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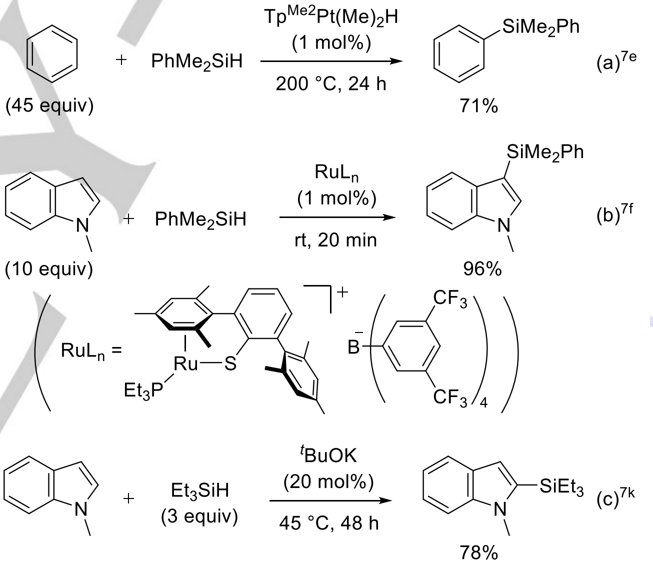
Rhodium-Catalyzed Silylative and Germylative Cyclization with Dehydrogenation Leading to 9-Sila- and 9-Germafluorenes: A Combined Experimental and Computational Mechanistic Study

Masahito Murai,*[a] Ryo Okada,[a] Sobi Asako,[a] and Kazuhiko Takai*[a]

Abstract: Stoichiometric amounts of oxidants are widely used as promoters (hydrogen acceptors) in dehydrogenative silylation of C–H bonds. However, the present study demonstrates that silylative and germylative cyclization with dehydrogenation can proceed efficiently, even without hydrogen acceptors. The combination of $[RhCl(cod)]_2$ and PPh_3 was effective for both transformations, and allowed a reduction in reaction temperature compared with our previous report. Monitoring of the reactions revealed that both transformations had an induction period for the early stage, and that the rate constant of dehydrogenative germylation was greater than that of dehydrogenative silylation. Competitive reactions in the presence of 3,3-dimethyl-1-butene indicated that the ratio of dehydrogenative metalation and hydrometalation was affected by reaction temperature when a hydrosilane or hydrogermane precursor was used. Further mechanistic insights of oxidant-free dehydrogenative silylation, including the origin of these unique reactivities, were obtained by density functional theory studies.

Introduction

Catalytic silylation with hydrosilanes provides synthetically valuable organosilicon compounds with high atom-efficiency.[1] The resulting C–Si bonds are stable, but can be derivatized easily to a wide variety of functional groups by reactions such as oxidative halogenation, Tamao oxidation, and Hiyama cross-coupling reaction.[2] Hydrosilylation with unsaturated carbon–carbon multiple bonds, such as alkenes and alkynes, represents one of the most important C–Si bond-forming reactions.[3] In addition, dehydrogenative silylation of unactivated C–H bonds with hydrosilanes has received attention as a convenient, economical, and environmentally benign approach in the past decades.[4] Considerable progress has been made in this field using catalysts, such as scandium, ruthenium, rhodium, iridium, and platinum complexes, for the formation of C–Si bonds from ubiquitous C–H bonds without preactivation of the starting compounds. However, most of the reported methods require a stoichiometric amount of the oxidant as a hydrogen acceptor, including olefins, a Lewis acid,[5] and peroxides,[6] to overcome the generally thermodynamically unfavorable formation of C–Si bonds with hydrogen elimination. The development of a catalytic dehydrogenative silylation without any hydrogen acceptors is limited.[7-9] The reported methods usually require high temperatures (above 150 °C), microwave heating, and/or a large excess of aromatic substrates (benzene or toluene) as solvents (Scheme 1a).[7a-e,h,j,l] The exception was reported by Oestreich and Tatsumi on the ruthenium-catalyzed C–H silylation of indole derivatives, in which the unique electrophilic aromatic substitution with sulfur-stabilized silicon cation species was proposed as a reaction mechanism (Scheme 1b).[7f] Using pyridine-based directing groups, Sato *et al.* reported that dehydrogenative silylation occurred without any hydrogen acceptors under iridium catalysis.[7g,i] More recently, ^{t}BuOK-catalyzed radical silylation of C–H bonds of heterocycles was reported by Stoltz and Grubbs *et al.* (Scheme 1c).[7k]



Scheme 1. Catalytic dehydrogenative silylation of C–H bonds without hydrogen acceptors (Tp^{Me2} = hydridotris(3,5-dimethylpyrazolyl)borate)

Prior to the work of Oestreich, Sato, Stoltz, and Grubbs, we reported the rhodium-catalyzed synthesis of 9-silafluorenes via intramolecular dehydrogenative silylation of 2-biphenylsilanes (Scheme 2).[8] Wilkinson complex, $RhCl(PPh_3)_3$, was effective for this transformation, and the reaction did not require external oxidants (hydrogen acceptors)[10] or heteroatom-containing directing groups. Stemming from this seminal work, *oxidant-free* dehydrogenative silylation was applied to the synthesis of various silacycles using a combination of $[RhCl(cod)]_2$ and phosphines as a catalyst and ligands, respectively.[9] Despite these rapid experimental advances, the reaction mechanism, and the reason why the reaction proceeds without oxidant have not been fully elucidated. Experimental observations that the choice of oxidant (hydrogen acceptor) was crucial in the following similar types of dehydrogenative silylation, were

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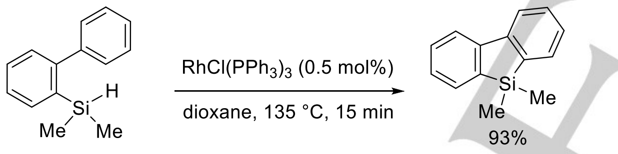
especially interesting: (i) iridium-catalyzed intramolecular silylation of C–H bonds,[11] (ii) rhodium-catalyzed intramolecular silylation of C(sp^3)–H bonds,[12] and (iii) rhodium- or iridium-catalyzed intermolecular silylation of C–H bonds.[13]

The present study describes experimental and computational results related to the unique oxidant-free dehydrogenative silylation of C(sp^2)–H bonds. Analogous DFT studies on the intermolecular dehydrogenative silylation of C(sp^2)–H bonds and the intramolecular dehydrogenative silylation of C(sp^3)–H bonds in the presence of cyclohexene or norbornene as a hydrogen acceptor have been previously performed by Sunoj and Hartwig.[13b,14] Their mechanistic studies revealed that the catalytic cycle comprised by the following three steps: 1) oxidative addition of hydrosilane to a hydrorhodium species; 2) dehydrogenation of the resulting metal silyl dihydride complexes by hydrogen acceptors; and 3) C–H bond activation by the metal silyl species followed by the reductive elimination to form C–Si bond. Hartwig reported that the resting state of the catalyst is metal silyl dihydride complex, and its dehydrogenation by hydrogen acceptor is the rate-determining step in the rhodium-catalyzed intermolecular dehydrogenative silylation of C(sp^2)–H bonds. On the other hand, the rate-determining step is suggested to be Si–C forming reductive elimination in the iridium-catalyzed intramolecular dehydrogenative silylation of C(sp^3)–H bonds by Sunoj. The comparative study of rhodium- and iridium-catalyzed intramolecular silylation of C(sp^2)–H bonds in the current study provides several clues for the development of oxidant-free functionalization of C–H bonds with dehydrogenation.

