Synthesis of Novel Dimeric Allylpalladium(II) Complexes from $PdCl_2$-Promoted Ring-Opening Reactions of Vinylidenecyclopropanes

Xingxing Gu,[†] Feijun Wang,*[,†] Ming-hui Qi,[†] Li-xiong Shao,[†] and Min Shi*[,†,‡]

School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 MeiLong Road, Shanghai 200237, People's Republic of China, and State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, People's Republic of China

Received November 23, 2008

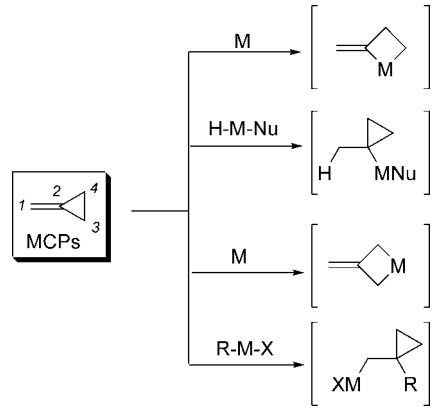
Novel dimeric allylpalladium(II) complexes have been successfully synthesized from the transition metal $PdCl_2$-promoted ring-opening reactions of VDCPs **1** in good yields. These dimeric allylpalladium(II) complexes have been characterized by X-ray crystal structure diffraction.

Introduction

Transition metal-catalyzed reactions of strained cyclic hydrocarbons such as methylenecyclopropanes (MCPs) and cyclopropenes have been widely explored and have received considerable attention from synthetic and mechanistic viewpoints since the middle of the 20th century.[1] The reaction course of MCPs with transition metal catalysts (M) may be categorized into the following four patterns (Scheme 1).[2] Among them the most significant findings are the selective cleavage of the proximal (C^2-C^3 or C^2-C^4) and/or distal bonds (C^3-C^4) of MCPs catalyzed by palladium to afford the corresponding ring-opening products under mild conditions. So far, only two papers have been reported regarding the transition metal-catalyzed reactions of vinylidenecyclopropanes (VDCPs),[3] which are also highly strained but readily accessible and stable molecules that serve as useful building blocks in many organic synthesis.[4] It is necessary to study the coordination behavior of VDCPs with transition metal so as to develop novel synthetic methods using VDCPs in the presence of transition metals.

It is well known that allylpalladium complexes, as the active intermediates or the precursors of active organometallic complexes, have been widely used as the catalysts or reagents in numerous palladium-catalyzed reactions, offering many synthetically useful methods for organic chemists.[5] These allylpalladium complexes are mainly prepared from oxidative addition of Pd(0) complexes and insertion reactions of Pd(II) complexes with the corresponding allylic compounds. Recently, Battiste and co-workers have reported the ring-opening reaction of cyclopropenes by using $[(PhCN)_2PdCl_2]$ under mild conditions to give a novel type of allylpalladium complexes in good yields (Scheme 2).[6] Furthermore, we have recently also disclosed that the ring-opening reaction of MCPs and VDCPs could take place to give the corresponding ring-opened products under mild conditions in the presence of Lewis acids such as $BF_3 \cdot OEt_2$, MCl_n (M = Al, Zn or Sn etc), or $Ln(OTf)_m$ (Ln = Yb, Sm, Sc,

Scheme 1. Transition Metal-Catalyzed Reactions of Methylenecyclopropanes (MCPs)



* Corresponding author. (M.S.) Fax: 86-21-64166128. E-mail: Mshi@mail.sioc.ac.cn. (F.W.) E-mail: feijunwang@ecust.edu.cn.
† East China University of Science and Technology.
‡ Shanghai Institute of Organic Chemistry.

(1) (a) Krief, A. *Top. Curr. Chem.* **1987**, *135*, 1. (b) Binger, P.; Büch, H. M. *Top. Curr. Chem.* **1987**, *135*, 77. (c) Ohta, T.; Takaya, H. In *Comprehensive Organic Synthesis*; Pergamon Press: Oxford, 1991; Vol. 5, p 1185. (d) *Carbocyclic Three-Membered Ring Compounds*, *Houben-Weyl*; de Meijere, A., Ed.; Thieme: Stuttgart, 1996; Vol. E17. (e) Brandi, A.; Goti, A. *Chem. Rev.* **1998**, *98*, 589. (f) Brandi, A.; Cicchi, S.; Cordero, F. M.; Goti, A. *Chem. Rev.* **2003**, *103*, 1213.

(2) Nakamura, I.; Yamamoto, Y. *Adv. Synth. Catal.* **2002**, *344*, 111.

(3) (a) Lu, J.-M.; Shi, M. *Tetrahedron* **2006**, *62*, 9115. (b) Stepakov, A. V.; Larina, A. G.; Molchanov, A. P.; Stepakova, L. V.; Starova, G. L.; Kostikov, R. R. *Russ. J. Org. Chem.* **2007**, *43*, 40.

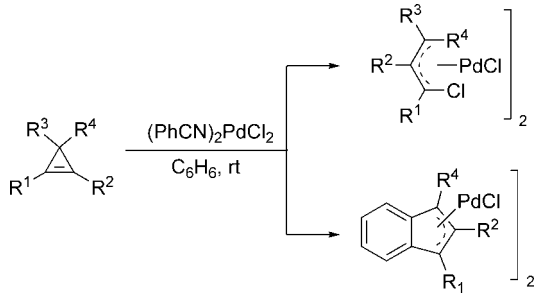
(4) (a) Lu, J.-M.; Shi, M. *Org. Lett.* **2008**, *10*, 1943. (b) Liu, L.-P.; Lu, J.-M.; Shi, M. *Org. Lett.* **2007**, *9*, 1303. (c) Shi, M.; Lu, J.-M. *J. Org. Chem.* **2006**, *71*, 1920. (d) Mizuno, K.; Nire, K.; Sugita, H.; Maeda, H. *Tetrahedron Lett.* **2001**, *42*, 2689. (e) Maeda, H.; Hirai, T.; Sugimoto, A.; Mizuno, K. *J. Org. Chem.* **2003**, *68*, 7700. (f) Su, C.; Huang, X.; Liu, Q. *J. Org. Chem.* **2008**, *73*, 6421. (g) Mizuno, K.; Maeda, H.; Sugita, H.; Nishioka, S.; Hirai, T.; Sugimoto, A. *Org. Lett.* **2001**, *3*, 581. (h) Mizuno, K.; Ichinose, N.; Yoshimi, Y. *J. Photochem. Photobiol. C: Photochem. Rev.* **2000**, *1*, 167. (i) Ma, S.; He, Q. *Tetrahedron* **2006**, *62*, 2769. (j) Li, W.; Shi, M. *J. Org. Chem.* **2008**, *73*, 4151.

