ORGANOMETALLICS
Article

Organometallics **2011,** *30,* 627–632
DOI: 10.1021/om1009846

Preparation of Di-μ-chlorobis[π-1-chloro-1-aryl-2-(2′,2′-diarylvinyl)allyl]palladium(II) Complexes and a Novel Dehydrogenative Rearrangement of Arylvinylcyclopropenes for the Synthesis of 7*H*-Benzo[*c*]fluorene Derivatives

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Received October 14, 2010

A new synthetic method for the preparation of di-μ-chlorobis[π-1-chloro-1-aryl-2-(2′,2′-diarylvinyl)allyl]palladium(II) complexes has been developed from the reaction of arylvinylcyclopropenes with a Pd(II) complex along with a novel dehydrogenative rearrangement of arylvinylcyclopropenes via di-μ-chlorobis[π-1-chloro-1-aryl-2-(2′,2′-diarylvinyl)allyl]palladium(II) complexes to produce 7*H*-benzo[*c*]fluorene derivatives in good yields under mild conditions. A stoichiometric amount of silver salts or a catalytic amount of strong Brønsted acid HOTf can be the promoter or the catalyst for this interesting dehydrogenative rearrangement.

Introduction

Cyclopropenes[1] are well known as a large class of excellent ligands for various π-philic transition metals.[2] The driving force of coordination between cyclopropenes and metal centers is the relief of ring strain[3] via donation of filled π-orbital electrons from cyclopropene moieties to the hybrid spd-orbital of the metals along with the formation of π-back-bonding.[4] Since the first Pd-promoted ring-opening reaction of cyclopropenes reported by Battiste and co-workers,[5] numerous investigations have been focused on the transition-metal-mediated ring-opening/ring-expanding of cyclopropenes, such as 3-vinylcyclopropenes.[6] For example, complexation of transition metals with cyclopropenes along with the C−C bond cleavage of ring structure including transformation of cyclopropenes into vinylcarbene metal complexes[7] and

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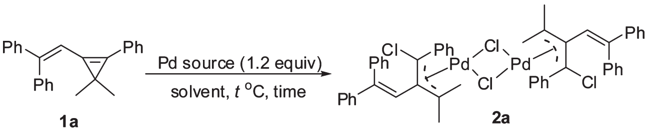
metallabenzenes[8] has been realized during the last several decades. On the other hand, isolable η^2-cyclopropenylmetal complexes containing transition metals Ni,[9] Ir,[10] Pt,[11] Mo,[12] W,[13] Ti, and Zr,[14] which involve complexation with cyclopropenes along with the retention of ring structure, have also been characterized by NMR spectroscopic analyses and X-ray diffraction. To the best of our knowledge, transition-metal-promoted reactions of 1-vinylcyclopropenes are rarely reported.[15] On the basis of the previous studies on $PdCl_2$-promoted ring-opening reactions of methylenecyclopropanes/vinylidenecyclopropanes (MCPs/VDCPs)[16] as well as transformation of vinylidenecyclopropanes to 1-vinylcyclopropenes,[17] we attempted to examine the reaction of arylvinylcyclopropenes **1** with palladium dichloride. Herein we wish to report the synthesis of di-μ-chlorobis[π-1-chloro-1-aryl-2-(2′,2′-diarylvinyl)allyl]palladium(II) complexes from the reaction of **1** with $PdCl_2$ as well as dehydrogenative rearrangement of arylvinylcyclopropenes to construct 7*H*-benzo[*c*]fluorene skeletons[18] via palladium-promoted ring-opening of **1** under mild conditions.

Table 1. Chloropalladation of Arylvinylcyclopropene 1a



entry[a]	Pd source	solvent	T (°C)	time (h)	yield (%)[b]
1	$PdCl_2$	THF	50	3	40
2	$PdCl_2$	THF	20	24	51
3	$PdCl_2$	THF	0	48	33
4	$PdCl_2$	THF	−10	48	31
5	$PdCl_2(PhCN)_2$	THF	20	12	84
6	$PdCl_2(PhCN)_2$	DCM	20	12	68
7	$PdCl_2(PhCN)_2$	toluene	20	12	90 (77)
8	$PdCl_2(PhCN)_2$	toluene	5	12	70

[a] All reactions were carried out using **1** (0.2 mmol) in the presence of Pd sources (0.24 mmol) and solvents (2.0 mL). [b] Isolated yield. Value in parentheses: isolated yield after second time flash column chromatography using toluene as eluent.