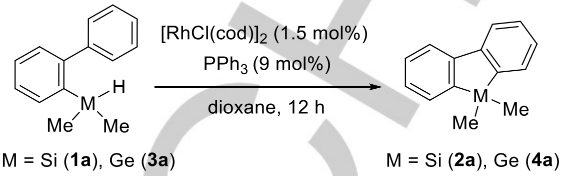


Scheme 2. Rhodium-catalyzed synthesis of 9-silafluorenes via dehydrogenative silylation of C(sp^2)–H bonds

Results and Discussion

We first found that the combination of $[RhCl(cod)]_2$ with PPh_3 (Rh:P = 1:3) as a catalyst gave the expected 9-silafluorene **2a** in 90% yield, even at 70 °C from reaction with dimethyl[(2-phenyl)phenyl]silane (**1a**) (Table 1, entry 1). Compared with Wilkinson complex,[8] $RhCl(PPh_3)_3$, which was the best catalyst in our previous report, the efficiency of the reaction improved (entry 2). The yield decreased to 21% when $[IrCl(cod)]_2$ was used in place of $[RhCl(cod)]_2$ (entry 3). The yield decreased to 63% when the reaction was conducted at 60 °C, but increased slightly at 80 °C (entries 4 and 5). The combination of $[RhCl(cod)]_2$ and PPh_3 was also effective for the dehydrogenative germylation of the C–H bonds of hydrogermane **3a** to afford 9-germafluorene **4a** in 92% yield (entry 6).[15] This is a rare example of dehydrogenative functionalization involving bonds between fourth-row atoms and hydrogen.[16] The reaction proceeded even at lower temperatures; however, the yield of **4a** decreased due to competitive decomposition of the precursor **3a** (entries 7 and 8).

Table 1. Catalytic dehydrogenative silylation and germylation of C–H bonds



Entry	M	temp / °C	Yield / %
1	Si	70	90
2^a	Si	70	78
3^b	Si	70	21
4	Si	80	93
5	Si	60	63
6	Ge	80	92
7	Ge	70	78
8	Ge	60	52

^{a} $RhCl(PPh_3)_3$ (3 mol%) and ^{b} $[IrCl(cod)]_2/PPh_3$ were employed as catalysts.

As mentioned above, dehydrogenative germylation of unactivated C–H bonds is rare. To compare the reaction profiles of germylation and silylation, reactions of hydrosilane **1a** and hydrogermane **3a** were monitored at 80 °C. The time-course of the formation of **2a** and **4a** is shown in Figure 1, which suggests that both reactions have an induction period during the early stage, but the rate constant for dehydrogenative germylation was 1.5 times greater than that for silylation (k_{Ge}/k_{Si}).

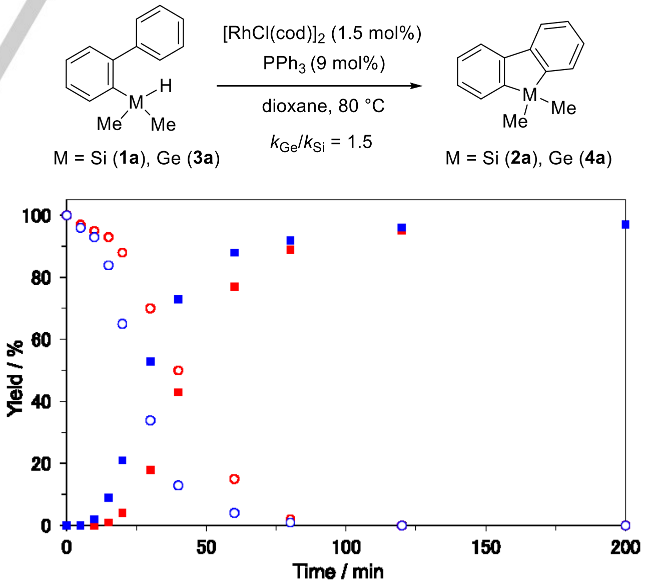


Figure 1. Time-conversion curves for reaction of **1a** and **3a** (recovery of **1a** (red circles) and **3a** (blue circles), yield of **2a** (red squares) and **4a** (blue squares)).

Although dehydrogenative silylation occurred without any oxidants, reaction of **1a** and **3a** was next examined in the presence of olefins. Among olefins, 3,3-dimethyl-1-butene, which is a widely used hydrogen acceptor, was chosen due to its mild reactivity considering the result obtained from our previous examination.[12,13c] The competitive intermolecular hydrosilylation of 3,3-dimethyl-1-butene leading to **5** suppressed the desired dehydrogenative silylation of C–H bonds, and the yield of **2a** decreased to 63% at 70 °C (Figure 2(a)).[17] Note that the ratio of dehydrogenative silylation product **2a** and hydrosilylation product **5** was greatly affected by the reaction temperature. **2a** was obtained selectively at high temperature, while the formation of **5** via intermolecular hydrosilylation occurred preferentially at low temperature.[18] In contrast, 3,3-dimethyl-1-butene successfully promoted the germylative cyclization of hydrogermane **3a**, and the yield of 9-germafluorene **4a** increased from 52% to 83% at 60 °C (Table 1, entry 8 *vs* Figure 2(b)). Competitive intermolecular hydrogermylation to 3,3-dimethyl-1-butene leading to **6** did not occur efficiently at any temperature examined (40~80 °C).[19,20]

