C–H Activation

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Synthesis of Fluorene Derivatives through Rhodium-Catalyzed Dehydrogenative Cyclization**

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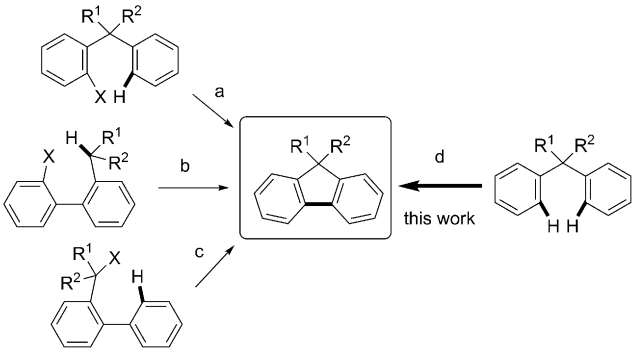
Polycyclic aromatic hydrocarbons (PAHs) have attracted considerable attention because of their optical and electronic properties, and their application as π-conjugated functional materials.[1] Fluorene is one of the simplest motifs in PAHs and its derivatives have been employed as important building blocks in a broad range of fields, including light-emitting devices, organic field-effect transistors (OFET), organic photovoltaic cells (OPV), biosensors, etc.[2] Fluorenyl functions have also played important roles in the field of organic synthesis, mainly as unique protecting groups in peptide synthesis.[3] In spite of the simple structures, their construction has been conducted under harsh reaction conditions or through complicated multistep procedures.[4]

Meanwhile, transition-metal-catalyzed organic reactions involving C–H bond cleavage have been significantly developed in recent years as atom- and step-economical tools in precise organic synthesis.[5] Such procedures can provide simple, functional-group-tolerable methods for fluorene synthesis. As shown in Scheme 1, several palladium-catalyzed cyclization reactions of halogenated aromatic substrates were recently reported (routes a–c).[6]

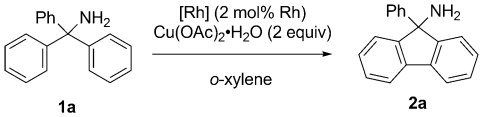
Although valuable, the development of a straightforward method involving the cleavage of two C–H bonds (route d, Scheme 1)[7–9] is strongly desired. Herein, we report such a dehydrogenative cyclization. Thus, in the course of our study of rhodium-catalyzed direct oxidative coupling,[10,11] we have found that 1-amino-1,1-diarylalkanes efficiently undergo cyclization to furnish 9*H*-fluoren-9-amine derivatives without any protection of the amine. Furthermore, related substrates such as 2,2-diphenylalkanoic acids can also be transformed into the corresponding fluorenes through dehydrogenative cyclization and subsequent decarboxylation.



Scheme 1. Synthesis of fluorenes through C–H bond cleavage. Precedents for a, b, and c. No precedent for d.

In an initial attempt, triphenylmethylamine (**1a**) was treated under the standard reaction conditions for our rhodium-catalyzed oxidative coupling. The reaction of **1a** in the presence of $[\{Cp^*RhCl_2\}_2]$ (2 mol% Rh) and $Cu(OAc)\cdot H_2O$ (2 equiv) as a catalyst and an oxidant, respectively, in *o*-xylene at 130 °C for 10 h gave the dehydrogenative cyclization product 9-phenyl-9*H*-fluoren-9-amine (**2a**) in 65% yield (Table 1, entry 1). Upon elevating the reaction temperature to 150 °C, the yield was improved up to 96% (entry 2). The reaction proceeded quantitatively in the presence of $[\{Cp^ERhCl_2\}_2]$ (Cp^E = 1,3-bis(ethoxycarbonyl)-2,4,5-trimethylcyclopentadienyl), which was recently employed for the oxidative coupling of acetanilides with alkynes[12] as a catalyst in place of $[\{Cp^*RhCl_2\}_2]$, even at 130 °C (entry 3). To our surprise, the reaction was effectively

Table 1: Reaction of triphenylmethylamine (**1a**).[a]



