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Electrophilic C(sp²)-H Silylation by Supported Gold Catalysts

Hiroki Miura,*^[a,b,c] Ryuji Hirata, Toyomasu Tomoya, and Tetsuya Shishido*^[a,b,c]

[a]	Prof. Dr. H. Miura, R. Hirata, T. Toyomasu, Prof. Dr. T. Shishido
	Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Sciences
	Tokyo Metropolitan University
	Minami-Osawa, Hachioji, Tokyo 192-0397(Japan)
	E-mail: miura-hiroki@tmu.ac.jp; shishido-tetsuya@tmu.ac.jp
[b]	Prof. Dr. H. Miura, Prof. Dr. T. Shishido
	Research Center for Hydrogen Energy-based Society
	Minami-Osawa, Hachioji, Tokyo 192-0397(Japan)

[c] Prof. Dr. H. Miura, Prof. Dr. T. Shishido
 Elements Strategy Initiative for Catalysts & Batteries
 Kyoto University
 1-30 Goryo-Ohara, Nishikyo-ku, Kyoto 615-8245(Japan)

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Abstract: Heterogeneous gold-catalyzed $C(sp^2)$ –H silylation is described. A variety of heteroarenes and electron-rich arenes participated in gold-catalyzed silylation to afford the corresponding heteroaryl and arylsilanes in good to excellent yields. A detailed mechanistic investigation corroborated that the cooperative catalysis of ether and O₂-activated gold nanoparticles realized heterolysis of the Si–H bond to generate silyl cations, which enabled subsequent electrophilic C–Si bond formation. The high activity, reusability and environmentally-friendly nature of the heterogeneous gold catalysts as well as the scalability of the reaction system realize the sustainable synthesis of aryl and heteroarylsilanes.

Introduction

Silylation of aromatic compounds is highly significant since aryland heteroarylsilanes are ubiquitous in synthetic, pharmaceutical and material chemistry.^[1] Nucleophilic attack of organolithium and Grignard reagents to silicon electrophiles is a classic, and still the most reliable method for delivering a silyl moiety to arenes and heteroarenes. Nevertheless, its severe drawbacks which include the prefunctionalization of substrates and the formation of a stoichiometric amount of toxic metallic salts, has forced us to replace the strategy for constructing C(sp²)-Si bonds with catalytic alternatives. Transition metal-catalyzed cross-coupling of aryl halides with hydrosilanes or disilanes has appeared as a reliable method for the regio-controlled silvlation of arenes,[2] while the formation of stoichiometric salt as a byproduct is unavoidable. In sharp contrast, direct C(sp²)-H bond silvlation with hydrosilanes is the most straightforward and atom-economical approach for accessing aryl- and heteroarylsilanes since the only potential by-products are non-toxic molecular hydrogen and water.^[2g,3] Extensive research in this field over the past decade has revealed that transition-metal complexes,^[4] Lewis acids,^[3d,3e,5] and strong bases^[6] enable catalytic C(sp²)-H silvlation. However, severe problems with homogeneous catalysis, such as the difficulty of separating and recycling catalysts, still forces us to devise alternative protocol for the sustainable synthesis of arylsilanes. On the other hand, one of the most reliable solutions for achieving environmentally-friendly organic transformation is the use of heterogeneous catalysts since they can facilitate the recycling of precious metals and prevent contamination of the products by toxic metals.^[7] Over the past decade, supported Au nanoparticles (NPs) have been reported to be effective for catalytic silylation of unsaturated organic molecules.^[8] Mitsudome and Yamaguchi independently demonstrated that supported Au catalysts exhibit high activity for the silylation of alcohols,^[9] and the C(sp)–H bond of terminal alkynes^[10] in the presence of molecular oxygen. However, there has been no reports on the efficient silylation of C(sp²)-H bonds under the influence of supported metal nanoparticles.

Herein, we report an electrophilic $C(sp^2)$ -H silylation by supported Au catalysts. Au NPs supported on SiO₂ in the presence of ether efficiently catalyzed the silylation of C–H bonds in various heteroarenes and electron-rich arenes under an O₂ atmosphere at ambient pressure. A detailed mechanistic investigation corroborated that O₂-activated Au NPs and ethers cooperatively functioned to generate silyl cation, thereby enabling electrophilic C–Si bond formation. The excellent activity, reusability and environmentally-friendly nature of the supported Au catalyst contribute to realization of the environmentaly-benign synthesis of aryl and heteroarylsilanes.

