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Cite this: DOI: 10.1039/c6cc09650f

Received 5th December 2016,
Accepted 2nd February 2017

DOI: 10.1039/c6cc09650f

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Silver(I)-promoted insertion into X–H (X = Si, Sn, and Ge) bonds with *N*-nosylhydrazones†

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Silver(I)-promoted carbene insertion into X–H (X = Si, Sn, and Ge) bonds has been realized by using unstable diazo compounds, which are generated *in situ* from *N*-nosylhydrazones as carbene precursors. The reaction tolerates a wide range of functional groups and delivers a number of valuable silicon-containing compounds in very high yields (up to 96%). Moreover, organostannanes and organogermanes were as well effectively obtained in very good yields under optimal conditions.

Organosilicon compounds are well known to be highly attractive scaffolds and valuable compounds, which have broad applications in organic synthesis,[1] materials chemistry,[2] and pharmaceuticals.[3] Transition-metal-catalyzed carbenoid insertion into Si–H bonds with diazo compounds represents a particularly important contribution to synthesize such compounds.[4] In 1962, Kramer and Wright first reported the carbene insertion into Si–H bonds from diazoalkanes with organosilicon.[5] Since then, great efforts based on transition metal catalysts, such as rhodium,[6] copper,[7] iron,[8] iridium,[9] and silver salts,[10] have been made in inducing Si–H insertion from diazo compounds. Among them, electron-withdrawing-group (EWG)- or trimethylsilyl (TMS)-group-stabilized diazo compounds were successfully implemented as carbene precursors in Si–H insertion reactions (Fig. 1a). However, the utilization of donor diazo compounds in such transformations was not well documented, which significantly limits their further application in organic synthesis. For this reason, the exploration of new strategies and reagents for the rapid assembly of silicon-containing compounds *via* transition-metal-catalyzed Si–H insertion from unstable diazoalkanes would be highly desirable.

On the other hand, sulfonylhydrazones as reliable diazo sources have been widely used in transition-metal catalyzed transformations,[11] particularly in heteroatom–hydrogen insertion reactions such as N–H,[12] O–H,[13] P–H[14] and S–H[15] insertions. To the best of our knowledge, there is no report that demonstrates the direct use of such diazo precursors in Si–H insertions. Promoted by these facts and given the continuous interest in silver catalysis,[16] we envisaged that silver salts could be employed in catalyzing Si–H insertion reactions with *N*-tosylhydrazones as diazo sources. Herein, we report the first example of donor and donor/donor carbenoid insertion into Si/Sn/Ge–H bonds to access a wide range of tetraorganosilanes/stannanes/germanes, which are difficult to access using other methods (Fig. 1b).[17]

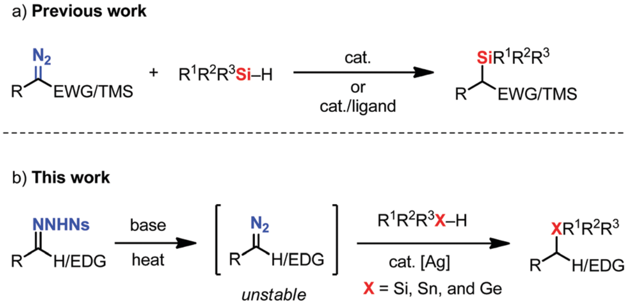

Fig. 1 Transition-metal-catalyzed insertion into the Si–H bond.

An exploratory experiment was conducted with *N*-tosylhydrazone **1a′** and triethylsilane **2a** in the presence of 30 mol% of AgOTf in CH_2Cl_2 at 40 °C under a N_2 atmosphere. The desired insertion product **3aa** was obtained, although the yield was only 15% (Table 1, entry 1). To improve the yield of the desired product, a nitro group was introduced into the aromatic ring, which stemmed from our previous observation of the rapid decomposition of *o*-nosylhydrazide at room temperature.[18] Notably, the yield was significantly improved to 57% when *N*-nosylhydrazone **1a** was used to generate the diazo intermediate. Inspired by these results, further optimization of the reaction conditions was performed. The reaction temperature was found to be a crucial parameter for this transformation. When the reaction was carried out at 80 °C, the yield was increased to 84% (Table 1, entry 3). Notably,