1a **2a**

Entry	[Rh]	*T* [°C]	*t* [h]	Yield [%][b]
1	$[\{Cp^*RhCl_2\}_2]$	130	10	65
2	$[\{Cp^*RhCl_2\}_2]$	150	6	96
3	$[\{Cp^ERhCl_2\}_2]$	130	6	>99
4	$[\{RhCl(cod)\}_2]$	130	2	>99 (98)
5	$RhCl_3\cdot 3H_2O$[c]	130	10	27
6	–	130	10	0
7	$[\{RhCl(cod)\}_2]$	100	10	88

[a] Reaction conditions: **1a** (0.5 mmol), [Rh] (0.005 mmol), $Cu(OAc)_2\cdot H_2O$ (1 mmol), *o*-xylene (3 mL) under N_2. [b] GC yield based on the amount of **1a** used. Value within parentheses indicates yield after purification. [c] $RhCl_3\cdot 3H_2O$ (0.01 mmol) was used.

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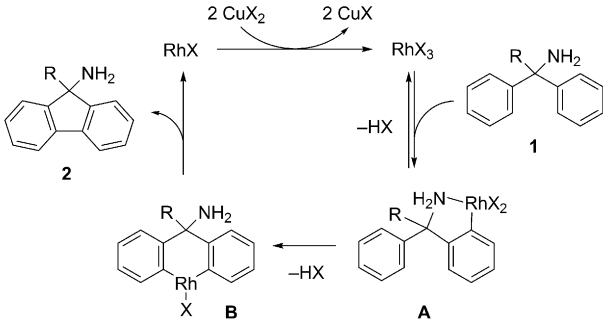
promoted by the use of [{RhCl(cod)}$_2$] as a catalyst precursor. Thus, in the absence of any Cp ligand, **2a** was obtained in a quantitative yield within 2 hours (entry 4).[13] Under similar reaction conditions, treatment of N-acetylated triphenylmethylamine gave no cyclization product. $RhCl_3 \cdot 3H_2O$ showed poor activity (entry 5). It was confirmed that the reaction did not proceed at all without any rhodium catalyst (entry 6). Under the reaction conditions using [{RhCl(cod)}$_2$], **2a** was formed in 88% yield even at 100°C (entry 7).

Under the optimized reaction conditions (Table 1, entry 4), various 1-amino-1,1-diphenylalkanes (**1b–e**) also underwent the cyclization to produce the corresponding 9-alkyl-9*H*-fluoren-9-amines **2b–e** in good to excellent yields (Table 2, entries 1–4). Note that a series of fluorenes bearing branched- and long-chain alkyl groups at their 9-position can be prepared through this reaction. 3,6-The disubstituted 9-methyl-9*H*-fluoren-9-amines **2f** and **2g** were smoothly synthesized from the 1-amino-1,1-diarylethanes **1f** and **1g**, respectively (entries 5 and 6). The reaction of tris(4-methylphenyl)methylamine (**1h**) also gave a cyclized product **2h** in 95% yield (entry 7). Expectedly, the reaction of an unsymmetrically substituted substrate, (4-chlorophenyl)bis(4-methoxyphenyl)methylamine, gave a mixture of two cyclization products. It was found that the present procedure is applicable to constructing a pentacyclic system. Thus, 12-methyl-12*H*-dibenzo[*b*,*h*]fluoren-12-amine (**2i**) was obtained predominantly upon treatment of 1-amino-1,1-di(2-naphthyl)ethane (**1i**), along with a minor amount of an unidentified isomer (entry 8).

A plausible mechanism for the reaction of **1** is illustrated in Scheme 2, in which neutral ligands are omitted. In either the case of using Rh^I or Rh^{III} precursors, an RhX_3 active species seems to be formed under oxidative conditions. Coordination of the amino nitrogen of **1** to the rhodium center and amino-directed C–H rhodation takes place to give the five-membered rhodacycle intermediate **A**. Subsequently, the second cyclorhodation to form the six-membered species **B** and reductive elimination may occur to produce **2**.



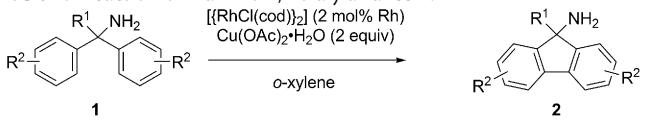
Scheme 2. Plausible mechanism for the reaction of **1**.

