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Rhodium-Catalyzed Dehydrogenative Germylation of C−H Bonds: New Entry to Unsymmetrically Functionalized 9-Germafluorenes

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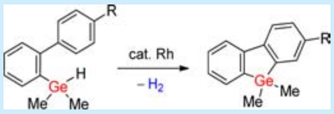
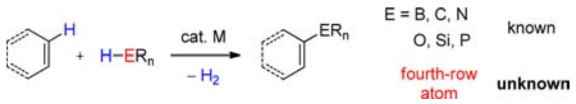
Supporting Information

ABSTRACT: Rhodium-catalyzed dehydrogenative germylation leading to unsymmetrically functionalized 9-germafluorenes via Ge−H and C−H bond activation is described. Despite the significant achievements made in dehydrogenative functionalization of C−H bonds, only a limited number of examples with the fourth-row atom−H bonds have been reported. The current method enabled the synthesis of various 9-germafluorene derivatives, including tetracyclic as well as donor−acceptor substituted germoles, which may be useful for electronic device applications.



Catalytic dehydrogenative functionalization of C−H or heteroatom−H bonds with unactivated C−H bonds is of interest because of its ability to introduce groups with broad synthetic potential for the construction of complicated molecules without preactivation of starting compounds.[1] Dehydrogenative functionalization involving borylation (B−H), arylation (C−H), carbonylation (C−H), amination (N−H), hydroxylation (O−H), silylation (Si−H), and phosphination (P−H) has been developed using transition metal complexes as catalysts (Scheme 1).[2] In contrast to the well-studied bonding reactions between second- or third-row atoms and hydrogens, much less attention has been paid to *the dehydrogenative functionalization of C−H bonds involving bonds between the fourth-row atom and hydrogens*.[3] The present study focused on germanium as a fourth-row atom and demonstrated the transition-metal-catalyzed synthesis of 9-germafluorenes via dehydrogenative germylation (Ge−H) of the unactivated C−H bonds. Although formal dehydrogenative germylation of styrene derivatives via regioselective hydrogermylation followed by β-elimination has been reported by Murai and co-workers using $Ru_3(CO)_{12}$ as a catalyst,[3] the present work describes the direct dehydrogenative germylation of unreactive aromatic C−H bonds. Interestingly, the reaction proceeded *without the addition of external or internal oxidants*,[4] which is usually required in catalytic dehydrogenative functionalization to induce catalytic turnover.

Scheme 1. Challenge in the Catalytic Dehydrogenative Functionalization



Heterocycles are important because of their unique photophysical and electronic properties. A recent report described the rhodium-catalyzed dehydrogenative silylation of unactivated $C(sp^2)$−H bonds leading to 9-silafluorenes.[5,6] The results suggested that similar dehydrogenative functionalization of other group 14 atom-containing substrates would allow new syntheses of the corresponding 9-heterofluorenes. Germole-based π-electron systems, especially in 9-germafluorenes, have received attention as key components for new organic functional materials, including solar cells, thin-film transistors, and host materials for electroluminescent devices, due to their unique photophysical as well as electronic properties.[7] It has been reported that incorporation of a germanium atom stabilizes the LUMO through interaction of the low lying π^* orbital of the germanium with the π^* orbital of the conjugated π-system, and also enhances the solid-state ordering compared to the carbon- and silicon-fused analogues, leading to improved charge transport.[8] Therefore, development of new methods for the facile synthesis and easy modification of their π-frameworks is highly desirable. Conventional syntheses of 9-germafluorenes often require stoichiometric organolithium or magnesium reagents, which limits the choice of functional groups on the substrates.[7] A transition-metal-catalyzed synthesis has been reported based on the cross-coupling reaction of hydrogermane with haloaromatics,[9a] and a reaction via cleavage of the germanium−carbon bonds.[9b] However, limitations in substrate scope remain for these reactions.