(5) (a) Maitlis, P. M. *The Organic Chemistry of Palladium*; Academic Press: New York, 1971; Vols. *1 and 2*. (b) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980. (c) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985. (d) Larock, R. C. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: London, 1994; Vol. 5, Chapter 3. (e) Tsuji, J. *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*; Wiley and Sons: New York, 1995. (f) Li, J. J.; Gribble, G. W. *Palladium in Heterocyclic Chemistry*; Pergamon: New York, 2000. (g) Negishi, E. *Handbook of Organopalladium Chemistry for Organic Synthesis*; Wiley and Sons: New York, 2002; Vols. 1 and 2.

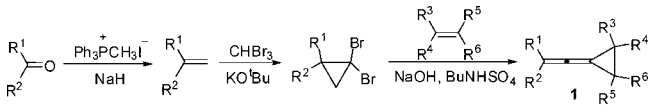
(6) (a) Mushak, P.; Battiste, M. A. *J. Organomet. Chem.* **1969**, *17*, 46. (b) Battiste, M. A.; Friedrich, L. E.; Fiato, R. A. *Tetrahedron Lett.* **1975**, *45*. (c) Fiato, R. A.; Mushak, P.; Battiste, M. A. *J. Chem. Soc., Chem. Commun.* **1975**, 869.

10.1021/om801117g CCC: $40.75
Publication on Web 02/11/2009

Scheme 2. Pd(II) Complex-Promoted Ring-Opening Reactions of Cyclopropenes



Scheme 3. Synthesis of VDCPs 1



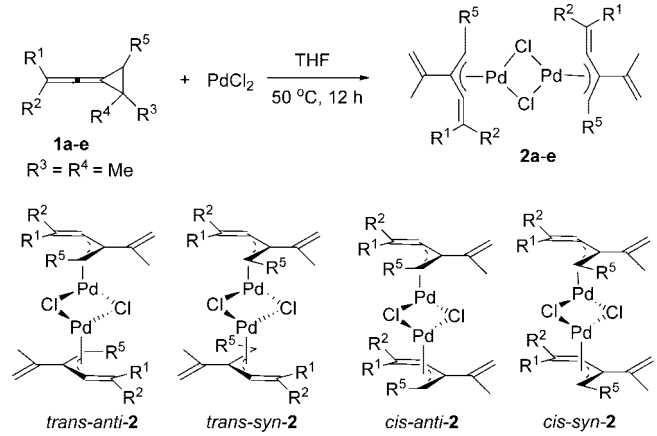
	R^1	R^2	R^3	R^4	R^5	R^6
1a	C_6H_5	C_6H_5	Me	Me	C_6H_5	H
1b	4-MeC_6H_4	4-MeC_6H_4	Me	Me	C_6H_5	H
1c	C_6H_5	C_6H_5	Me	Me	4-MeC_6H_4	H
1d	C_6H_5	C_6H_5	Me	Me	4-ClC_6H_4	H
1e	C_6H_5	C_6H_5	Me	Me	4-BrC_6H_4	H
1f	C_6H_5	C_6H_5	C_6H_5	C_6H_5	Me	H
1g	4-FC_6H_4	4-FC_6H_4	C_6H_5	C_6H_5	Me	H
1h	4-MeC_6H_4	4-MeC_6H_4	C_6H_5	C_6H_5	Me	H
1i	C_6H_5	C_6H_5	4-FC_6H_4	4-FC_6H_4	Me	H
1j	C_6H_5	C_6H_5	4-MeC_6H_4	4-MeC_6H_4	Me	H
1k	C_6H_5	C_6H_5	4-MeOC_6H_4	4-MeOC_6H_4	Me	H

La, etc.).[7] These interesting results stimulated us to further investigate the reactions of $PdCl_2$ with VDCPs **1**. Herein we report a novel synthetic method of allylpalladium complexes from the ring-opening reactions of VDCPs **1** with $PdCl_2$ along with their application in Suzuki coupling reactions.

Results and Discussion

Reactions of VDCPs 1 with Transition Metal $PdCl_2$. A series of multiaryl-substituted VDCPs **1** was synthesized according to the previously reported procedures, and their structures are shown in Scheme 3.[8] First, triaryl-substituted VDCPs **1a**−**e** (R^1, R^2, and R^5 = aryl group) were used as the substrates to react with $PdCl_2$ in tetrahydrofuran (THF) at 50 °C (Scheme 4). It was found that a novel type of dimeric allylpalladium(II) complexes, **2a**−**e**, was obtained in moderate yields. These dimeric allylpalladium(II) complexes are air and

Scheme 4. Reactions of $PdCl_2$ with VDCPs 1a−e



moisture stable in the solid state and even in the solution state. Their structures were determined by microanalysis, IR and NMR spectroscopic data, and ESI-MS spectroscopy. It should be noted that complex **2** may exist in four isomers (*trans-anti*-**2**, *trans-syn*-**2**, *cis-anti*-**2**, and *cis-syn*-**2**) (Scheme 4).[9] On the basis of their ^{1}H NMR spectroscopic data, complex **2** was assigned as only two isomers in a nearly equimolar ratio. The signal for the allylic proton of these two isomers was relatively close in chemical shift, suggesting that the two isomers were *trans-anti*-**2** and *cis-anti*-**2**. Moreover, the *syn*-isomer did not exist because of the steric interaction between the R^5 group and the isopropenyl group.[9,10] Single crystals of **2e** were obtained by recrystallization from a mixed solvent of dichloromethane/petroleum ether (1:4), and its structure was unambiguously determined by X-ray diffraction.[11] An ORTEP drawing of **2e** is depicted in Figure 1. As can be seen from Figure 1, the palladium(II) center is in a slightly distorted planar geometry, defined by two chloride atoms and one allyl group. The angle of the C(2)−Pd(1)−C(4) plane is 69.6°, smaller than the sum angle of C(2)−Pd(1)−C(3) and C(3)−Pd(1)−C(4), which is 38.8° and 38.9°, respectively. The bond length of Pd−C is comparable to its analogues.[10,12]