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cc09650f

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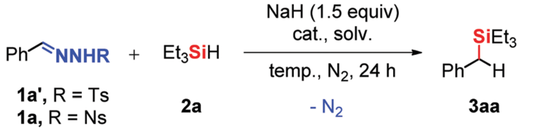
Table 1 Optimization of the reaction conditions[a]



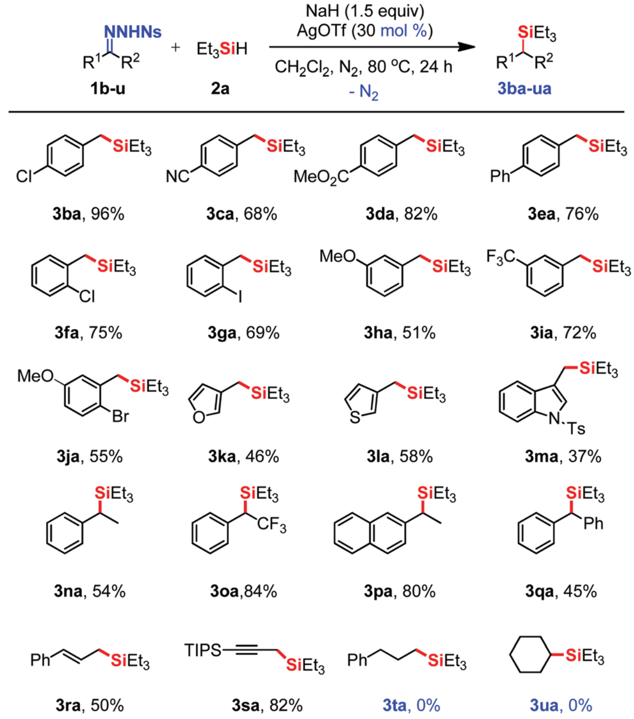
Entry	R	Cat. (30 mol%)	Solvent	Temp. (°C)	Yield **3aa**[b] (%)
1	Ts	AgOTf	CH_2Cl_2	40	15
2	Ns	AgOTf	CH_2Cl_2	40	57
3	Ns	AgOTf	CH_2Cl_2	80	84 (81)[d]
4	Ns	AgOAc	CH_2Cl_2	80	55
5	Ns	AgOTAF	CH_2Cl_2	80	60
6	Ns	AgF	CH_2Cl_2	80	28
7	Ns	Ag_2CO_3	CH_2Cl_2	80	34
8	Ns	AgOTf	1,4-Dioxane	80	20
9	Ns	AgOTf	PhCl	80	6
10	Ns	AgOTf	MeCN	80	<5
11	Ns	AgOTf	$ClCH_2CH_2Cl$	80	32
12	Ns	$Cu(OTf)_2$	CH_2Cl_2	80	7
13	Ns	$Cu(MeCN)_4PF_6$	CH_2Cl_2	80	10
14[c]	Ns	$Rh_2(OAc)_4$	CH_2Cl_2	80	25

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (1.5 mmol), NaH (0.45 mmol), and the catalyst (30 mol%) in solvent (6.0 mL) for 24 h under a N_2-atmosphere. [b] Yield calculated by ^{1}H-NMR spectroscopy with CH_2Br_2 as the internal standard. [c] $Rh_2(OAc)_4$ (5 mol%) was used. [d] Isolated yield in brackets.

side products like H_2 and NaNs were probably produced from the decomposition of *N*-nosylhydrazones. Compared to AgOTf, other silver catalysts (AgOAc, AgOTAF, AgF and Ag_2CO_3; Table 1, entries 4–7) are less effective in this transformation, although the desired products were obtained. The screening of solvents (Table 1, entries 8–11) identified CH_2Cl_2 as the most suitable solvent. Other commonly used transition-metal catalysts in catalytic Si–H insertion reaction with diazo compounds, such as $Cu(OTf)_2$,[7b] $Cu(MeCN)_4PF_6$,[7d] and $Rh_2(OAc)_4$,[6] were also tested but did not produce better results (Table 1, entries 12–14).