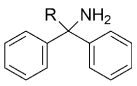
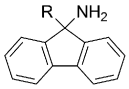
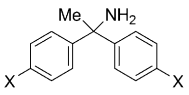
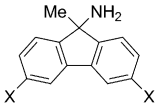
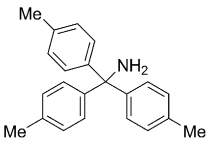
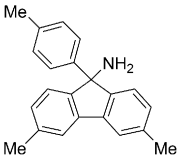
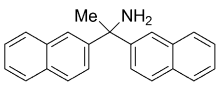
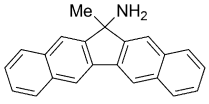
Notably, in the early stages of the reaction of an isotope-labeled substrate, 1-amino-1,1-bis(d_5-phenyl)ethane ([D_{10}]-**1b**), considerable contamination by protons at the *ortho* positions of recovered [D_n]-**1b** and at the 1- and/or 8-positions of produced fluorene [D_n]-**2b** took place (see the Supporting Information). This result indicates that at least the first cyclorhodation step to form **A** seems to be reversible.

Besides the amino group, a carboxylic function was also found to act as a good directing group to trigger the cyclization.[14] Although treatment of 2,2-diphenylpropionic acid (**3a**) under the optimized reaction conditions for the reaction of amine **1** did not give any cyclized product (Table 3, entry 1), the corresponding fluorene product could be obtained under modified reaction conditions. Thus, in the presence of [{Cp*$RhCl_2$}$_2$] (4 mol% Rh) and K_2CO_3 (1 equiv) in diglyme, **3a** underwent dehydrogenative cyclization/decarboxylation to afford 9-methyl-9*H*-fluorene (**4a**) in 27% yield (entry 3). Addition of $AgSbF_6$ (8 mol%) improved the **3a** yield, in spite of retarding the reaction (entry 4). In this reaction, [{$Cp^E RhCl_2$}$_2$] was found to be the catalyst precursor of choice. Especially, with further addition of 2,6-$Me_2C_6H_3CO_2H$ (0.5 equiv) **4a** was obtained in 73% yield (entry 6).

Even under milder reaction conditions (100°C), 2,2-diphenylacetic acid (**3b**) underwent the reaction smoothly to produce 9-unsubstituted 9*H*-fluorene (**4b**) in 56% yield

Table 2: Reaction of 1-amino-1,1-diarylalkanes **1**.[a]



Entry	**1**	*T* [°C]	*t* [h]	Product	Yield [%][b]
					
1	**1b**: R = Me	130	4	**2b**: R = Me	98
2	**1c**: R = *n*Pr	130	2	**2c**: R = *n*Pr	96
3	**1d**: R = *i*Pr	130	4	**2d**: R = *i*Pr	78
4	**1e**: R = *n*-C_9H_{19}	130	2	**2e**: R = *n*-C_9H_{19}	87
					
5	**1f**: X = OMe	130	4	**2f**: X = OMe	76
6[c]	**1g**: X = Cl	150	2	**2g**: X = Cl	87
					
7	**1h**	130	2	**2h**	95
					
8[c]	**1i**	130	2	**2i**	73[d]

[a] Reaction conditions: **1** (0.5 mmol), [{RhCl(cod)}$_2$] (0.005 mmol), $Cu(OAc)_2 \cdot H_2O$ (1 mmol), *o*-xylene (3 mL) under N_2. [b] Yield of isolated product based on the amount of **1** used. [c] The reaction was conducted on half the scale: **1** (0.25 mmol), [{RhCl(cod)}$_2$] (0.0025 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.5 mmol) in *o*-xylene (2 mL). [d] Contaminated with an isomer (**2i**/isomer = 81:19).

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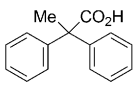
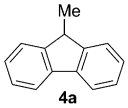
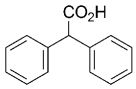
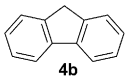
Table 3: Reaction of 2,2-diphenylalkanoic acids **3**.[a]