To optimize the reaction conditions of $PdCl_2$ with VDCPs **1**, various solvents, reaction temperatures, and employed amounts of $PdCl_2$ were investigated using **1a** as a model reactant. The results of these experiments are shown in Table 1. It was found that THF is the solvent of choice, affording the corresponding dimeric allylpalladium(II) complex **2a** in 68% yield at 50 °C (Table 1, entries 1−6). Raising or lowering the reaction temperature did not improve the yield of **2a** (Table 1, entries 7 and 8). Increasing the employed amounts of $PdCl_2$ produced **2a** in 60% and 53% yield, respectively (Table 1, entries 9 and 10). Under these optimized reaction conditions, as for other reactants **1b**−**e** having different electronic properties of aryl groups, the corresponding dimeric allylpalladium(II) complexes

(7) (a) Shi, M.; Xu, B. *Org. Lett.* **2002**, *4*, 2145. (b) Shi, M.; Chen, Y.; Xua, B.; Tang, J. *Tetrahedron Lett.* **2002**, *43*, 8019. (c) Xu, B.; Shi, M. *Org. Lett.* **2003**, *5*, 1415. (d) Shi, M.; Chen, Y. *J. Fluorine Chem.* **2003**, *122*, 219. (e) Huang, J.-W.; Shi, M. *Tetrahedron Lett.* **2003**, *44*, 9343. (f) Shi, M.; Chen, Y.; Xu, B.; Tang, J. *Green Chem.* **2003**, *5*, 85. (g) Shao, L.-X.; Huang, J.-W.; Shi, M. *Tetrahedron* **2004**, *60*, 11895. (h) Liu, L.-P.; Shi, M. *Chem. Commun.* **2004**, 2878. (i) Wang, B.-Y.; Jiang, R.-S.; Li, J.; Shi, M. *Eur. J. Org. Chem.* **2005**, 4002. (j) Shi, M.; Liu, L.-P.; Tang, J. *J. Am. Chem. Soc.* **2006**, *128*, 7430. (k) Shi, M.; Liu, L.-P.; Tang, J. *Org. Lett.* **2006**, *8*, 4043. (l) Shi, M.; Jiang, M.; Liu, L.-P. *Org. Biomol. Chem* **2007**, *5*, 438. (m) Lu, J.-M.; Shi, M. *Tetrahedron* **2007**, *63*, 7545. (n) Lu, J.-M.; Shi, M. *J. Org. Chem.* **2008**, *73*, 2206. (o) Shi, M.; Wu, L.; Lu, J.-M. *Tetrahedron* **2008**, *64*, 3315. (p) Xu, G.-C.; Liu, L.-P.; Lu, J.-M.; Shi, M. *J. Am. Chem. Soc.* **2005**, *127*, 14552. (q) Zhang, Y.-P.; Lu, J.-M.; Xu, G.-C.; Shi, M. *J. Org. Chem.* **2007**, *72*, 509.

(8) (a) Isagawa, K.; Mizuno, K.; Sugita, H.; Otsuji, Y. *J. Chem. Soc., Perkin Trans 1* **1991**, 2283. (b) Sugita, H.; Mizuno, K.; Mori, T.; Isagawa, K.; Otsuji, Y. *Angew. Chem.* **1991**, *103*, 1000. ; *Angew. Chem. Int. Ed. Engl*. **1991**, *30*, 984.

(9) Rosset, J.-M.; Glenn, M. P.; Cotton, J. D.; Willis, A. C.; Kennard, C. H. L.; Byriel, K. A.; Riches, B. H.; Kitching, W. *Organometallics* **1998**, *17*, 1968–1983.

(10) Lukas, J.; Ramakers-Blom, J. E.; Hewitt, T. G.; De Boer, J. J. *J. Organomet. Chem.* **1972**, *46*, 167.

(11) The crystal data of **2e** have been deposited in the CCDC with number 671929. Empirical formula: $C_{50}H_{40}Br_2Cl_2Pd_2$; formula weight: 1084.34; crystal color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: a = 15.4519(12) Å, b = 7.9145(6) Å, c = 18.5937(15) Å, α = 90°, β = 99.013(2)°, γ = 90°, V = 2245.8(3) Å^3; space group: $P2(1)/c$; Z = 2; D_{calc} = 1.604 g/cm^3; F_{000} = 1072; diffractometer: Rigaku AFC7R; residuals: R, R_w: 0.0568, 0.1132.

(12) (a) Zhang, T.; Wang, W.; Gu, X.; Shi, M. *Organometallics* **2008**, *27*, 753. (b) Liu, Z.; Zhang, T.; Shi, M. *Organometallics* **2008**, *27*, 2668. (c) Larock, R. C.; Song, H.; Kim, S.; Jacobson, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 834.

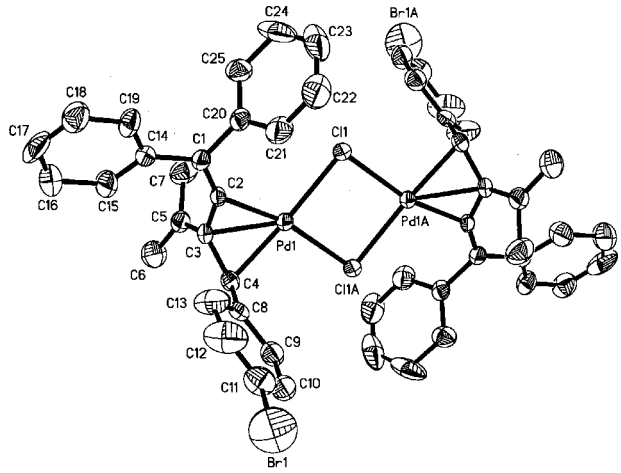
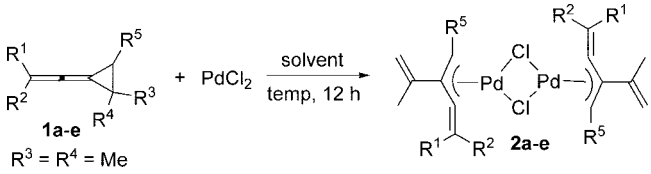


Figure 1. ORTEP drawing of dimeric allylpalladium(II) complex **2e** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): C1−C2 = 1.315(8), C2−C3 = 1.384(8), C3−C4 = 1.415(8), C4−C8 = 1.449(8), Pd1−C2 = 2.034(6), Pd1−C3 = 2.121(6), Pd1−C4 = 2.127(6), C2−Pd1−C3 = 38.8(2), C3−Pd1−C4 = 38.9(2), C2−Pd1−C4 = 69.6(2), C2−C3−C4 = 116.2(6).