Results and Discussion

The effect of metal nanoparticles on the reaction of benzo[b]thiophene (1a) and triethylsilane (2a) under an ambient pressure of O2 was examined (Table 1). Among the SiO2supported catalysts examined, only a Au catalyst was effective for the C-H silylation of 1a, in which the C2-silylated benzothiophene (3aa) was obtained as a sole product in 52% yield (entries 1 and 2). The keys for obtaining the aryl silanes under the heterogeneous gold catalysis are the supporting material, the reaction solvent, and the reaction atmosphere. The replacement of SiO₂ support with TiO₂ or ZrO₂ significantly decreased the yield of 3aa (entries 3 and 4). SiO₂-supported catalysts with larger Au NPs showed higher activity than the Au catalysts supported on TiO₂ and ZrO₂ (entry 5), which indicated that the SiO₂ support positively affects the catalytic activity of Au NPs. The reaction under an argon atmosphere resulted in no conversion of 1a and 2a regardless of the presence of cyclohexene as a hydrogen acceptor (entries 6 and 7), suggesting that molecular oxygen

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served not only as a hydrogen acceptor, but also as an activating reagent for the supported Au catalyst. The reaction solvents also critically dominate the reaction efficiency, and the reaction in diglyme as a solvent remarkably increased the yield of 3aa (entry 8), whereas toluene, THF and 1,4-dioxane were inappropriate (entries 9-11). In contrast, a cyclic siloxane, namely octamethylcyclotetrasiloxane, was a good solvent for the Aucatalyzed silylation to furnish 3aa quantitatively (entry 12). Furthermore, the addition of diglyme (2 equiv. to 1a) to the reaction in toluene significantly increased the yield of 3aa (entry 13), which implies that a polyether structure in the solvent and a SiO₂ support are crucial for efficient silylation by Au catalysts (vide infra). The reaction with a quite low catalyst loading (1a/Au = 4000) corroborates high activity and durability of the supported Au catalyst to furnish 1a in 90% yield, in which the turnover number reached 3600 (entry 14). Although this is the first report of heterogeneous C(sp²)-H silvlation, this value is the highest ever reported in the catalytic silvlation of C(sp²)-H bonds.^[11] Furthermore, the reaction at a large scale (1.0 g (7.45 mmol) of 1a) proceeded smoothly to give 3aa in an isolated yield of 84% (1.5 g), which clearly indicates that the supported Au catalysts

Table 1. Optimization of reaction conditions.

	> + H−SiEt₃ ·	Au/SiO ₂ (1 mol%)	SiEt ₃	
S 1a	2a	dibutyl ether, 100 °C 3 h, under O ₂	S 3aa	
Entry	Variation from t	yield of 3aa (%) ^[b]		
1	none	52		
2	Ni, Cu, Ru, Rh, Au	0		
3	Au/TiO ₂ ^[c] instea	4		
4	Au/ZrO ₂ ^[d] instea	18		
5	Au/SiO ₂ with lar	40		
6	under Ar	0		
7	with addition of under Ar	0		
8	diglyme instea	97		
9	toluene instead	9		
10	THF instead of	1		
11	1,4-dioxane inst	2		
12	cyclo-siloxane	99		
13	toluene instead and the addition	87		
14	Au/SiO ₂ (0.025	90 (TON=3600)		
15	gram-scale read	ction in diglyme ^[g]	84 ^h	
0			/ i	
(Octamethylcyclotetrasiloxane)				

[a] Standard reaction condition: **1a** (0.50 mmol), **2a** (2.5 mmol), Au/SiO₂ (loading weight: 1wt%, Au NPs: 1.6 nm, 1.0 mol% as Au was used), dibutyl ether (1 mL), O₂ (1 atm, baloon), 100 °C, 3 h. [b] Determined by GC. [c] Au NPs: 2.5 nm. [d] Au NPs: 2.7 nm. [e] Au/SiO₂ (loading weight: 3wt%, Au NPs: Au NPs: 5.5 nm). [f] Cyclo-siloxane: octamethylcyclotetrasiloxane. [g] Reaction of **1a** (1.0 g (7.45 mmol)). [h] Isolated yield.