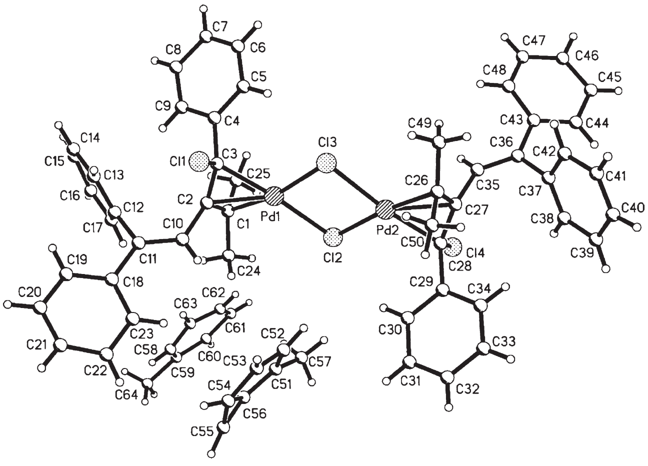


Figure 1. ORTEP drawing of Pd complex **2a**.

Results and Discussion

Our initial experiments were carried out to investigate the reaction of 1-(2′,2′-diphenylvinyl)-2-phenyl-3,3-dimethylcyclopropene (**1a**) with $PdCl_2$ (1.2 equiv) at 50 °C in THF for 3 h, which were the best reaction conditions for the complexation of VDCPs with palladium dichloride.[16b] The reaction proceeded smoothly to produce di-μ-chlorobis[π-1-chloro-1-phenyl-2-(2′,2′-diphenylvinyl)-3,3-dimethylallyl]palladium(II) complex **2a** in 40% isolated yield, which is an air- and moisture-stable solid (Table 1, entry 1). The structure of *trans*-*anti*-**2a** was unambiguously determined by X-ray diffraction. Its ORTEP drawing having two toluene molecules is shown in Figure 1, and its CIF data are presented in the Supporting Information.[19] The formation of *anti*-**2a**, having a configuration opposite the similar π-1-chloro-3-arylallylpalladium(II) complexes that have been previously reported by Battiste and co-workers,[5] is presumably due to the steric interaction between the R^2 ring and 2,2-diphenylvinyl substitution in the *syn*-configuration of **2a** (Figure 2). A slightly higher isolated yield was obtained by reducing the temperature to 20 °C with lengthening of the reaction time

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(19) The crystal data of **2a** have been deposited in the CCDC with number 759635. Empirical formula: $C_{64}H_{60}Cl_4Pd_2$ ($C_{50}H_{44}Cl_4Pd_2$ + toluene*2); formula weight: 1183.72; crystal color, habit: colorless, prismatic; crystal dimensions: 0.265 × 0.123 × 0.069 mm; crystal system: monoclinic; lattice type: primitive; lattice parameters: a = 19.611(5) Å, b=11.893(3) Å, c=25.775(7) Å, α=90°, β = 108.957(6)°, γ = 90°, V = 5686(3) Å^3; space group: $P2(1)/n$; Z = 4; D_{calc} = 1.383 g/cm^3; F_{000} = 2416; diffractometer: Rigaku AFC7R; residuals: R; R_w: 0.0669, 0.1152.

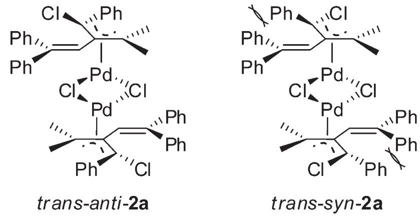
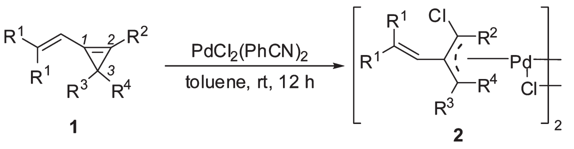


Figure 2. Steric hindrance in *trans-syn*-**2a**.

Table 2. Substrate Scope of the Palladium Complex Promoted Ring-Opening of Arylvinylcyclopropenes 1



entry[a]	**1** ($R^1/R^2/R^3/R^4$)	yield (%)[b]
1	**1b** (C_6H_5/4-$CH_3C_6H_4$/CH_3/CH_3)	**2b**, 92 (71)
2	**1c** (C_6H_5/4-ClC_6H_4/CH_3/CH_3)	**2c**, 87 (74)
3	**1d** (C_6H_5/3-ClC_6H_4/CH_3/CH_3)	**2d**, 68 (61)
4	**1e** (C_6H_5/4-BrC_6H_4/CH_3/CH_3)	**2e**, 83 (71)
5	**1f** (4-$CH_3C_6H_4$/C_6H_5/CH_3/CH_3)	**2f**, 86 (74)
6	**1g** (4-ClC_6H_4/C_6H_5/CH_3/CH_3)	**2g**, 73 (63)
7	**1h** (C_6H_5/C_6H_5/$-(CH_2)_5-$)	**2h**, 81 (70)
8	**1i** (C_6H_5/C_6H_5/$-(CH_2)_4-$)	**2i**, 68 (60)
9	**1j** (C_6H_5/C_6H_5/CH_3/H)	**2j**, 76 (55)
10	**1k** (C_6H_5/C_6H_5/H/H)	

