Intermolecular Carbon−Carbon Bond Formation with an Electrophilic Trimethylenemethane−Palladium(II) Intermediate Arising from (η^3-2-(Chloromethyl)allyl)(η^5-cyclopentadienyl)palladium

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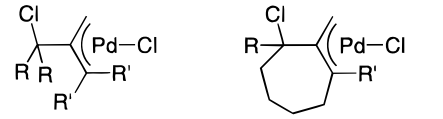
[Pd{η^3-$CH_2C(CH_2Cl)CH_2$}(η^5-C_5H_5)] (**2a**) was spontaneously transformed into [Pd{η^3-$CH_2C(CH_2C_5H_5)CH_2$}Cl]$_2$ (**3a**) in polar solvents such as $CDCl_3$, CD_2Cl_2, and CD_3NO_2. The rate of decay of **2a** was found to be second order in the concentration of **2a** and to increase with the solvent polarity. [Pd{η^3-$CH_2C(CMe_2Cl)CH_2$}(η^5-C_5H_5)] (**2b**) was also transformed into a mixture of [Pd{η^3-$CH_2C(CMe_2C_5H_5)CH_2$}Cl]$_2$ (**3b**) and [Pd{η^3-$CH_2C(CH_2C_5H_5)CMe_2$}Cl]$_2$ (**3c**; **3c**/**3b** = 86/14). The decay of **2b** in CD_2Cl_2 was much faster than that of **2a**. [Pd{η^3-$CH_2C(CH_2Cl)CMe_2$}(η^5-C_5H_5)] (**2c**), generated by treatment of [Pd{η^3-$CH_2C(CH_2Cl)CMe_2$}Cl]$_2$ (**1c**) with TlC_5H_5, isomerized to **2b**. In CD_3OD, **2a** or **2b** instantaneously gave not only **3a** or **3b** and **3c** but solvolysis products [Pd{η^3-$CH_2C(CR_2OCD_3)CH_2$}Cl]$_2$ **7a** (R = H) or **7b** (R = Me), together with deuteriocyclopentadiene. A mechanism consistent with these observations is proposed, which involves a cationic trimethylenemethane−Pd(II) intermediate. The further reaction of **3a** or **3c**, leading to the formation of the cyclic (π-allyl)palladium complexes (7-methylenebicyclo[3.3.0]oct-2-en-4-yl)(chloro)palladium (**4a**) or (6,6-dimethyl-7-methylenebicyclo[3.3.0]oct-2-en-4-yl)(chloro)palladium (**4b**) via insertion of a Pd−allyl bond to the diene part of C_5H_5, is also reported.

Introduction

Trimethylenemethane (TMM) has been of theoretical interest for several decades in relation to the acyclic Y-aromaticity. Though the TMM diradical is so short-lived and highly reactive that it can be detected only at low temperature by ESR,[1] many TMM−metal complexes have been synthesized and found to be stable at room temperature[2] since Emerson prepared (η^4-TMM)$Fe(CO)_3$ in 1966.[3] As to the palladium analogs, much attention has been paid to TMM−Pd(0) intermediates which have played key roles in [3 + 2] cycloaddition,[4a,b] and TMM−Pd(0) complexes bearing electron-withdrawing substituents have actually been prepared recently.[4c] In contrast to the TMM−Pd(0) species which is nucleophilic in origin in catalytic cycles, much less is known about the reactivities of electrophilic TMM−Pd(II) complexes.[5−8] Lukas and Kramer briefly described the possible generation of [Pd{$CH_2C(CH_2)CH_2$}Cl]$^+$ through chloride abstraction of **1a** by a strong acid.[5] In addition,



1a : R = R' = H
1b : R = Me, R' = H
1c : R = H, R' = Me
1d : R = Ph, R' = H
1e : R = H, R' = Ph

1f : R = Ph, R' = H
1g : R = H, R' = Ph
1h : R = R' = H

Hughes[6] and Donaldson[7] proposed that a TMM−Pd(II) intermediate produced by C−Cl cleavage of **1d** and **1f** undergoes rearrangement to accomplish the isomerization to **1e** and **1g**, respectively. Here, we demonstrate the first example of intermolecular C−C bond formation with a TMM−Pd(II) complex during an apparently intramolecular rearrangement of (η^3-2-(chloromethyl)allyl)(η^5-cyclopentadienyl)palladium complexes represented by the rearrangement of [Pd{η^3-$CH_2C(CH_2Cl)CH_2$}(η^5-C_5H_5)] (**2a**) to [Pd{η^3-$CH_2C(CH_2C_5H_5)CH_2$}Cl]$_2$ (**3a**).

Results

Isomerization of the 2-(Chloromethyl)allyl Complex. Red complex **2a**, prepared readily by treatment of **1a** with TlC_5H_5 in C_6H_6, was stable in C_6D_6 at 25 °C for several days. In CD_3NO_2, however, **2a** was almost quantitatively transformed into the yellow complex **3a** at 25 °C in 4 min (Scheme 1). On prolonged reaction, **3a** further underwent both a reversible 1,5-hydrogen shift to give **3a′**, as is seen in the isomerization of

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(1) Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587.
(2) For a review, see: Jones, M. D.; Kemmit, R. D. *Adv. Organomet. Chem.* **1987**, *27*, 279.
(3) Emerson, G. F.; Ehrlich, K.; Griering, W. P.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1966**, *88*, 3172.
(4) (a) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. (b) For a recent reiew paper, see: Harrington, P. J. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 12, p 923. (c) Su, C. C.; Chen, J. T.; Lee, G. H.; Wang, Y. *J. Am. Chem. Soc.* **1994**, *116*, 4999.
(5) Lukas, J.; Kramer, P. A. *J. Organomet. Chem.* **1971**, *31*, 111.
(6) Dallas, B. K.; Hughes, R. P.; Schumann, K. *J. Am. Chem. Soc.* **1982**, *104*, 5380.
(7) Donaldson, W. A.; North, J. T.; Gruetzmacher, J. A.; Fineley, M.; Stepuszek, D. J. *Tetrahedron* **1990**, *46*, 2263.
(8) For the C−Cl bond activation in analogous Pt(II) complexes, see: Kemmitt, D.; Andrew, W. G. P. *J. Chem. Soc., Dalton. Trans.* **1986**, 1603.