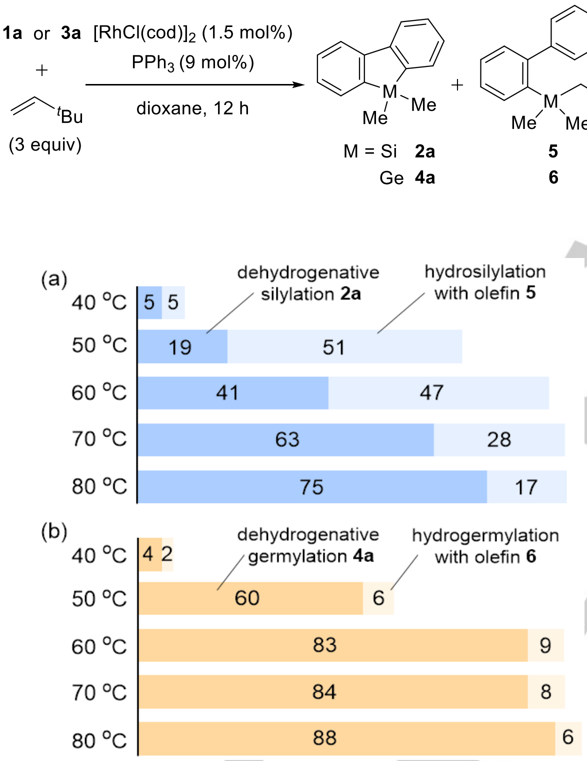
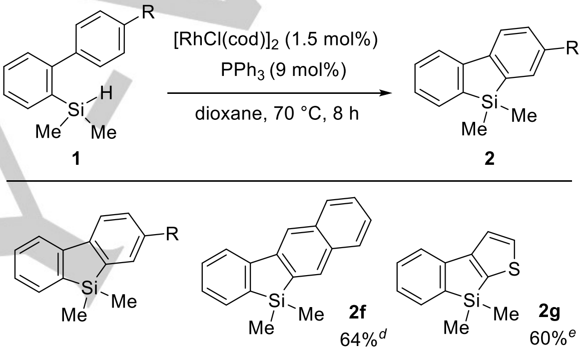


Figure 2. Competition between intramolecular dehydrogenative metalation and intermolecular hydrometalation with 3,3-dimethyl-1-butene. M = Si for (a) and M = Ge for (b).

Based on the above results, the effect of substitution pattern of hydrosilane **1** and hydrogermane **3** on dehydrogenative silylation ($[RhCl(cod)]_2$ / PPh_3 at 70 °C) and germylation ($[RhCl(cod)]_2$ / PPh_3 with 3,3-dimethyl-1-butene at 60 °C) was investigated (Tables 2 and 3). A variety of (2-biaryl)hydrosilanes and hydrogermanes possessing electron-withdrawing and -donating substituents gave the corresponding 9-sila- and 9-germafluorenes **2** and **4** in high yields. Unfortunately, partial reductive dechlorination occurred during silylative cyclization of biarylsilane containing a chloro group to produce a mixture of the 9-silafluorenes **2c** and **2a**. In contrast, chemoselective formation of 9-germafluorene **4c** occurred preferentially in the corresponding germylative cyclization with dehydrogenation. Note that cyclization of hydrosilane containing an electron-donating methoxy group leading to **2d** proceeded smoothly when 3,3-dimethyl-1-butene was treated as an additive. In the absence of 3,3-dimethyl-1-butene, the reaction was sluggish even at 120 °C. This result indicates that 3,3-dimethyl-1-butene promoted the dehydrogenative silylation as a hydrogen acceptor although a similar positive effect was not observed for cyclization of **1a** as shown in Figure 2.[20] Silylative and germylative cyclization occurred selectively at the β-position of the

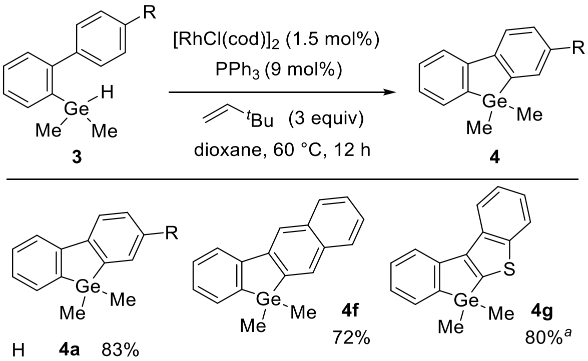
Table 2. Rhodium-catalyzed silylative cyclization of **1** leading to 9-silafluorene derivatives **2**



H	**2a**	90%			
CF_3	**2b**	94%	MeO	**2d**	68%[b], 82%[c]
Cl	**2c**	70%[a]	ᵗBu	**2e**	83%[d]

[a] Silafluorene **2a** was obtained in 18% yield via the dechlorination. [b] At 120 °C for 12 h. [c] With 3,3-dimethyl-1-butene (3 equiv) at 100 °C for 12 h. [d] 90 °C for 18 h. [e] 80 °C for 12 h.

Table 3. Rhodium-catalyzed germylative cyclization of **3** leading to 9-germafluorene derivative **4**

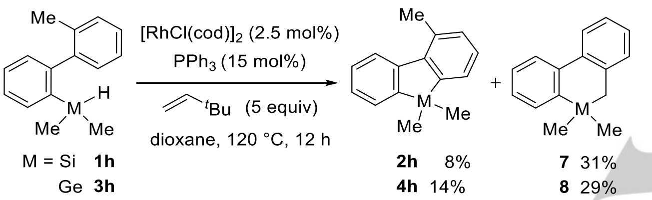


H	**4a**	83%			
CF_3	**4b**	83%	MeO	**4d**	82%
Cl	**4c**	86%	Me	**4e**	80%

[a] 80 °C.

naphthalene ring to furnish benzo[*b*]silafluorene **2f** and benzo[*b*]germafluorene **4f** in moderate yields. The current dehydrogenative cyclization was applicable to 2-(biaryl)silane and germane containing thienyl or benzothienyl groups to afford thiophene-fused benzosilole **2g** and benzogermole **4g** in good yields.

Reaction of hydrosilane containing a methyl group *ortho* to the silylphenyl group afforded a mixture of 9-silafluorene **2h** and 9,10-dihydro-9-silaphenanthrene **7** in 8% and 31% yield, respectively (Scheme 3).[12] Addition of 3,3-dimethyl-1-butene was again effective for this dehydrogenative silylation. Similar selectivity was observed for dehydrogenative cyclization of the corresponding biarylgermane **3h**, in which 9,10-dihydro-9-germaphenanthrene **8** was obtained as a major product along with 9-germafluorene **4h**. These results demonstrate that dehydrogenative silylation and germylation of the C(sp^3)–H bonds occurred preferentially over the aryl C(sp^2)–H bonds. This outcome is unique, because dehydrogenative functionalization generally favors C(sp^2)–H bonds under neutral conditions, and selective functionalization of C(sp^3)–H bonds remains difficult.