[a] All reactions were carried out using **1** (0.40 mmol) and $PdCl_2(PhCN)_2$ (0.48 mmol) in toluene (2.0 mL) at room temperature for 12 h. [b] Isolated yields. Value in parentheses: isolated yields after second time flash column chromatography using toluene as eluent.

(Table 1, entry 2). When the reaction was carried out at 0 or −10 °C, the complexation proceeded much slower, affording **2a** in lower yields (Table 1, entries 3 and 4). Using $PdCl_2(PhCN)_2$ as the palladium precursor, the reaction completed within 12 h to produce **2a** in 84% isolated yield (Table 1, entry 5). Further examination of the solvent effects revealed that toluene is the solvent of choice for this transformation (Table 1, entries 6−8). Moreover, it should also be noted that when **2a** was purified by flash column chromatography [petroleum ether (PE)/ethyl acetate (EA) = 10:1 as the eluent], small amounts of PE could not be removed from the product, even with high-vacuum pumping. Therefore, we carried out a second time flash column chromatography by employing toluene as the eluent and calculated a more accurate yield by ^{1}H NMR spectroscopic data of the isolated product (toluene cannot be removed by high-vacuum pumping either, Table 1, entry 7).

With these optimized conditions in hand, we next examined a variety of arylvinylcyclopropenes **1** in this reaction, and the results of these experiments are shown in Table 2. A variety of π-allylpalladium chloride complexes **2** were attained in moderate to good yields (Table 2, entries 1−10). The reaction of arylvinylcyclopropenes **1b** and **1f**, bearing electron-donating methyl group(s) on the benzene ring of R^1 or R^2, produced the corresponding π-allylpalladium chloride complexes **2b** and **2f** in relatively higher yields than those of arylvinylcyclopropenes **1c**, **1d**, **1e**, and **1g**, which have electron-withdrawing groups on the benzene ring presumably due to the electronic property (Table 2, entries 1−6). The reaction also proceeded smoothly to produce π-allylpalladium chloride complexes **2h** and **2i** in good yields when substituted spiro[2.5]oct-1-ene **1h** and spiro[2.4]hept-1-ene **1i** were used (Table 2, entries 7 and 8). 3-Monosubstituted arylvinylcyclopropene **1j** produced the corresponding palladium(II) complex **2j** in lower yield, and when 3-nonsubstituted arylvinylcyclopropene **1k** was employed as the substrate, the isolation of the corresponding Pd complex was not observed under the standard conditions (Table 2, entries 9 and 10).

We have previously reported a stepwise dehydrogenative rearrangement of arylvinylcyclopropenes **1** to produce benzofulvene derivatives in good yields in the presence of $Pd(OAc)_2$ (Scheme 1).[17e] In the present case, we assumed that abstraction of a Cl^- in the produced π-allylpalladium chloride complex **2** to generate a cationic palladium species followed by intramolecular electrophilic addition would also possibly produce a dehydrogenative rearrangement product in good yield. Therefore, we next employed a variety of silver(I) salts to generate cationic palladium species for the dehydrogenative rearrangement reaction. It was found that the reaction of **2a** with stoichiometric amounts of AgOTf, $AgSbF_6$, and $AgBF_4$ indeed produced 7,7-dimethyl-5-phenyl-7*H*-benzo[*c*]fluorene **3a** in excellent isolated yields in toluene at 80 °C within 8 h (Table 3, entries 1−3). The structure of **3a** was determined by X-ray diffraction. Its ORTEP drawing is shown in Figure 3, and its CIF data are presented in the Supporting Information.[20] Silver nitrate did not promote the transformation, leading to decomposition of **2a** rapidly (Table 3, entry 4). We also observed that a trace of **3a** was formed along with the decomposition of **2a** when a catalytic amount of $AgSbF_6$ was used (Table 3, entry 5). Upon heating and without addition of silver(I) salt, **2a** decomposed to produce complex product mixtures (Table 3, entry 6). Product **3a** was also isolated in 99% yield when the reaction was carried out in the presence of inorganic base Na_2CO_3 (2.0 equiv) and 2.0 equiv of $AgSbF_6$ (Table 3, entry 7).