Once the optimal reaction conditions were established, efforts were then focused on the scope of this method. As shown in Table 2, a series of *N*-nosylhydrazones **1b–s** worked well with triethylsilane **2a**, furnishing the corresponding insertion products **3ba–sa** efficiently. For *N*-nosylhydrazones derived from benzaldehyde derivatives, a variety of electron-donating (Ph or MeO) or electron-withdrawing groups (Cl, CN, CO_2Me, I, Br, or F_3C) located at the *para*-, *meta*- or *ortho*-position of the aromatic ring were all compatible, thus affording the corresponding insertion products (**3ba–ja**) in good to high yields. Among these cases, the tolerance of iodo (**3ga**) and bromo (**3ja**) groups on the aromatic rings, which provide a basis for subsequent derivatization of the product into more-complex molecules, is especially noteworthy. More importantly, this reaction is compatible with *N*-nosylhydrazones bearing a heteroaryl group such as furan (**3ka**), thiophene (**3la**) and indole (**3ma**). This feature makes the reaction particularly useful for the synthesis of silicon-based materials.[2] Furthermore, *N*-nosylhydrazones derived from aromatic ketones can be employed without loss in efficiency (**3na–qa**, 45–84% yields). Finally, the reaction was also efficient with *N*-nosylhydrazones derived from unsaturated aldehydes and gave allylic and propargylic silane products (**3ra** and **3sa**), which are hard to access using conventional methods. Unfortunately, *N*-nosylhydrazones generated from aliphatic aldehydes or ketones, such as **3ta** and **3ua**, were not compatible under the current conditions (Table 2).

Table 2 Reaction scopes with respect to *N*-nosylhydrazones[a,b]



[a] Reaction conditions: **1b–1u** (0.3 mmol), **2a** (1.5 mmol), NaH (0.45 mmol), and AgOTf (30 mol%) in CH_2Cl_2 (6.0 mL) for 24 h under a N_2-atmosphere. [b] Isolated yield.

Next, the scope of silanes was evaluated. A broad range of silanes reacted smoothly with *N*-nosylhydrazone **1b**. As illustrated in Table 3, the reaction between trialkyl-substituted silanes and *N*-nosylhydrazone **1b** proceeded efficiently to afford the insertion products **3bb–be** in very high yields. For aryl-substituted silanes, there is a significant drop in yields with the increasing number of aryl substituents on the silicon atom (**3bg**, **3bh**), presumably due to steric hindrance. It is worth mentioning that strong electron-withdrawing groups, *i.e.*–CF_3, have a negative impact on the yield of the desired insertion product (**3bf**). Silane bearing flexible tri-TMS groups was amenable to this transformation, affording desired compounds in 68% yield (**3bi**).

Encouraged by the successful carbenoid Si–H bond insertion, we proceeded to explore the same strategy for other similar types of σ bonds, including Sn–H and Ge–H bonds, which have received little attention to date.[5a,7a,19] As shown in Table 3, a variety of *N*-nosylhydrazones, both derived from aldehydes and ketones, were excellent substrates for Sn–H bond (**3bj–br**) and Ge–H bond (**3bs**) insertions, thus affording the desired products in moderate-to-good yields, which further expanded the scope of this protocol in X–H bond insertion.