Scheme 3. Competitive dehydrogenative germylation of C(sp^3)–H *vs* C(sp^2)–H bonds

The proposed reaction mechanism for rhodium-catalyzed dehydrogenative silylation and germylation is shown in Figure 3. According to previous reports, reaction is initiated by oxidative addition of hydrosilane **1a** to a hydrorhodium species (H–Rh in Figure 3) to generate silylrhodium complex **A**.[21] Intermediate **A** then reacts through two possible pathways (Path a or b). In Path a, C(sp^2)–H bond activation *via* σ-complex-assisted metathesis (σ-CAM)[22] forms six-membered rhodacycle intermediate **B**. Subsequent elimination of H_2 followed by reductive elimination furnishes 9-silafluorene **2a** along with regeneration of the hydrorhodium species. In Path b, silylrhodium intermediate **A** first undergoes reductive elimination of H_2 to become intermediate **C**. Oxidative addition of the rhodium center in **C** to an aryl C–H bond generates intermediate **D**, which then undergoes reductive elimination to give **2a**. Path b is essentially the same mechanism proposed by Hartwig for rhodium-catalyzed intermolecular dehydrogenative silylation of aromatic compounds in the presence of cyclohexene as a hydrogen acceptor.[13b]

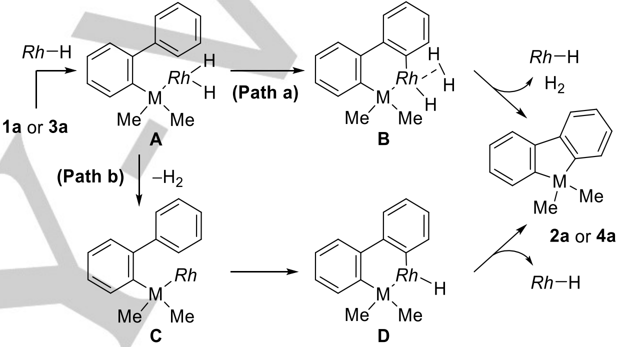


Figure 3. Proposed reaction mechanism (phosphine ligands omitted for clarity)

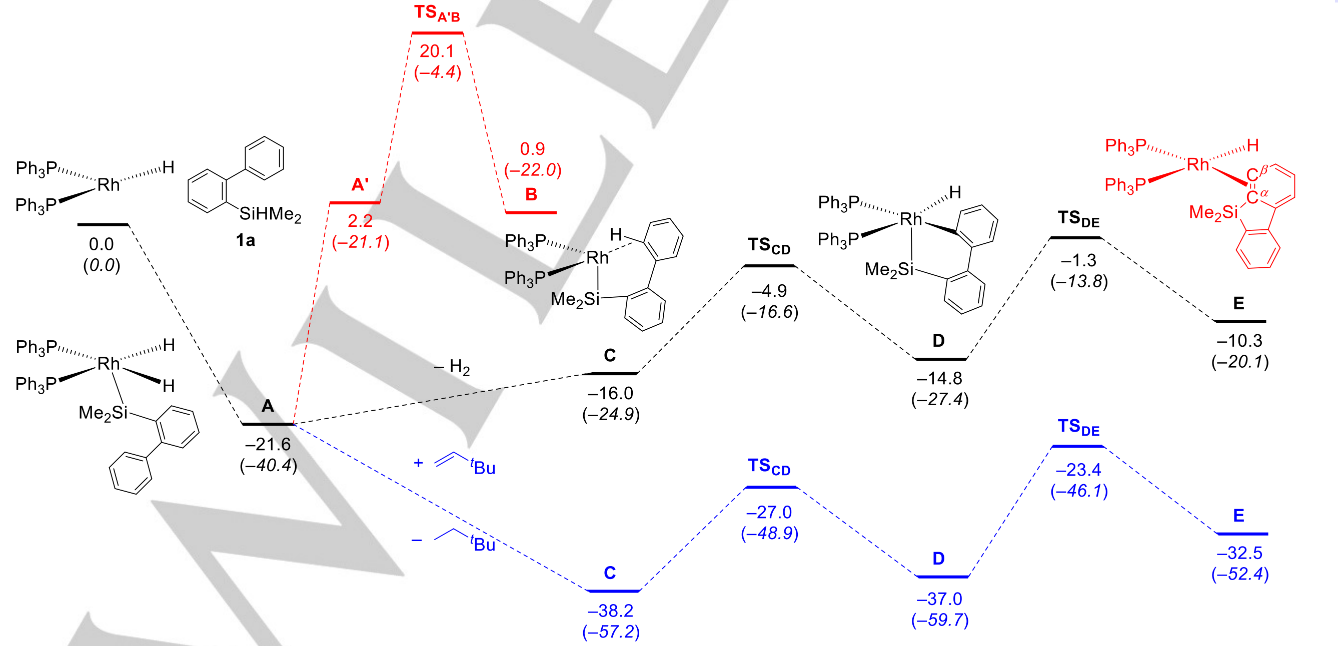
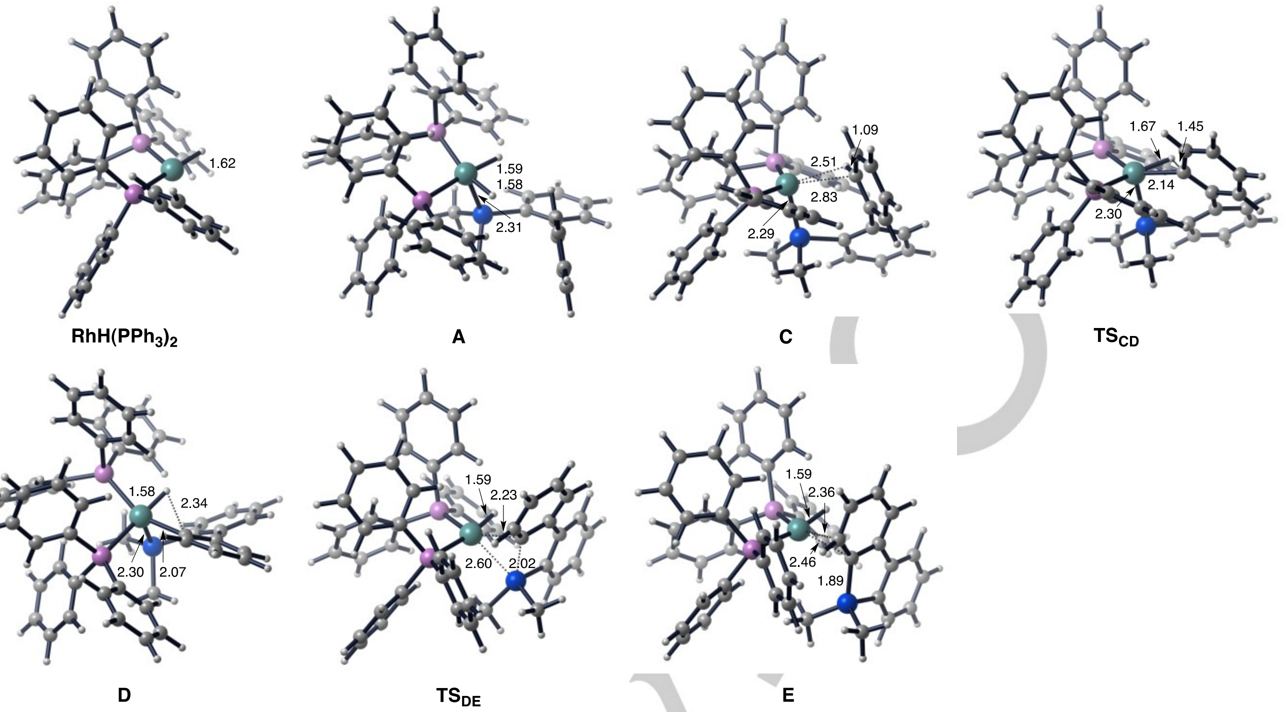


Figure 4. Energy profiles for rhodium-catalyzed dehydrogenative silylation of **1a** (Path a (red), Path b (black), and Path b with 3,3-dimethyl-1-butene (blue)). Relative Gibbs free energies and *enthalpies* calculated at the B3LYP-D3/SDD:6-31G(d) level of theory in dioxane at 70 °C are given in kcal/mol.