Hereafter, we examined the substrate scope of this transformation. Substrates **2**, bearing electron-donating groups on the benzene ring, underwent the reactions smoothly to provide the corresponding 7*H*-benzo[*c*]fluorene derivatives **3** in excellent yields (Table 4, entries 1 and 5). Using AgOTf as the promoter, the rearrangement reactions of π-allylpalladium chloride complexes **2**, bearing electron-withdrawing groups on the benzene ring, proceeded smoothly to give the corresponding products **3** in moderate to good isolated yields at 100 °C (Table 4, entries 2−4 and 6). We also isolated formal rearrangement product 7-chloro-4-(4-chlorophenyl)-2-isopropyl-1-phenylnaphthalene **4**[17a] in 34% yield in addition to **3g** in 45% yield when Pd(II) complex **2g** was used as the substrate (Table 4, entry 6). The reaction of palladium(II) complex **2h**, bearing a six-membered ring, produced 5-phenylspiro[benzo[*c*]fluorene-7,1′-cyclohexane] **3h** in 83% yield under the standard conditions (Table 4, entry 7). However, the reaction of **2i** under various conditions produced only unidentified complex product mixtures (Table 4, entry 8), presumably due to the steric difference between the five-membered ring and six-membered ring. The reaction of **2j** produced the corresponding product **3i** in 72% isolated yield in the presence of AgOTf (1.0 equiv) at 100 °C (Table 4, entry 9).

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(20) The crystal data of **3a** have been deposited in the CCDC with number 759636. Empirical formula: $C_{25}H_{20}$; formula weight: 320.41; crystal color, habit: colorless, prismatic; crystal dimensions: 0.408 × 0.322 × 0.074 mm; crystal system: orthorhombic; lattice type: primitive; lattice parameters: $a = 8.1602(14)$ Å, $b = 13.070(2)$ Å, $c = 16.940(3)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 1806.6(5)$ Å^3; space group: $P2(1)2(1)2(1)$; Z = 4; $D_{calc} = 1.178$ g/cm^3; $F_{000} = 680$; diffractometer: Rigaku AFC7R; residuals: R; R_w: 0.0475, 0.1060.

Scheme 1. Dehydrogenative Rearrangement of Arylvinylcyclopropene 1 Promoted by Pd(OAc)$_2$/*p*-BQ

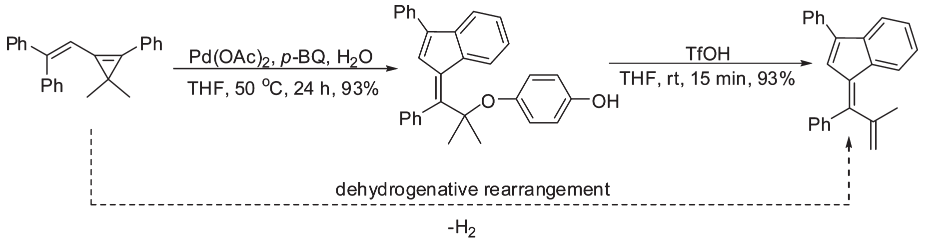
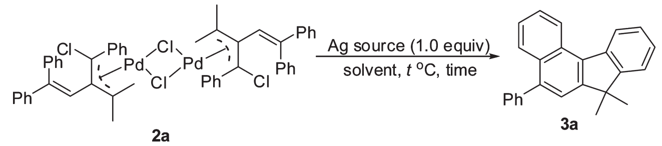


Table 3. Dehydrogenative Rearrangement to Produce 7*H*-Benzo[*c*]fluorene Derivative 3a



entry[a]	Ag source	solvent	T (°C)	time (h)	yield (%)[b]
1	AgOTf	toluene	80	8	95
2	$AgSbF_6$	toluene	80	8	99
3	$AgBF_4$	toluene	80	8	95
4	$AgNO_3$	toluene	80	12	complex
5	$AgSbF_6$	toluene	80	12	trace[c]
6		toluene	80	12	complex
7	$AgSbF_6$	toluene	80	8	99[d]

[a] All reaction were carried out using **1** (0.1 mmol, as monomer) in the presence of Ag sources (0.1 mmol) and solvents (1.0 mL). [b] Isolated yield. [c] $AgSbF_6$ (0.1 equiv) was used. [d] $AgSbF_6$ (2.0 equiv) was used in the presence of Na_2CO_3 (2.0 equiv).