Table 1. Optimized Reaction Conditions of $PdCl_2$ with Triaryl-Substituted VDCPs 1a−e



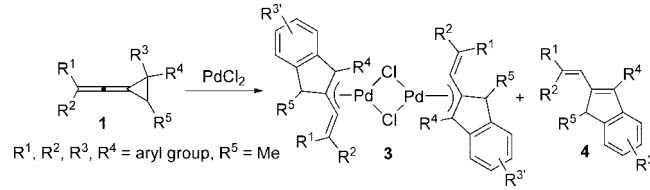
entry[a]	reactant	solvent	$PdCl_2$ (equiv)	temp (°C)	yield (%)[b]
1	**1a**	CH_2Cl_2	1.2	40	**2a**, 48
2	**1a**	CH_3CN	1.2	50	**2a**, 36
3	**1a**	DMF	1.2	50	**2a**, 48
4	**1a**	toluene	1.2	50	**2a**, 58
5	**1a**	DCE	1.2	50	**2a**, 59
6	**1a**	THF	1.2	50	**2a**, 68
7	**1a**	THF	1.2	rt	**2a**, 45
8	**1a**	THF	1.2	65	**2a**, 60
9	**1a**	THF	1.5	50	**2a**, 60
10	**1a**	THF	2.0	50	**2a**, 53
11	**1b**	THF	1.2	50	**2b**, 59
12	**1c**	THF	1.2	50	**2c**, 53
13	**1d**	THF	1.2	50	**2d**, 42
14	**1e**	THF	1.2	50	**2e**, 39

[a] All reactions were carried out using **1** (0.2 mmol) in the presence of the solvent (3 mL) for 12 h. [b] Isolated yields as mixtures of *trans-anti*-**2** and *cis-anti*-**2** (1:1).

2b−**e** were also obtained in moderate yields as mixtures of *trans-anti*-**2** and *cis-anti*-**2**, suggesting that the substituents on the aromatic rings did not have a significant effect on the reaction outcomes (Table 1, entries 11−14).

With the optimized reaction conditions in hand, the reactions of $PdCl_2$ with tetraaryl-substituted VDCPs **1f**−**k** were investigated, and the results of these experiments are summarized in Table 2. A novel type of dimeric allylpalladium(II) complexes **3** was attained in moderate to good yields (Table 2, entries 1−6). On the basis of their ^{13}C NMR spectroscopic data, a *cis*−*trans* isomerization equilibrium also existed in complex **3**. The two isomers were assigned as *trans-syn*-**3** and *cis-syn*-**3** by X-ray diffraction.[9,10] Furthermore, it was found that the electronic properties of aryl groups had a remarkable influence on the reactions of $PdCl_2$ with tetraaryl-substituted VDCPs **1f**−**k**.

Table 2. Reactions of $PdCl_2$ with Tetraaryl-Substituted VDCPs 1f−k



		yield (%)[b]	
entry[a]	**1**	**3**	**4**
1	**1f**	**3a**, 69	trace
2	**1g**	**3b**, 82	trace
3	**1h**	**3c**, 48	**4c**, 41
4	**1i**	**3d**, 79	trace
5	**1j**	**3e**, 70	**4e**, 20
6	**1k**	**3f**, 59	**4f**, 32

[a] All reactions were carried out using **1** (0.2 mmol) and $PdCl_2$ (1.2 equiv) in THF (3 mL) at 50 °C for 3 h. [b] Isolated yields as mixtures of *trans-syn*-**3** and *cis-syn*-**3** (1:1).

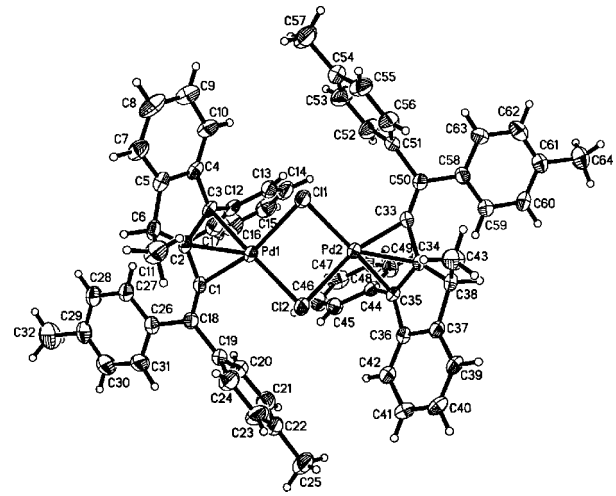
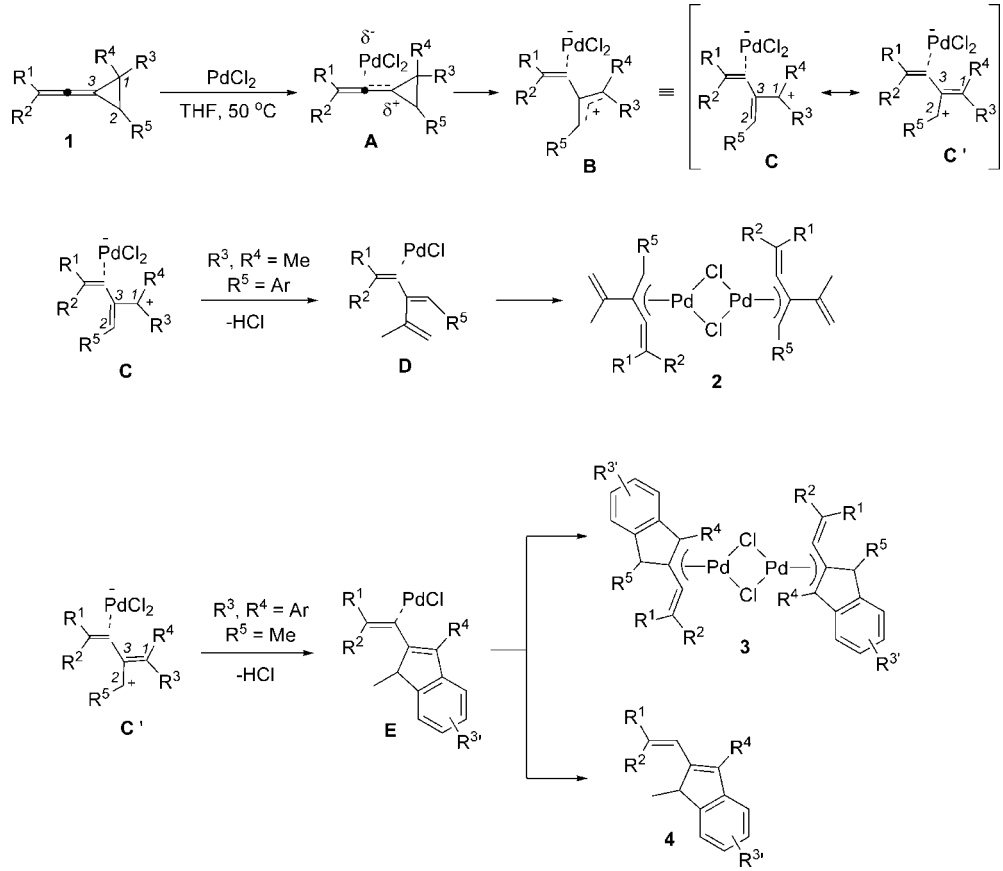