With the optimized catalyst in hand, we next investigated the scope of substrates in the supported Au-catalyzed C(sp²)-H silvlation. The appropriate solvent depended on the substrate and should be chosen from among several ethers, such as diglyme, dibutylether and cyclosiloxanes. As for benzothiophene and its derivatives, silylation predominantly took place at the C2 position (Table 2). Although a methyl group at the C2 position of benzothiophene did not allow the silvlation at the C3 position of benzothiophene, the reaction of 3-methylbenzothiophene proceeded efficiently to give C2-silylated product (3ca) in 88% yield. A cyclopropyl group at the C3 position was tolerated, thus giving the corresponding product (3da) in 92% yield. No ringopening of the cyclopropyl group during this reaction suggests that no radical intermediates are involved in the Au-catalyzed silvlation (vide infra). A methyl substituent at the C5 position did not affect the reaction efficiency or product selectivity. A characteristic of silvlation by the supported Au catalysts is the broad scope of hydrosilanes. Not only primary alkyl group, but also secondary and tertiary alkyl group-substituted silyl moieties could be installed into benzo[b]thiophene to give 3ab-3ad in high yields. Interestingly, bulky bis(trimethylsiloxy)methylsilane and tris(trimethylsiloxy)silane also participated in Au-catalyzed C-H silvlation to provide 3ae and 3af in respective yields of 98% and 93%. Aryl groups were also acceptable as a substituent of hydrosilanes to furnish bisarylsilanes (3ag-3ai).

Table 2. Au/SiO₂-catalyzed silylation of benzothiophene derivatives^[a].





Table 3 summarizes the silylation of benzo-fused *N*- and *O*heterocycles. In contrast to benzo[*b*]thiophenes, silylation of these heteroarenes took place at both the C2 and C3 positions, to give the corresponding products as a mixture of regioisomers. For instance, the reaction of *N*-methylindole (**1f**) gave the corresponding silylated adducts (**3fa**) in 95% yield, while the C2/C3 regioselectivity was 51:49. The substituents at the *N* atom of indole influenced regioselectivity. The reaction of *N*-ethyl indole afforded **3ga** in 81% yield, where a C3 adduct was formed preferentially. Phenyl and benzyl substituents also increased the C3 selectivity of the products (**3ha** and **3ia**). Although a pyridyl

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group is often used as a directing group for C-H functionalization at the C2 position of indole,^[12] no dramatic effect on regioselectivity was observed in the present Au-catalyzed C-H silylation. N-Methylindoles with a methyl substituent at the C2 or C3 position underwent silvlation at the C3 or C2 position to provide 3ka and 3la, respectively. The reactions of Nmethylindoles bearing a methyl group at C5, C6, C7 or C8 proceeded smoothly to give the corresponding silvlated indoles (3ma-3pa) in good to high yields, where a C5 methyl group particularly enhanced C2 selectivity. The electronic impact of the substituents at the C6 position of indoles was examined to gain the insight into the reaction mechanism. The preferential conversion of substrates with an electron-donating MeO group implies that the present Au-catalyzed reaction proceeds via the formation of cationic intermediates (vide infra). Benzo[b]furan also participated in Au/SiO₂-catalyzed silylation to afford 3sa in 79% vield, in which C2/C3 regioselectivity was 68:32. As is the case with benzo[b]thiophene (Table 2), Au/SiO₂ catalyst installed a bulky triisopropylsilyl group into N-methylindole and benzo[b]furan to give the corresponding arylsilanes (3fd and 3sd) in excellent yields, whereas its bulkiness did not affect the regioselectivity of the products. The lower reactivity of indoles and benzo[b]furan compared to benzo[b]thiophenes allows for the fast oxidative consumption of hydrosilanes. Hence, dropwise addition of 2 using a syringe pump was indispensable to obtain the silvlated N- and O-heterocycles in high yields.

Table 3. Au/SiO₂-catalyzed silylation of benzo-fused N- and O-heterocycles^[a].



[a] Reaction conditions: 1 (0.50 mmol), 2 (2.5 mmol; added to the reaction mixture over 1 h by a syringe pump), Au/SiO₂ (1.0 mol% as Au), solvent (1 mL). Isolated yields were given. [b] Reaction in decamethylcyclopentasiloxane. [c] No dropwise addition of 2.

In addition, C-H silylation of simple heterocycles was investigated (Table 4). The reaction of 3-butylthiophene (4a) with 2a allowed silylation predominantly at C-H bonds adjacent to the S atom to

give mono and disilylated thiophenes (**5aa** and **5aa**') in a total yield of 86%. As for *N*-methylpyrrole, disilylation mainly occurred to give disilylpyrroles as a mixture of regioisomers (**5ba** and **5ba**') in a total yield of 79%. In contrast, 2-butylfuran underwent C-H silylation only at the C5 position to give **5ca** in 66% yield.

