Carbon−Carbon Bond Formation by Electrophilic Addition at the Central Carbon of the μ-η^3-Allenyl/Propargyl Ligand on the Pd−Pd Bond

Sensuke Ogoshi,* Takuma Nishida, Ken Tsutsumi, Motohiro Ooi, Tsutomu Shinagawa, Tenpei Akasaka, Mariko Yamane, and Hideo Kurosawa*

Contribution from the Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

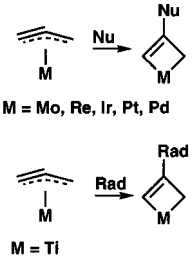
Received October 23, 2000

Abstract: The μ-η^3-allenyl/propargyldipalladium complexes were synthesized by the reaction of the corresponding η^1-allenyl- or η^1-propargylpalladium complexes with $Pd_2(dba)_3$. The X-ray diffraction analysis indicates that the dinuclear complex has a unique structure, in which two palladium, three carbon, two phosphorus, and one halogen atoms are in the same plane. These dinuclear complexes react with electrophiles, such as HCl or AcCl, at the central carbon of the μ-η^3-allenyl/propargyl ligand to give the μ-η^3-vinylcarbenedipalladium complexes. Intramolecular reaction proceeded smoothly to give cyclization products quantitatively. Addition of a catalytic amount of a palladium(0) complex dramatically accelerated the carbon−carbon bond formation. The MO calculations on the μ-η^3-allenyl/propargyl complexes indicated that the reaction proceeds via orbital control.

Introduction

The chemistry of allenyl/propargyl transition metal complexes had been considered as a simple extension of the chemistry of allyl transition metal complex. However, recent studies on η^3-allenyl/propargyl transition metal complexes reveal unique structures and reactivity patterns different from those of η^3-allyl complexes.[1−3] The characteristic structural feature of the η^3-allenyl/propargyl ligand is that the center metal is on the plane defined by the three carbons.[3] The reactivity of the η^3-allenyl/propargyl ligand can be summarized as "exclusive enhancement of the reactivity toward nucleophiles at the central carbon when compared to that of the η^3-allyl transition metal complexes". In fact, the reaction of the η^3-allenyl/propargyl complexes with carbon nucleophiles gives metalacyclobutene complexes (Scheme 1), which is the key step in the palladium-catalyzed reaction of propargyl electrophiles with carbon nucleophiles.[3e,n] Recently, the addition of alkyl radicals to η^3-allenyl/propargyltitanium(III) complexes to form carbon−carbon bonds has been reported as well.[3p] Thus, the formation of carbon−carbon bonds by electrophilic addition to the η^3-allenyl/propargyl ligand is the remaining challenging transformation, which, however, has not yet been realized. Moreover, MO calculations on mononuclear cationic η^3-allenyl/propargylplatinum complexes suggest that this step is disfavouerd.[4]

Scheme 1



Our previous study on the μ-η^3-allyldipalladium complexes including MO calculations suggested much more electron-rich nature for the allyl ligand bridging the metal−metal bond than that in mononuclear complexes owing to a significantly larger contribution of η^3-allyl π^* orbital in HOMO in the dinuclear than mononuclear complexes.[5] Although the μ-η^3-allyl ligand was not reactive enough toward electrophiles, the reactivity of the μ-η^3-allenyl/propargyl ligand at the central carbon is

(1) Reviews: (a) Chen, J.-T. *Coord. Chem. Rev.* **1999**, *190*−*192*, 1143. (b) Kurosawa, H.; Ogoshi, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 973. (c) Doherty, S.; Corrigan, J. F.; Carty, A. J.; Sappa, E. *Adv. Organomet. Chem.* **1995**, *37*, 39. (d) Wojcicki, A. *New J. Chem.* **1994**, *18*, 61.

(2) For a review of reactions proceeding via η^3-propargyl intermediates, see: Tsuji, J.; Mandai, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2589.

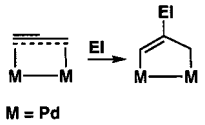
(3) Isolated η^3-propargyl complexes: (a) Mo: Krivykh, V. V.; Taits, E. S.; Petrovskii, P. V.; Struchkov, Y. T.; Yanovski, A. I. *Mendeleev Commun.* **1991**, 103 (b) Ru: Wakatsuki, Y.; Yamazaki, H.; Maruyama, Y.; Shimizu, I. *J. Chem. Soc., Chem. Commun*. **1991**, 261. (c) Re: Casey, C. P.; Yi, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 6597. (d) Re: Casey, C. P.; Selmeczy, A. D.; Nash, J. R.; Yi, C. S.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1996**, *118*, 6698. (e) Re: Casey, C. P.; Nash, J. R.; Yi, C. S.; Selmeczy, A. D.; Chung, S.; Powell, D. R.; Hayashi, R. K. *J. Am. Chem. Soc.* **1998**, *120*, 722. (f) Zr: Blosser, P. W.; Gallucci, J. C.; Wojcicki, A. *J. Am. Chem. Soc.* **1993**, *115*, 2994. (g) Zr: Rodriguez, G.; Bazan, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 343. (h) Pt: Huang, T.-M.; Chen, J.-T.; Lee, G.-H.; Wang, Y. *J. Am. Chem. Soc*. **1993**, *115*, 1170. (i) Pt: Blosser, P. W.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1993. (j) Pt: Stang, P. J.; Crittell, C. M.; Arif, A. M. *Organometallics* **1993**, *12*, 4799. (k) Pd: Ogoshi, S.; Tsutsumi, K.; Kurosawa, H. *J. Organomet. Chem.* **1995**, *493*, C19. (l) Pd: Baize, M. W.; Blosser, P. W.; Plantevin, V.; Schimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1996**, *15*, 164. (m) Tsutsumi, K.; Ogoshi, S.; Nishiguchi, S.; Kurosawa, H. *J. Am. Chem. Soc*. **1998**, *120*, 1938. (n) Tsutsumi, K.; Kawase, T.; Kakiuchi, K.; Ogoshi, S.; Okada, Y.; Kurosawa, H. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2687. (o) Mo: Carfagna, C.; Deeth, R. J.; Green, M.; Mahon, M. F.; Mclnnes, J. M.; Pellegrini, S.; Woolhouse, C. M. *J. Chem. Soc., Dalton Trans*. **1995**, 3975. (p) Ti: Ogoshi, S.; Stryker, J. M. *J. Am. Chem. Soc*. **1998**, *120*, 3514.

(4) Graham, J. P.; Wojcicki, A.; Bursten, B. E. *Organometallics* **1999**, *18*, 837.

10.1021/ja003754m CCC: $20.00
Published on Web 03/16/2001

expected to be much more enhanced than that in the μ-η^3-allyl ligand, if the different reactivity of the two ligands in the mononuclear complexes is taken into account. In such a case, the carbon−carbon bond formation would be attained by the attack of carbon electrophiles at the central carbon of the μ-η^3-allenyl/propargyl ligand (Scheme 2).