Figure 2. ORTEP drawing of dimeric allylpalladium(II) complex **3c** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (deg): C1−C2 = 1.386(8), C2−C3 = 1.438(8), C1−Pd1 = 2.041(6), C2−Pd1 = 2.130(6), C3−Pd1 = 2.176(6), Pd1−Cl1 = 2.3617(15), Pd1−Cl2 = 2.4466(26), C1−Pd1−C2 = 38.7(2), C2−Pd1−C3 = 39.0(2), C1−Pd1−C3 = 70.4(2), C1−C2−C3 = 119.1(5), Cl1−Pd1−Cl2 = 87.00(6).

Besides that, a novel type of dimeric allylpalladium(II) complexes **3** was obtained; tetraaryl-substituted VDCPs **1h**, **1j**, and **1k**, bearing electron-donating groups on the aromatic rings of R^3 and R^4 as well as R^1 and R^2, could also give other products, **4**, in moderate yields at the same time, which are derived from $PdCl_2$-catalyzed rearrangement of **1** (Table 2, entries 3, 5 and 6).[7o−q] The single crystals of **3c** were grown from a mixed solvent of dichloromethane/petroleum ether (1:4), and its X-ray crystal structure is shown in Figure 2.[13] The palladium(II) center is in a slightly distorted planar geometry, defined by two chloride atoms and one allyl group. The angle of the C(1)−Pd(1)−C(3) plane is 70.4°, smaller than the sum angle of C(1)−Pd(1)−C(2) and C(2)−Pd(1)−C(3), which is 38.7° and 39.0°, respectively. The bond length of Pd−C is comparable to its analogue **2e**.

(13) The crystal data of **3c** have been deposited in the CCDC with number 661676. Empirical formula: $C_{64}H_{54}Cl_2Pd_2$; formula weight: 1106.77; crystal color, habit: colorless, prismatic; crystal system: monoclinic; lattice type: primitive; lattice parameters: a = 16.1405(11) Å, b = 16.7692(11) Å, c = 22.9735(16) Å, α = 90°, β = 104.3370(10)°, γ = 90°, V = 6024.4(7) Å^3; space group: $P2(1)/c$; Z = 4; D_{calc} = 1.220 g/cm^3; F_{000} = 2256; diffractometer: Rigaku AFC7R; residuals: R, R_w: 0.0630, 0.1951.

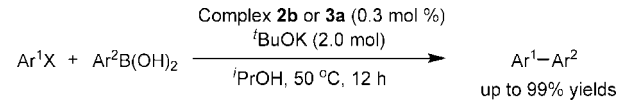
Scheme 5. Plausible Mechanism for $PdCl_2$-Promoted Ring-Opening Reactions of 1a−k



On the basis of the above results, a plausible mechanism for this interesting $PdCl_2$ promoted ring-opening reaction and the formation of dimeric allylpalladium(II) complexes is tentatively outlined in Scheme 5. The coordination of **1** with $PdCl_2$ produces the initial zwitterionic intermediate **A**, from which the corresponding cyclopropyl ring-opened zwitterionic intermediate **B** is formed. The intermediate **B** can exist as intermediate **C** and its resonance-stabilized intermediate **C′**. As for VDCPs **1a−e** (R^3, R^4 = Me, R^5 = aryl group), intermediate **C** is a more reactive species since it bears two alkyl groups R^3 and R^4 at the C-1 position, which can be easily transformed to the corresponding intermediate **D** along with the elimination of HCl. Then, the corresponding dimeric allylpalladium(II) complexes **2a−e** are produced from intermediate **D**. On the other hand, as for VDCPs **1f−k** (R^3, R^4 = aryl group, R^5 = Me), intermediate **C′** is a more reactive species, which easily undergoes intramolecular Friedel−Crafts reaction with the adjacent aromatic group at the C-1 position (R^3 group) to afford the corresponding intermediate **E** along with the elimination of HCl. Intermediate **E** can be transformed to the products **4** by protonation as well as the corresponding dimeric allylpalladium(II) complexes **3a−f**. In the case of VDCPs **1h**, **1j**, and **1k**, the formation of **4c**, **4e**, and **4f** is favored since R^3 and R^4 are electron-rich aromatic groups, which can facilitate the intramolecular Friedel−Crafts reaction.

Catalytic Abilities in Suzuki Coupling Reaction. Allylpalladium complexes as catalysts have been widely applied in many organic reactions such as coupling reactions, polymerization, and allylation.[14] Therein, we turned our interest to investigate the catalytic abilities of these dimeric allylpalladium(II) complexes in Suzuki coupling reactions. As shown in Scheme 6, complexes **2b** and **3a** are effective catalysts in the Suzuki coupling reaction. The details of these results have been summarized in the Supporting Information.

Scheme 6. Allylpalladium(II) Complexes-Catalyzed Suzuki Coupling Reaction



Conclusion

In conclusion, we have developed a novel synthetic method for the preparation of dimeric allylpalladium(II) complexes from the ring-opening reactions of $PdCl_2$ with VDCPs **1**. These dimeric allylpalladium(II) complexes have been isolated and characterized by IR and NMR spectroscopic data and ESI-MS spectroscopy. Moreover, two of them have been characterized by X-ray crystal structure analyses. The catalytic activities of these interesting complexes have been tested in the Suzuki coupling reaction, and we have found that those complexes are quite effective in the Suzuki coupling reaction under mild conditions. Efforts are underway to develop novel synthetic methods for transition metal-promoted ring-opening reactions of VDCPs **1**.