Treatment of dimethyl((2-phenyl)phenyl)germane (**1a**) with a catalytic amount of Wilkinson catalyst, $RhCl(PPh_3)_3$, which was the most effective catalyst for the synthesis of 9-silafluorenes via the dehydrogenative silylation of $C(sp^2)$−H bonds,[5a] in dioxane at 110 °C gave the 9-germafluorene **2a** in 71% yield (Table 1, entry 1). The biphenyl **3** was obtained as a byproduct in 18% yield under these reaction conditions. In contrast, similar cleavage of the Si−C bond was not observed

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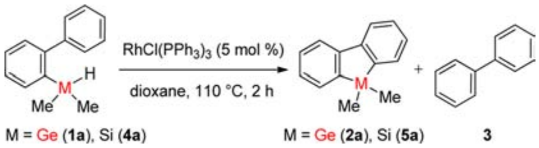
Table 1. Catalytic Dehydrogenative Cyclization Leading to 9-Germafluorene 2a and 9-Silafluorene 5a



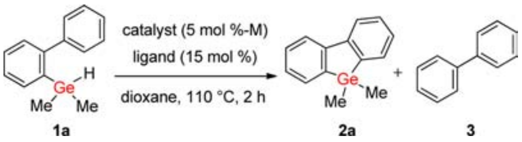
entry	M	results[a]
1	Ge (**1a**)	71% (**2a**), 18% (**3**), 10% (**1a**)
2	Si (**4a**)	97% (**5a**), 0% (**3**)

[a] Determined by ^{1}H NMR.

when the corresponding biarylhydrosilane **4a** was employed as a precursor instead of **1a** (entry 2). In this case, 9-silafluorene **5a** was obtained in 97% yield without producing any byproducts. The Ge−C bond is inherently weaker than the Si−C bond based on bonding energy (Ge−C 246.87 vs Si−C 292.88 kcal/mol). Thus, the Ge−C bond in **1a** is cleaved more easily than the Si−C to form **3**.

These successful results prompted an examination of the catalytic activity of various transition-metal complexes for the synthesis of 9-germafluorene **2a** (Table 2). Among the catalysts screened, the combination of [RhCl(cod)]$_2$ with 3 equiv of PPh$_3$ was the most effective to furnish **2a** in 93% yield (entry 1).[10] Under the reaction conditions, the formation of biphenyl **3** was limited to 6% yield. Although other rhodium and iridium catalysts including [Rh(OMe)(cod)]$_2$, [IrCl(cod)]$_2$, and [Ir(OMe)(cod)]$_2$ exhibited marginal catalytic activity (entries 2 and 3), [Rh(OAc)$_2$]$_2$, Re$_2$(CO)$_{10}$, Ru$_3$(CO)$_{12}$,[3] and Ir$_4$(CO)$_{12}$ were almost ineffective, with the recovery of **1a** in >95% yield. Examination of the solvents revealed that the best yield was obtained in dioxane.[11] Next, the effect of ligands using [RhCl(cod)]$_2$ and dioxane as the metal complex and solvent, respectively, were investigated. Triarylphosphines with electron-donating and -withdrawing substituents displayed good activity to afford 9-germafluorene **2a** in 63% and 74% yield, respectively (entries 4 and 5). When PCy$_3$ was used as a ligand, selective formation of **2a** was observed albeit in low yield without cleavage of the Ge−C bond leading to biphenyl **3** (entry 6). Several ligands promoted the reaction, but none were superior to PPh$_3$ (entry 7). Using the combination of [RhCl(cod)]$_2$ with PPh$_3$, **2a** was isolated in 92% yield, even when the reaction temperature was lowered to 80 °C (entry 8). Note that the reaction proceeded efficiently even in the absence of hydrogen acceptors and oxidants, which are usually needed for catalytic dehydrogenative functionalizations.[1]