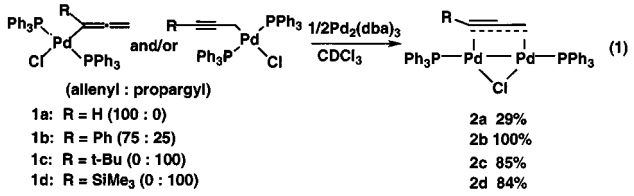
Scheme 2



Here, we report the synthesis of the μ-η^3-allenyl/propargylpalladium complexes and the facile carbon−carbon bond formation by the electrophilic addition at the central carbon to give μ-η^3-vinylcarbenedipalladium complexes.[6] The unique acceleration of the reaction by the addition of a catalytic amount of palladium(0) complexes is also described. MO analysis of the μ-η^3-allenyl/propargyldipalladium complexes is also discussed.

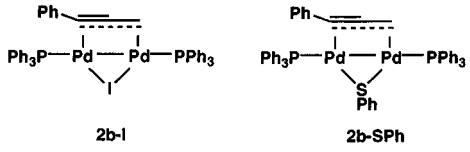
Results and Discussion

Synthesis and Structure of μ-η^3-Allenyl/Propargyldipalladium Complexes. The reaction of η^1-allenyl or η^1-propargyl bistriphenylphosphine palladium chloride (**1a**−**d**) with $Pd_2(dba)_3$ in $CDCl_3$ at room temperature gave μ-η^3-allenyl/propargyldipalladium complexes (**2a**−**d**) (eq 1). The fragmentation of **2a**−**d**

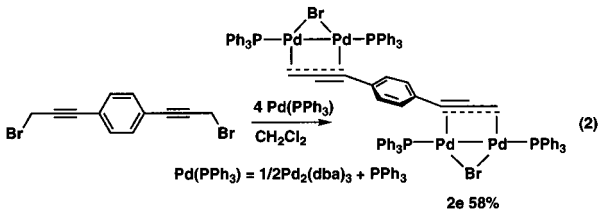


to **1a**−**d** and $Pd(PPh_3)_2$ was realized by the addition of PPh_3 to these dinuclear complexes. The analogous reaction of **1b** with $Pd_2(dba)_3$ in the presence of NaI and NaSPh gave the iodide and phenyl thiolate analogues, respectively (**2b**-I 63%, **2b**-SPh 78%) (Scheme 3). The dinuclear complexes **2a**−**d** can also be prepared by the reaction of propargyl chlorides RC≡CCH_2Cl

Scheme 3



(R = H, Ph, ^{t}Bu, $SiMe_3$) with 2 equiv of $Pd(PPh_3)$ generated in situ from $Pd_2(dba)_3$ and PPh_3 (Pd/PPh_3 = 1/1). The reaction of 1,4-di-(3-bromopropynyl)benzene[7] with 4 equiv of $Pd(PPh_3)$ also gave bisdinuclear complex (**2e**) (eq 2).[8]



The P−P coupling constants for these dinuclear complexes (80−100 Hz) are extremely large for a $^4J_{PP}$ value, which indicates the four atoms P−Pd−Pd−P are arrayed almost in a straight line. In fact, the X-ray diffraction analyses on **2a** and **2b**-SPh show unique structures, which are consistent with the large P−P coupling constant (Figure 1 and 2 and Table 1). In both **2a** and **2b**-SPh, the μ-η^3-allenyl/propargyl group is almost linear and parallels the Pd−Pd bond. Thus, the Pd1−C1 distance is almost equal to the Pd2−C3 distance. Moreover, the Pd−Pd distance is almost equal to the C1−C3 distance. Two palladiums, μ-η^3-allenyl/propargyl carbons, chlorine (**2a**) or sulfur (**2b**-SPh) atom, and two phosphorus atoms are located on the same plane.

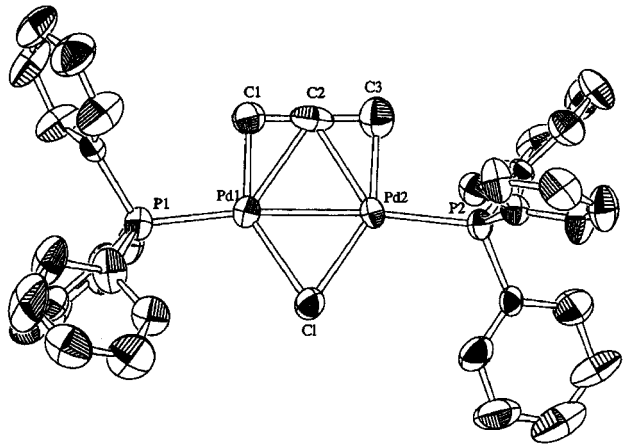


Figure 1. Molecular structure of **2a**.

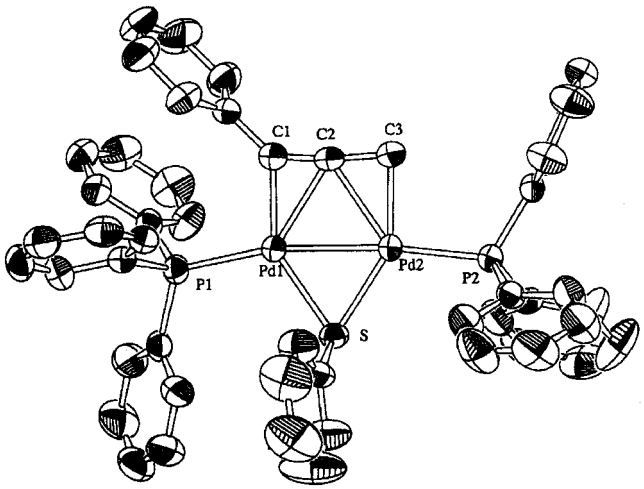


Figure 2. Molecular structure of **2b**-SPh.

Reaction of μ-η^3-Allenyl/Propargyldipalladium Complexes with HCl. The dinuclear complexes **2b** and **2b**-I reacted with HCl (generated from a reaction of H_2O with Me_3SiCl in situ)

(5) (a) Kurosawa, H.; Hirako, K.; Natsume, S.; Ogoshi, S.; Kanehisa, N.; Kai, Y.; Sakaki, S.; Takeuchi, K. *Organometallics* **1996**, *15*, 2089. (b) Sakaki, S.; Takeuchi, K.; Sugimoto, M.; Kurosawa, H. *Organometallics* **1997**, *16*, 2995.

(6) Portions of this work have been communicated previously. (a) Ogoshi, S.; Tsutsumi, K.; Ooi, M.; Kurosawa, H. *J. Am. Chem. Soc.* **1995**, *117*, 10415. (b) Ogoshi, S.; Tsutsumi, K.; Shinagawa, T.; Kakiuchi, K.; Kurosawa, H. *Chem. Lett.* **1999**, 123.

(7) Hopf, H.; Jones, P. G.; Bubenitschek, P.; Werner, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2367.

(8) Although the reaction proceeded quantitatively, the isolated yield is moderate due to poor solubility of **2e**.