(14) (a) Son, S. U.; Kim, D. H.; Jung, I. G.; Chung, Y. K.; Lee, S.-G.; Chun, S.-H. *J. Polym. Sci., Part A: Polym. Chem* **2002**, *41*, 76. (b) Joo, J.-E.; Lee, K.-Y.; Pham, V.-T.; Ham, W.-H. *Eur. J. Org. Chem.* **2007**, 1586. (c) Terao, J.; Naitoh, Y.; Kuniyasu, H.; Kambe, N. *Chem. Commun.* **2007**, 825. (d) Tilley, S. D.; Francis, M. B. *J. Am. Chem. Soc.* **2006**, *128*, 1080. (e) Thomas, I. W.; Bruce, M. N. *J. Org. Chem.* **1994**, *59*, 5034. (f) Nakamura, H.; Nakamura, K.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4242. (g) Nakamura, H.; Shim, J.-G.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 8113.

Experimental Section

General Procedure for the Synthesis of Dimeric Allylpalladium(II) Complexes 2a−e. A mixture of VDCPs **1** (0.20 mmol) and $PdCl_2$ (0.24 mmol) was stirred in anhydrous THF (3 mL) at 50 °C for 12 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (eluent: CH_2Cl_2 and petroleum ether) to give dimeric allylpalladium(II) complex **2**.

Dimeric Allylpalladium(II) Complex 2a (*trans-anti*-2a and *cis-anti*-2a). Yellow solid. Mp: 194.8−199.5 °C. IR (CH_2Cl_2): ν 3080, 3057, 3025, 1943, 1884, 1801, 1625, 1594, 1577, 1492, 1464, 1443, 1421, 1375, 1264, 1180, 1167, 1098, 1072, 1031, 1000, 913, 840, 824, 693 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.82−2.01 (3H, m, CH_3), 5.09−5.14 (1H, m, CH_2), 5.43−5.47 (1H, m, CH_2), 6.11−6.14 (1H, m, CH), 7.02−7.26 (15H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.8, 21.0, 99.4, 99.6, 117.0, 127.0, 127.2, 127.4, 127.9, 128.0, 128.3, 128.5, 128.7, 130.4, 135.5, 135.6, 136.8, 137.0, 137.5, 139.8, 140.3. MS (ESI) *m/z* (%): 889 $[M - Cl]^+$, 427 $[1/2M - Cl]^+$. Anal. Calcd for $C_{50}H_{42}Cl_2Pd_2$: C, 64.81; H, 4.57. Found: C, 64.40; H, 4.40.

Dimeric Allylpalladium(II) Complex 2b (*trans-anti*-2b and *cis-anti*-2b). Yellow solid. Mp: 115.7−119.4 °C. IR (CH_2Cl_2): ν 3084, 3023, 2920, 2852, 2395, 2294, 1655, 1624, 1608, 1508, 1492, 1459, 1448, 1420, 1375, 1265, 1181, 1108, 1097, 1020, 914, 821, 783, 752, 738, 720 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.87−1.98 (3H, m, CH_3), 2.32 (3H, s, CH_3), 2.40−2.43 (3H, m, CH_3), 5.08−5.12 (1H, m, CH_2), 5.41−5.44 (1H, m, CH_2), 6.05−6.10 (1H, m, CH), 6.98−7.36 (13H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.9, 21.1, 21.4, 21.5, 99.3, 99.8, 116.6, 116.8, 127.0, 127.1, 127.8, 128.0, 128.5, 128.7, 129.2, 130.3, 130.4,134.2, 134.8, 135.0, 135.8, 136.6, 136.7, 137.3, 140.1, 140.7. MS (ESI) *m/z* (%): 957 $[M - Cl]^+$, 461 $[1/2M - Cl]^+$. Anal. Calcd for $C_{54}H_{50}Cl_2Pd_2$: C, 66.00; H, 5.13. Found: C, 66.09; H, 5.11.

Dimeric Allylpalladium(II) Complex 2c (*trans-anti*-2c and *cis-anti*-2c). Yellow solid, Mp: 213.6−219.5 °C. IR (CH_2Cl_2): ν 3076, 3048, 3023, 2909, 2852, 2387, 2298, 1599, 1491, 1455, 1443, 1377, 1263, 1184, 1157, 1095, 1072, 1030, 916, 904, 840, 807, 765 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.81−1.95 (3H, m, CH_3), 2.17−2.21 (3H, m, CH_3), 5.07−5.12 (1H, m, CH_2), 5.40−5.45 (1H, m, CH_2), 6.08−6.11 (1H, m, CH), 6.86−6.92 (2H, m, ArH), 7.12−7.42 (12H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 20.9, 21.0, 21.4, 21.45, 98.8, 99.1, 116.8, 127.0, 127.2, 127.4, 127.9, 128.2, 128.5, 129.5, 129.6, 130.4, 132.5, 132.7, 136.9, 137.2, 138.2, 139.9, 140.4. MS (ESI) *m/z* (%): 917 $[M - Cl]^+$, 441 $[1/2M - Cl]^+$. Anal. Calcd for $C_{52}H_{46}Cl_2Pd_2+1/5CH_2Cl_2$: C, 63.66; H, 4.77. Found: C, 63.67; H, 4.66.

Dimeric Allylpalladium(II) Complex 2d (*trans-anti*-2d and *cis-anti*-2d). Yellow solid, Mp: 210.1−215.9 °C. IR (CH_2Cl_2): ν 3082, 3056, 3022, 2376, 2296, 1958, 1592, 1490, 1443, 1377, 1261, 1175, 1164, 1092, 1072, 1029, 1013, 999, 929, 916, 905, 831, 816, 765, 748 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.85−1.95 (3H, m, CH_3), 5.15−5.18 (1H, m, CH_2), 5.44−5.48 (1H, m, CH_2), 6.05 (1H, s, CH), 7.02−7.32 (14H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.8, 21.0, 99.8, 100.0, 117.3, 127.0, 127.4, 127.7, 128.0, 128.7, 129.0, 130.4, 133.7, 134.1, 136.7, 137.0, 137.5, 139.8, 140.2. MS (ESI) *m/z* (%): 957 $[M - Cl]^+$, 461 $[1/2M - Cl]^+$. Anal. Calcd for $C_{50}H_{40}Cl_4Pd_2+1/6CH_2Cl_2$: C, 59.05; H, 4.00. Found: C, 59.30; H, 3.99.