$RhH(PPh_3)_2$ **A** **C** **TS_{CD}**

D **TS_{DE}** **E**

Figure 5. Optimized structures of rhodium complexes involved in Path (b) calculated at the B3LYP-D3/SDD:6-31G(d) level. Color code: gray, carbon; white, hydrogen; pink, phosphine; blue, silicon; green, rhodium.

To obtain insight into the transformation, DFT calculations were performed at the B3LYP-D3/SDD:6-31G(d) level of theory using hydrosilane **1a** and $HRh(PPh_3)_2$ as active species (Figures 4 and 5, see SI for details).[14] The free energies were calculated for the reaction in dioxane at 70 °C (the conditions in Table 2). The results suggested that the reaction proceeds preferentially via Path b (Figure 4, black line) involving reductive elimination of H_2, and an alternative mechanism following Path a (Figure 4, red line) via the σ-CAM is energetically disfavored. Oxidative addition of **1a** to $HRh(PPh_3)_2$ is highly exergonic (ΔG = –21.6 kcal/mol) and gives intermediate **A**. In Path a, one of the two hydrogen atoms moves from the equatorial position to the axial position to form **A’**, which is ready for σ-CAM through $TS_{A'B}$ ($TS_{A'B}$ = 20.1 kcal/mol) leading to **B**.[23] In Path b, which does not involve hydrogen acceptors, elimination of H_2 from **A** leads to silylrhodium intermediate **C**, in which an ortho C–H bond of a benzene ring of **1a** weakly coordinates to the rhodium center in an η^2-fashion (Rh–C: 2.83 Å, Rh–H: 2.51 Å). The transition state for the reductive elimination of H_2 could not be located. The energy monotonously increased as the distance between the two hydrogen atoms decreased, which indicates that the reverse reaction, the rebound of H_2 and subsequent oxidative addition, is virtually barrierless and proceeds rapidly once the intramolecular η^2-coordination is removed. Oxidative addition of the aryl C–H bond (**C** to **D**) followed by C–Si bond-forming reductive elimination (**D** to **E**) occurs smoothly with a barrier of 11.2 and 13.5 kcal/mol, respectively. The benzene ring of **E** coordinates to the rhodium center in an η^2-fashion (Rh–C^{α}: 2.46 Å, Rh–C^{β}: 2.36 Å).[24] Finally, product dissociation from **E** regenerates the active rhodium species, completing the catalytic cycle.

Calculations for the reaction using 3,3-dimethyl-1-butene were performed next. The energy profile is outlined in Figure 4 with blue line. The system, in which 3,3-dimethyl-1-butene accepts H_2, gains a driving force as much as 22.2 kcal/mol greater than

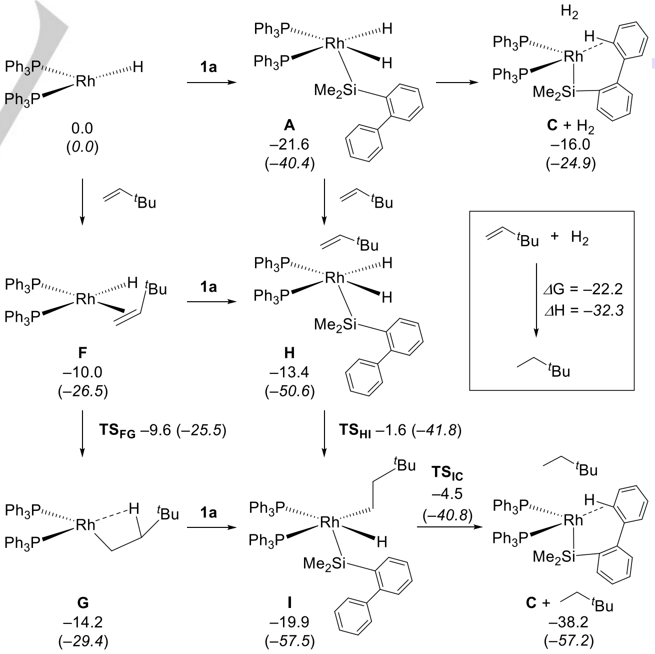


Figure 6. Possible reaction pathways from $HRh(PPh_3)_2$ to intermediate **C** in the presence of 3,3-dimethyl-1-butene. The relative Gibbs free energies and *enthalpies* calculated at the B3LYP-D3/SDD:6-31G(d) level of theory in dioxane at 70 °C are given in kcal/mol.

the acceptor-less system (–16.0 *vs* –38.2 kcal/mol for the energy of intermediate **C** in Figure 4), which suggests that the reaction is accelerated by 3,3-dimethyl-1-butene. Since 3,3-dimethyl-1-butene could not be located to $\mathbf{TS_{CD}}$ or **D**, probably because of strong σ-donation by a *trans*-silyl group, the reaction profile is essentially the same after formation of **C**. In contrast, coordination of 3,3-dimethyl-1-butene to **C** affords olefin adduct **K** (see Figure 7) by replacing the η^2-coordinated benzene ring, which inhibits C–H bond cleavage leading to 9-silafluorene **2a**, and causes the undesired side reaction, hydrosilylation of alkene to produce **5** (vide infra). Detailed reaction pathways for the formation of intermediate **C** starting from $HRh(PPh_3)_2$ are depicted in Figure 6. The most energetically favored pathway is $HRh(PPh_3)_2$ → **A** → **H** → **I** → **C**.[25] An alternative mechanism starting from insertion of 3,3-dimethyl-1-butene to the *Rh*–H bond followed by oxidative addition of **1a** leading to **I** may also be plausible.[26]

