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Pd(0)-Catalyzed Carbene Insertion into Si−Si and Sn−Sn Bonds

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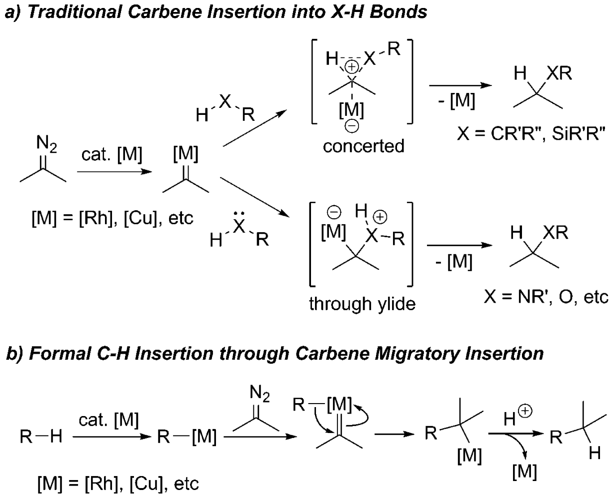
Supporting Information

ABSTRACT: The first Pd(0)-catalyzed carbene insertion into Si−Si and Sn−Sn bonds has been realized by using *N*-tosylhydrazones as the carbene precursors. Geminal bis(silane) and geminal bis(stannane) derivatives were obtained in good to excellent yields under mild conditions. Migratory insertion of Pd carbene is supposed to be the key step for the reaction.

Catalytic carbene insertions into σ bonds are attractive transformations for their versatility and high efficiency.[1] Up to date, X−H (X = C, N, O, etc.) insertions are the most popular and have become one of the carbene's symbolic reactions. Typically, transition-metal catalysts such as rhodium and copper complexes are used to ensure reactivity and selectivity.[2] Mechanistically, the insertion reactions are initiated by the formation of metal carbene species, then followed by two possible pathways. For nonpolar bonds (C−H, Si−H bonds), the reaction goes through concerted mechanism; while for the polar bonds (O−H, N−H bonds), the reaction proceeds through ylide formation and subsequent 1,2-proton migration (Scheme 1a).[3]

Scheme 1. Catalytic Carbene Insertion into σ Bonds



These types of carbene insertion reactions have been extensively studied and have found wide applications in organic synthesis. However, examples of carbene insertion into other type of σ bonds are limited. Recently, we have proposed a formal C−H insertion process which follows stepwise mechanism: C−H bond metalation, carbene formation, migratory insertion, and the protonation (Scheme 1b).[4a] We have conceived that such a process that involves metal carbene migratory insertion may be applied to other types of σ bonds. Besides, we have recently achieved a Rh(I)-catalyzed formal C−C bond insertion.[4b] Herein we report the Pd(0)-catalyzed carbene insertion into Si−Si and Sn−Sn bonds based on the similar mechanistic paradigm.

The hypothetical carbene insertion into Si−Si bond is shown in Scheme 2. The reaction starts with oxidative addition of Si−Si bond to transition-metal catalyst [M], followed by metal carbene formation, silyl migratory insertion, and finally reductive elimination of C−Si bond to afford the insertion product. Among the four steps of this catalytic cycle, the first and last steps have been known in transition-metal-catalyzed Si−Si bond additions to alkynes and alkenes, mostly with nickel, palladium, and platinum as the catalysts.[5] A recent example is reported by Spencer, Navarro et al. who have synthesized a novel NHC-bearing palladium complex, which could efficiently catalyze Si−Si bonds addition to internal alkynes using unactivated $Me_3SiSiMe_3$.[6] The last step has also been reported in transition-metal-catalyzed hydrosilylation of alkenes.[7] Metal carbene formation and the subsequent migratory insertion have been supposed as the key steps in many transition-metal-catalyzed cross-coupling reactions. The migratory inserted moieties have been demonstrated to include aryl, alkenyl, alkynyl, benzyl, etc.[8] However, the metal carbene formation by a metal−silyl complex (**B** to **C**) and the subsequent silyl migratory insertion (**C** to **D**) are unprecedented in catalytic reactions.[9]

