ring through a lithiation/silylation procedure. Subsequently, a cyclobutanone moiety was installed through [2 + 2]-cycloaddition with dichloroketene followed by dechlorination, furnishing the substrate **1a**.[11]

Scheme 1. Palladium-Catalyzed Reactions of Substrate 1



Scheme 2. Preparation of Substrate 1a



The substrate **1a** thus obtained was treated with palladium(0) catalysts,[12] prepared in situ from Pd(π-allyl)Cp (Cp = cyclopentadienyl) and a variety of phosphine ligands (Table 1).[13] The outcomes obtained at a temperature range of 130–150 °C widely varied depending upon the ligand employed.[14] The use of bulky $P(Ad)_2(n\text{-}Bu)$ selectively gave eight-membered silacycle **2a** in 86% yield as a single diastereomer having two methyl group in a *cis* arrangement.[15] On the other hand, sterically less demanding trialkylphosphine ligands gave rise to ring-opened aldehyde **3a** in addition to the silacycle **2a**. The two methyl groups of **3a** were *cis*, as with the case of **2a**. The ratio of **3a**/**2a** increased as the steric bulkiness

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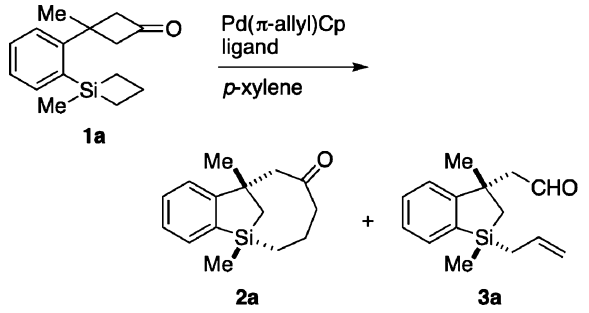
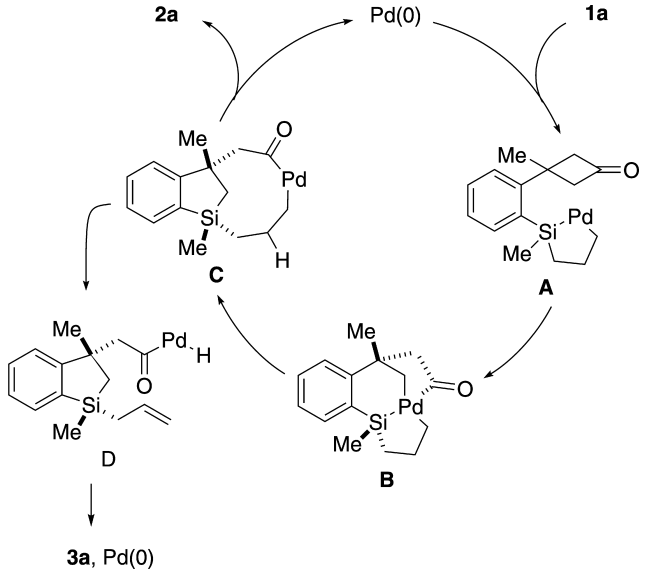
Table 1. Influence of the Ligands on the Product Selectivity



entry	ligand (Pd:P)	yield/%[a] 2a	3a
1[b]	$P(Ad)_2(n\text{-Bu})$ (1:2)	86	0
2[c]	$P(t\text{-Bu})(cyclohexyl)_2$ (1:2)	62	37[d]
3[c]	$P(cyclohexyl)_3$ (1:2)	24	71[d]
4[c]	$P(n\text{-Bu})_3$ (1:4)	10	77[d]
5[e]	PMe_3 (1:4)	trace	86

[a]Isolated yields. [b]Pd(π-allyl)Cp (10 mol %), 150 °C, 24 h. [c]Pd(π-allyl)Cp (5 mol %), 130 °C, 48 h. [d]A small amount of an isomeric mixture of the internal olefins was included. [e]Pd(π-allyl)Cp (5 mol %), 130 °C, 3 h.

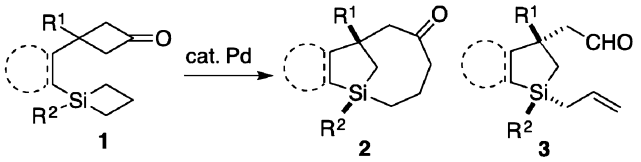
Scheme 3. Plausible Mechanism

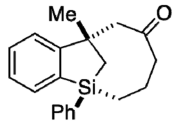
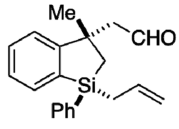
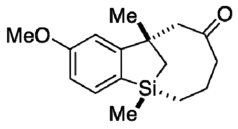
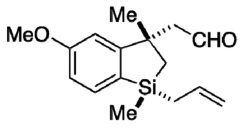
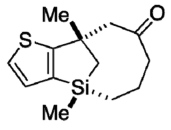
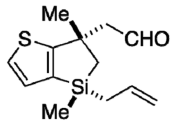
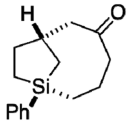
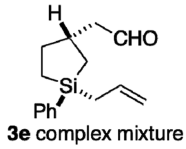
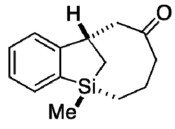
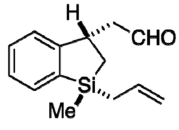
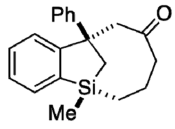
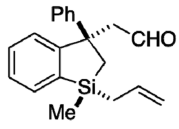
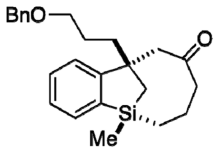
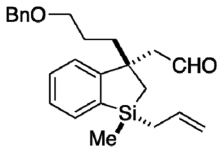


of the ligand decreased (entries 2–5).[16] The least bulky trialkylphosphine ligand PMe_3 produced **3a** in 86% isolated yield almost exclusively.