Table 1. Relevant Bond Lenghs (Å) and Angles (deg)

	2a	**2a**-SPh	B3LYP
Pd−Pd	2.642(2)	2.6291(4)	2.65
Pd1−C1	2.06(2)	2.066(3)	2.03
Pd1−C2	2.47(3)	2.361(3)	2.53
Pd2−C2	2.42(3)	2.431(3)	2.46
Pd2−C3	2.08(2)	2.096(3)	2.13
C1−C2	1.33(3)	1.257(4)	1.27
C2−C3	1.36(3)	1.406(5)	1.39
Pd1-X	2.405(6)	2.361(8)	2.55
Pd2-X	2.397(6)	2.3679(9)	2.54
Pd1−P2	2.252(6)	2.2595(9)	2.41
Pd2−P2	2.282(6)	2.2626(9)	2.42
P1−Pd1−Pd2	173.0(2)	167.98(3)	171.8
P2−Pd2−Pd1	173.8(1)	173.39(3)	167.3
C1−C2−C3	178(2)	173.2(3)	183.3

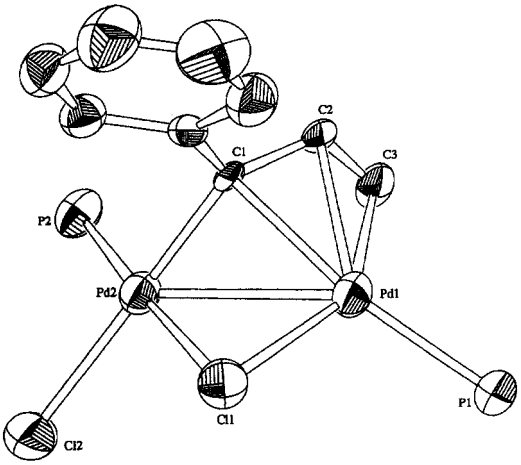
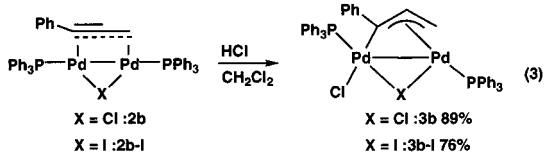
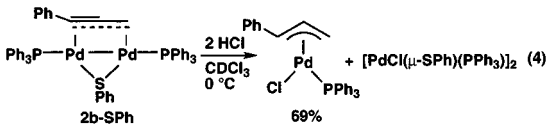


Figure 3. Molecular structure of **3b**.

to give unusual dinuclear complexes **3b** (89%) and **3b**-I (76%) (eq 3). The structure of **3b** was determined by X-ray diffraction

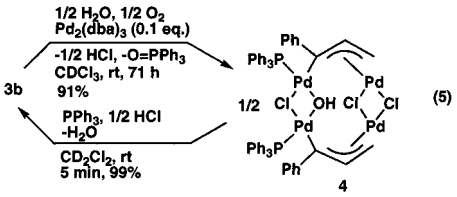


(Figure 3). The structure reveals the first example of a μ-vinylcarbene complex of palladium, which is similar to μ-vinylcarbene complexes of other transition metals.[9,10] On the other hand, the reaction of **3b**-SPh with 2 equiv of HCl gave (η^3-PhCHCHCH$_2$)PdCl(PPh$_3$) in 69% yield, which is a formal hydrogenation product of starting complex **1b** (eq 4). The Pd-



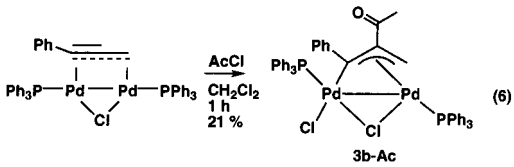
(II) complex [PdCl(μ-SPh)(PPh$_3$)]$_2$ was identified by comparison of ^{31}P NMR spectra of the reaction mixture with that of an authentic sample,[11] which indicated that one palladium of the dinuclear complex was a reductant in the reaction. The reaction employing 1 equiv of HCl gave 28% of Pd(η^3-PhCHCHCH$_2$)-Cl(PPh$_3$) with 0.5 equiv of **2b**-SPh remaining unchanged, while **3b** and **3b**-I were stable to the attack of HCl.

In the presence of a catalytic amount of Pd$_2$(dba)$_3$ (dba = dibenzylideneacetone), the complex **3b** reacted with H$_2$O and O$_2$ to give hydroxo-bridged μ-η^3-vinylcarbenedipalladium dimer (**4**) in an excellent yield (eq 5). The structure of the complex **4**



was determined by X-ray diffraction analysis. This complex has a unique structure in which one of four bridging ligands is OH group. The coordination mode and geometry of the μ-η^3-vinylcarbene group in **4** are quite similar to those in **3b**. However, the distance between two Pd atoms bridged by the vinylcarbene ligand in **4** (3.17 Å) is considerably longer than that in **3b** (2.87 Å). The electron count on each Pd of **3b** and **4** should be the same as that in A-frame complex [Pd$_2$(μ-CO)-Cl$_2$(dmpm)$_2$], which has a nonbonded Pd−Pd separation (3.17 Å).[12] The short Pd−Pd distance in **3b** possibly reflected the presence of the Cl bridge over the Pd−Pd opposite to the vinylcarbene bridge. The transformation shown in eq 5 did not work well without Pd$_2$(dba)$_3$, which might have a role of oxidizing PPh$_3$ to O=PPh$_3$ and was confirmed by ^{31}P NMR spectra. Treatment of **4** with PPh$_3$ and HCl regenerated the dinuclear complex **3b** quantitatively.

Reaction of μ-η^3-Allenyl/Propargyldipalladium with Carbon Electrophiles. The reaction of dinuclear complex **2b** with acetyl chloride also gave μ-vinylcarbene complex (**3b**-Ac), where the intriguing electrophilic carbon−carbon bond formation occurred at the central carbon (eq 6). On the other hand, in both mononuclear complexes[3] including palladium and dinuclear complexes of other metals,[13] the η^3-allenyl/propargyl group is prone to be attacked by a nucleophile at the central carbon.



Although the other electrophiles, such as PhC≡CCH$_2$Cl and PhCH$_2$Cl, did not undergo electrophilic addition to the central carbon of **2b**, the corresponding intramolecular reaction proceeded. Thus, the reaction of 1,2-di(3-chloropropynyl)benzene[7] with 2 equiv of Pd(PPh$_3$) generated in situ gave the cyclized μ-η^3-vinylcarbene complex (**3f**) possibly by very rapid intramolecular electrophilic addition to the central carbon of the intermediate dinuclear complex (**2f**) (eq 7).[14] Even with 4 equiv

(9) A review on palladium carbene complexes: Maitlis, P. M.; Espinet, P.; Russell, M. J. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 6, pp 292−299.

(10) Mitsudo, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1525 and references therein.