Dimeric Allylpalladium(II) Complex 2e (*trans-anti*-2e and *cis-anti*-2e). Yellow solid. Mp: 212.5−216.7 °C. IR (CH_2Cl_2): ν 3071, 3010, 2915, 2843, 2368, 2300, 1600, 1585, 1489, 1443, 1377, 1266, 1180, 1165, 1095, 1072, 1029, 1010, 999, 929, 916, 904, 829, 765, 760, 746, 700 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.85−1.99 (3H, m, CH_3), 5.16−5.19 (1H, m, CH_2), 5.45−5.48 (1H, m, CH_2), 6.03 (1H, s, CH), 7.00−7.44 (14H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.8, 21.0, 99.8, 100.0, 117.3, 122.1, 127.0, 127.4, 127.7, 128.0, 128.7, 129.3, 130.4, 132.0, 134.6, 136.7, 136.9, 139.8, 140.2. MS (ESI) *m/z* (%): 1045 $[M - Cl]^+$, 505 $[1/2M - Cl]^+$. Anal. Calcd for $C_{50}H_{40}Br_2Cl_2Pd_2$: C, 55.38; H, 3.72. Found: C, 55.11; H, 3.50.

General Procedure for the Synthesis of Dimeric Allylpalladium(II) Complexes 3a−f and Indene Compounds 4c, 4e, and 4f. A mixture of VDCPs **1** (0.20 mmol) and $PdCl_2$ (0.24 mmol) was stirred in anhydrous THF (3 mL) at 50 °C for 3 h. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (eluent: CH_2Cl_2 and petroleum ether) to give dimeric allylpalladium(II) complexes **3** and products **4**.

Dimeric Allylpalladium(II) Complex 3a (*trans-syn*-3a and *cis-syn*-3a). Yellow solid. Mp: 155.2−158.4 °C. IR (CH_2Cl_2): ν 3055, 3024, 2960, 2922, 2853, 1490, 1470, 1443, 1375, 1335, 1155, 1075, 1028, 971, 771, 745, 731 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.66−1.73 (3H, m, CH_3), 3.60−3.67 (1H, m), 7.07−7.47 (19H, m, ArH), 7.70−7.72 (1H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.0, 44.7, 45.0, 103.9,104.2, 106.4, 106.7, 124.1, 124.5, 127.4, 127.5, 127.8, 128.0, 128.4, 130.3, 130.5, 133.1, 133.3, 137.8, 139.7, 140.1, 142.4, 142.6, 147.6, 154.3. MS (ESI) *m/z* (%): 1013 $[M - Cl]^+$, 489 $[1/2M - Cl]^+$. Anal. Calcd for $C_{60}H_{46}Cl_2Pd_2$: C, 68.58; H, 4.41. Found: C, 68.64; H, 4.31.

Dimeric Allylpalladium(II) Complex 3b (*trans-syn*-3b and *cis-syn*-3b). Yellow solid. Mp: 159.2−163.8 °C. IR (CH_2Cl_2): ν 3067, 2960, 2924, 2854, 1600, 1505, 1469, 1261, 1231, 1156, 1015, 836, 746 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.60−1.76 (3H, m, CH_3), 3.45−3.70 (1H, m), 6.62−7.49 (17H, m, ArH), 7.63−7.75 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 38.7, 39.0, 44.7, 45.1, 104.3, 104.7, 106.4, 106.6, 114.4, 114.5, 114.6, 114.7, 114.9, 115.2, 115.3, 115.4, 115.6, 123.9, 124.1, 124.2, 124.5, 124.6, 127.6, 127.9, 128.0, 128.2, 128.3, 128.4, 128.6, 128.9, 129.0, 129.1, 129.2, 129.3, 129.4, 132.0, 132.2, 132.96, 133.02, 133.1, 133.3, 133.6, 133.7, 134.0, 134.0, 135.9, 142.2, 142.4, 147.4, 147.5, 147.6, 154.3, 154.4, 160.9, 161.0, 161.1, 163.4, 163.4, 163.5. MS (ESI) *m/z* (%): 1085 $[M - Cl]^+$, 525 $[1/2M - Cl]^+$. HRMS (ESI): calcd for $C_{60}H_{42}F_4ClPd_2$ $[M - Cl]^+$ 1085.0981, found 1085.0975.

Dimeric Allylpalladium(II) Complex 3c (*trans-syn*-3c and *cis-syn*-3c). Yellow solid. Mp: 162.4−170.4 °C. IR (CH_2Cl_2): ν 3018, 3058, 2959, 2922, 2853, 1736, 1507, 1469, 1444, 1372, 1332, 1180, 1155, 1071, 1022, 918, 819, 773, 745, 730 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.64−1.72 (3H, m, CH_3), 2.19−2.41 (6H, m, $2CH_3$), 3.52−3.65 (1H, m), 6.80−6.88 (1H, m, ArH), 7.07−7.46 (17H, m, ArH), 7.65−7.74 (1H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.0, 21.1, 21.4, 22.6, 31.6, 31.9, 106.4, 106.8, 124.1, 124.5, 127.4, 127.5, 127.8, 128.1, 128.4, 129.1, 130.2, 130.4, 133.4, 134.8, 136.7, 137.1, 142.6, 142.8, 147.7, 153.7. MS (ESI) *m/z* (%): 1069 $[M - Cl]^+$, 517 $[1/2M - Cl]^+$. Anal. Calcd for $C_{64}H_{54}Cl_2Pd_2$: C, 69.45; H, 4.92. Found: C, 68.68.70; H, 5.01.

Dimeric Allylpalladium(II) Complex 3d (*trans-syn*-3d and *cis-syn*-3d). Yellow solid. Mp: 158.5−163 °C. IR (CH_2Cl_2): ν 3056, 2974, 2921, 2379, 1874, 1713, 1613, 1602, 1509, 1489, 1477, 1441, 1369, 1336, 1292, 1278, 1244, 1224, 1160, 1137, 1065, 1027, 950, 905, 872, 821, 807, 775, 766, 734 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.69−1.79 (3H, m, CH_3), 3.49−3.72 (1H, m), 6.70−7.41 (17H, m, ArH), 7.49−7.70 (1H, m). ^{13}C NMR (75 MHz, DMSO): δ 16.2, 49.4, 113.1 (d, J_{C-F} = 23.0 Hz), 114.3 (d, J_{C-F} = 21.6 Hz), 120.0, 120.1, 125.0, 126.6, 126.8, 127.0, 129.0, 130.3 (d, J_{C-F} = 8.3 Hz), 131.2, 131.9, 139.4, 140.5, 141.4, 142.9, 145.7, 151.7 (d, J_{C-F} = 8.6 Hz), 153.7, 160.5 (d, J_{C-F} = 240.5 Hz), 160.7 (d, J_{C-F} = 241.4 Hz). MS (ESI) *m/z* (%): 1085 $[M - Cl]^+$, 525 $[1/2M - Cl]^+$. HRMS (ESI): calcd for $C_{60}H_{42}F_4ClPd_2$ $[M - Cl]^+$ 1085.0981, found 1085.0975.