Table 2. Optimization of Reaction Conditions

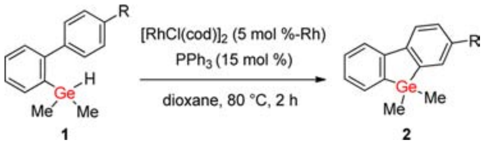


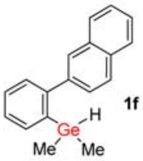
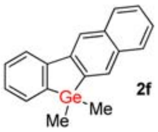
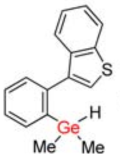
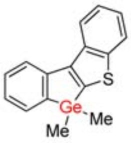
		yield[a]/%		
entry	catalyst/ligand	**2a**	**3**	recovery of **1a**[b]/%
1	[RhCl(cod)]$_2$/PPh$_3$	93	6	0
2	[Rh(OMe)(cod)]$_2$/PPh$_3$	51	12	6
3	[Ir(OMe)(cod)]$_2$/PPh$_3$	15	15	57
4	[RhCl(cod)]$_2$/P(4-MeOC$_6$H$_4$)$_3$	63	6	0
5	[RhCl(cod)]$_2$/P(4-CF$_3$C$_6$H$_4$)$_3$	74	12	0
6	[RhCl(cod)]$_2$/PCy$_3$	21	0	73
7	[RhCl(cod)]$_2$/P(C$_6$F$_5$)$_3$	9	30	46
8[b]	[RhCl(cod)]$_2$/PPh$_3$	97 (92)	2 (2)	0

[a] Determined by ^{1}H NMR. The value in parentheses is isolated yield. [b] At 80 °C for 2 h.

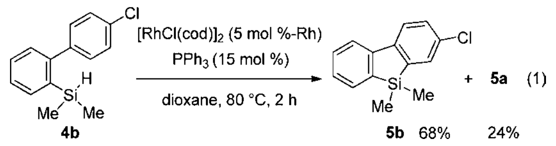
With optimized reaction conditions established, the scope of substrates for the dehydrogenative germylation of the C(sp^2)−H bond leading to unsymmetrical 9-germafluorenes was examined (Table 3). The reaction of biarylgermanes with an electron-withdrawing trifluoromethyl group and electron-neutral methyl group gave the corresponding 9-germafluorenes **2b** and **2c** in 88% and 85% yields, respectively (entries 1 and 2).[12] Even hydrogermane containing an electron-donating methoxy group was a good substrate for the current dehydrogenative cyclization and afforded the 2-methoxy-9-germafluorene **2d** in 92% yield (entry 3). It is noteworthy that reaction with the corresponding hydrosilane containing a methoxy group was sluggish, and addition of 3,3-dimethyl-1-butene as a hydrogen acceptor was required to obtain 2-methoxy-9-silafluorene in good yield, as described in a previous report.[5a] A chlorine group, which can be used subsequently in various cross-coupling reactions, was also tolerated to afford **2e** in 90% yield, which indicates the potential utility of the present reaction in various functional material syntheses (entry 4). In contrast, reductive dechlorination occurred to afford 9-silafluorene **5a** as a byproduct when the corresponding biarylsilane **4b** was employed as a precursor under the current reaction conditions (eq 1).[5a] In all cases, cleavage of the Ge−C bonds to afford the corresponding biaryl did not occur under the optimized reaction conditions. The current method can be also applied to the construction of a germylene-bridged

Table 3. Rh-Catalyzed Germylative Cyclization Leading to Germole-Fused Tri- and Tetracycles 2



entry	R		product	yield[a] / %
1	CF$_3$	**1b**	**2b**	88 (92)
2	Me	**1c**	**2c**	85 (93)
3	MeO	**1d**	**2d**	92 (94)
4	Cl	**1e**	**2e**	90 (94)
5		**1f**	 **2f**	80 (81)
6[b]		**1g**	 **2g**	80 (85)
7		**1g**	**2g**	17 (18)