Table 4. Au/SiO₂-catalyzed silylation of S-, N- and O-heterocycles [a].



[a] Reaction conditions: 1 (0.50 mmol),), 2a (2.5 mmol; added to the reaction mixture over 1 h by a syringe pump), Au/SiO₂ (1.0 mol% as Au), solvent (1 mL), 120 °C. Isolated yields were given.

Furthermore, the supported Au NPs efficiently catalyzed the silylation of electron-rich arenes (Table 5). Although dropwise addition of hydrosilanes was required to obtain the products in satisfactory yields, arenes with more than two methoxy groups underwent silylation to give mono- and disilylarenes in good to high total yields. A silyl group was also installed into naphthalene, albeit the total yield was low. Methods to improve both the yield and regioselectivity of the products in Au-catalyzed C-H silylation are currently being investigated in our laboratory.

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Au/SiO2 (1 mol%) Ar-H Ar-SiEt₃ + H-SiEt₃ Diglyme, 120 °C 7 6 2a 3 h, under O₂ product entry arene SiEt₃ SiEt₃ 1 MeO -OMe OMe MeC 6a 7aa 7aa Et₂S 14% 52% MeC MeO MeO MeC 2 MeO OMe MeO OMe MeO MeO OMe

Table 5. Au/SiO₂-catalyzed silylation of electron-rich arenes^[a].



[a] Reaction conditions: 1 (0.50 mmol),), 2a (2.5 mmol; added to the reaction mixture over 1 h by a syringe pump), Au/SiO₂ (1.0 mol% as Au), diglyme (1 mL), 100 °C. Isolated yields were given. [b] Reaction at 100 °C for 3 h.

The most advantageous feature of supported catalysts is their high reusability. The Au/SiO₂ catalyst exhibited excellent reusability without remarkable decreases in the yield of the product in five consecutive silylations of benzo[b]thiophene (Figure 1).





Figure 1. Catalyst reuse test^[a].

Furthermore, hot filtration of the solid catalyst completely retarded the further progress of the reaction, which indicates that the supported Au catalyst operates heterogeneously during the silvlation of C(sp²)-H bonds (Figure 2). Besides, atomic absorption spectrometry identified no leaching of Au species into the reaction mixture. These environmentally friendly characteristics and the scalability of the reaction system (Table 1, entry 15) clearly indicate that the Au/SiO₂ catalysts can be an attractive tool for the green and sustainable synthesis of arylsilanes.



[a] Reaction conditions: 1a (0.50 mmol), 2a (2.5 mmol), catalyst (1.0 mol% as metal), digly me (1 mL), 100 °C.

Figure 2. Hot filtration of Au/SiO₂ catalyst^[a].

Previously proposed mechanisms for catalytic C(sp²)-H silylation can be briefly classified into three modes (Scheme 1). Mechanism (A) involves the formation of aryl silyl metal species formed via C-H and Si-H bond cleavage at the metal center.^[4d,4n] Mechanism (B) includes the generation of silyl radicals via homolysis of the Si-H bond.^[13] In mechanism (C), Lewis acid catalysts abstract hydride of Si-H to form electrophilic silyl cation, which enables Friedel-Crafts type C–Si bond formation.[3d,14]

Mechanism (A): Reductive elimination from aryl silyl metal

$$Ar-H + H-SiR_3 \xrightarrow{M} Ar-M-SiR_3 \xrightarrow{} Ar-SiR_3$$

Mechanism (B): Silvl radical formation by radical initiator

$$RI \cdot H \xrightarrow{G} SiR_3 \xrightarrow{RI-H} SiR_3 \xrightarrow{Ar-H} Ar-SiR_3$$

Mechanism (C): Silvl cation formation by strong Lewis acid

$$LA \cdots H SiR_3 \xrightarrow{+SiR_3} H^+ Ar - SiR_3$$

Scheme 1. Brief classification of the reaction mechanisms of C(sp2)-H silylation (RI: radical initiator).

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To gain insight into the mechanism of the supported Au-catalyzed silylation, several control experiments were performed. The treatment of benzo[*b*]thiophene with D₂O in the presence of Au/SiO₂ did not allow the incorporation of D at the C2 position (Scheme 2-1). Furthermore, the reaction of C2-deuterated benzo[*b*]thiophene with both H₂O and *N*-methylindole allowed no H-D exchange (Scheme 2-2 and 2-3). These results suggest that the reaction dos not involve direct activation of C(sp²)–H bond by Au nanoparticles, thus enabling us to exclude mechanism (A).