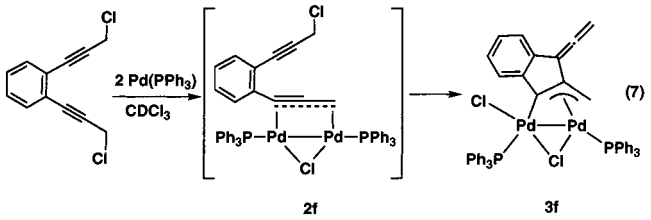
(11) Boschi, T.; Crociani, B.; Toniolo, L.; Belluco, V. *Inorg. Chem.* **1970**, *9*, 532. Jain, V. K. *Inorg. Chim. Acta* **1987**, *133*, 251.

(12) Kullberg, M. L.; Kubiak, C. P. *Organometallics* **1984**, *3*, 632.

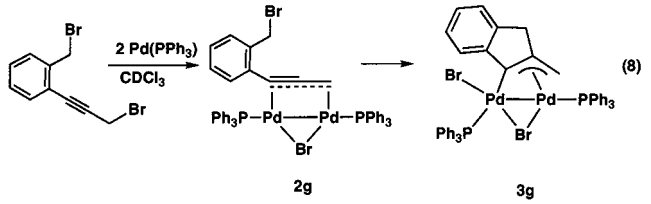
(13) Carleton, N.; Corrigan, J. F.; Doherty, S.; Pixner, R.; Sun, Y.; Taylor, N. J.; Carty, A. J. *Organometallics* **1994**, *13*, 4179.

(14) The corresponding bromide compound, 1,2-di(3-bromopropynyl)-benzene, underwent a unique radical coupling reaction in the presence of Ti(III) complex and SmI$_2$.[3p]

of $Pd(PPh_3)$, 1,2-di(3-chloropropynyl)benzene gave no spectral evidence for tetranuclear complex (an ortho isomer of **2e**) but only the cyclization proceeded.



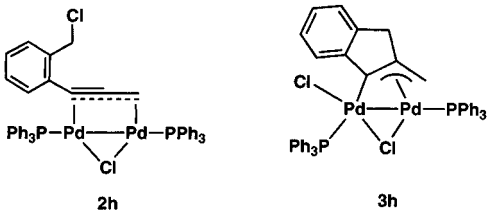
The reaction of the 1-bromomethyl-2-(3-bromopropynyl)-benzene with 2 equiv of $Pd(PPh_3)$ generated in situ from $Pd_2(dba)_3$ and PPh_3 gave the dinuclear complex (**2g**) quantitatively, which subsequently underwent slow cyclization to give μ-η^3-vinylcarbene complex (**3g**), as confirmed by ^1H NMR in $CDCl_3$



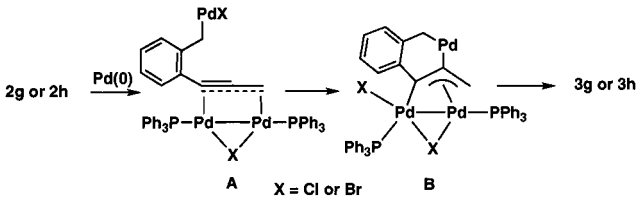
(eq 8). On the other hand, the reaction of dinuclear complex **2b**-Br with benzyl bromide did not occur at all, which suggests that the intramolecular reaction is much more advantageous to this electrophilic addition. The isolation of the dinuclear complex **2g** by column chromatography (silica, alumina) failed due to the occurrence of the quantitative cyclization on column chromatography to give **3g**. Reprecipitation from the benzene/hexane solution of the initial reaction mixture gave a sample of **2g** contaminated by a trace amount of **3g**. This sample was used without further purification for kinetic analysis of the cyclization of **2g**, since it was confirmed that further addition of **3g** to the above sample did not affect the rate of cyclization at all; apparently the reaction rate is insensitive to the amount of **3g** present. The rate of cyclization of the dinuclear complex **2g** to **3g** was determined at 25 °C in $CDCl_3$ and C_6D_6 (k_{obs} = 2.1×10^{-5} s^{-1} and 5.1×10^{-6} s^{-1}, respectively). The rate is first order in the concentration of **2g** and no autocatalytic behavior was observed. These observations indicate that this electrophilic addition proceeded intramolecularly and is not catalyzed by Pd(0) species dissociated from dinuclear complex (see next section). A similar benzyl chloride analogue (**2h**) underwent no cyclization under the same condition, which would be attributed to the lower electrophilicity of benzyl chloride than that of benzyl bromide (Scheme 4).

Palladium-Catalyzed Intramolecular Reaction. Although an isolated sample of **2h** did not undergo spontaneous cyclization at all, generation of **2h** from 1-chloromethyl-2-(3-chloropropynyl)benzene and 2 equiv of $Pd(PPh_3)$ was always accompanied by the formation of a small amount of the cyclization product **3h**, as confirmed by the ^1H NMR and ^{31}P NMR spectrum. We presumed that the cyclization would have occurred in the early stage of the dinuclear complex forming reaction, where the inevitable presence of a large amount of palladium(0) species may have some role in facilitating the cyclization. In fact, we found that the addition of a catalytic amount of $Pd_2(dba)_3$ to **2h** caused smooth cyclization to occur in 1.5 h to give **3h** in 90% yield. The cyclization of **2g** also was significantly accelerated by the addition of the catalytic amount of palladium(0) complexes in C_6D_6 (k_{obs} = 5×10^{-6} s^{-1} for no catalyst, k_{obs} = 1.0×10^{-3} s^{-1} for 10 mol % of $Pd(PPh_3)_4$, $k_{obs} \gg 1.0 \times 10^{-3}$ s^{-1} for 5 mol % of $Pd_2(dba)_3$). The reaction would proceed as follows (Scheme 5). The oxidative addition of benzyl halide moiety of **2** to palladium(0) would generate the intermediate **A** followed by the electrophilic attack of the benzylpalladium moiety at the central carbon to give palladacyclohexene **B** accompanied by the halogen migration. The reductive elimination of **B** then gives rise to the cyclization complex **3**. In the electrophilic attack, the μ-η^3-allenyl/propargyl dinuclear moiety acts as a novel alkylation reagent.