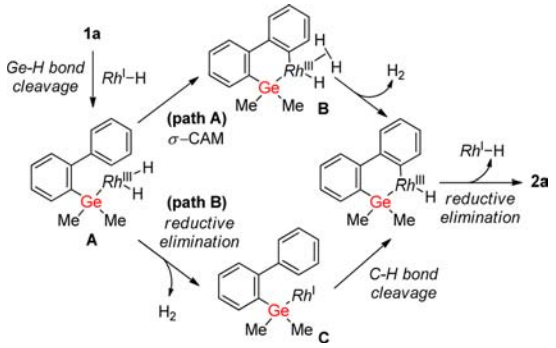
[a] Isolated yields. Yields determined by ^{1}H NMR are in parentheses. [b] 3,3-Dimethyl-1-butene (5 equiv) was added.



expanded π-conjugated system.[13] 2-(2′-Naphthyl)phenylgermane **1f** containing naphthyl groups cyclized smoothly to furnish benzo[*b*]germafluorene **2f** in 80% yield (entry 5). The reaction occurred selectively at the β-position of the naphthalene ring without producing its regioisomer, benzo[*a*]germafluorene. Diarylgermane **1g** containing a benzothienyl group also underwent dehydrogenative germylation, affording the benzothiophene-fused tetracyclic germole **2g**[14] in 80% yield in the presence of 3,3-dimethyl-1-butene (entry 6). Due to the competitive decomposition of hydrogermane **1g**, the yield decreased to 17% without the addition of 3,3-dimethyl-1-butene (entry 7). Therefore, 3,3-dimethyl-1-butene may be useful not as a hydrogen acceptor, but as the ligand coordinated to the rhodium center to control its reactivity.[15]

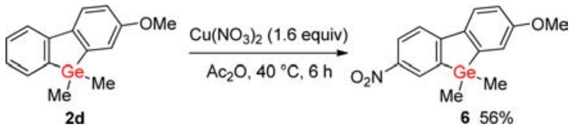
Based on these results, a plausible mechanism for the formation of 9-germafluorene **2a** is illustrated in Scheme 2 (phosphine ligands are omitted for clarity). The reaction was initiated by the oxidative addition of hydrogermane **1a** to a Rh^{I}–H species to generate germylrhodium complex **A**.[16] Intermediate **A** then reacted through two possible pathways (path A or B). In path A, C(sp^2)–H bond activation via σ-complex-assisted metathesis (σ-CAM)[17] forms six-membered rhodacycle intermediate **B**. Subsequent elimination of hydrogen followed by the reductive elimination furnishes 9-germafluorene **2a** along with the regeneration of the Rh^{I}–H species. In path B, reductive elimination followed by oxidative addition of the Rh^{I} center in **C** to an aryl C–H bond generates a Rh^{III}–H intermediate, which then undergoes reductive elimination to give **2a**. Although C–H bond activation without participation of a heteroatom containing directing group under neutral conditions is rare,[18] the position of the Ge–Rh moiety in intermediate **A** or **C**, which is near the aryl C–H bond, is thought to be very important for the promotion of this energetically unfavored step.

Scheme 2. Proposed Reaction Mechanism



Although 9-germafluorenes with expanded π-conjugation are candidates as new components of light-emitting materials and solar cells,[7,13] reports on the synthesis of unsymmetrical 9-germafluorenes are limited. The current reaction can provide such a rare example of unsymmetrical 9-germafluorenes. In addition, further transformations of the resulting 2-methoxy-9-germafluorene (**2d**) were done to examine its synthetic utility (Scheme 3). For example, nitration of **2d** with Cu(NO$_3$)$_2$ occurred smoothly to afford donor–acceptor substituted 9-germafluorene **6** in 56% yield with the germylene moiety intact.[19,20] Reaction occurred mainly at the 7-position, indicating that nucleophilic substitution of germoles occurs preferentially at this position.