Intermediate **I** can potentially undergo two different reactions: dehydogenative silylation leading to 9-silafluorene **2** and hydrosilylation leading to **5**. Figure 7 shows possible reaction pathways for hydrosilylation of **1a** with 3,3-dimethyl-1-butene. Intermediate **I** may reductively eliminate **5** via $\mathbf{TS_{IJ}}$ (9.8 kcal/mol). However, C–H reductive elimination to produce 2,2-dimethylbutane and **C** occurs more easily via $\mathbf{TS_{IC}}$ (–4.5 kcal/mol), thus excluding the first mechanism. The following silylrhodation of olefin adduct **K** proceeds via $\mathbf{TS_{KL}}$ (–14.0 kcal/mol) to form alkylrhodium species **L**, which eventually affords **5** after reaction with another molecule of **1a**. $\mathbf{TS_{KL}}$ is 9.4 kcal/mol higher in energy than $\mathbf{TS_{DE}}$ (–23.4 kcal/mol, see Figure 4) leading to intermediate **E** at 70 °C. Calculations at 25 °C predicts a smaller energy difference between the transition state of the silylrhodation and that for the desired reaction ($\Delta\Delta G$ = 7.3 kcal/mol, $\mathbf{TS_{KL/25}}$: –19.1 kcal/mol, $\mathbf{TS_{DE/25}}$: –26.4 kcal/mol). These results explain the experimental observation demonstrated in Figure 2 that intramolecular dehydrogenative silylation occured preferentially over intermolecular alkene hydrosilylation at high temperatures, and are rationalized by considering the entropy effect. Intramolecular η^2-coordination of the benzene ring in **C** followed by the oxidative addition to C–H bond is preferred at high temperature over intermolecular coordination of another molecule of 3,3-dimethyl-1-butene leading to intermediate **K** with an entropic cost. Thus, the hydrogen acceptor functions as a thermodynamic promoter by making H_2 release irreversible and gaining driving force, but also acts as a kinetic inhibitor by forming an olefin adduct, such as **K**, and causing the undesired side reaction.

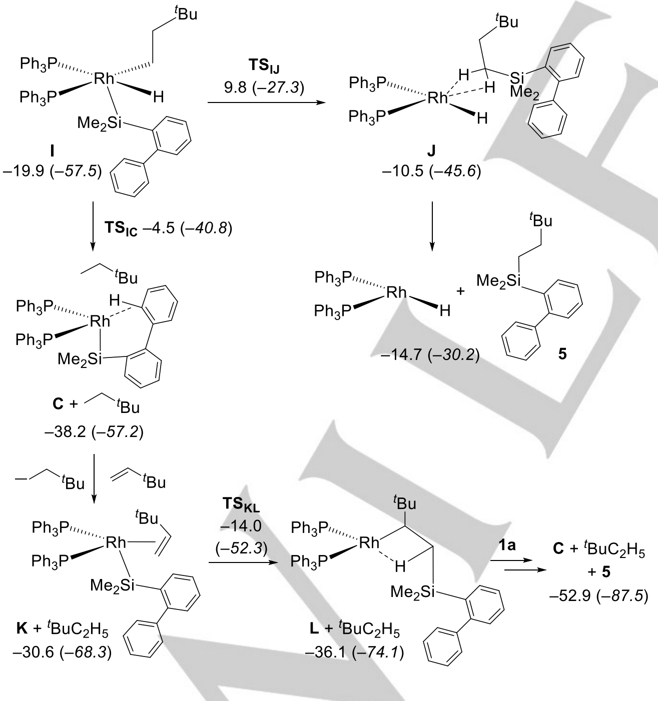


Figure 7. Possible reaction pathways for formation of hydrosilylation product **5**. The relative Gibbs free energies and *enthalpies* calculated at the B3LYP-D3/SDD:6-31G(d) level of theory in dioxane at 70 °C are given in kcal/mol.

Further insight was obtained by comparing the driving force of intramolecular dehydrogenative silylation with the intermolecular version, *i.e.*, reaction of $PhMe_2SiH$ with benzene (Figure 8).[13] The results clearly suggested that the intermolecular reaction is endergonic even at 70 °C (ΔG = +4.2 kcal/mol), and does not proceed efficiently without the assistance of a hydrogen acceptor, while the intramolecular reaction is exergonic (ΔG = –4.1 kcal/mol). Besides these thermodynamic considerations, the intramolecular coordination of a benzene ring to a rhodium center in intermediate **C** (Figure 4) is thought to be helpful for prohibiting the reverse reaction, oxidative addition of H_2, as well as facilitating C–H bond cleavage. These are the major advantages for the current rare example of oxidant-free C–H bond functionalization under neutral conditions.

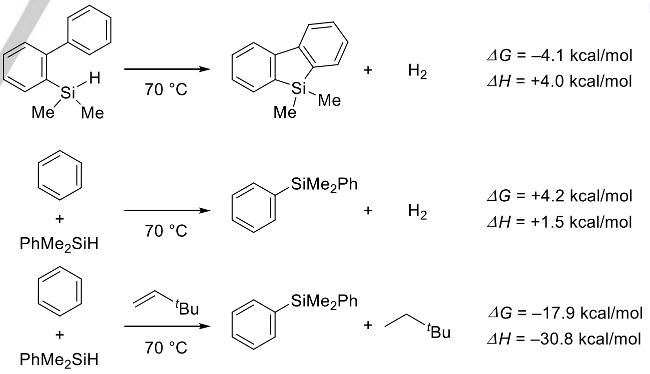


Figure 8. Comparison of Gibbs free energies and *enthalpies* of $C(sp^2)$–H bonds dehydrogenative silylation in dioxane at 70 °C.

Finally, the energy profile for iridium-catalyzed intramolecular dehydrogenative silylation was compared with that for the rhodium-catalyzed system (Figure 9). The Ir^{III} species $\mathbf{A_{Ir}}$ is thermodynamically stable compared with the other Ir^{I} species, much more than the corresponding Rh^{III} species are when compared with the Rh^{I} species (see Figure 4). Therefore, oxidative addition leading to Ir^{III} is energetically favored compared to the reductive elimination back to Ir^{I}. The energy difference between $\mathbf{A}_{\mathbf{Ir}}$ and $\mathbf{C}_{\mathbf{Ir}}$ in the absence of a hydrogen acceptor is greater than that of the rhodium-catalyzed system (14.0 *vs* 5.6 kcal/mol), and hence the reverse oxidative addition of intermediate $\mathbf{C}_{\mathbf{Ir}}$ to H_2 leading back to $\mathbf{A}_{\mathbf{Ir}}$ occurs more easily. These results provide a rationale for the experimental observations that most of the reported iridium-catalyzed dehydrogenative silylations require hydrogen acceptors.[11-13] Iridium catalysis with a hydrogen acceptor may be suitable for dehydrogenative silylation of C–H bonds, in which oxidative addition is included as a difficult step, but not effective for the current oxidant-free intramolecular system, as shown by Table 1, entry 3.