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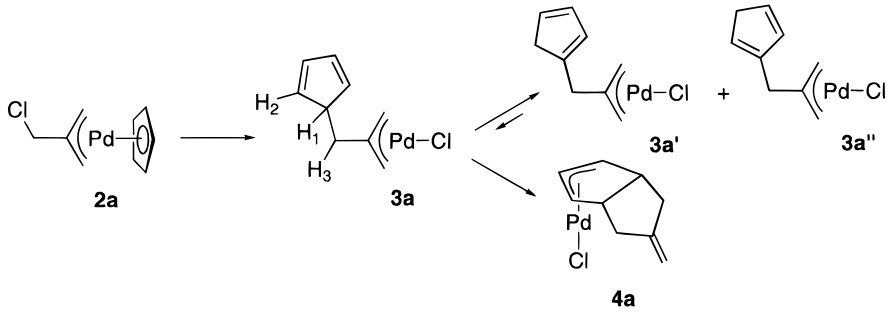
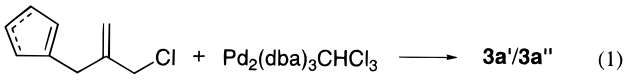
Scheme 1



alkylcyclopentadienes,[9] and an insertion of the diene part of the C_5H_5 ring into the palladium−allyl bond to give **4a** (**3a**:**3a′**:**4a** = trace:32:68 after 1 h). On standing further for a few days, **3a′** isomerized to **3a″** to give similar amounts of **3a′** and **3a″** while the ratio of **3a′**/**3a″**:**4a** remained almost unchanged. The mixture of **3a′**/**3a″** (1:1) and **4a** could be easily separated by column chromatography on a large scale in 27% and 48% isolated yields, respectively. Isolated **3a′**/**3a″** converted into **4a** in 9% yield in $CDCl_3$ at 25 °C for 3 days with the ratio of **3a′**/**3a″** remaining still 1:1.

The identification of **3a** and **3a′**/**3a″** was made on the basis of the ^1H NMR spectra. The most characteristic signal of **3a** was a triplet of triplets due to H_1 (see Scheme 1) at δ 3.31 with $J_{H_1H_2}$ and $J_{H_1H_3}$ being 1.6 and 6.8 Hz, respectively, and a doublet signal due to H_3 at δ 2.56. **3a′**/**3a″** was synthesized independently by the reaction between $Pd_2(dba)_3CHCl_3$ (bda = dibenzylideneacetone) and 2-(chloromethyl)-3-cyclopentadienylpropene (1:1 isomeric mixture) in CH_2Cl_2 in 69% isolated yield (eq 1).

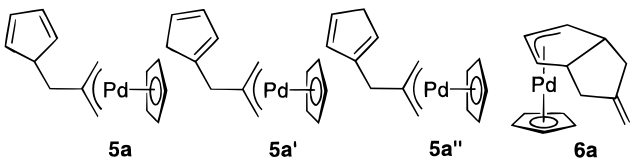


(1)

The PPh_3 adduct of **4a** was formed by mixing **4a** with PPh_3, and its structure was characterized by X-ray diffraction (Figure 1). The Pd atom was located inside the bicyclo skeleton.

The transformation of **2a** to **3a**/**3a′**/**3a″** and **4a** proceeded more slowly in $CDCl_3$ at 25 °C. The time dependence for the amounts of **2a** and the products (**1a**, **3a**/**3a′**/**3a″**, and **4a**) recorded by ^1H NMR spectroscopy is shown in Figure 2.

The decay of **2a** was accompanied by an increase of **3a**/**3a′**/**3a″** and **4a**. Also, temporary accumulation of a small amount of **1a** (<10%) was notable. Other byproducts confirmed spectroscopically include **5a**/**5a′**/**5a″** (<7%) and **6a** (<5%). Authentic samples of **5a′**/**5a″** and



6a were generated in NMR tubes by adding TlC_5H_5 to **3a′**/**3a″** and **4a**. **5a** was generated by adding 2 equiv of TlC_5H_5 to **1a** in CD_3NO_2, but readily underwent a 1,5-H shift to give **5a′** as **3a** did.

Next, we analyzed the kinetics of the decay of **2a** in $CDCl_3$. Though a plot of $\ln([\mathbf{2a}]/[\mathbf{2a}]_0)$ vs time did not give a straight line, a plot of $1/[\mathbf{2a}]$ gave a better line

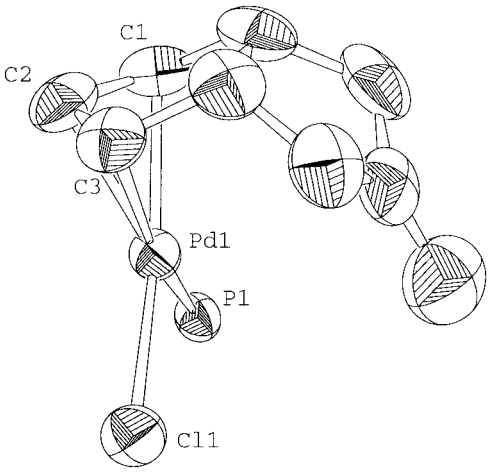


Figure 1. ORTEP drawing of complex **4a**-PPh_3 with thermal ellipsoids at 50% probability levels: side view (all hydrogen atoms and Ph groups are omitted for clarity). Selected bond lengths (Å): Pd1−C1 = 2.138(4), Pd1−C2 = 2.121(4), Pd−C3 = 2.225(4), Pd1−Cl1 = 2.3961(9), Pd1−P1 = 2.341(1), C1−C2 = 1.401(5), C2−C3 = 1.378(6).