Scheme 4



Scheme 5



MO Calculation on the μ-η^3-Allenyl/Propargyldipalladium Complexes. To understand why μ-η^3-alleny/propargyl ligand reacts with electrophiles, the B3LYP geometry optimization and the ab initio MO/MP2 calculation were performed on the model complex $Pd_2(\mu$-η^3-$CHCCH_2)(\mu$-$Cl)(PH_3)_2$. The optimized geometry of this model is also given in Table 1. Although calculated Pd−Cl and Pd−P distances are longer than the experimental ones, the other calculated distances agree with experimental values. The calculations also showed that all atoms except for some hydrogen atoms are on the same plane. From these results, it is reasonably concluded that the B3LYP optimization can reproduce well the characteristic features of the bonding interaction between (μ-η^3-$CHCCH_2$) and $Pd_2(\mu$-$Cl)(PH_3)_2$. The electron distribution in $Pd_2(\mu$-η^3-$CHCCH_2)(\mu$-$Cl)(PH_3)_2$ shows that all the allenyl/propargyl carbons are negatively charged, but the central carbon (C2, −0.10088) is less negative compared with the terminal carbons (C1, −0.37892; C3, −0.61412). Thus, the regioselectivity of the electrophilic addition would not have been governed by the atomic charge, but perhaps by the molecular orbital coefficients (Figure 4). In

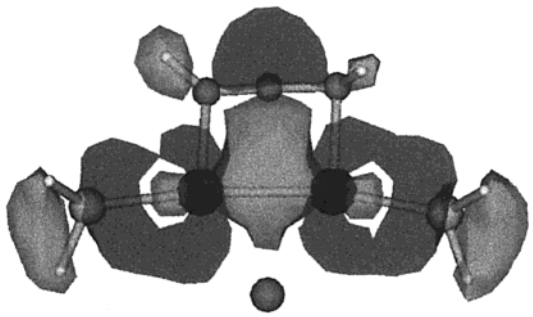
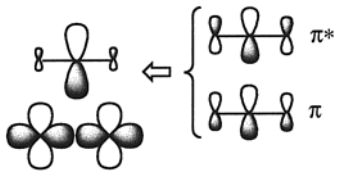


Figure 4.

fact, the HOMO mainly consists of an antibonding combination between two filled orbitals, η^3-allenyl/propargyl π and (dσ +

Scheme 6



dσ), into which the η^3-allenyl/propargyl π^* orbital mixes, in an antibonding way with ligand π and a bonding way with dσ + dσ, giving rise to a big lobe at the p orbital of the central carbon (Scheme 6). This would force electrophiles to add to the central carbon.

Conclusion

The novel μ-η^3-allenyl/propargyldipalladium complexes were synthesized for the first time and a unique structure was determined by the X-ray diffraction analysis. The reaction with electrophiles occurred at the central carbon of the μ-η^3-allenyl/propargyl ligand, which was the remaining challenging transformation of the allenyl or propargyl ligand. The electrophilic addition was catalyzed by Pd(0) complexes. MO calculations on the μ-η^3-allenyl/propargyl ligand suggested that this interesting reactivity is governed not by charge control but by orbital control.

Experimental Section

General Procedures. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on JEOL JNM-GSX 270 (270 MHz), JEOL JNM-GSX 400 (400 MHz), and Bruker AM600 (600 MHz) spectrometers as solutions in $CDCl_3$ or C_6D_6 with a reference to $SiMe_4$ (δ 0.00) and H_3PO_4 (δ 0.00). IR spectra were recorded on a Hitachi 270-50 infrared spectrophotometer as KBr pellets. Melting points were determined on a Kyoto Keiryoki Seisakujo micro melting point apparatus and are uncorrected.

Typical procedure for reaction of 1b with $Pd_2(dba)_3$·$CHCl_3$: Under an argon atmosphere, 120.0 mg (0.154 mmol) of **1b** and 124.0 mg (0.12 mmol) of $Pd_2(dba)_3$·$CHCl_3$ were dissolved in 3.0 mL of CH_2Cl_2. After 30 min, the reaction mixture was separated by column (silica gel, 100−200 mesh, CH_2Cl_2) and the first yellow-orange eluent was concentrated to give **2b** (88.0 mg) in 65% isolated yield.

(μ-η^3-HCCCH$_2$)(μ-Cl)Pd$_2$(PPh$_3$)$_2$ (2a): yield 12%; mp 129−131 °C dec; IR (KBr) 2180 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.18 (ddd, J_{HH} = 2.3 Hz, J_{HP} = 6.4, 0.7 Hz, 2H), 5.64 (tdd, J_{HH} = 2.3 Hz, J_{HP} = 32.1, 1.0 Hz, 1H), 7.40 (m, 20H), 7.65 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 11.49 (s, CCH_2), 79.23 (t, J_{CP} = 5.7 Hz, CCH_2), 108.49 (d, J_{CP} = 4.9 Hz, HCC); ^{31}P NMR δ 27.4 (d, J_{PP} = 98.2 Hz), 22.7 (d, J_{PP} = 98.2 Hz). Anal. Calcd for $C_{39}H_{33}P_2Pd_2Cl$: C, 57.69; H, 4.10. Found: C, 57.52; H, 4.32. Crystal data for **2a**·THF: $C_{43}H_{41}ClP_2Pd_2O$, triclinic, $P1$(No. 1); a = 10.090(2) Å, b = 11.768(2) Å, c = 8.747(1) Å, α = 94.16(1)°, β = 108.35(1)°, γ = 78.19(1)°, Z = 1, D_{calc} = 1.521 g/cm^3. The data were collected at 23 °C with Mo Kα radiation: μ = 11.17 cm^{-1}, $2\theta_{max}$ = 55.0°, 440 variables refined with 4437 unique reflections with $I > 3.00\sigma(I)$ to $R(F)$ = 0.056 and $Rw(F)$ = 0.045.

(μ-η^3-PhCCCH$_2$)(μ-Cl)Pd$_2$(PPh$_3$)$_2$ (2b): yield 65%; mp 105−109 °C dec; IR (KBr) 2190 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.22 (dd, J_{HP} = 4.32, 2.43 Hz, 2H), 6.85 (m, 5H), 7.26 (m, 9H), 7.39 (m, 9H), 7.48 (m, 6H), 7.67 (m, 6H); ^{13}C NMR δ 9.52 (s, CCH_2), 96.14 (dd, J_{CP} = 5.1, 2.0 Hz, CCH_2), 102.96 (dd, J_{CP} = 10.3, 4.2 Hz, PhCC); ^{31}P NMR δ 25.7 (d, J_{PP} = 85.6 Hz), 24.7 (d, J_{PP} = 85.6 Hz). Anal. Calcd for $C_{45}H_{37}ClP_2Pd_2$: C, 60.86; H, 4.20. Found: C, 60.12; H, 4.22.

(μ-η^3-^{t}BuCCCH$_2$)(μ-Cl)Pd$_2$(PPh$_3$)$_2$ (2c): yield 85% (NMR); ^{1}H NMR ($CDCl_3$) δ 0.86 (s, 9H), 2.07 (d, J_{HP} = 5.9 Hz, 2H), 7.38 (m, 18H), 7.62 (m, 6H), 7.73 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 10.31 (d, J_{CP} = 3.3 Hz, CCH_2), 93.59 (dd, J_{CP} = 12.3, 2.8 Hz, CCH_2), 111.66 (d, J_{CP} = 4.5 Hz, ^{t}BuCC); ^{31}P NMR δ 22.1 (d, J_{PP} = 80.4 Hz), 25.8 (d, J_{PP} = 80.4 Hz).

(μ-η^3-Me$_3$SiCCCH$_2$)(μ-Cl)Pd$_2$(PPh$_3$)$_2$ (2d): yield 84% (NMR); ^{1}H NMR ($CDCl_3$) δ −0.21 (s, 9H), 2.08 (d, J_{HP} = 6.6 Hz, 2H), 7.40 (m, 18H), 7.55 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 7.67 (s, CCH_2), 84.55 (d, J_{CP} = 6.2 Hz, CCH_2), 117.85 (s, Me_3SiCC); ^{31}P NMR δ 20.5 (d, J_{PP} = 101.8 Hz), 23.9 (d, J_{PP} = 101.8 Hz).