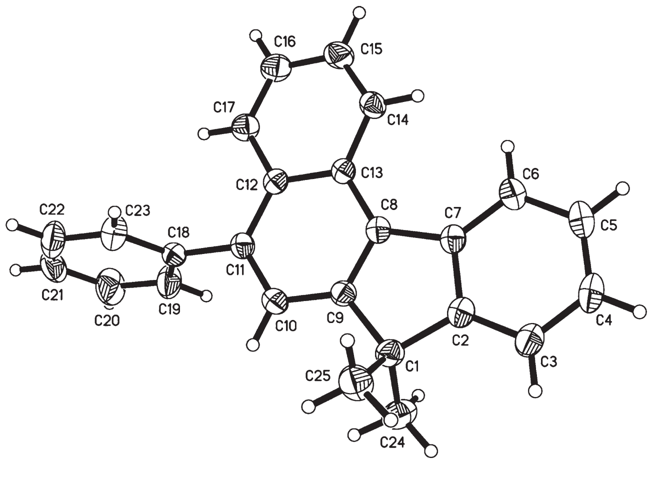


Figure 3. ORTEP drawing of compound **3a**.

According to the above silver(I) salt promoted reactions of π-allylpalladium chloride complexes **2** to produce 7*H*-benzo[*c*]fluorene derivatives **3**, it is worth noting that the addition of 1.0 equiv of silver(I) salt (relative to the monomer of **2**) has the capability to abstract only 1.0 equiv of Cl^- in the absence of a base (Table 3, entry 7). However, both chloride atoms have been abstracted from starting material **2** to produce product **3**. Thus, we considered the possibility of a second abstraction of Cl^- by the *in situ* generated trifluoromethanesulfonic acid CF_3SO_3H (HOTf) to give a new cationic palladium species and HCl. In this case, using a catalytic amount of strong Brønsted acid to abstract Cl^- instead of stoichiometric silver(I) salt would also promote the transformation. Further examination of the dehydrogenative rearrangement of **2** using a 0.1 equiv amount of HOTf as the catalyst was carried out, and we found that the reaction proceeded smoothly to produce **3a** in 99% isolated yield within 1 h (Table 5, entry 1). This result is totally different from our previous report on the direct treatment of arylvinylcyclopropenes **1** with catalytic Lewis acid or Brønsted acid in which different naphthalene derivatives could be obtained in good yields under mild conditions (Scheme 2).[17a] We also examined the reactions of **2c** and **2g** using a catalytic amount of HOTf instead of a stoichiometric amount of AgOTf and found that the reaction proceeded smoothly, producing the corresponding products **3c** and **3g** in excellent yields within 1 h (Table 5, entries 2 and 3). Unfortunately, transformation of **2i** in the presence of a catalytic amount of HOTf still failed (Table 5, entry 4). Furthermore, when a catalytic amount of AgOTf (0.1 equiv) was used instead of HOTf, the reaction of **2a** produced **3a** in 90% isolated yield under the standard conditions. Compared to a catalytic amount of $AgSbF_6$ in the reaction (Table 3, entry 5), the *in situ* generated strong Brønsted acid HOTf may be the real catalytic species in this case, driving the transformation more efficiently than the *in situ* generated $HSbF_6$. It should be emphasized here that the catalytic amount of AgOTf (0.1 equiv) cannot catalyze the reaction in the presence of inorganic base Na_2CO_3 (2.0 equiv) presumably because the *in situ* generated HOTf was quenched under basic conditions. Finally, the one-pot dehydrogenative rearrangement of **1a** has been carried out without isolation of palladium(II) complex **2a** using HOTf (0.1 equiv) as the catalyst, affording **3a** in 75% overall yield (Scheme 3).

A plausible mechanism for the formation of these 7*H*-benzo[*c*]fluorene derivatives **3** is outlined in Scheme 4. Abstraction of Cl^- in π-allylpalladium chloride complexe **2** by strong Brønsted acid HOTf or silver(I) salt generates cationic palladium specie **A**,[21] which undergoes intramolecular electrophilic addition[22] to the phenyl ring of R^1 to afford intermediate **B**. Reductive elimination and oxidative addition[23] of intermediate **C**, which is generated from intermediate **B** via deprotonation, produce a

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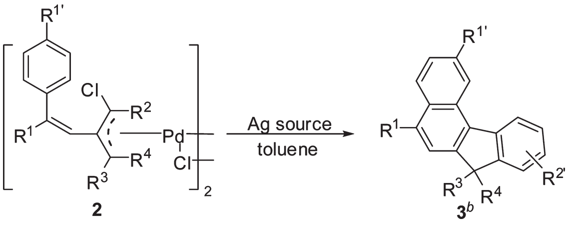
(21) Chloride ligands can be converted to the corresponding triflates in the presence of HOTf; see: Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M.; Taube, H. *Trifluoromethanesulfonates and Trifluoromethanesulfonato-O Complexes*; John Wiley & Sons, Inc.: New York, 2007; p 70.