To establish practical laboratory-scale utility, scale-up experiments were carried out for *N*-nosylhydrazones **1a** and **1b** (Scheme 1). The reaction proceeded efficiently, and the corresponding silanes could be isolated on a gram scale. Furthermore, the silane **3aa** can be further transformed into diversely

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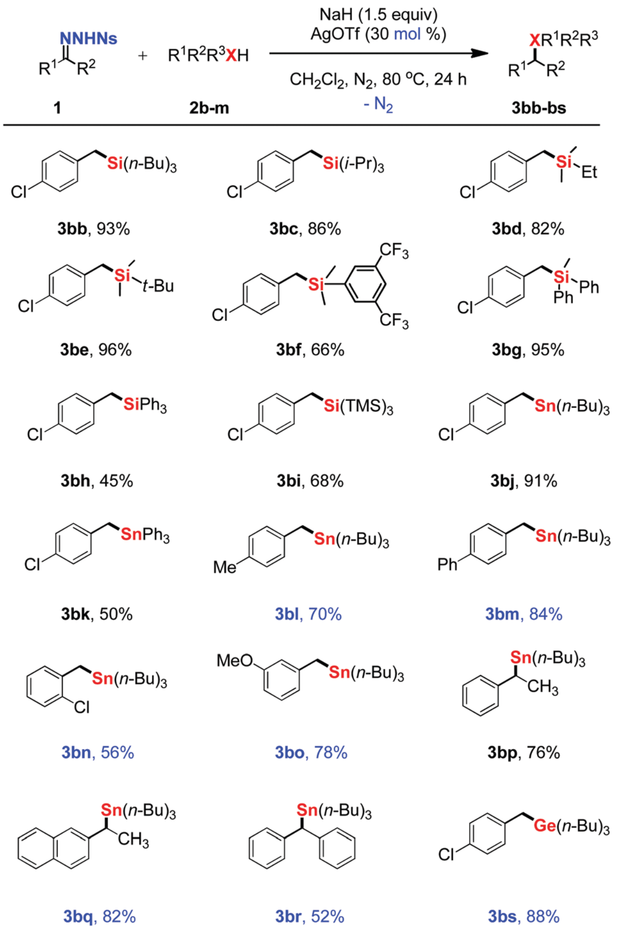
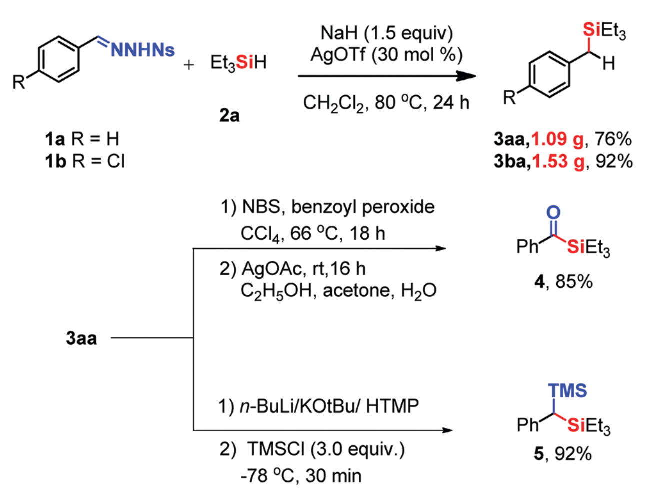
Table 3 Reaction scopes with respect to organic Si/Sn/Ge–H[a,b]



[a] Reaction conditions: **1** (0.3 mmol), **2b–2m** (1.5 mmol), NaH (0.45 mmol), and AgOTf (30 mol%) in CH_2Cl_2 (6.0 mL) for 24 h under a N_2-atmosphere. [b] Isolated yield.



Scheme 1 Gram-scale experiment and synthetic application.

functionalized silanes. For example, phenyl-(triethylsilyl)-methanone **4** and geminal bis(silane) product **5** can be readily prepared from **3aa** *via* multi-step procedures, respectively. Obviously, these functionalized organosilicon compounds are potentially powerful synthetic intermediates.[20]

In summary, we have developed the first practical and efficient silver(I)-promoted carbenoid insertion into X–H (X = Si, Sn, and Ge) bonds with donor diazo compounds generated *in situ* from *N*-nosylhydrazones. Moreover, the wide substrate scope and high efficiency of the current transformations make them attractive methods to access organosilanes, organostannanes and organogermanes.

Notes and references

1 P. L. Fuchs, *Handbook of Reagents for Organic Synthesis: Reagents for Silicon-Mediated Organic Synthesis*, Wiley, Chichester, UK, 2011.