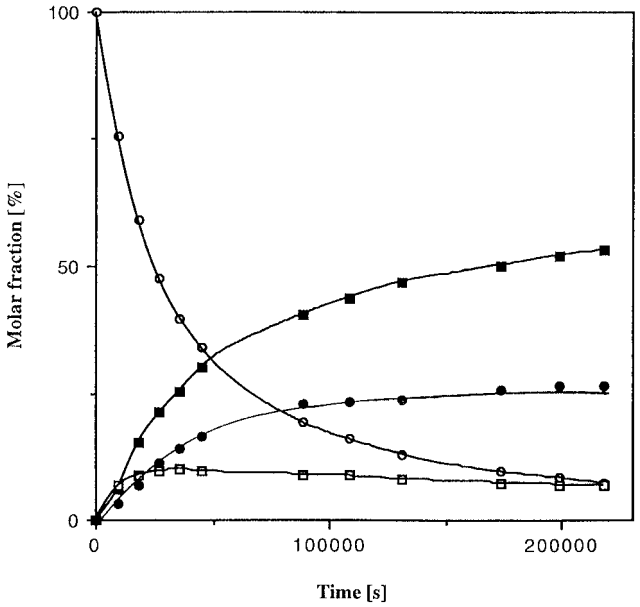


Figure 2. Time dependence for the transformation of **2a** in $CDCl_3$ at 25 °C: **2a** (○), **1a** (□), **3a**/**3a′**/**3a″** (●), **4a** (■). $[\mathbf{2a}]_0 = 7.3 \times 10^{-2}$M.

(9) Korenevsky, V. A.; Sergeyev, N. M. *J. Am. Chem. Soc.* **1972**, *94*, 8586.

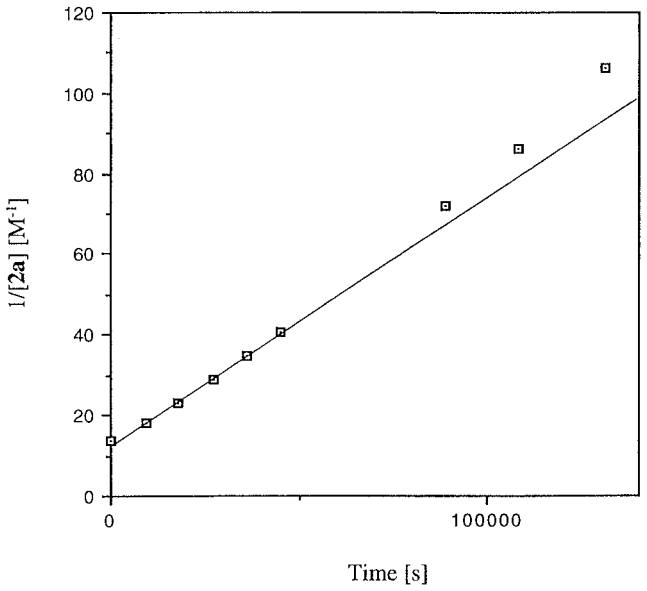
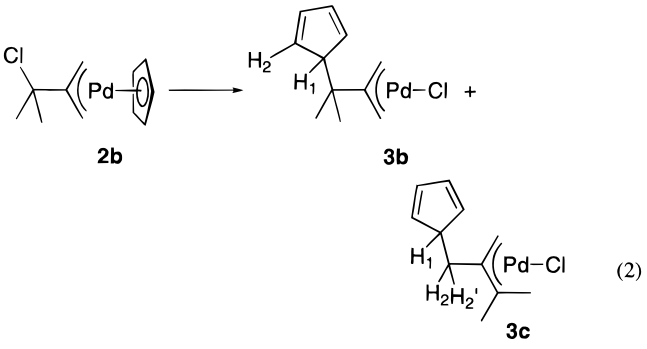


Figure 3. Time dependence for 1/[**2a**] in $CDCl_3$ at 25 °C. $[\mathbf{2a}]_0 = 7.3 \times 10^{-2}$M.

(until 60% decay of **2a**; Figure 3). Furthermore, theslope of the latter plot was independent of the initial concentration $[\mathbf{2a}]_0$ (see Experimental Section). Thus, the rate of decay of **2a** may be approximated as second order in the concentration of **2a.** The second-order rate constant k (M^{-1} s^{-1}, $-d[\mathbf{2a}]/dt = k[\mathbf{2a}]^2$) at 25 °C was found to be $(6.2 \pm 0.2) \times 10^{-4}$. A similar result was observed in CD_2Cl_2. The k value at 25 °C was much greater ($(1.0 \pm 0.1) \times 10^{-2}$) than that in $CDCl_3$.

Isomerization of Methyl-Substituted 2-(Chloromethyl)allyl Complexes. The methyl-substituted analog **2b**, prepared from **1b** and TlC_5H_5, was stable in C_6H_6 for several days. As shown in eq 2, **2b** was transformed quantitatively to a mixture of two isomers, **3b** and **3c**, in CD_3NO_2 at 25 °C in 4 min, with the geometrical rearrangement product **3c** dominating (**3c**/**3b** = 86/14). The structures of **3b** and **3c** were assigned

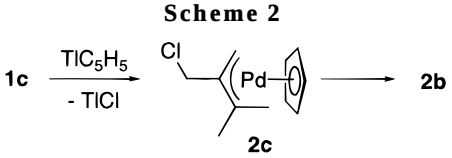


(2)

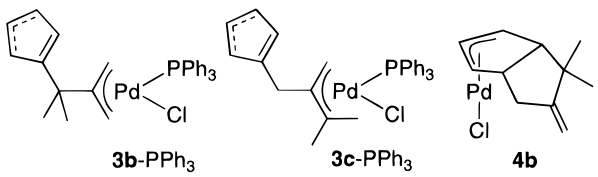
by ^{1}H NMR spectra. In particular, **3b** showed a broad singlet due to H_1 at δ 3.10, which is expected to result from a very small vicinal coupling with H_2, while the spectrum of **3c** showed two doublets of doublets due to H_2 and $H_{2'}$ at δ 2.28 and 2.83 ($J_{H_2H_{2'}} = 13.5$ Hz) and a doublet of doublets due to H_1 at δ 3.28.