(22) For enhancement of the aromatic C−H bonds' metalation via electrophilic C−H activation with cationic Pd(II) species, see: (a) Nishikata, T.; Abela, A. R.; Huang, S.; Lipshutz, B. H. *J. Am. Chem. Soc.* **2010**, *132*, 4978. (b) Jia, C.; Piao, D.; Kitamura, T.; Fujiwara, Y. *J. Org. Chem.* **2000**, *65*, 7516.

(23) For recent studies on oxidative addition of Pd(0) to allyl/benzylic chlorides, see: (a) Lu, S.; Xu, Z.; Bao, M.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 4366. (b) Kabalka, G. W.; Dadush, E.; Al-Masum, M. *Tetrahedron Lett.* **2006**, *47*, 7459. (c) Carvajal, M. A.; Miscione, G. P.; Novoa, J. J.; Bottoni, A. *Organometallics* **2005**, *24*, 2086. (d) Bao, M.; Nakamura, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **2001**, *123*, 759. (e) Nakamura, H.; Shibata, H.; Yamamoto, Y. *Tetrahedron Lett.* **2000**, *41*, 2911.

Table 4. Substrate Scope of Stoichiometric Silver(I)-Promoted Transformation of π-Allylpalladium Chloride Complexes 2 to 7*H*-Benzo[*c*]fluorene Derivatives 3



entry^a	**2** ($R^1/R^2/R^3/R^4$)^b	Ag source	*T* (°C)	yield (%)^c
1	**2b** (C_6H_5/4-$CH_3C_6H_4$/CH_3/CH_3)	$AgSbF_6$	80	**3b**, 99
2	**2c** (C_6H_5/4-ClC_6H_4/CH_3/CH_3)	AgOTf	100	**3c**, 68
3	**2d** (C_6H_5/3-ClC_6H_4/CH_3/CH_3)	AgOTf	100	**3d**, 86^d
4	**2e** (C_6H_5/4-BrC_6H_4/CH_3/CH_3)	AgOTf	100	**3e**, 88
5	**2f** (4-$CH_3C_6H_4$/C_6H_5/CH_3/CH_3)	$AgSbF_6$	80	**3f**, 99
6	**2g** (4-ClC_6H_4/C_6H_5/CH_3/CH_3)	AgOTf	100	**3g**, 45^e **4**^{f}
7	**2h** (C_6H_5/C_6H_5/$-(CH_2)_5-$)	$AgSbF_6$	80	**3h**, 83
8	**2i** (C_6H_5/C_6H_5/$-(CH_2)_4-$)	AgOTf/$AgSbF_6$	80/100	complex
9	**2j** (C_6H_5/C_6H_5/CH_3/H)	AgOTf	100	**3i**, 72

^{a} All reactions were carried out using **2** (0.1 mmol, as monomer) and Ag source (0.1 mmol) in toluene (1.0 mL) for 8 h. ^{b} $R^{1\prime}/R^{2\prime}$ are the substituent on the aromatic rings R^1/R^2. ^{c} Isolated yields. ^{d} 1.2:1 mixture of regioisomers. ^{e} 7-Chloro-4-(4-chlorophenyl)-2-isopropyl-1-phenylnaphthalene **4** was isolated in 34% yield. ^{f}

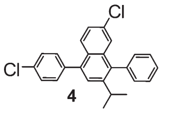


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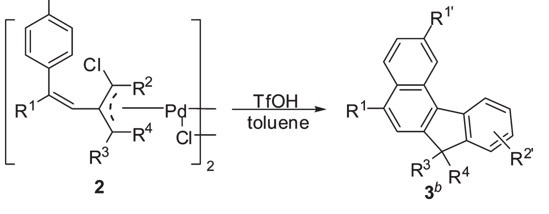
Table 5. Substrate Scope of HOTf-Catalyzed Transformation of π-Allylpalladium Chloride Complexes 2 to 7*H*-Benzo[*c*]fluorene Derivatives 3