2 (*a*) N. Auner and J. Weis, *Organosilicon Chemistry V: From Molecules to Materials*, Wiley-VCH, Weinheim, Germany, 2004; (*b*) B. A. Kamino and T. P. Bender, *Chem. Soc. Rev.*, 2013, **42**, 5119.

3 (*a*) Z. Rappoport and Y. Apeloig, *The Chemistry of Organic Silicon Compounds*, Wiley, Chichester, UK, 1998; (*b*) A. K. Franz and S. O. Wilson, *J. Med. Chem.*, 2013, **56**, 388.

4 For selected reviews, see: (*a*) A. Ford, H. Miel, A. Ring, C. N. Slattery, A. R. Maguire and M. A. McKervey, *Chem. Rev.*, 2015, **115**, 9981; (*b*) X. Zhao, Y. Zhang and J. Wang, *Chem. Commun.*, 2012, **48**, 10162; (*c*) M. P. Doyle and D. C. Forbes, *Chem. Rev.*, 1998, **98**, 911.

5 (*a*) K. A. W. Kramer and A. N. Wright, *J. Chem. Soc.*, 1963, 3604; (*b*) K. Kramer and A. Wright, *Angew. Chem.*, 1962, **74**, 468.

6 For selected examples of rhodium-catalyzed carbenoid Si–H insertion, see: (*a*) V. Bagheri, M. P. Doyle, J. Taunton and E. E. Claxton, *J. Org. Chem.*, 1988, **53**, 6158; (*b*) H. M. L. Davies, T. Hansen, J. Rutberg and P. R. Bruzinski, *Tetrahedron Lett.*, 1997, **38**, 1741; (*c*) M. P. Doyle, W. Hu, I. M. Phillips, C. J. Moody, A. G. Pepper and A. G. Z. Slawin, *Adv. Synth. Catal.*, 2001, **343**, 112; (*d*) Z. Qu, W. Shi and J. Wang, *J. Org. Chem.*, 2001, **66**, 8139; (*e*) F. M. Wong, J. Wang, A. C. Hengge and W. Wu, *Org. Lett.*, 2007, **9**, 1663; (*f*) R. Sambasivan and Z. T. Ball, *J. Am. Chem. Soc.*, 2010, **132**, 9289; (*g*) D. Chen, D. Zhu and M. Xu, *J. Am. Chem. Soc.*, 2016, **138**, 1498; (*h*) During the preparation of our manuscript, a rhodium(II)-alkynyl carbenoid insertion into Si–H bonds was published, which provides an entry to propargylic geminal bis(silanes). T. Courant, R. Kumar, S. Turcaud and L. Micouin, *Org. Lett.*, 2016, **18**, 4818.

7 For copper-catalyzed carbenoid Si–H insertion examples, see: (*a*) F. Rijkens, M. J. Janssen, W. Drenth and G. J. M. Van der Kerk, *J. Organomet. Chem.*, 1964, **2**, 347; (*b*) Y. Zhang, S. Zhu, L. Wang and Q. Zhou, *Angew. Chem., Int. Ed.*, 2008, **47**, 8496; (*c*) J. Barluenga, L. Riesgo, R. Vicente, L. A. Lopez and M. Tomas, *J. Am. Chem. Soc.*, 2008, **130**, 13528; (*d*) S. Hyde, J. Veliks, B. Liegault, D. Grassi and M. Taillefer, V Gouverneur, *Angew. Chem., Int. Ed.*, 2016, **55**, 3785.

8 E. Scharrer and M. Brookhart, *J. Organomet. Chem.*, 1995, **497**, 61.

9 (*a*) Y. Yasutomi, H. Suematsu and T. Katsuki, *J. Am. Chem. Soc.*, 2010, **132**, 4510; (*b*) J. Wang, Z. Xu, Z. Guo, Q. Deng, C. Zhou, X. Wan and C. Che, *Chem. Commun.*, 2012, **48**, 4299.