Entry	Catalyst	Additive	*T* [°C]	*t* [h]	Yield [%][b]
	 **3a** →  **4a**				
1[c]	[{RhCl(cod)}$_2$]	–	120	8	0
2[c]	[{Cp*RhCl$_2$}$_2$]	–	120	8	0
3	[{Cp*RhCl$_2$}$_2$]	K_2CO_3	120	8	27
4	[{Cp*RhCl$_2$}$_2$]/$AgSbF_6$	K_2CO_3	120	20	45
5	[{Cp^{E}RhCl$_2$}$_2$]/$AgSbF_6$	K_2CO_3	120	20	65
6	[{Cp^{E}RhCl$_2$}$_2$]/$AgSbF_6$	K_2CO_3/acid[d]	120	20	73 (63)
	 **3b** →  **4b**				
7	[{Cp^{E}RhCl$_2$}$_2$]/$AgSbF_6$	K_2CO_3/acid[d]	120	20	51
8	[{Cp^{E}RhCl$_2$}$_2$]/$AgSbF_6$	K_2CO_3/acid[d]	100	48	56
9	[{Cp^{E}RhCl$_2$}$_2$]/$AgSbF_6$	K_2CO_3	100	48	57 (57)

[a] Reaction conditions: **3** (0.5 mmol), Rh-cat (0.01 mmol), ($AgSbF_6$ (0.04 mmol)), (K_2CO_3 (0.5 mmol)), Cu(OAc)$_2$·H$_2$O (1 mmol), diglyme (3 mL) under N_2. [b] GC yield based on the amount of **3** used. Value within parentheses indicates yield after purification. [c] In *o*-xylene (3 mL). [d] acid = 2,6-$Me_2C_6H_3CO_2H$ (0.25 mmol).

(Table 3, entry 8). In this case, the addition of 2,6-$Me_2C_6H_3CO_2H$ was not necessary (entry 9). In contrast, the corresponding amine, diphenylmethylamine, could not be used for the cyclization. Under standard oxidative conditions, only a small amount of dehydrogenation/condensation[15] product was detected (8%).

In summary, we have demonstrated that a series of fluorene derivatives can be constructed through dehydrogenative cyclization of diphenylmethane moieties of substrates under rhodium catalysis. Work is underway toward further development of relevant reactions.

Experimental Section

General procedure for cyclization of 1-amino-1,1-diarylalkenes: The amine **1** (0.5 mmol), [{RhCl(cod)}$_2$] (0.005 mmol, 2.5 mg), Cu(OAc)$_2$·H$_2$O (1 mmol, 200 mg), 1-methylnaphthalene (ca. 50 mg) as internal standard, and *o*-xylene (3 mL) were added to a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup. The resulting mixture was then stirred under nitrogen at 100–150 °C (bath temperature) for 2–10 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed by water (100 mL, three times), and dried over Na_2SO_4. After evaporation of the solvents under vacuum, the product **2** was isolated by column chromatography on silica gel using *n*-hexane/ethyl acetate (3:1 or 1:1, v/v) as the eluant. Characterization data of products are summarized in the Supporting Information.

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[13] Under the reaction conditions using $[\{RhCl(cod)\}_2]$, AgOAc was found to be less effective as oxidant. Thus, the yield of **2a** decreased to 21%.

[14] In contrast, treatment of triphenylmethanol, benzophenone imine, and benzanilide gave no or trace amounts of cyclization products.

[15] a) K. Morimoto, K. Hirano, T. Satoh, M. Miura, *Chem. Lett.* **2011**, *40*, 600; b) X. Lang, H. Ji, C. Chen, W. Ma, J. Zhao, *Angew. Chem.* **2011**, *123*, 4020; *Angew. Chem. Int. Ed.* **2011**, *50*, 3934. Similar dehydrogenation also took place upon treatment of N-methylated triphenylmethylamine.

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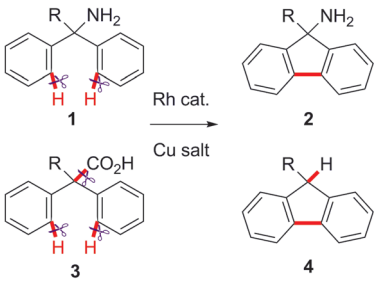
Communications

C–H Activation

K. Morimoto, M. Itoh, K. Hirano, T. Satoh,* Y. Shibata, K. Tanaka, M. Miura* _____ ■■■■–■■■■

Synthesis of Fluorene Derivatives through Rhodium-Catalyzed Dehydrogenative Cyclization



Doubling up: Two C–H bond activations took place efficiently upon treatment of **1** with a rhodium catalyst to form dehydrogenative cyclization products **2**. Furthermore, **3** undergoes similar cyclization and subsequent decarboxylation through the cleavage of two C–H bonds and one C–C bond. Both reactions provide straightforward routes to the fluorene framework.

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