(μ-η^3-PhCCCH$_2$)(μ-I)Pd$_2$(PPh$_3$)$_2$ (2b-I): yield 63%; ^{1}H NMR ($CDCl_3$) δ 2.55 (dd, J_{HP} = 4.6, 1.9 Hz, 2H), 7.16 (m, 5H), 7.26 (m, 9H), 7.40 (m, 9H), 7.51 (m, 6H), 7.68 (m, 6H); ^{31}P NMR δ 33.13 (d, J_{PP} = 94.6 Hz), 33.70 (d, J_{PP} = 94.6 Hz). Anal. Calcd for $C_{45}H_{37}IP_2Pd_2$: C, 55.18; H, 3.81. Found: C, 55.03; H, 3.96.

(μ-η^3-PhCCCH$_2$)(μ-SPh)Pd$_2$(PPh$_3$)$_2$ (2b-SPh): yield 78%; ^{1}H NMR ($CDCl_3$) δ 2.13 (dd, J_{HP} = 5.4, 2.2 Hz, 2H), 6.65 (t, J_{HH} = 7.3 Hz, 2H), 6.82 (m, 8H), 7.13 (m, 6H), 7.31 (m, 18H), 7.54 (m, 6H); ^{31}P NMR δ 26.31 (d, J_{PP} = 92.8 Hz), 27.12 (d, J_{PP} = 92.8 Hz). Anal. Calcd for $C_{51}H_{42}ClP_2Pd_2S$: C, 63.69; H, 4.40; S, 3.33. Found: C, 63.67; H, 4.70; S, 3.40. Crystal data for **2b**-SPh: $C_{51}H_{42}ClP_2Pd_2S$, monoclinic, $P2_1/n$ (No. 14); a = 16.809(2) Å, b = 16.608(3) Å, c = 17.238(2) Å, β = 114.871(8)°, Z = 4, D_{calc} = 1.463 g/cm^3. The data were collected at 23 °C with Mo Kα radiation: μ = 9.64 cm^{-1}, $2\theta_{max}$ = 55.0°, 505 variables refined with 10400 unique reflections with $I > 3.00\sigma(I)$ to $R(F)$ = 0.036 and $Rw(F)$ = 0.029.

1,4-Bisdinuclear complex (2e): To a solution of 82.9 mg of 1,4-di(3-bromopropynyl)benzene[15] (0.266 mmol) and 279.0 mg of PPh_3 (1.06 mmol) in 6.5 mL of dry CH_2Cl_2 was added 549.1 mg of $Pd_2(dba)_3$·$CHCl_3$ (0.530 mmol) at room temperature with stirring for 20 h to give yellow solids. The yellow solids were filtered and washed with CH_2Cl_2 and hexane to give **2e** (274.0 mg) in 58% yield. ^{1}H NMR ($CDCl_3$) δ 2.34 (s, 4H), 6.26 (s, 4H), 7.16−7.52 (m, 60H); ^{31}P NMR δ 31.8 (s, 4P). Anal. Calcd for $C_{84}H_{68}Br_2P_4Pd_4$·$(CH_2Cl_2)_{0.5}$: C, 55.48; H, 3.80. Found: C, 55.42; H, 3.80.

(μ-η^3-PhCCHCH$_2$)PdCl(PPh$_3$)Pd(μ-Cl)(PPh$_3$) (3b): To a solution of 29.9 mg (0.034 mmol) of **2b** in 0.5 mL of CH_2Cl_2 were added 0.1 mL of H_2O and 4.6 mg (0.042 mmol) of $(CH_3)_3SiCl$ at room temperature. The mixture changed to a yellow suspension within 10 min. After 45 min, addition of 0.35 mL of hexane to the suspension yielded yellow solids (24.4 mg, 78%). ^{1}H NMR spectra of **3b** showed the presence of two isomers which we tentatively assume to arise from different disposition of P2 and Cl2 on Pd2 (see Figure 3). Selected spectral data for **3b** (major:minor = 67:33): major isomer ^{1}H NMR ($CDCl_3$) δ 3.28 (dd, J_{HH} = 7.5 Hz, J_{HP} = 1.2 Hz, 1H), 3.62 (d, J_{HH} = 10.7 Hz, 1H), 5.31 (ddd, J_{HH} = 7.5, 10.7 Hz, J_{HP} = 6.3 Hz, 1H), 6.98−7.89 (m, 35H); ^{31}P NMR δ 28.9 (d, J_{PP} = 4.0 Hz), 24.7 (d, J_{PP} = 4.0 Hz); minor isomer ^{1}H NMR ($CDCl_3$) δ 2.58 (dd, J_{HH} = 13.0 Hz, J_{HP} = 1.6 Hz, 1H), 3.04 (d, J_{HH} = 6.7 Hz, J_{HP} = 1.0 Hz, 1H), 5.52 (ddd, J_{HH} = 13.0, 6.7 Hz, J_{HP} = 3.4 Hz, 1H), 6.98−7.89 (m, 35H); ^{31}P NMR δ 26.6 (s), 21.2 (s). Anal. Calcd for $C_{45}H_{38}P_2Pd_2Cl_2$·$(CH_2Cl_2)_{1.5}$: C, 53.10; H, 3.93. Found: C, 53.03; H, 4.02. Crystal data for **3b**·$(H_2O)_3$: $C_{45}H_{44}P_2Cl_2Pd_2O_3$, triclinic, $P1$ (No. 2); a = 10.233(2) Å, b = 24.617(7) Å, c = 9.028(2) Å, α = 97.69(2)°, β = 108.69(1)°, γ = 87.23(2)°, Z = 2, D_{calc} = 1.551 g/cm^3. The data were collected at 23 °C with Mo Kα radiation: μ = 11.42 cm^{-1}, $2\theta_{max}$ = 55.0°, 488 variables refined with 7851 unique reflections with $I > 3.00\sigma(I)$ to $R(F)$ = 0.065 and $Rw(F)$ = 0.082.

(μ-η^3-PhCCHCH$_2$)PdCl(PPh$_3$)Pd(μ-I)(PPh$_3$) (3b-I): yield 76%; ^{1}H NMR ($CDCl_3$) δ 3.47 (d, J_{HH} = 12.0 Hz, 1H), 3.85 (d, J_{HH} = 6.8 Hz, 1H), 5.18 (ddd, J_{HH} = 12.0, 6.8 Hz, J_{HP} = 6.2 Hz, 1H), 7.16 (m, 3H), 7.26 (m, 4H), 7.47 (m, 13H), 7.65 (m, 13H), 7.88 (d, J_{HH} = 9.4 Hz, 2H); ^{31}P NMR δ 26.33 (s), 24.38 (s). Anal. Calcd for $C_{45}H_{38}P_2Pd_2ClI$: C, 53.20; H, 3.77. Found: C, 52.48; H, 4.04.