Scheme 2. Hypothetical Catalytic Cycle for Si−Si Bond Insertion

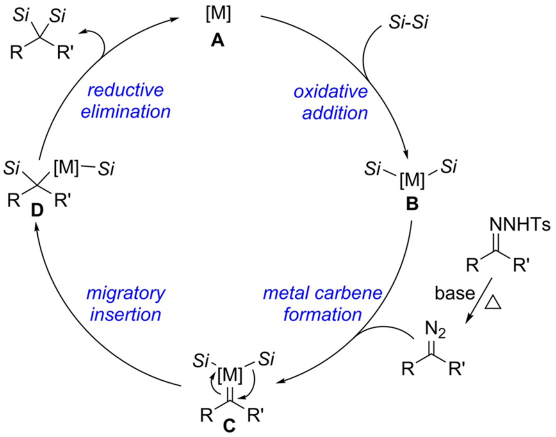


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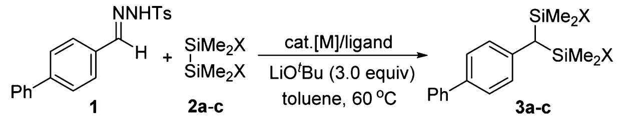
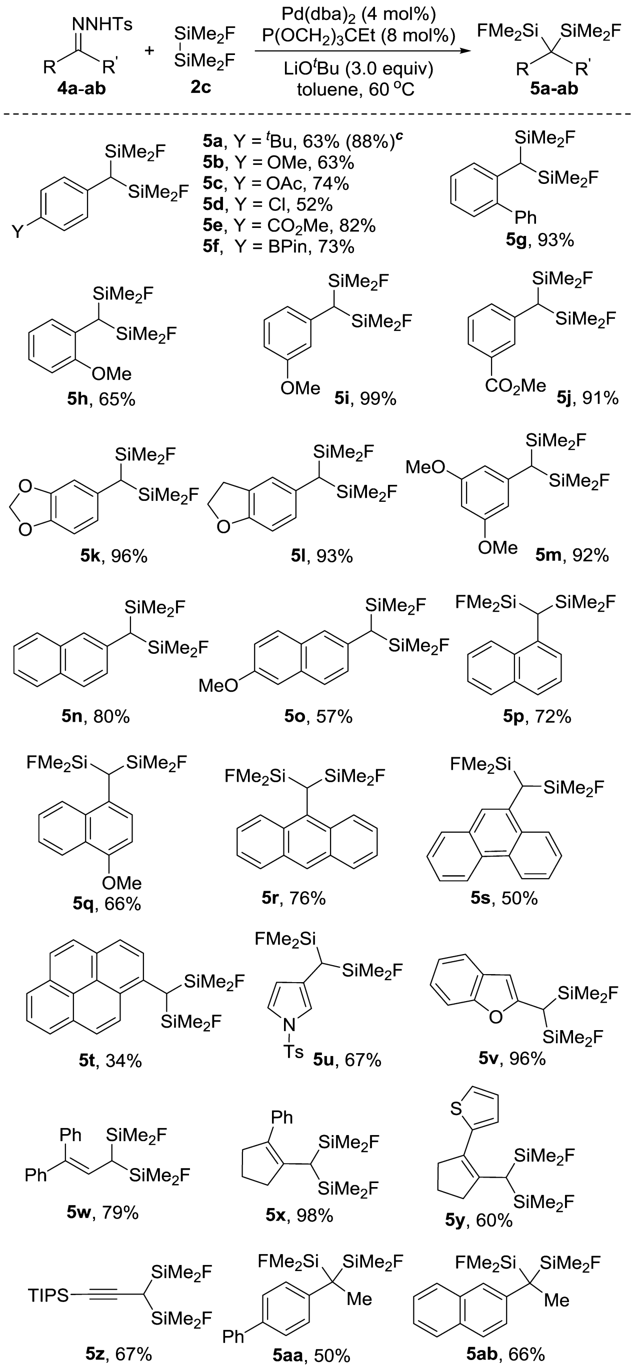
Table 1. Optimization of Transition-Metal-Catalyzed Carbene Si−Si Insertion[a]