Scheme 2. D-labeling experiments over Au/SiO₂ catalysts.

On the other hand, Raffa and coworkers proposed that silyl radical intermediates were generated from hydrosilane in the silylation of aldehyde over supported Au catalysts.^[15] However, as described in Table 2, no ring-opening during the C2 silylation of 3-cyclopropyl benzo[*b*]thiophene (**2d**) suggests that a silyl radical intermediate did not participate in the Au-catalyzed C-H silylation. Moreover, the addition of TEMPO as a radical scavenger did not affect the progress of the silylation of benzo[*b*]thiophene (**1a**) (Scheme 3), which further supports the exclusion of mechanism (B). These results enable us to surmise that C-H silylation under supported Au catalysis proceeds through the formation of an electrophilic silyl cation intermediate.



Scheme 3. Effect of TEMPO on Au/SiO2-catalyzed C-H silylation of 1a.

To identify the generation of silyl cation during silylation of a C-H bond by Au/SiO₂ catalysts, the ring-opening reaction of epoxide was carried out. The treatment of epoxide (8) with triethylsilane (2a) in the presence of Au/SiO₂ catalyst under an O₂ atmosphere gave allyloxysilane (9) in 51% yield (Scheme 4). This dehydrogenative silvlation including ring cleavage between O and quaternary carbon should involve an electrophilic migration of silyl cation to O atom and subsequent formation of tertiary carbocation. Notably, the addition of TEMPO did not influence the silvlation of the epoxide, which indicates that the silvl radical does not contribute to the oxidative silvlation by Au/SiO₂ catalyst. Furthermore, molecular O2 was also indispensable for this reaction to proceed. These results indicate that O₂ is crucial for generating an electrophilic silyl cation via heterolysis of a Si-H bond over Au NPs. Although Au/TiO₂ was reported to promote ring-opening rearrangement of epoxides to allylic alcohols,^[16] the present Au/SiO₂ catalyst was not effective for the rearrangement of 8 in the absence of hydrosilane. This indicates that the pathway to 9 by Au/SiO₂ catalyst did not involve sequential isomerization and silvlation.



Scheme 4. Reaction of epoxide and hydrosilane.

To gain further information about the effect of the reaction atmosphere and solvent on Si–H cleavage over Au NPs catalysts, the reactions of TEMPO (**10**) and triethylsilane (**2a**) were investigated (Scheme 5). The reaction in toluene under an argon atmosphere gave a considerable amount of TEMPO-silyl adduct (**11**). In contrast, the use of diglyme as a solvent significantly retarded the formation of silyl adduct. Furthermore, the reaction under O_2 dramatically suppressed the radical coupling reaction. These results clearly support the notion that molecular O_2 and ethers are essential for preventing the formation of silyl radical via the homolysis of Si–H bonds and for promoting heterolysis to form a silyl cation.



Scheme 5. Reaction of TEMPO with hydrosilane.

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To identify the rate-determining step in the Au-catalyzed silylation of $C(sp^2)$ –H bond, we performed several kinetic studies. As shown in Scheme 6, the kinetic isotope effect (KIE) estimated by the silylation of d-benzo[*b*]thiophene (**1a**-*d*) was 1.7. In contrast, a remarkable KIE of 5.1 was confirmed in the reaction of dtriethylsilane (**2a**-*d*). Although further detailed investigation is necessary to understand the reason why such large KIE value appeared in the reaction of **2a**-*d*, these results enable us to deduce that activation of Si-H bond is more important than that C–H bond of arenes for C-Si bond formation.



Scheme 6. Kinetic isotope effect in C-H silylation by Au/SiO₂ catalyst.

Besides, the reaction orders of benzo[*b*]thiophene and hydrosilane were estimated to be -0.4 and 0.3, respectively (Figure 3). On the other hand, the first-order dependency of the partial pressure of O_2 suggests that O_2 acts as part of a real catalyst. These results clearly indicate that the rate-determining step of the present C–H silylation should be the heterolysis of Si– H bonds with the assistance of molecular O_2 . Previous reports stated that strong Lewis acids were required to generate silyl cation via the abstraction of hydride from hydrosilanes.^[17] Although Au NPs are known to exhibit Lewis acidic character,^[18] adsorption of molecular O_2 promotes electron-transfer from Au NPs to O_2 , thereby further increasing the Lewis acidity of the Au NPs.^[18]



Figure 3. Effects of the concentration of 1a, 2a, and the partial pressure of O_2 on the reaction rate.