On prolonged reaction (several minutes), **3b** and **3c** were further transformed to a complicated mixture whose complete ^{1}H NMR assignment was difficult.

Scheme 2



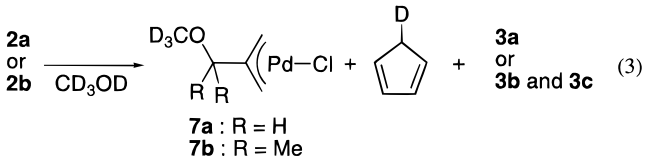
From the mixture **4b** was isolated in 38% by column chromatography on a large scale. We could not con-



firmthe products arising from the 1,5-H shift of **3b** and **3c** spectroscopically, but we succeeded in isolating PPh_3 adducts of such products. In CD_2Cl_2, we found that the decay of **2b** was much faster than that of **2a**. The first half-life of the decay of **2b** ($[\mathbf{2b}]_0 = 8.3 \times 10^{-3}$ M) was 670 s, which can be compared with that of **2a** (12 000 s) under the same conditions.

Although **3c** was the major product in the transformation shown in eq 2, we observed no evidence to show the isomerization of **2b** to **2c** (Scheme 2). On the contrary, we confirmed that **2c** was by far less stable than **2b**. Thus, treatment of **1c** with TlC_5H_5 in C_6D_6 initially led to formation of **2c**, whose structure was established by comparison of its ^{1}H NMR data with **1c**. **2c** isomerized to **2b** almost completely in 15 h in C_6D_6 (Scheme 2). The same treatment of **1c** with TlC_5H_5 in $CDCl_3$ gave **2b** exclusively in 4 min.

Solvolysis in CD_3OD. When dissolved in CD_3OD, **2a** gave a mixture of **3a** and the solvolysis product $[Pd\{\eta^3\text{-}CH_2C(CH_2OCD_3)CH_2\}Cl]_2$ (**7a**), together with deuteriocyclopentadiene, in 4 min (eq 3). Significantly,



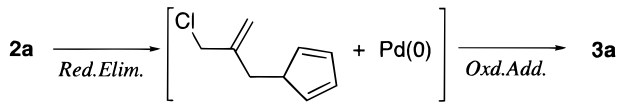
(3)

as the initial concentration of **2a** became higher, the amount of **7a** decreased while **3a** increased; the ratio **7a**/**3a** was 87/13, 82/18, 71/29, and 41/59 when the initial concentration of **2a** was 1.75×10^{-3}, 3.83×10^{-3}, 7.02×10^{-3}, and 1.66×10^{-2} M, respectively. This trend is understood if we assume that formation of **3a** is a bimolecular process (concentration of MeOH can be assumed constant; see below for more detail). **2b** in CD_3OD (3.8×10^{-3} M) also gave an almost quantitative amount of $[Pd\{\eta^3\text{-}CH_2C(CMe_2OMe)CH_2\}Cl]_2$ (**7b**), together with trace amounts of **3b** and **3c**. Importantly, in **7b** the CD_3O group is attached to the tertiary carbon.

Discussion

Mechanism of Transformation of 2a to 3a via a Cationic TMM−Pd Intermediate. Conversion of **2a** to **3a** might have proceeded via reductive elimination of **2a** giving Pd(0) and the allyl chloride bearing the cyclopentadienylmethyl substituent at C-2, followed by oxidative addition (Scheme 3). Donaldson proposed this reductive elimination−oxidative addition sequence in

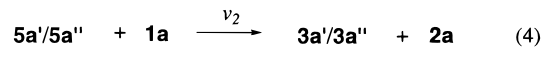
Scheme 3



the reaction of **1h** with $NaBPh_4$, which gave the (η^3-2-benzylcycloheptenyl)palladium chloride dimer.[10] However, we exclude this mechanism since it is inconsistent with the second-order rate law for the decay of **2a**. Moreover, we found no C−C bond coupling in Pd{η^3-$CH_2C(CH_2R)CH_2$}(η^5-C_5H_5) (R = H, SO_2Ph) under the conditions for Scheme 1; these conditions give Pd(0) complexes and the coupling products only when 2 equiv of PR_3 is added.[11]

The observed rate increase with the solvent polarity ($C_6D_6 \ll CDCl_3 < CD_2Cl_2 \ll CD_3NO_2$) and the accelerated rate by attaching methyl groups to the carbon bearing Cl atom suggest formation of a carbocation species at a key step. Here, we propose that the cationic TMM−Pd(II) intermediate **8a**, formed by C−Cl bond heterolysis in **2a**, represents the reactive species (Scheme 4). This would undergo an electrophilic substitution with the ligand of **2a** to give **5a**. Complex **5a** thus formed may undergo two transformations, Cp−Cl exchange between **5a** and **1a** to yield **3a** and **2a**[12] and a 1,5-H shift to yield **5a′**/**5a″**, with the relative degree of these steps being dependent on the nature of the solvents.