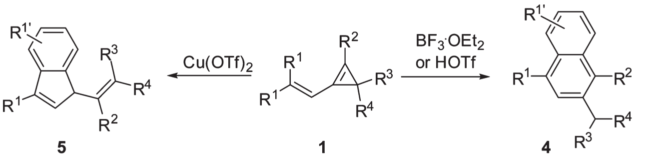


entry^a	**2** ($R^1/R^2/R^3/R^4$)^b	yield (%)^c
1	**2a** (C_6H_5/C_6H_5/CH_3/CH_3)	**3a**, 99
2	**2c** (C_6H_5/4-ClC_6H_4/CH_3/CH_3)	**3c**, 99
3	**2g** (4-ClC_6H_4/C_6H_5/CH_3/CH_3)	**3g**, 99
4	**2i** (C_6H_5/C_6H_5/$-(CH_2)_4-$)	complex

^{a} All reactions were carried out using **2** (0.1 mmol, as monomer) and HOTf (0.01 mmol) in toluene (1.0 mL) at 80 °C for 1 h. ^{b} $R^{1\prime}/R^{2\prime}$ are the substituents on the aromatic rings R^1/R^2. ^{c} Isolated yields.

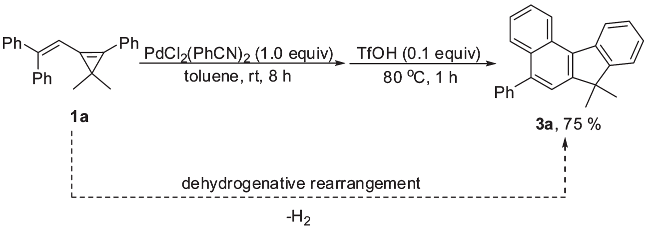
new π-allyl-palladium(II) complex **D**. Aromatization followed by an allylic rearrangement affords intermediate **E**, which undergoes abstraction of Cl^- by silver(I) salts or the *in situ* generated Brønsted acid along with an intramolecular electrophilic addition to the phenyl ring of R^2 to give cyclic-palladium intermediate **F**. Further deprotonation of **F** along with reductive elimination produces the final product **3** and regenerates H^+. Alternatively, since the protonolysis of an electron-deficient palladium complex is easier than that of an electron-rich

Scheme 2. Acid-Catalyzed Rearrangement of Arylvinylcyclopropene 1



$R^{1\prime}$ is the substituents on the aromatic rings R^1

Scheme 3. One-Pot Dehydrogenative Rearrangement of Arylvinylcyclopropene 1a



one,[24h] direct protonolysis[24] of intermediate **E** would also produce the corresponding formal rearrangement product **4**

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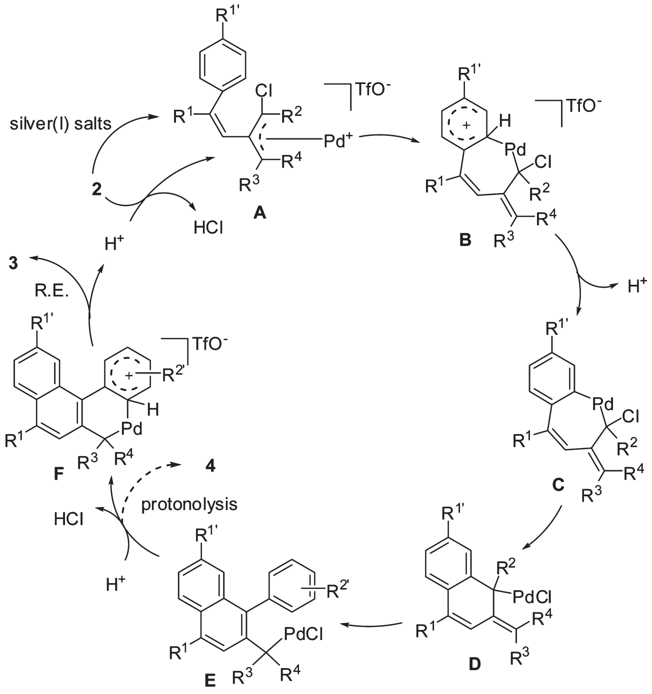
[24] For recent studies on protonolysis of the Pd—C bond, see: (a) Yang, S.-R.; Jiang, H.-F.; Li, Y.-Q.; Chen, H.-J.; Luo, W.; Xu, Y.-B. *Tetrahedron* **2008**, *64*, 2930. (b) Cochran, B. M.; Michael, F. E. *J. Am. Chem. Soc.* **2008**, *130*, 2786. (c) Bercaw, J. E.; Chen, G. S.; Labinger, J. A.; Lin, B.-L. *J. Am. Chem. Soc.* **2008**, *130*, 17654. (d) Shen, Z.; Lu, X. *Tetrahedron* **2006**, *62*, 10896. (e) Feducia, J. A.; Campbell, A. N.; Anthis, J. W.; Gagne, M. R. *Organometallics* **2006**, *25*, 3114. (f) Zhao, L. G.; Lu, X. Y.; Xu, W. *J. Org. Chem.* **2005**, *70*, 4059. (g) Wang, Z.; Zhang, Z.; Lu, X. *Organometallics* **2000**, *19*, 775. (h) Liu, H.; Yu, J.; Wang, L.; Tong, X. *Tetrahedron Lett.* **2008**, *49*, 6924.