Reaction of 3b with Ph_4Sn: A solution of 84.6 mg of **3b** (0.092 mmol) and 39.1 mg of Ph_4Sn (0.092 mmol) in 3.1 mL of dry CH_2Cl_2 was heated at 40 °C for 47 h. The reaction mixture was concentrated in vacuo and the residue was separated by column chromatography (Florisil, CH_2Cl_2, and EtOAc). The yellow EtOAc eluent was concentrated to give yellow solids[6b] (35.8 mg, 62%). ^{1}H NMR ($CDCl_3$) 2.76 (dd, J_{HH} = 7.3, 2.2 Hz, 1H), 2.92 (dd, J_{HH} = 12.5, 2.2 Hz, 1H), 5.83 (dd, J_{HH} = 12.5, 7.3 Hz, 1H), 7.31−7.70 (m, 25H). ^{31}P NMR ($CDCl_3$) δ 28.45 (s). Anal. Calcd for $C_{33}H_{28}ClPPd$·CH_2Cl_2: C, 59.85; H. 4.43. Found: C, 59.84; H, 4.47.

(15) Hay. P. J.; Wadt. W. R. *J. Chem. Phys.* **1985**, *82*, 299.

Generation of 4: At room temperature, 9.5 mg of **3b** (0.0103 mmol) and 1.0 mg of $Pd_2(dba)_3$ (0.0010 mmol) were dissolved in 0.6 mL of $CDCl_3$. The reaction was followed by ^1H NMR. After 71 h, the complex **4** was observed in excellent yield (91%, NMR yield).

Isolation of 4: To a solution of 162.8 mg of **3b** (0.176 mmol) in 6.0 mL of CH_2Cl_2 was added 18.3 mg of $Pd_2(dba)_3$·$CHCl_3$ (0.0176 mmol) at room temperature and the mixture was stirred for 63 h. The reaction mixture was concentrated in vacuo and the concentrate was separated by column (silica gel, 100−200 mesh, CH_2Cl_2 then EtOAc). The yellow eluent was concentrated to give yellow solids (68.9 mg, 60%). ^1H NMR ($CDCl_3$) δ 2.17 (t, J_{HP} = 2.0 Hz, 1H), 3.73 (d, J = 6.6 Hz, 2H), 4.37 (d, J = 11.4 Hz, 2H), 4.66 (ddd, J = 6.6, 11.4 Hz, J_{HP} = 5.0 Hz, 2H), 7.02−7.81 (m, 40H). ^{13}C NMR ($CDCl_3$) δ 57.68, 112.68 (J_{CP} = 9.3 Hz), 122.83; ^{31}P NMR ($CDCl_3$) δ 30.85 (s). Anal. Calcd for $C_{54}H_{47}Cl_3OP_2Pd_4$: C, 49.66; H. 3.63. Found: C, 49.44; H, 3.82.

Reaction of 2b with AcCl (**3b**-Ac): To a solution of 92.2 mg (0.104 mmol) of dinuclear complex **2b** in 1.5 mL of dry CH_2Cl_2 was added 12.2 mg (0.155 mmol) of AcCl at room temperature and the mixture was stirred for 1 h. The reaction mixture was filtered and the filtrate was separated by column (silica gel, 100−200 mesh, CH_2Cl_2/EtOAc = 10/1) to give a wine-red oil followed by reprecipitation from a CH_2Cl_2/*n*-hexane solution to give orange solids (**3b**-Ac). Yield 20.7 mg (21%). ^1H NMR ($CDCl_3$) δ 2.67 (s, 1H), 3.30 (s, 3H), 3.37 (s, 1H), 6.98 (m, 2H), 7.13 (m, 2H), 7.2−7.5 (m, 28H), 7.68 (m 2H). ^{31}P NMR ($CDCl_3$) δ 27.24 (s), 28.53 (s). Anal. Calcd for $C_{53}H_{40}Cl_2OP_2Pd_2$: C, 58.41; H, 4.17. Found: C, 58.14; H, 4.20.

Reaction of 1,2-di(3-chloropropynyl)benzene with Pd(PPh$_3$) (3f): To a solution of 22.3 mg (0.0215 mmol) of $Pd_2(dba)_3$·$CHCl_3$ and 11.2 mg (0.0427 mmol) of PPh_3 was added 5.1 mg (0.0220 mmol) of 1,2-di(3-chloropropynyl)benzene[15] in $CDCl_3$ at room temperature. After 1 h, the solution changed from violet to orange. Yield 80%. ^1H NMR ($CDCl_3$) δ 3.30 (s, 1H), 3.34 (s, 1H), 5.25 (d, J_{HH} = 14.6 Hz, 1H), 5.32 (d, J_{HH} = 14.6 Hz, 1H), 6.98 (m, 2H), 7.15−7.25 (m, 2H), 7.37−7.49 (m, 20H), 7.59−7.63 (m, 12H). ^{13}C NMR ($CDCl_3$) δ 203.4 (central carbon of allene). ^{31}P NMR ($CDCl_3$) δ 29.63 (d, J_{PP} = 6.1 Hz), 33.53 (d, J_{PP} = 6.1 Hz).

Reaction of 1-bromomethyl-2-(3-bromopropynyl)benzene with Pd(PPh$_3$) (generation of 2 g): To a solution of 19.0 mg of $Pd_2(dba)_3$·$CHCl_3$ (0.00184 mmol) and 9.6 mg of PPh_3 (0.00366 mmol) in 0.6 mL of $CDCl_3$ was added 5.3 mg of 1-bromomethyl-2-(3-bromopropynyl)benzene (0.00184 mmol) at room temperature. The reaction mixture changed to orange and dinuclear complex **2g** and small amounts of cyclization complex **3g** were generated quantitatively. The rate of cyclization of complex **2g** was measured by ^1H NMR spectra (k_{obs} = 2.1×10^{-5} s^{-1}). The rate in C_6D_6 was also measured as well (k_{obs} = 5.1×10^{-6} s^{-1}). ^1H NMR ($CDCl_3$) δ 2.34 (d, J_{PH} = 3.1 Hz, 1H), 4.07 (s, 2H), 6.68 (m, 2H), 6.93 (m, 2H), 7.06−7.71 (m, 30H). ^{31}P NMR ($CDCl_3$) δ 31.9 (s, 2P).

Reaction of 1-bromomethyl-2-(3-bromopropynyl)benzene with Pd(PPh$_3$) (attempt of isolation): To a solution of 107.5 mg (0.104 mmol) of $Pd_2(dba)_3$ and 55.3 mg (0.211 mmol) of PPh_3 in 3.6 mL of C_6H_6 was added 31.2 mg (0.108 mmol) of 1-bromomethyl-2-(3-bromopropynyl)benzene at room temperature and the mixture was stirred for 30 min. The solution changed from violet to brown. The reaction mixture was concentrated in vacuo followed by the reprecipitation from a CH_2Cl_2/*n*-hexane solution to give yellow solids (a mixture of dinuclear complex **2g** and a small amount of cyclization complex **3g**). Yield 24.6 mg (23%).