Moreover, to understand the role of the ether solvent, we investigated the time course of the reaction with different diglyme concentrations in toluene (Figure 4A). As described in Table 1, although no C-H silylation took place with the use of toluene as a sole solvent, the reaction-rate increased with an increase in the



Figure 4 Effect of the concentration of diglyme on C-H silylation by Au/SiO $_2$ catalyst.

Based on these results, we propose a possible reaction mechanism for C(sp²)–H silylation over Au/SiO₂ catalyst (Scheme 7). Initially, molecular O₂ coordinates with Au NPs, which enhances their Lewis acidity.^[20] Subsequently, the activated Au NPs abstract hydride of hydrosilane to form a silyl cation. In this step, the coordination of ethers and the siloxane network of SiO₂ to Si atom would facilitate the heterolysis of Si-H bonds. Next, electrophilic migration of the silyl cation to an arene gives an arenium ion. Finally, an adsorbed O2 on Au NPs abstracts a proton of arenium ion to furnish arylsilanes. Since surface basicity of ZrO₂ is stronger than that of SiO₂, excess stabilization of silyl cation reduces reaction efficiency. On the other hand, surface acidic nature of TiO₂ would decrease electron density of arenes, which causes the decrease the rate of electrophilic C-Si bond formation. Thus, neutral surface nature of SiO₂ should be suitable for the present Au-catalyzed C-Si coupling. Notably, no hydrogen evolution was detected during the present oxidative silylation by GC analysis, which suggests that molecular O2 functioned not only as an activator of Au NPs, but also as a hydrogen acceptor. Although the origin of the regioselectivity of the present C-H silylation by Au/SiO2 is still under discussion, this can be explained by the stability of carbocation intermediates. As for the silylation of heterocycles, the carbocation formed via the migration of a silyl cation to the C2 carbon is stable since it is located at a benzylic position. Besides, the carbocation formed at the C2 position of benzo[b]furan and indoles via the migration of a silyl cation to C3 carbon can be stabilized due to delocalization of the positive charge by adjacent O and N atoms, thus leading to the formation of mixture of regioisomers. In contrast, the contribution of delocalization of the positive charge by an adjacent S atom is much smaller than those for O and N atoms,^[21] thereby enabling the regioselective C2 silvlation of benzo[b]thiophene. Although interaction between Au and S atoms^[22] can be attributed to the regioselective silvlation of benzo[b]thiophene, further

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Scheme 7. Possible Mechanism of C(sp²)-H silylation by Au/SiO₂ catalyst.

detailed investigations based on theoretical study is necessary to understand the reaction mechanism.

Conclusion

In summary, versatile C(sp²)-H bond silvlation by supported Au catalysts was described. Au/SiO₂ catalyst showed high activity for the silvlation of a C-H bond in a variety of heteroarenes and electron-rich arenes to give the corresponding aryl- and heteroarylsilanes. Furthermore, the present heterogeneous Au catalysts was effective for the installation of not only simple trialkylsilyl groups but also bulky triisopropyl and tris(trimethylsiloxy) groups into heterocycles. Detailed mechanistic investigation revealed that cooperative catalysis by ethers and O₂-activated Au NPs promoted the heterolysis of Si-H bonds to form silvl cation, which enabled electrophilic silvlation of C(sp²)-H. The high activity, reusability and environmentally friendly nature of the supported Au NPs catalyst as well as the scalability of the reaction system should be advantageous for the environmentaly-benign synthesis of important aryl and heteroarylsilanes. Further applications of supported Au catalysts in other synthetic reactions including regioselective synthesis of arylsilanes are currently under investigation in our laboratory.

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Keywords: gold • heterogeneous catalyst • silylation • C-H functionalization • arylsilane

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FULL PAPER

Entry for the Table of Contents



Aid of oxygen and ether: SiO_2 -supported gold nanoparticle catalysts showed high activity for silylation of $C(sp^2)$ –H bond to afford a series of aryl and heteroarylsilanes. Detailed mechanistic investigation revealed that O_2 -activated Au NPs and ethers cooperatively functioned to generate silyl cation, thereby enabling electrophilic C–Si bond formation.