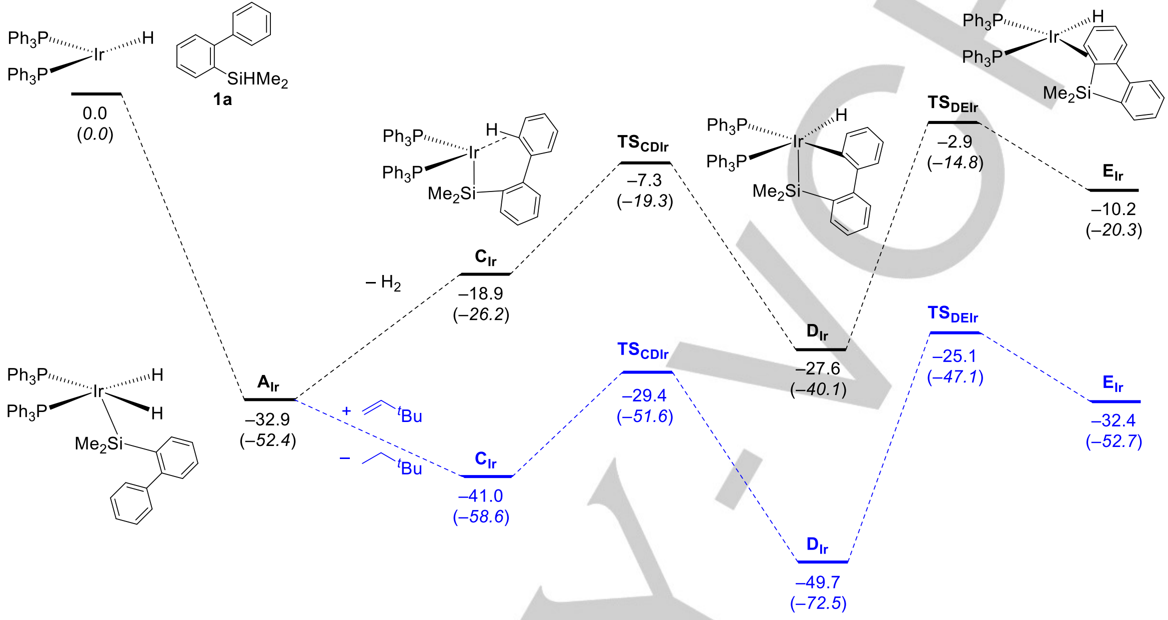


Figure 9. Energy profile for iridium-catalyzed intramolecular dehydrogenative silylation of **1a**. The relative Gibbs free energies and *enthalpies* calculated at the B3LYP-D3/SDD:6-31G(d) level of theory in dioxane at 70 °C are given in kcal/mol.

Conclusions

A rare example of *oxidant-free* dehydrogenative silylation and germylation of C(sp^2)–H bonds leading to 9-sila- and 9-germafluorenes was demonstrated. The combination of $[RhCl(cod)]_2$ with PPh_3 was effective as a catalyst, enabling the reaction to proceed at temperatures lower than those reported previously.[8] Competitive reactions in the presence of 3,3-dimethyl-1-butene revealed that the ratio of dehydrogenative metalation and hydrometalation was affected by reaction temperature and the hydrosilane or hydrogermane precursors used. The experimentally observed unique reactivity was supported by results of theoretical calculations, and a plausible reaction mechanism, including insights into why the current rhodium-catalyzed dehydrogenative silylation and germylation did not require hydrogen acceptors was proposed. In addition to a thermodynamic preference for the dehydrogenative cyclization (ΔG = –4.1 kcal/mol) and the relatively easy elimination of H_2 from Rh^{III} species (ΔG_{AC} = 5.6 kcal/mol), intramolecular coordination of a benzene ring to a rhodium center appeared to kinetically promote oxidative cleavage of a C–H bond and block oxidative addition of the released H_2. This work provides fundamental understanding of the oxidant-free catalytic functionalization of C–H bonds with dehydrogenation.[27] Further study of the design of substrates as well as ligands to determine the novel type of dehydrogenative metalation of C–H bonds is underway.

Experimental Section

General Methods. All reactions were carried out in dry solvent under an argon atmosphere. 1,4-Dioxane was purchased from Wako Pure Chemical Industries, distilled from benzophenone / Na ketyl solution, and degassed with an argon gas for 20 min before use. $[RhCl(cod)]_2$ was purchased from Kanto Chemical Co. PPh_3 was purchased from Wako Pure Chemical Industries and recrystallized before use. Unless otherwise noted, other chemicals obtained from commercial suppliers were used without further purification. 2-Bromobiaryls were prepared by Suzuki-Miyaura cross-coupling reaction between aryl iodides (or aryl bromides) and aryl boronic acids.[28] ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL ECS-400 spectrometer. Proton chemical shifts are reported in ppm based on the solvent resonance resulting from incomplete deuteration ($CDCl_3$ at 7.26 ppm) as the internal standard. ^{13}C NMR was recorded with complete proton decoupling and the chemical shifts are reported relative to $CDCl_3$ at 77.00 ppm. The following abbreviations are used; br s: broad singlet, s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. IR spectra were recorded on a SHIMADZU IRAFFINITY-1 100V J. High-resolution mass spectra (HRMS) were measured with JEOL JMS-700 MStation FAB-MS. Melting points (mp) were measured with Yanako MP-J3 and uncorrected.

Preparation of 2-(dimethylgermyl)-2’-methylbiphenyl (3h). ^nBuLi (1.6 M in hexane, 2.8 mL, 4.5 mmol) was added to a solution of 2-bromo-2’-methylbiphenyl (741 mg, 3.0 mmol) in Et_2O (10 mL) at -78 °C, and the mixture was stirred for 30 min. A solution of dimethyldichlorogermane (775 mg, 4.5 mmol) in Et_2O (2.0 mL) was added dropwise, and the resulting mixture was gradually warmed to 25 °C. After stirring for 12 h, a suspension of $LiAlH_4$ (0.23 g, 6.0 mmol) in Et_2O (5.0 mL) was added at 0 °C, and the mixture was further stirred at 25 °C for 14 h. The reaction mixture was quenched with H_2O (0.2 mL), aqueous NaOH (15 wt%, 0.2 mL), and H_2O (0.6 mL). The mixture was filtered through a Celite pad, and the solvent was removed under the reduced pressure. The residue was purified by flash column chromatography on silica gel with *n*-hexane and ethyl acetate (*v* / *v* = 50 / 1) as eluent to give 2-(dimethylgermyl)-2'-methylbiphenyl (**3h**) (700 mg, 2.4 mmol, 80% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.11 (d, *J* = 3.6 Hz, 3H), 0.16 (d, *J* = 3.6 Hz, 3H), 2.07 (s, 3H), 4.14 (sept, *J* = 3.6 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 1H), 7.15-7.41 (m, 4H), 7.33 (dt, *J* = 2.0, 7.2 Hz, 1H), 7.38 (dt, *J* = 2.0, 7.2 Hz, 1H), 7.59 (dd, *J* = 1.6, 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ-3.73, -3.59, 20.3, 125.1, 126.4, 127.4, 128.3, 129.1, 129.7, 129.9, 134.3, 136.0, 138.5, 142.8, 147.9. IR (neat / cm^{-1}): 3055, 3017, 2976, 2914, 2029, 1464, 1423, 1246, 1117, 835, 756, 729. HRMS (FAB$^+$): calcd for $C_{14}H_{15}ClGe$ ([M]$^+$) 292.0620; found 292.0608.