Isolation of 3g: To a solution of 101.2 mg (0.0980 mmol) of $Pd_2(dba)_3$·$CHCl_3$ and 51.2 mg (0.195 mmol) of PPh_3 in 3.0 mL of CH_2Cl_2 was added 28.1 mg (0.0980 mmol) of 1-bromomethyl-2-(3-bromopropynyl)benzene at room temperature and the mixture was stirred for 3 h. The solution changed from violet to orange. The reaction mixture was concentrated in vacuo and the concentrate was separated by column (silica gel, 100−200 mesh, CH_2Cl_2) followed by concentration of the second yellow eluent to give a yellow oil. Reprecipitation from a CH_2Cl_2/hexane solution gave yellow solids. Yield 27.0 mg (27%). ^1H NMR ($CDCl_3$) δ 2.75 (d, J = 21.1 Hz, 1H), 2.97 (d, J = 21.1 Hz, 1H), 3.48 (s, 2H), 7.06−7.69 (m, 34H). ^{31}P NMR ($CDCl_3$) δ 29.4 (d, J_{PP} = 5.4 Hz), 33.7 (d, J_{PP} = 5.4 Hz). Anal. Calcd for $C_{46}H_{38}Br_2P_2Pd_2$: C, 53.88; H, 3.74. Found: C, 53.70; H, 3.72.

Reaction of 2b-Br with benzyl bromide: To a solution of 11.7 mg of **2b**-Br (0.0125 mmol) in 0.5 mL of C_6D_6 was added 2.16 mg of benzyl bromide (1.5 μL, 0.0126 mmol) and the reaction was followed by ^1H and ^{31}P NMR. After 120 h no reaction occurred.

(μ-η^3-PhCCCH$_2$)(μ-Br)Pd$_2$(PPh$_3$)$_2$ (**2b**-Br): To a solution of 81.3 mg of **2b** (0.0916 mmol) in CH_2Cl_2 was added a solution of 18.9 mg of NaBr (0.184 mmol) in 1 mL of MeOH at room temperature and the mixture was stirred for 20 min. The reaction mixture was concentrated in vacuo and the residue was separated by column chromatography (silica gel, 100−200 mesh, CH_2Cl_2). The orange eluent was concentrated to give red solids (65.2 mg, 76%). ^1H NMR (C_6D_6) δ 2.47 (dd, J_{HP} = 4.0, 2.5 Hz, 2H), 6.74 (m, 3H), 6.93 (m, 9H), 7.00 (m, 9H), 7.13 (d, J = 6.9 Hz, 2H), 7.74 (m, 12H); ^{31}P NMR (C_6D_6) δ 32.29 (d, J_{PP} = 87.3 Hz), 33.19 (d, J_{PP} = 87.3 Hz). Anal. Calcd for $C_{45}H_{37}BrP_2Pd_2$: C, 57.96; H, 4.00. Found: C, 57.95; H, 4.27.

Reaction of 1-chloromethyl-2-(3-chloropropynyl)benzene with Pd(PPh$_3$) (generation of 2h): To a solution of 19.0 mg of $Pd_2(dba)_3$·$CHCl_3$ (0.00184 mmol) and 9.6 mg of PPh_3 (0.00366 mmol) in 0.6 mL of C_6D_6 was added 3.7 mg of 1-chloromethyl-2-(3-chloropropynyl)-benzene (0.00186 mmol) at room temperature. The reaction mixture changed to yellow and a mixture of dinuclear complex **2h** and a small amount of **3h** was generated quantitatively. ^1H NMR ($CDCl_3$) δ 2.18 (d, J_{PH} = 6.5 Hz, 1H), 4.16 (s, 2H), 6.69 (m, 2H), 6.99 (m, 2H), 7.12−7.72 (m, 30H). ^{31}P NMR ($CDCl_3$) δ 28.5 (d, J_{PP} = 83.8 Hz) 29.6 (d, J_{PP} = 83.8 Hz).

Cyclization of 2h: To a solution of 21.0 mg of $Pd_2(dba)_3$·$CHCl_3$ (0.00203 mmol) and 10.2 mg of PPh_3 (0.00389 mmol) in 0.6 mL of C_6D_6 was added 3.7 mg of 1-chloromethyl-2-(3-chloropropynyl)benzene (0.00186 mmol) at room temperature. A mixture of dinuclear complex **2h** and a small amount of **3h** was generated quantitatively; however, the reaction mixture was still violet due to the use of slightly excess $Pd_2(dba)_3$·$CHCl_3$. The cyclization proceeded completely in 1.5 h to give **3h** quantitatively.

Isolation of 3h: To a solution of 110.6 mg (0.107 mmol) of $Pd_2(dba)_3$·$CHCl_3$ and 56.9 mg (0.217 mmol) of PPh_3 in 3.0 mL of CH_2Cl_2 was added 18.4 mg (0.092 mmol) of 1-chloromethyl-2-(3-chloropropynyl)benzene at room temperature and the mixture was stirred for 1.5 h. The solution changed from violet to orange. The reaction mixture was concentrated in vacuo and the concentrate was separated by column (silica gel, 100−200 mesh, CH_2Cl_2/EtOAc) followed by concentration of the second yellow eluent to give a yellow oil. Reprecipitation from a CH_2Cl_2/hexane solution gave yellow solids (**3h**). Yield 30.8 mg (36%). ^1H NMR ($CDCl_3$) δ 2.72 (d, J_{HH} = 20.9 Hz, 1H), 2.97 (d, J_{HH} = 20.9 Hz, 1H), 3.24 (s, 1H), 3.48 (s, 1H), 7.06−7.69 (m, 34H). ^{31}P NMR ($CDCl_3$) δ 29.1 (d, J_{PP} = 6.1 Hz), 33.4 (d, J_{PP} = 6.1 Hz). Anal. Calcd for $C_{46}H_{38}Cl_2P_2Pd_2$·(H_2O): C, 57.88; H, 4.22. Found: C, 58.22; H, 4.09.

MO Calculation. Molecular geometry optimization followed by analytical frequency calculations was performed at the B3LYP/BS-1 (BS-1, Pd: valence electrons (5s 5p 4d)/[3s 3p 2d], core electrons ECPs (up to 3d),[15] P: valence electrons (3s 3p)/[2s 2p], core electrons ECPs (up to 2p),[16] others 6-31G*) levels of theory with the Gaussian 94 programs.[17] The ab initio MO/MP2 calculation with BS-2 (BS-2, Pd: valence electrons (5s 5p 4d)/[3s 3p 2d], core electrons ECPs (up to 3d), others 6-31G*) was carried out on the optimized geometry.

Acknowledgment. Partial support of this work through CREST of Japan Science and Technology Corporation and Grants-in-aid for Scientific Research from Ministry of Education, Science and Culture, Japan is gratefully acknowledged.

JA003754M

(16) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Oritiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Chalacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; People, J. A. Gsussian 94; Gaussian, Inc.: Pittsburgh, PA, 1995.