entry	[M] (mol %)/ligand (mol %)	2, X	conc. (M)	3, %[b]
1	NiCl$_2$(PPh$_3$)$_2$ (2)	2a, Me	0.1	3a, 0
2	Pt(PPh$_3$)$_4$ (2)	2a, Me	0.1	3a, 0
3	Pd(OAc)$_2$ (2)/^{t}OctNC (30)	2a, Me	0.1	3a, 0
4	Pd(dba)2 (2)/P(OCH$_2$)$_3$CEt (4)	2a, Me	0.1	3a, 10
5	Pd(dba)2 (2)/P(OCH$_2$)$_3$CEt (4)	2b, Ph	0.1	3b, 30
6	Pd(dba)2 (2)/P(OCH$_2$)$_3$CEt (4)	2c, F	0.1	3c, 50
7	Pd(dba)2 (2)/P(OCH$_2$)$_3$CEt (4)	2c, F	0.2	3c, 40
8	Pd(dba)2 (2)/P(OCH$_2$)$_3$CEt (4)	2c, F	0.05	3c, 69
9	Pd(dba)2 (2)/P(OCH$_2$)$_3$CEt (4)	2c, F	0.03	3c, 75
10	Pd(dba)2 (4)/P(OCH$_2$)$_3$CEt (8)	2c, F	0.025	3c, 90 (81)[c]
11	Rh$_2$(OAc)$_4$ (2)	2c, F	0.025	3c, 0
12	none	2c, F	0.025	3c, 0

[a] The reaction was carried out with *N*-tosylhydrazone **1** (0.10 mmol), XMe$_2$SiSiMe$_2$X **2** (0.20 mmol) and LiO^{t}Bu (0.30 mmol) in the presence of catalyst in toluene at 60 °C for 12 h. [b] The yields were determined by ^{1}H NMR with mesitylene as the internal standard. [c] The yield in parentheses refers to isolated yield. ^{t}OctNC: 1,1,3,3-tetramethylbutyl isocyanide.

Scheme 3. Scope of Pd(0)-Catalyzed Carbene Insertion into Si−Si Bonds[a,b]



[a] The reaction was carried out with *N*-tosylhydrazones **4** (0.10 mmol), FMe$_2$SiSiMe$_2$F **2c** (0.20 mmol), and LiO^{t}Bu (0.30 mmol) in the presence of Pd(dba)$_2$ (4 mol %)/P(OCH$_2$)$_3$CEt (8 mol %) in 4.0 mL toluene at 60 °C for 12 h. [b] All the yields refer to isolated yield by bulb-to-bulb distillation. [c] The yield refers to a 0.5 mmol scale reaction.

With the hypothesis in mind, we started to examine the reaction with *N*-tosylhydrazone derived from 4-biphenylcarboxaldehyde and Me$_3$SiSiMe$_3$ as the substrates (Table 1). *N*-Tosylhydrazones have been recently widely used as the precursors for the in situ generation of nonstabilized diazo compounds in transition-metal-catalyzed cross-coupling reactions involving carbene species.[10,11] Screening of the catalysts with nickel, palladium, and platinum revealed that only Pd(dba)$_2$/P(OCH$_2$)$_3$CEt system could afford the expected product in 10% NMR yield (entries 1−4).[12] The failure of other catalysts might be attributed to the difficulty in the metal carbene forming step (entries 1−3),[13] while in the case of entry 4 the low efficiency might be due to the inert nature of the Si−Si bonds. To tune the reactivity of Si−Si bond, we have switched Me$_3$SiSiMe$_3$ to PhMe$_2$SiSiMe$_2$Ph and FMe$_2$SiSiMe$_2$F (entries 5 and 6). This could indeed improve the yields of insertion products (entries 5 and 6). It was observed that the concentration significantly affected the reaction (entries 7−9). The reaction worked better under lower concentration, in which there were fewer side products due to the reactions of carbene species (entries 8 and 9). With concentration of 0.025 M and slightly increased catalyst loading (from 2 to 4 mol%), the yield of product was improved to 90% (^{1}H NMR). The product was isolated by bulb-to-bulb distillation in 81% yield (entry 10). Finally, control experiments indicated that with Rh$_2$(OAc)$_4$ as the catalyst or in the absence of catalyst the reaction did not give the product **3c** (entries 11 and 12).