10 M. J. Iglesia, M. C. Nicasio, A. Caballero and P. J. Perez, *Dalton Trans.*, 2013, **42**, 1191.

11 (*a*) Z. Shao and H. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 560; (*b*) Q. Xiao, Y. Zhang and J. Wang, *Acc. Chem. Res.*, 2013, **46**, 236; (*c*) J. Barluenga and C. Valdés, *Angew. Chem., Int. Ed.*, 2011, **50**, 7486; (*d*) Y. Xia, Y. Zhang and J. B. Wang, *ACS Catal.*, 2013, **3**, 2586; (*e*) J. R. Fulton, V. K. Aggarwal and J. de Vicente, *Eur. J. Org. Chem.*, 2005, 1479.

12 (*a*) P. Xu, F. Qi, F. Han and Y. Wang, *Chem. – Asian J.*, 2016, **11**, 2030; (*b*) J. Aziz, J. D. Brion, A. Hamze and M. Alamia, *Adv. Synth. Catal.*, 2013, **355**, 2417; (*c*) A. Hamze, B. Tŕeguier, J. D. Brion and M. Alamia, *Org. Biomol. Chem.*, 2011, **9**, 6200.

13 J. Barluenga, M. Tomás-Gamasa, F. Aznar and C. Valdés, *Angew. Chem., Int. Ed.*, 2010, **49**, 4993.

14 (*a*) W. J. Miao, Y. H. Gao, Y. X. Gao, G. Tang and Y. F. Zhao, *Adv. Synth. Catal.*, 2012, **354**, 2659; (*b*) L. Wu, X. Zhang, Q. Q. Chen and A. K. Zhou, *Org. Biomol. Chem.*, 2012, **10**, 7859.

15 Q. Ding, B. Cao, J. Yuan, X. Liu and Y. Peng, *Org. Biomol. Chem.*, 2011, **9**, 748.

16 For examples of our reports on silver catalysis, see: (*a*) J. Liu, Z. Liu, P. Liao, L. Zhang, T. Tu and X. Bi, *Angew. Chem., Int. Ed.*, 2015, **54**, 10618; (*b*) Z. Liu, J. Liu, L. Zhang, P. Liao, J. Song and X. Bi, *Angew. Chem., Int. Ed.*, 2014, **53**, 5305; (*c*) J. Q. Liu, Z. X. Fang, Q. Liu

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and X. Bi, *Angew. Chem., Int. Ed.*, 2013, **52**, 6953; (*d*) G. Fang and X. Bi, *Chem. Soc. Rev.*, 2015, **44**, 8124.

17 For recent examples of the synthesis of tetraorganosilanes, see: (*a*) C. Chu, Y. Liang and G. C. Fu, *J. Am. Chem. Soc.*, 2016, **138**, 6404; (*b*) Y. Hua, P. Asgari, T. Avullala and J. Jeon, *J. Am. Chem. Soc.*, 2016, **138**, 7982; (*c*) A. A. Toutov, W. B. Liu, K. N. Betz, A. Fedorov, B. M. Stoltz and R. H. Grubbs, *Nature*, 2015, **518**, 80.

18 (*a*) Z. Liu, P. Liao and X. Bi, *Chem. – Eur. J.*, 2014, **20**, 17277; (*b*) Z. Yang, R. K. Kumar, P. Liao, Z. Liu, X. Li and X. Bi, *Chem. Commun.*, 2016, **52**, 5936; (*c*) A. Myers and B. Zheng, *J. Am. Chem. Soc.*, 1996, **118**, 4492.

19 During the review of this manuscript, a related work on carbene insertion into Sn–H bonds was reported by Wang and co-workers, D. Qiu, S. Wang, H. Meng, S. Tang, Y. Zhang and J. Wang, *J. Org. Chem.*, 2017, **82**, 624.

20 (*a*) J. Cossrow and S. D. Rychnovsky, *Org. Lett.*, 2002, **4**, 147; (*b*) M. Das, A. Manvar, M. Jacolot, M. Blangetti, R. C. Jones and D. F. O'Shea, *Chem. – Eur. J.*, 2015, **21**, 8737.