Cleavage of the C–C and C–Si σ-bonds and their exchange in the subsequent formation of new σ-bonds are the mechanistic events requisite for the production of **2a** from **1a**. One plausible mechanism is depicted in Scheme 3, although there are many other possibilities. It assumes simultaneous oxidative addition of the C–Si and C–C bonds onto palladium and crossing in the bond formation by reductive elimination. Initially, the C–Si bond of the silacyclobutane moiety undergoes oxidative addition onto palladium(0) to generate silapalladacycle **A**.[17] The palladium(II) center having carbon and silicon atoms on it is relatively electron-rich if compared with other palladium(II) species having other anionic ligands such as acetate and chloride. It is located in close proximity to

Table 2. Palladium-Catalyzed Reactions of 1



entry	yield / %[a] 2 under conditions A[b]	3 under conditions B[c]
1	 **2b** 76%	 **3b** 87%
2	 **2c** 80%	 **3c** 84%
3	 **2d** 78%	 **3d** 82%
4	 **2e** 87%[d]	 **3e** complex mixture
5	 **2f** 84%	 **3f** 79%
6	 **2g** 78%	 **3g** 72%
7	 **2h** 80%	 **3h** 79%

[a]Isolated yields. [b]Pd(π-allyl)Cp (10 mol %), $P(Ad)_2(n\text{-Bu})$ (20 mol %), *p*-xylene (0.1 M), 150 °C, 24 h. [c]Pd(π-allyl)Cp (5 mol %), PMe_3 (20 mol %), *p*-xylene (0.1 M), 130 °C, 3 h. [d]*N*,*N*-Dimethylformamide (DMF) was used instead of *p*-xylene.

the cyclobutanone moiety so that the σ-bond between the carbonyl carbon and the α-carbon also undergoes oxidative addition to furnish the palladium(IV) intermediate **B**.[18,19] Although both diastereotopic C–C bonds potentially undergo oxidative addition, the resulting *cis* isomer **B** and its *trans* isomer may be in equilibrium through reversible extrusion/insertion of the CO group. Ensuing reductive elimination

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forming the C(sp^3)−Si bond occurs only with the *cis* isomer because of the geometrical constraints, giving rise to the *cis*-fused bicyclic palladium(II) **C** stereoselectively. Further reductive elimination forming the bond between the carbonyl carbon and the sp^3 carbon[20] produces **2a** along with regeneration of the palladium(0) species. From the intermediate **C**, another mechanistic pathway branches off leading to the ring-opened aldehyde **3a**; it undergoes β-hydride elimination to generate acylpalladium hydride **D**. Reductive elimination follows to produce **3a** together with palladium(0).

The origin of the dichotomy observed between the two phosphine ligands is presumably ascribed to the difference in their steric bulkiness. The sterically less bulky PMe_3 allows an agostic interaction between the β-hydrogen and the palladium center, resulting in β-hydride elimination leading to the production of **3a**. By sharp contrast, the sterically bulkier $P(Ad)_2(n\text{-Bu})$ disfavors such an agostic interaction. Rather, it facilitates reductive elimination producing **2a** to relieve the steric congestion around the palladium center.

The results with various substrates are listed in Table 2. The products **2** and **3** were both selectively produced in good yield depending on the ligand employed. For example, the substrate **1b** afforded the corresponding silaindane **2b** in 76% yield and allylsilane **3b** in 87% yield, respectively (entry 1). A thiophene ring was also suitable as the tether of the substrate (entry 2). Whereas the ethylene-tethered substrate **1e** gave the bicyclic product **2e** in 87% isolated yield, a complex mixture was generated with the PMe_3 ligand (entry 4). Hydrogen, phenyl, and alkyl substituents were all allowed at the 3-position of the cyclobutanones (entries 5−7).

In summary, we have disclosed that σ-bond exchange takes place between C−C and C−Si single bonds; the cyclobutanone/silacyclobutane substrates **1** undergo structural rearrangement upon treatment with a palladium catalyst to furnish bicyclic 5-silacyclooctanone **2** diastereoselectively. Whereas the reactivities of most organic compounds derive from π-bonds and/or polar σ-bonds, the net reactivity of the present reaction consists only in nonpolar σ-bonds between group 14 elements.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, and spectral data for all compounds, including scanned images of ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(15) The *cis* arrangement of the two methyl groups on the silacyclopentene ring was elucidated by analyses of a set of NMR spectra (^1H, ^{13}C, COSY, DEPT, HMQC, HMBC, INADEQUATE, and NOE).
(16) Cone angles: PCy_3 170°, $P(n\text{-Bu})_3$ 132°, PMe_3 118°. Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
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(19) A general review on palladium(IV) complexes: Sehnal, P.; Taylor, R. J. K.; Fairlamb, I. J. S. *Chem. Rev.* **2010**, *110*, 824.
(20) The alternative order of the two reductive elimination steps, i.e., initial $C(sp^3)-C(=O)$ formation followed by $C(sp^3)-Si$ formation, is also conceivable.

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