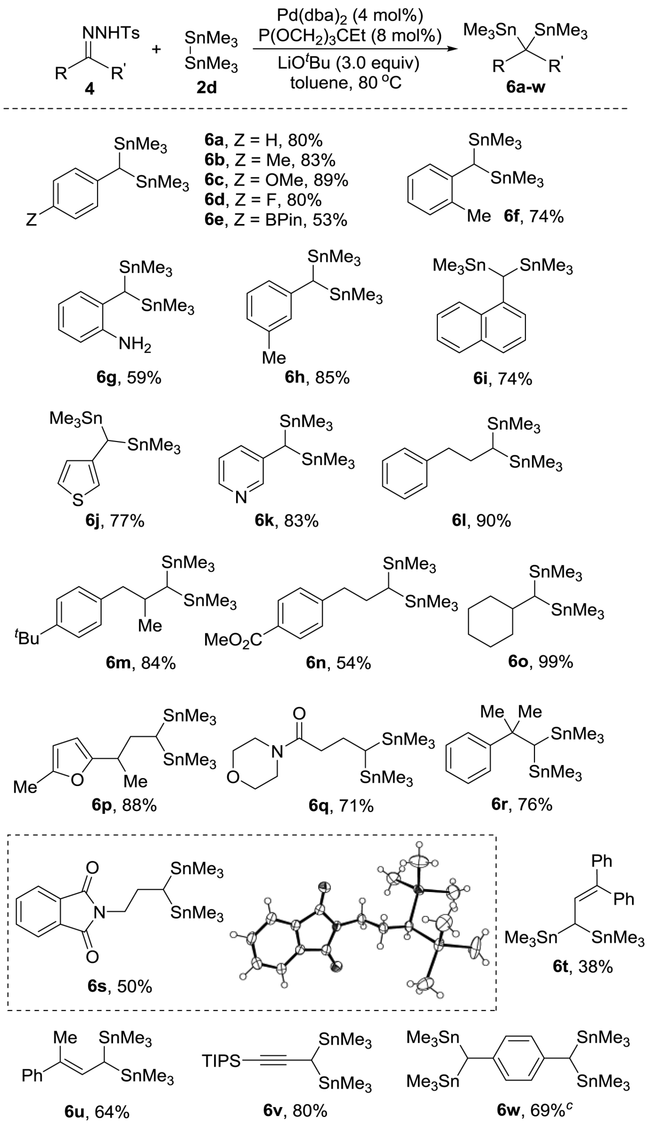
Next, we proceeded to explore the scope of the reaction under the optimized reaction conditions (see Supporting Information). As shown in Scheme 3, a series of *N*-tosylhydrazones could be employed as substrates in the reaction, affording the corresponding geminal bis(silane) derivatives **5a−ab** efficiently. For monosubstituted aromatic aldehyde derived *N*-tosylhydrazones, the substrates bearing substituents in *para*-, *meta*-, and *ortho*-position with different electronic properties all proceeded well in the reaction (**5a−e, j−g**). Notably, Bpin could be tolerated under current conditions (**5f**). The reactions with the *N*-tosylhydrazones bearing two substituents on the aromatic rings also proceeded well to give the corresponding products in excellent yields (**5k−m**).

