

Communication

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

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Supporting Information Placeholder

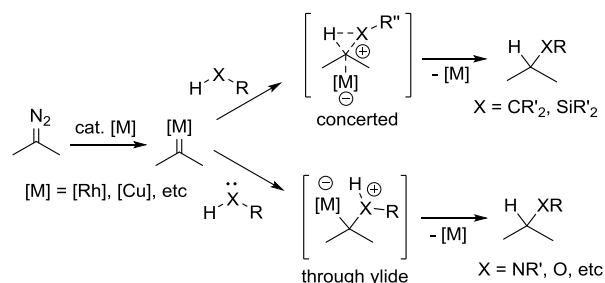
**ABSTRACT:** The first Pd(0)-catalyzed carbene insertion into Si-Si and Sn-Sn bonds have been realized by using *N*-tosylhydrazones as the carbene precursors. Geminal bis(silane) and geminal bis(stannane) derivatives were obtained in good to excellent yields under mild conditions. Migratory insertion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

Catalytic carbene insertions into  $\sigma$  bonds are attractive transformations for their versatility and high efficiency.<sup>1</sup> 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.<sup>2</sup> Mechanistically, the insertion reactions are initiated by the formation of metal carbene species, then followed by two possible pathways. For non-polar bonds (C-H, Si-H bonds), the reaction goes through concerted mechanism; while for the polar bonds (O-H, N-H bond), the reaction proceeds through ylide formation and subsequent 1,2-proton migration (Scheme 1a).<sup>3</sup> This type 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  $\sigma$  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). We have conceived that such a process that involves metal carbene migratory insertion may be applied to other types of  $\sigma$  bonds. In this context we have recently achieved a Rh(I)-catalyzed formal C-C bond insertion.<sup>4</sup> Herein we report the Pd(0)-catalyzed carbene insertion into Si-Si and Sn-Sn bonds based on the same mechanistic paradigm.

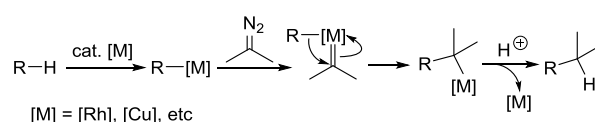
The hypothetical carbene insertion into Si-Si bond is shown in Scheme 2. The reaction starts with oxidative addition of Si-Si bond to transition-metal catalyst [M], followed by metal carbene formation, silyl migratory insertion, and finally reductive elimination of C-Si bond to afford the insertion product. Amongst the four steps of this catalytic cycle, the first and last steps have been known in transition-metal catalyzed Si-Si bond additions

## Scheme 1. Catalytic Carbene Insertion into $\sigma$ bonds

### a) Traditional Carbene Insertion into X-H Bonds

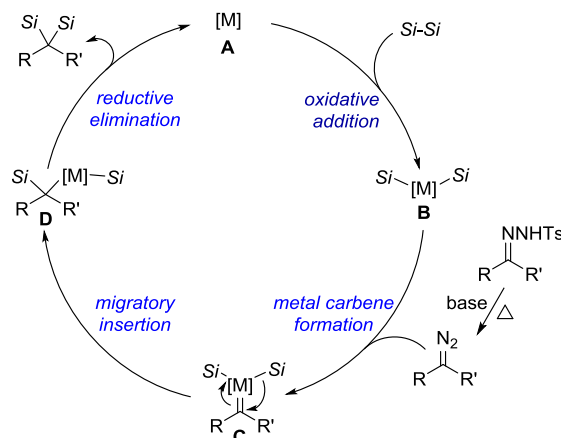


### b) Formal C-H Insertion through Carbene Migratory Insertion



to alkynes and alkenes, mostly with nickel, palladium and platinum as the catalysts.<sup>5</sup> A recent example is by Spencer, Navarro and co-workers who have synthesized a novel NHC-bearing palladium complex, which could efficiently catalyze Si-Si bonds addition to internal alkynes using unactivated Me<sub>3</sub>SiSiMe<sub>3</sub>.<sup>6</sup> The last step has

## Scheme 2. Hypothetical Catalytic Cycle for Si-Si Bond Insertion



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