In CD_3NO_2, since the formation of **5a** would be sufficiently fast to allow accumulation of the high concentration of **5a** and efficient consumption of **2a**, the ligand exchange between **5a** and **1a** would predominate, eventually leading to the formation of **3a** as the sole initial product. In $CDCl_3$ or CD_2Cl_2, in which formation of **5a** and consumption of **2a** are not so fast, the driving force to the **5a**−**1a** ligand exchange would be weaker, and thus, the isomerization of **5a** to **5a′**/**5a″**, though to a lesser extent, would compete with the ligand exchange. **3a** formed in the latter step would isomerize to **3a′**/**3a″** and **4a**. The rate of the decrease of **2a** is not straightforward since it is formed or consumed in several Cp−Cl ligand exchange steps, e.g., that between **5a** and **1a** to give **3a** and **2a**, **5a′**/**5a″** and **1a** to give **3a′**/**3a″** and **2a** (eq 4), or **6a** and **1a** to give **4a** and **2a** (eq 5).[13] Then eqs 6 and 7 can be deduced[13] from



Scheme 4 and eqs 4 and 5, and combining a steady-state approximation for the concentration of **8a** (eq 8) with eqs 6 and 7 gives eq 9. Equation 9 seems to be difficult

$$\frac{d[\mathbf{2a}]}{dt} = -k_1[\mathbf{2a}] + k_{-1}[\mathbf{8a}] - k_2[\mathbf{2a}][\mathbf{8a}] + v_1 + v_2 + v_3 \quad (6)$$

$$\frac{d[\mathbf{1a}]}{dt} = k_2[\mathbf{2a}][\mathbf{8a}] - v_1 - v_2 - v_3 \quad (7)$$

$$\frac{d[\mathbf{8a}]}{dt} = k_1[\mathbf{2a}] - k_{-1}[\mathbf{8a}] - k_2[\mathbf{2a}][\mathbf{8a}] = 0 \quad (8)$$

$$\frac{d[\mathbf{2a}]}{dt} = -k_2[\mathbf{2a}][\mathbf{8a}] - \frac{d[\mathbf{1a}]}{dt} \quad (9)$$

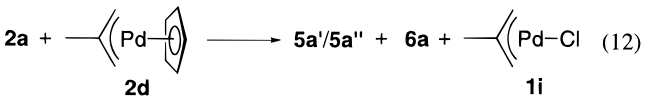
to solve, but we make the following assumption; if k_{-1} is much greater than k_2[**2a**], [**8a**] solves to eq 10. Also,

$$[\mathbf{8a}] = \frac{k_1[\mathbf{2a}]}{k_2[\mathbf{2a}] + k_{-1}} = \frac{k_1}{k_{-1}}[\mathbf{2a}] \quad (10)$$

$$\frac{d[\mathbf{2a}]}{dt} = \frac{-k_2k_1[\mathbf{2a}]^2}{k_{-1}} \quad (11)$$

since the change of **1a** is assumed to be considerably small compared to that of **2a** at the early stage (see Figure 2), d[**1a**]/d*t* may be neglected and eq 9 can be simplified to eq 11, leading to a pseudo-second−order rate equation. At the latter stage, however, the change of [**1a**] cannot be ignored.

The contribution of other complexes (**5a′**/**5a″** and **6a**) as a cyclopentadienyl source for trapping **8a** to give **5a** may be possible, but their effect is negligibly small at the early stage because of their low concentration. Then, we speculate that the excess external cyclopentadienyl source would greatly change the kinetics of the original reaction. In order to confirm the validity, we examined the transformation of **2a** in $CDCl_3$ in the presence of excess Pd{η^3-$CH_2C(CH_3)CH_2$}(η^5-C_5H_5) (**2d**; 10.4 equiv; 1.73×10^{-1} M). The reaction gave **5a′**/**5a″** and [Pd{η^3-$CH_2C(CH_3)CH_2$}Cl]$_2$ (**1i**) as the main products (84% and 94%), respectively, with 8% of **6a** also being obtained (after 1 day eq 12). More importantly,



the decay of **2a** obeyed the first-order rate law (until 75% decay of **2a**; first-order rate constant $k' = 7.6 \times 10^{-5}$ s^{-1}).

Solvolysis with CD_3OD. In MeOH, the C−C bond formation between the TMM−Pd intermediate **8a** and **2a** may compete with the solvolysis path which forms **9a** and DCl, which would immediately react with each other, affording **7a** and cyclopentadiene (Scheme 5). The concentration dependence of the ratio **7a**/**3a** observed in MeOH is consistent with the bimolecular nature of the C−C bond-forming reaction where the concentration of MeOH can be assumed constant. Also, it is well-known that (π-allyl)(cyclopentadienyl)palladium reacts with HCl to afford the corresponding (π-allyl)palladium chloride dimer instantaneously.[14]

Migration of the Metal Along the TMM Fragment. Facile isomerization of **2c** to **2b** and formation of both **3b** and **3c** from **2b** suggest that the dimethyl-substituted TMM−Pd(II) complex underwent a very rapid migration of the metal (Scheme 6) as does the

(10) Donaldson, W. A.; Wang, J. *J. Organomet. Chem.* **1990**, *395*, 113.