Likewise, the reaction with *N*-tosylhydrazones derived from fused polycyclic or heterocyclic aromatic aldehydes could afford the corresponding geminal bis(silane) products in moderate yields (**5n−v**). The reaction also worked well with *N*-tosylhydrazones derived from unsaturated aldehydes (**5w−z**). Finally, for

N-tosylhydrazones derived from aromatic ketones, the yields were slightly diminished, presumably due to steric effect (**5aa**–**ab**).

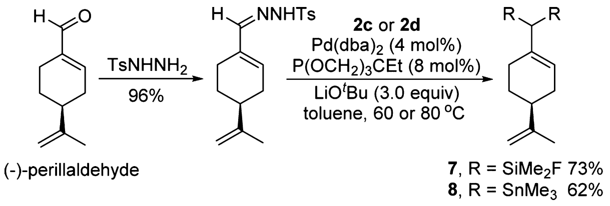
Encouraged by the successful carbene Si–Si bond insertion, we proceed to explore the same strategy for other similar types of σ bonds. Sn–Sn bonds have been applied in transition-metal-catalyzed addition to unsaturated organic molecules as Si–Si bonds.[14] Accordingly, we conceived that carbene insertion into Sn–Sn bonds might also be realized under similar conditions and this indeed proved to be the case. As shown in Scheme 4, for a series of *N*-tosylhydrazones the Pd(0)-catalyzed reaction with hexamethyldistannane ($Me_3SnSnMe_3$, **2d**) afforded the corresponding geminal bis(stannane) derivatives **6a**–**w** in moderate to excellent yields. It is worth mentioning that the *N*-tosylhydrazones derived from alkyl aldehydes are also excellent substrates for the Sn–Sn bonds insertion, while the corresponding Si–Si insertion reaction failed to afford the desired products. The structure of **6s** was confirmed by X-ray crystallography (see Supporting Information).

Scheme 4. Scope of Pd(0)-Catalyzed Carbene Insertion into Sn–Sn Bonds[a,b]



[a] The reaction was carried out with *N*-tosylhydrazones **4** (0.10 mmol), $Me_3SnSnMe_3$ **2d** (0.15 mmol), and LiO^tBu (0.30 mmol) in the presence of $Pd(dba)_2$ (4 mol %)/$P(OCH_2)_3CEt$ (8 mol %) in 1.0 mL toluene at 80 °C for 12 h. [b] All the yields refer to isolated product by silica gel chromatography. [c] The reaction was carried out with bis-*N*-tosylhydrazones (0.10 mmol), $Me_3SnSnMe_3$ (0.30 mmol), and LiO^tBu (0.60 mmol) in the presence of $Pd(dba)_2$ (8 mol %)/$P(OCH_2)_3CEt$ (16 mol %) in 2.0 mL toluene at 80 °C for 12 h.

To further assess the applicability of the Pd(0)-catalyzed carbene Si–Si and Sn–Sn bond insertion, the natural product (−)-perillaldehyde was first converted to the corresponding *N*-tosylhydrazone and then was subjected to the Pd(0)-catalyzed reaction. The Si–Si insertion and Sn–Sn insertion products were obtained in 73% and 62% yields, respectively (eq 1).



(1)

In conclusion, we have developed the first Pd(0)-catalyzed carbene insertion into Si–Si and Sn–Sn bonds.[15] The study further demonstrates the generality of carbene migratory insertion/reductive elimination sequence as a novel strategy to achieve σ bond insertion, which may open new possibilities in carbene chemistry. Besides, the mild conditions, wide substrate scope, and high efficiency of the current reactions make them attractive methods to access geminal bis(silane) and geminal bis(stannane) derivatives.[16]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b09135.

Experimental procedure, characterization data, copies of ^1H and ^{13}C NMR spectra (PDF)

X-ray crystallographic data for **6s** (CIF)

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Notes

The authors declare no competing financial interest.

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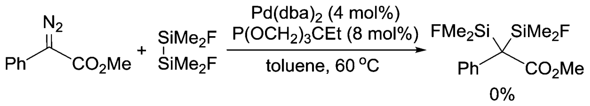

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