Scheme 4. Plausible Mechanism of Dehydrogenative Rearrangement Promoted by Stoichiometric Amount of Silver(I) Salt and Catalytic Amount of HOTf



$R^{1'}/R^{2'}$ are the substituents on the aromatic rings R^1/R^2

when **2g** was used as the substrate with a stoichiometric amount of AgOTf as the promoter.

Conclusion

In summary, we have developed a new synthetic protocol for the preparation of di-μ-chlorobis[π-1-chloro-1-aryl-2-(2′,2′-diarylvinyl)allyl]palladium(II) complexes from arylvinylcyclopropenes with a Pd(II) complex as well as an unusual dehydrogenative rearrangement of arylvinylcyclopropenes promoted by a palladium(II) complex in the presence of silver(I) salts or HOTf to produce 7*H*-benzo[*c*]fluorene derivatives in good to excellent yields. This synthetic protocol furnishes 7*H*-benzo[*c*]fluorene derivatives straightforwardly from simple starting materials under mild conditions. A plausible mechanism that is based on an intramolecular electrophilic addition pathway has been also proposed. Clarification of the reaction mechanism and further application of this chemistry are currently in progress.

Experimental Section

General Procedure for the Synthesis of Di-μ-Chlorobis[π-1-chloro-1-phenyl-2-(2′,2′-diphenylvinyl)-3,3-dimethylallyl]palladium(II) Complex 2a. Under an argon atmosphere, 1-(2′,2′-diphenylvinyl)-2-phenyl-3,3-dimethylcyclopropene **1a** (64.0 mg, 0.2 mmol), $PdCl_2(PhCN)_2$ (92.0 mg, 0.24 mmol), and toluene (2.0 mL) were added into a flame-dried Schlenk tube. The reaction mixture was stirred at rt for 8 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on a silica gel column (PE/EA = 10:1) to provide **2a** (90 mg, 90%). A second purification by flash chromatography on a silica gel column (toluene as eluent) was required to determine the yield (**2a**/toluene = 1:2, determined by X-ray diffraction and ^{1}H NMR spectroscopic data). We found that recrystallization of these complexes from toluene for the elementary analysis was very difficult because only a small amount of the complex could be isolated. However, recrystallization of these complexes in hexane with addition of a very small amount of CH_2Cl_2 was successful, affording an acceptable amount of complexes for the elementary analyses. After filtration and drying under reduced pressure via a Büchi B-585 Kugelrohr at 50 °C for 2 h, these samples could pass the elementary analyses. We have calculated the corresponding components of hexane and palladium complex according to the analytical data, and these elemental analysis data are shown in the Experimental Section.

General Procedure for the Synthesis of 7*H*-Benzo[*c*]fluorene Derivative 3a. Di-μ-chlorobis[π-1-chloro-1-phenyl-2-(2′,2′-diphenylvinyl)-3,3-dimethylallyl]palladium(II) complex **2a** (59.0 mg, 0.1 mmol as monomer containing 0.1 mmol of toluene), $AgSbF_6$ (34.4 mg, 0.1 mmol) or HOTf (1.0 μL, 0.01 mmol), and toluene (1.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at 80 °C until the reaction was complete. Then, the solvent was removed under reduced pressure and the residue was purified by flash chromatography on a silica gel column (PE as eluent) to provide pure **3a** (32 mg, 99%).

Acknowledgment. We thank the Shanghai Municipal Committee of Science and Technology (08dj1400100-2), National Basic Research Program of China (973)-2009CB825300, the Fundamental Research Funds for the Central Universities, and the National Natural Science Foundation of China for financial support (20472096, 20872162, 20672127, 20821002, and 20732008).

Supporting Information Available: Detailed description of experimental procedures, full characterization of new compounds shown in tables and figures, along with the X-ray data of **2a** and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org or from the authors.