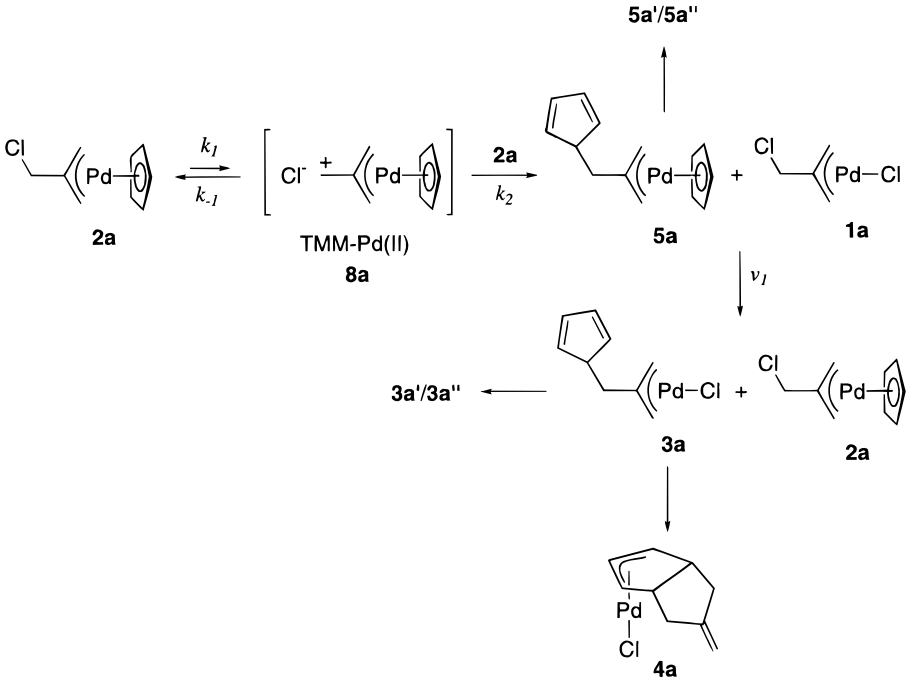
(11) (a) Harder, V.; Werner, H. *Helv. Chim. Acta* **1973**, *56*, 549. (b) Parker, G.; Werner, H. *Ibid.*, **1973**, *56*, 2819.

(12) We separately confirmed the occurrence of an equilibrium between **1a** + **5a′**/**5a″** and **2a** + **3a′**/**3a″** in $CDCl_3$ at 25 °C, with K (= [**2a**][**3a′**/**3a″**][**1a**]$^{-1}$[**5a′**/**5a″**]$^{-1}$) being larger than 10.

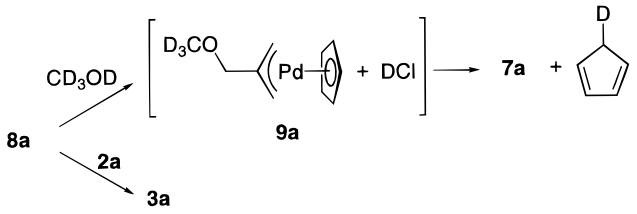
(13) The Cp−Cl exchanges may be more or less reversible, as confirmed in the case of eqs 4 and 5. During the transformation of **2a**, however, the rate of change of the concentration of each component involved in the equilibrium is not necessarily zero. v_n represents the rate of the overall concentration change and can be either positive or negative.

(14) Gubin, S. P.; Rubezhov, A. Z.; Winch, B. L.; Nesmeyanow, A. N. *Tetrahedron Lett.* **1964**, 2881.

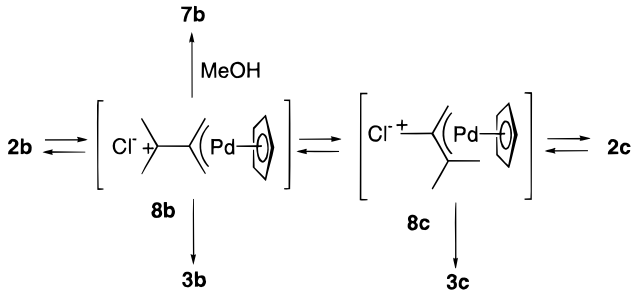
Scheme 4



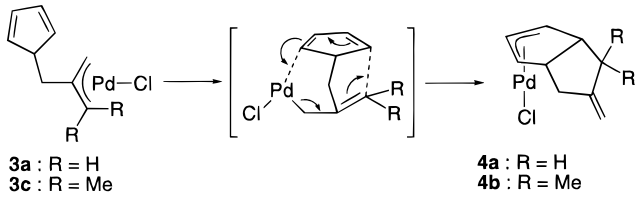
Scheme 5



Scheme 6



Scheme 7



TMM−Pd(0) complex.[4a,b,15] In addition, this migration is expected to be much faster than the trapping of **8b** and **8c** with nucleophiles. We believe that the exclusive formation of **2b** from the mixture of **8b** and **8c** reflects the thermodynamic stability of **2b** relative to **2c**, while more efficient trapping of **8c** than **8b** with the cyclopentadienyl ligand occurs by a kinetic control, forming the higher amount of **3c** than **3b**. Much less can be deduced concerning the origin of the formation of only **7b** from **2b** in MeOH. It should be noted, however, that treating **1c** with TlC_5H_5 in CD_3OD resulted in quantitative formation of **7b** in 4 min.

Intramolecular 1,3-Diene Insertion into the Allyl−Palladium Bond. It is estimated that the precursor of **4a** is not **3a′**/**3a″** but **3a**. Even after **3a** had been converted to **3a′** and **3a″**, the latter two may go back to **3a** from which the insertion may have proceeded. The precursor of **4b** is not assumed to be **3b** but **3c** because the isolated yield (38%) of **4b** exceeded the initial amount of **3b** (14%). These precursors would undergo the cyclization via the transition state involving σ-allyl bonding shown in Scheme 7, which is consistent with that proposed in the insertion of 1,3-diene (butadiene) into the allyl−palladium bond.[16]

Conclusion

In summary, we demonstrated the intermediacy of the cationic TMM−Pd complex in the apparently intramolecular C−C bond−forming transformation of (2-(chloromethyl)allyl)palladium complexes. It should be noted that **1a**−**c** showed no evidence of a C−Cl bond cleavage in the solvents used in this study.[6] This suggests that use of the electron-donating cyclopentadienyl ligand may have played a key role in stabilizing the TMM ligand coordinated to the d^8 ML_3 fragment[17] ($(\eta^5\text{-}C_5H_5)Pd^+$). Notice that Pd^{2+} has a d^8 configuration and that the $(\eta^5\text{-}C_5H_5)^-$ ligand is a formally tridentate six-electron donor.