General procedure for rhodium-catalyzed dehydrogenative silylation leading to 9-silafluorenes (Table 2). A flame dried 7.0 mL of sealed tube was charged with $[RhCl(cod)]_2$ (1.5 mg, 3.0 μmol), PPh_3 (4.7 mg, 18 μmol), 1,4-dioxane (0.20 mL), and stirred at 25 °C for 15 mins. 2-(Dimethylsilyl)biaryls **1** (0.20 mmol) was added, and the resulting mixture was stirred at 70 °C for 8 h. The solvent was removed under the reduced pressure, and the residue was subjected to flash column chromatography on silica gel with *n*-hexane as eluent to give the corresponding 9-silafluorenes **2**.

General procedure for rhodium-catalyzed dehydrogenative germylation leading to 9-germafluorenes (Table 3). A flame dried 7.0 mL of sealed tube was charged with $[RhCl(cod)]_2$ (1.5 mg, 3.0 μmol), PPh_3 (4.7 mg, 18 μmol), 1,4-dioxane (0.20 mL), and stirred at 25 °C for 15 mins. 2-(Dimethylgermyl)biaryls **3** (0.20 mmol) and 3,3-dimethyl-1-butene (50 mg 0.60 mmol) was added, and the resulting mixture was stirred at 60 °C for 12 h. The solvent was removed under the reduced pressure, and the residue was subjected to flash column chromatography on silica gel with *n*-hexane as eluent to give the corresponding 9-germafluorenes **4**.

9,9-Dimethyl-4-methyl-9-germafluorene (4h) and 9,9-dimethyl-9,10-dihydro-9-germaphenanthrene (8). These compounds were obtained as a mixture of inseparable constitutional isomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.35 (s, 6H for **8**), 0.58 (s, 6H for **4h**), 2.29 (s, 2H for **8**), 2.78 (s, 3H for **4h**), 7.17-7.24 (m, 4H), 7.26-7.32 (m, 3H), 7.38-7.49 (m, 2H), 7.50-7.54 (m, 3H), 7.62-7.69 (m, 2H), 8.12 (d, J = 8.1 Hz, 1H for **4h**). ^{13}C NMR (100 MHz, $CDCl_3$): δ-4.9, -2.7, 20.9, 24.7, 126.1, 126.3, 126.6, 126.7, 126.9, 127.3, 128.1, 128.8, 129.0, 129.1, 129.6, 130.4, 130.7, 132.3, 132.6, 132.8, 133.7, 134.7, 136.9, 137.6, 138.2, 142.8, 144.2, 148.1. IR (neat / cm^{-1}): 3051, 3022, 2970, 2907, 1584, 1466, 1443, 1234, 1123, 1086, 827, 808, 785, 731, 608. HRMS (FAB$^+$): calcd for $C_{15}H_{16}Ge$ ([M]$^+$) 270.0464; found 270.0461.

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Keywords: Rhodium • Dehydrogenation • C–H Bond Activation • Silylation • Germylation

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[21] HRh(PR$_3$)$_n$ species, generated via oxidative addition of ClRh(PR$_3$)$_n$ to R'$_3$SiH followed by reductive elimination of R'$_3$SiCl is reported to be active species of dehydrogenative silylation. See ref 13b. This species is also proposed as active catalytic species in the hydrosilylation of alkynes. See: a) Y. Nishihara, M. Takemura, K. Osakada, *Organometallics* **2002**, *21*, 825. b) M. A. Esteruelas, M. Oliván, A. Vélez, *Inorg. Chem.* **2013**, *52*, 12108. The active species was proposed to be HRh(PPh$_3$)$_2$ in the current study based on these reports, although the corresponding studies for reaction with hydrogermanes have not been reported.

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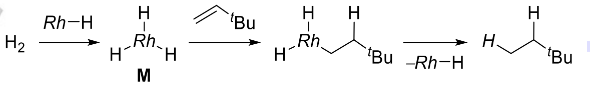
[24] Reversibility of C–Si bond forming reductive elimination and oxidative cleavage of C–Si bonds was proposed in our previous report on the enantioselective dehydrogenative silylation leading to spiro-9-silafluorenes. See ref 9f. η^2-Coordination of the rhodium center to the C–Si σ-bond was a key in this report, and the interconversion of two hydrosilanes with retention of stereochemistry was observed.

[25] Because silylrhodation of **H** to 3,3-dimethyl-1-butene would provide energetically less stable intermediates, hydrorhodation shown in Figure 6 is more plausible. The similar reactivity of H–Rh–*Si* species toward cyclohexene was reported previously in ref 13b.

[26] Hydrogen acceptance via insertion of rhodium trihydride **M** to 3,3-dimethyl-1-butene followed by reductive elimination can be ruled out as an alternative reaction mechanism due to the higher energy of the rhodium trihydride (–7.7 kcal/mol) than silylrhodium complex **A** (–21.6 kcal/mol).



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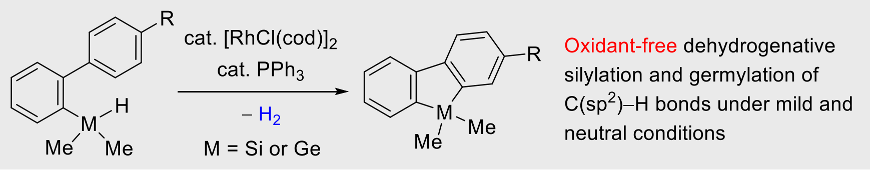

Masahito Murai, Ryo Okada, Sobi Asako, Kazuhiko Takai**

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Rhodium-Catalyzed Silylative and Germylative Cyclization with Dehydrogenation Leading to 9-Sila- and 9-Germafluorenes: Experimental and Computational Mechanistic Study

The combination of $[RhCl(cod)]_2$ and PPh_3 catalyzes the oxidant-free dehydrogenative silylation and germylation of unactivated $C(sp^2)$–H bonds under neutral conditions. The experimentally obtained unique reactivity is supported by the results of theoretical calculations, and a plausible reaction mechanism including insights into why the current transformation does not require hydrogen acceptors and heteroatom-containing directing groups is proposed.