Scheme 3. Synthetic Application to Donor–Acceptor Substituted 9-Germafluorene 6



Preliminary studies to determine the photophysical properties of unsymmetrical 9-germafluorenes as new molecular material candidates have been done (Figure 1).[21] The electron-donating methoxy group of **2d** at the 2-position of the 9-germafluorene ring caused a bathochromic shift in the absorption maximum by 11 nm (**2a** vs **2d**), indicating pronounced π-conjugation. A set of well-resolved absorption bands extending to 300 nm for the naphthalene-fused germole **2f** reflects its rigid structure and expanded π-conjugation. The red-shifted absorption band of donor–acceptor substituted 9-germafluorene **6**, in which the absorption tail extended to 443 nm, was also significant. The high intensity of the solar irradiation spectrum around this range indicates potential application of this compound as a component for solar cells. Furthermore, tetracycle **2f** and donor–acceptor substituted **6** exhibited fluorescence, in contrast with the absence of fluorescence for 9-germafluorene **2a**.

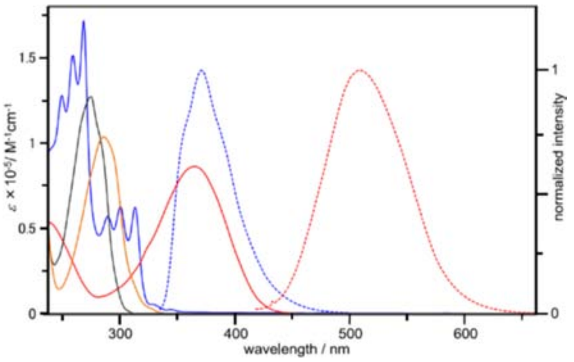


Figure 1. UV–vis (solid line) and fluorescence (dashed line) spectra of unsymmetrically fuctionalized germafluorene derivatives **2a** (black), **2d** (yellow), **2f** (blue), and **6** (red) in CH$_2$Cl$_2$ (8×10^{-6}) at 25 °C.

In conclusion, the rhodium-catalyzed dehydrogenative germylation of readily available ((2-aryl)phenyl)germanes has been shown to be a versatile synthetic route toward germylene-bridged π-conjugated systems via the activation of Ge–H and C–H bonds. This reaction is more efficient than the conventional methods for synthesizing 9-germafluorenes, because the only byproduct produced is hydrogen. Interestingly, addition of an external or internal oxidant, which is usually required for dehydrogenative functionalization, is not necessary for most of the transformations. The resulting 9-germafluorenes can be used as building blocks for the synthesis of novel unsymmetrically functionalized 9-germafluorenes.[20] Further investigations into the scope and reaction mechanisms, as well as synthetic applications, are currently in progress.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, spectroscopic data for all new compounds, and copies of ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) Investigation of the ratio of $[RhCl(cod)]_2/PPh_3$ at 110 °C: 43% (Rh/P = 1/1), 80% (Rh/P = 1/2), 93% (Rh/P = 1/3), 88% (Rh/P = 1/4).

(11) Investigation of solvents with the catalyst system of $[RhCl(cod)]_2/PPh_3$ at 110 °C: toluene 86%, $ClCH_2CH_2Cl$ 79%, MeCN 88%, DMF 28%.

(12) The reaction of a regioisomer of **1c**, 2-(dimethylgermyl)-2′-methylbiphenyl, has also been tested to afford the corresponding 9,9-dimethyl-4-methyl-9-germafluorene in 14% yield.

(13) Reports on the synthesis of π-expanded 9-germafluorenes are limited. For spirogermabifluorenes, see: (a) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 1883. (b) Russell, A. G.; Spencer, N. S.; Philp, D.; Kariuki, B. M.; Snaith, J. S. *Organometallics* **2003**, *22*, 5589. For a germa[5]helicene, see: (c) Yasuike, S.; Iida, T.; Okajima, S.; Yamaguchi, K.; Seki, H.; Kurita, J. *Tetrahedron* **2001**, *57*, 10047. For a trigermasumanene, see: (d) Tanikawa, T.; Saito, M.; Guo, J. D.; Nagase, S.; Minoura, M. *Eur. J. Org. Chem.* **2012**, 7135.