Experimental Section

All manipulations were carried out under argon with the use of standard vacuum line techniques. Solvents were dried by standard methods and distilled prior to use. The following

(15) For a theoretical consideration, see: Albright, T. A. *J. Organomet. Chem.* **1980**, *198*, 159.

(16) Hughes, R. P.; Powell, J. *J. Am. Chem. Soc.* **1972**, *94*, 7723.

(17) Albright, T. A.; Hoffmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546.

materials were prepared according to reported methods: $[Pd(\eta^3\text{-}CH_2C(CH_2Cl)CH_2)Cl]_2$ (**1a**),[5] $[Pd(\eta^3\text{-}CH_2C(CMe_2Cl)CH_2)Cl]_2$ (**1b**).[6] ^1H NMR and ^{31}P NMR spectra were recorded on a JEOL JNM-GSX-270 (270 MHz) spectrometer and a JEOL GSX-400 (400 MHz) spectrometer. Chemical shifts in the ^1H NMR and ^{31}P NMR spectra are referenced to residual protons of the solvents and external $P(OMe)_3$ (δ = 0.00), respectively. Molecular weights were measured by vapor pressure osmometry in benzene at 40 °C on a Corona 114 molecular weight apparatus.

Synthesis of $[Pd(\eta^3\text{-}CH_2C(CH_2Cl)CMe_2)Cl]_2$ (1c). A mixture of 2-isopropylidene-1,3-dichloropropane (330 mg, 2.16 mmol) and $Pd_2(dba)_3CHCl_3$ (999 mg, 0.965 mmol) (dba = dibenzylideneacetone) in CH_2Cl_2 (8 mL) was stirred for 30 h. **1c** (R_f = 0.60, CH_2Cl_2 100%) was separated from free dba by flash column chromatography. Recrystallization of crude **1c** with CH_2Cl_2−hexane gave yellow crystals of **1c**. Yield 64%; mp 137 °C. The ^1H NMR data were identical with those reported as one component of a mixture of isomers.[6] Anal. Calcd for $C_6H_{10}Cl_2Pd$: C, 27.77; H, 3.88. Found: C, 28.06; H, 4.00. 2-Isopropylidene-1,3-dichloropropane was easily made by the known chlorination of 2-isopropylidene-1,3-propanediol[18] with PPh_3/CCl_4/THF (45%).

Synthesis of $[Pd(\eta^3\text{-}CH_2C(CH_2Cl)CH_2)(\eta^5\text{-}C_5H_5)]$ (2a). To a benzene suspension (3 mL) of **1a** (233 mg, 1.01 mmol) was added TlC_5H_5 (290 mg, 1.10 mmol) at room temperature. The mixture was stirred for 5 min and filtered to remove TlCl. Evaporation of benzene under vacuum followed by recrystallization with pentane at −78 °C gave a red solid of pure **2a**. Yield 147 mg (55%); mp 51 °C. ^1H NMR (C_6D_6): δ 2.05 (s, 2H), 3.34 (s, 2H), 3.45 (s, 2H), 5.70 (s, 5H). Anal. Calcd for $C_9H_{11}ClPd$: C, 41.41; H, 4.25. Found: C, 41.03; H, 4.34.

Synthesis of $[Pd(\eta^3\text{-}CH_2C(CMe_2Cl)CH_2)(\eta^5\text{-}C_5H_5)]$ (2b). A similar treatment of **1b** with TlC_5H_5 in C_6H_6 gave a red solid of pure **2b**. Yield 47%; mp 44 °C. ^1H NMR (C_6D_6): δ 1.48 (s, 6H), 1.93 (s, 2H), 3.62 (s, 2H), 5.74 (s, 5H). Anal. Calcd for $C_{11}H_{15}ClPd$: C, 45.70; H, 5.23. Found: C, 45.00; H, 5.15.

Generation of $[Pd(\eta^3\text{-}CH_2C(CH_2Cl)CMe_2)(\eta^5\text{-}C_5H_5)]$ (2c). When a mixture of **1c** (2.9 mg, 0.011 mmol) and TlC_5H_5 (4.9 mg, 0.019 mmol) in C_6D_6 (1.0 mL) was monitored by ^1H NMR 4 min after mixing the reagents, the formation of **2c** was confirmed. ^1H NMR (C_6D_6): δ 1.06 (s, 3H), 1.54 (s, 3H), 2.50 (s, 1H), 3.16 (s, 1H), 3.37 (d, J = 11.3 Hz, 1H), 4.07 (d, J = 11.3 Hz, 1H), 5.62 (s, 5H). This compound gradually isomerized to **2b** (almost completely after 15 h).

Rearrangement of 2a to $[Pd(\eta^3\text{-}CH_2C(CH_2C_5H_5)CH_2)Cl]_2$ (3a) and (7-Methylenebicyclo[3.3.0]oct-2-en-4-yl)(chloro)palladium (4a). **3a** was formed instantaneously upon dissolving **2a** (0.023 mmol) in CD_3NO_2 (0.6 mL) at 25 °C, as confirmed by ^1H NMR. ^1H NMR (CD_3NO_2): δ 2.56 (d, J = 6.8 Hz, 2H), 2.86 (s, 2H), 3.31 (tt, J = 6.8, 1.6 Hz, 1H), 3.88 (s, 2H), 6.50 (br d, J = 4.9 Hz, 2H), 6.64 (br d, J = 4.9 Hz, 2H). On prolonged reaction time, the amount of **3a** decreased, and was replaced by new complexes **4a** (66% yield) and **3a′**/**3a″** (33% yield) after 1 h. These complexes were isolated as follows; a CH_2Cl_2 solution (15 mL) of **2a** (488 mg, 1.87 mmol) was stirred at 40 °C for 24 h. The color of the solution changed from red to yellow. The yellow solution was concentrated, and residual solids were subjected to flash column chromatography, yielding **3a′**/**3a″** (R_f = 0.49) and **4a** (R_f = 0.24) as yellow solids. **3a′**/**3a″**: Yield 131 mg (27%); mp 118 °C. ^1H NMR ($CDCl_3$): δ 2.92 (s, 4H), 3.00 (d, J = 1.6 Hz, 2H), 3.14 (d, J = 0.8 Hz, 2H), 3.40 (br s, 2H), 3.43 (br s, 2H), 3.84 (s, 2H), 3.87 (s, 2H), 6.2−6.7 (m, 6H). Anal. Calcd for $C_9H_{11}ClPd$: C, 41.41; H, 4.25. Found: C, 41.08; H, 4.42. MW calcd for the dimer: 522. Found: 515 at a concentration of 8.62×10^{-3} M. **4a.** Yield 233 mg (48%); mp 142 °C (dec). ^1H NMR ($CDCl_3$): δ 1.72 (d, J = 7.8 Hz, 2H), 2.29 (dddd, J = 15.7, 7.8, 1.9 Hz, 2H), 2.54 (d, J = 15.7 Hz, 2H), 5.03 (q, J = 3.0 Hz, 2H), 5.41 (br s, 2H), 5.77 (t, J = 3.0 Hz, 1H). Anal. Calcd for $C_9H_{11}ClPd$: C, 41.41; H, 4.25. Found: C, 40.92; H, 4.32. MW calcd for the dimer: 522. Found: 519 at a concentration of 1.05×10^{-2} M.