Dimeric Allylpalladium(II) Complex 3e (*trans-syn*-3e and *cis-syn*-3e). Yellow solid. Mp: 170.5−174.5 °C. IR (CH_2Cl_2): ν 3024, 2959, 2921, 2857, 1606, 1490, 1444, 1331, 1185, 1073, 820, 766, 729, 696 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 1.63−1.69 (3H, m, CH_3), 2.21−2.48 (6H, m, $2CH_3$), 3.46−3.67

(1H, m), 6.78−7.47 (17H, m, ArH), 7.57−7.64 (1H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.0, 19.2, 21.4, 21.9, 44.2, 44.8, 104.9, 106.1, 124.3, 124.7, 124.9, 127.2, 127.38, 127.45, 128.2, 128.4, 129.1, 130.3, 130.5, 137.3, 137.8, 137.9, 139.8, 140.1, 148.2, 154.2. MS (ESI) *m*/*z* (%): 1069 $[M - Cl]^+$, 517 $[1/2M - Cl]^+$. Anal. Calcd for $C_{64}H_{54}Cl_2Pd_2$: C, 69.45; H, 4.92. Found: C, 69.07; H, 4.77.

Dimeric Allylpalladium(II) Complex 3f (*trans-syn*-3f and *cis-syn*-3f). Yellow solid. Mp: 157.7−160.6 °C. IR (CH_2Cl_2): ν 2959, 2924, 2844, 1605, 1513, 1489, 1443, 1337, 1276, 1256, 1178, 1031, 831, 764, 697 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.604−1.71 (3H, m, CH_3), 3.46−3.63 (1H, m), 3.80−3.91 (6H, m, $2OCH_3$), 6.64−7.41 (17H, m, Ar), 7.56−7.67 (1H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.1, 19.2, 44.3, 44.7, 55.2, 55.5, 105.1, 109.7, 110.3, 113.3, 113.9, 125.5, 127.1, 127.3, 128.4, 129.6, 130.3, 130.5, 135.4, 138.0, 139.7, 140.2, 150.1, 154.0, 159.1, 159.9. MS (ESI) *m*/*z* (%): 549 $[1/2M - Cl]^+$. Anal. Calcd for $C_{64}H_{54}Cl_2O_4Pd_2+1/3CH_2Cl_2$: C, 63.28; H, 4.54. Found: C, 63.43; H, 4.23.

2-(2,2-Di-*p*-tolylvinyl)-1-methyl-3-phenyl-1*H*-indene (4c). Colorless liquid. IR (CH_2Cl_2): ν 3056, 3022, 2962, 2922, 2867, 1602, 1509, 1443, 1265, 1020, 818, 777 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.96 (3H, d, J = 7.5 Hz, CH_3), 2.25 (3H, s, CH_3), 2.33 (3H, s, CH_3), 3.05 (1H, q, J = 7.5 Hz), 6.66 (1H, m), 6.97−7.17 (11H, m, ArH), 7.25−7.29 (m, 2H, ArH), 7.33−7.38 (m, 2H, ArH), 7.44−7.47 (2H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.5, 21.1, 21.4, 43.8, 120.0, 122.0, 122.7, 125.2, 126.2, 127.4, 127.8, 128.3, 128.7, 128.8, 129.7, 131.0, 135.2, 137.2, 137.3, 137.9, 140.8, 142.2, 143.6, 143.7, 147.1, 149.2. MS (EI) *m*/*z* (%): 412 (100) $[M^+]$. HRMS (EI): calcd for $C_{32}H_{28}$ (M^+) 412.2191, found 412.2190.

2-(2,2-Diphenylvinyl)-1,6-dimethyl-3-*p*-tolyl-1*H*-indene (4e). Colorless liquid. IR (CH_2Cl_2): ν 3061, 2963, 2927, 2859, 1600, 1507, 1443, 1224, 1156, 1014, 834, 777 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 0.95 (3H, d, J = 7.2 Hz, CH_3), 2.28 (3H, s, CH_3), 2.33 (3H, s, CH_3), 2.95 (1H, q, J = 7.2 Hz), 6.71 (1H, d, J = 1.2 Hz), 6.97−7.02 (2H, m, ArH), 7.15−7.36 (15H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.6, 21.3, 21.5, 43.5, 119.9, 123.4, 123.7, 127.0, 127.2, 127.6, 127.8, 128.0, 128.1, 129.0, 129.2, 129.6, 130.0, 131.2, 132.2, 135.2, 137.2, 140.9, 142.80, 142.82, 143.4, 145.4, 149.5. MS (EI) *m*/*z* (%): 412 (100) $[M^+]$, 305 (35). HRMS (EI): calcd for $C_{32}H_{28}$ (M^+) 412.2191, found 412.2198.

2-(2,2-Diphenylvinyl)-6-methoxy-3-(4-methoxyphenyl)-1-methyl-1*H*-indene (4f). Green solid. Mp: 181.2−181.3 °C. IR (CH_2Cl_2): ν 3050, 3025, 2927, 2858, 1605, 1502, 1450, 1250, 1171, 1034, 835, 765 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 1.02 (3H, d, J = 7.2 Hz, CH_3), 3.02 (1H, q, J = 7.2 Hz), 3.79 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 6.76−6.80 (3H, m, ArH), 6.96−6.99 (2H, m, ArH), 7.23−7.26 (6H, m, ArH), 7.34−7.37 (5H, m, ArH), 7.44−7.48 (2H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.7, 43.6, 55.2, 55.5, 109.2, 111.8, 113.8, 120.6, 123.4, 127.1, 127.50, 127.53, 127.7, 128.0, 128.1, 130.9, 131.2, 136.6, 141.0, 142.1, 142.3, 143.5, 144.0, 151.2, 158.5, 159.0. MS (EI) *m*/*z* (%): 444 (100) $[M^+]$. Anal. Calcd for $C_{32}H_{28}O_2$: C, 86.45; H, 6.35. Found: C, 86.54; H, 6.28.

Acknowledgment. Financial support from the Shanghai Municipal Committee of Science and Technology (06XD14005 and 08dj1400100-2), National Basic Research Program of China (973-2009CB825300), and the National Natural Science Foundation of China (20872162, 20672127, 20732008, and 20702013) is greatly acknowledged.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM801117G