(14) Thiophene-fused germole derivatives have been thoroughly investigated as key components for photovoltaic devices. For selected examples, see: (a) Ohshita, J.; Hwang, Y.-M.; Mizumo, T.; Yoshida, H.; Ooyama, Y.; Harima, Y.; Kunugi, Y. *Organometallics* **2011**, *30*, 3233. (b) Fei, Z.; Ashraf, R. S.; Huang, Z.; Smith, J.; Kline, R. J.; D'Angelo, P.; Anthopoulos, T. D.; Durrant, J. R.; McCulloch, I.; Heeney, M. *Chem. Commun.* **2012**, *48*, 2955.

(15) The use of other alkenes, such as cyclooctene, cyclohexene, norbornene, and styrene, was less effective to afford **2g** in less than 20% yield. For representative reviews on the effect of unsaturated hydrocarbons in the catalytic transformation, see: (a) Johnson, J. B.; Rovis, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 840. (b) Jarvis, A. G.; Fairlamb, I. J. S. *Curr. Org. Chem.* **2011**, *15*, 3175. The yield of **2f** was decreased to 66% when 3,3-dimethyl-1-butene was added to the reaction of **1f** (see Table 3, entry 5).

(16) The $H{-}Rh(PPh_3)_n$ species, generated *via* oxidative addition of $Cl{-}Rh(PPh_3)_n$ to $H{-}SiR_3$ followed by reductive elimination of $Cl{-}SiR_3$, is proposed as an active catalytic species in the hydrosilylation of alkynes. See: (a) Nishihara, Y.; Takemura, M.; Osakada, K. *Organometallics* **2002**, *21*, 825. (b) Esteruelas, M. A.; Oliván, M.; Vélez, A. *Inorg. Chem.* **2013**, *52*, 12108. The active species is proposed to be $H{-}Rh(PPh_3)_n$ in Scheme 2 based on these reports, although corresponding studies for reaction with hydrogermanes have not been reported.

(17) For a review on a σ-CAM, see: Perutz, R. N.; Sabo-Etienne, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 2578.

(18) For a review, see: Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236.

(19) Regioisomer of **6**, 2-methoxy-3-nitro-9-germafluorene was also obtained in 23% yield along with the recovery of **2d** in 6% yield. For the nitrations with $Cu(NO_3)_2$, see: (a) Shin, D.-Y.; Kim, S. N.; Chae, J.-H.; Hyun, S.-S.; Seo, S.-Y.; Lee, Y.-S.; Lee, K.-O.; Kim, S.-H.; Lee, Y.-S.; Jeong, J. M.; Choia, N.-S.; Suh, Y.-G. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 4519. (b) Wei, W.-G.; Zhang, Y.-X.; Yao, Z.-J. *Tetrahedron* **2005**, *61*, 11882.

(20) Fluorenes with donor and acceptor substituents at the 2- and 7-positions are useful candidates for nonlinear optical and two-photon absorption materials. See: (a) Kannan, R.; He, G. S.; Yuan, L.; Xu, F.; Prasad, P. N.; Dombroskie, A. G.; Reinhardt, B. A.; Baur, J. W.; Vaia, R. A.; Tan, L. S. *Chem. Mater.* **2001**, *13*, 1896. (b) Stegeman, G. I.; Stegeman, R. A. In *Nonlinear Optics: Phenomena, Materials, and Devices*; Boreman, G., Ed.; Wiley Series in Pure and Applied Optics; John Wiley & Sons: Hoboken, NJ, 2012.

(21) For **2a**: λ_{max} = 276 nm (ε = 1.27 × 10^5). For **2d**: λ_{max} = 287 nm (ε = 1.04 × 10^5). For **2f**: λ_{max} = 262 (ε = 1.51 × 10^5), 271 (ε = 1.71 × 10^5), 292 (ε = 0.57 × 10^5), 303 (ε = 0.62 × 10^5), 315 nm (ε = 0.62 × 10^5). For **6**: λ_{max} = 365 nm (ε = 0.86 × 10^5).