(18) Marshal, J. A.; Werner, T. M., Jr. *J. Org. Chem.* **1971**, *36*, 178.

Table 1. Crystallographic Data for 4a-PPh_3

empirical formula	$C_{27}H_{26}ClPPd(C_6H_6)_{1.5}$
fw	642.52
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a Å	9.623(7)
b, Å	10.761(4)
c, Å	15.389(5)
α, deg	98.13(3)
β, deg	96.98(4)
γ, deg	96.98(4)
V, Å	1539(1)
Z	2
D_{calcd} g/cm^3	1.386
λ(Mo Kα), Å	0.710 69
μ(Mo Kα), cm^{-1}	7.65
temp, °C	23.0
$2\theta_{max}$, deg	55
no. of observations	5852 ($I > 3.00\sigma(I)$)
least squares weights	$\omega^{-1} = \sigma^2(F_o)$
R	0.037
R_w	0.039

Alternative Synthesis of $[Pd(\eta^3\text{-}CH_2C(CH_2C_5H_5)CH_2)Cl]_2$ (3a′/3a″). To a solution of 2-(chloromethyl)-3-cyclopentadienylpropene (138 mg, 0.893 mmol) (1:1 isomeric mixture) in CH_2Cl_2 (5 mL) was added $Pd_2(dba)_3CHCl_3$ (409 mg, 0.395 mmol), and the mixture was stirred at room temperature for 2.5 h. The yellow solution was concentrated and separated off by flash column chromatography with CH_2Cl_2, yielding **3a′**/**3a″** (126 mg, 69%). The spectral data agreed with those described above. 2-(Chloromethyl)-3-cyclopentadienylpropene was easily made by the reaction of 3-chloro-2-(chloromethyl)-1-propene with NaC_5H_5 in THF as a colorless oil in a 1:1 isomeric mixture (15%).

Synthesis and X-ray Structure Determination of 4a-PPh_3. This complex was readily formed by adding PPh_3 to **4a** in C_6H_6. Recrystallization with C_6H_6/hexane gave a yellow needle crystal of **4a**-PPh_3·$1.5C_6H_6$ suitable for X-ray characterization. The presence of 1.5 mol of C_6H_6 was also confirmed by X-ray analysis. Yield 84%; mp 118 °C. ^1H NMR ($CDCl_3$): δ 1.83 (m, 1H), 2.05 (m, 2H), 2.33 (d, J = 14.3 Hz, 2H), 2.96 (d, J = 12.7 Hz, 1H), 4.28 (br s, 1H), 4.71 (br s, 1H), 5.12 (br s, 1H), 5.68 (d, J_{HP} = 8.5 Hz, 1H), 5.91 (br s, 1H), 7.3−7.4 (m, 9H), 7.6−7.7 (m, 6H). ^{31}P NMR (162 Hz, $CDCl_3$): δ −124.93. Anal. Calcd for $C_{36}H_{35}ClPPd$: C, 67.51; H, 5.51. Found: C, 67.85; H, 5.66. A crystal (0.2 × 0.2 × 0.3 mm) for X-ray diffraction was mounted on a glass fiber. The data were obtained on a Rigaku AFC-5R diffractometer with graphite monochromated Mo Kα radiation. The calculation was carried out with the TEXSAN crystallographic software package of Molecular Structure Corp. The structure was solved by direct methods and refined by full-matrix least-squares procedures, the function minimized being $\Sigma\omega(|F_o| - |F_c|)^2$. The non-hydrogen atoms were refined anisotropically. The crystallographic data are summarized in Table 1.

Generation of $[Pd(\eta^3\text{-}CH_2C(CH_2C_5H_5)CH_2)(\eta^5\text{-}C_5H_5)]$ 5a′ + 5a″. Mixing **3a′** + **3a″** with TlC_5H_5 (1.2 equiv) in $CDCl_3$ generated **5a′** + **5a″** rapidly. **5a′** + **5a″**: ^1H NMR ($CDCl_3$) δ 2.28 (s, 4H), 2.95 (dd, J = 1.4, 3.0 Hz, 2H), 2.97 (m, 2H), 3.17 (br s, 2H), 3.19 (br s, 2H), 3.54 (s, 2H), 3.56 (s, 2H), 5.77 (s, 10H), 6.05−6.55 (m, 6H).

Generation of (7-Methylenebicyclo[3.3.0]oct-2-en-4-yl)$(\eta^5\text{-}C_5H_5)$palladium (6a). Treatment of **4a** with TlC_5H_5 in $CDCl_3$ generated **6a**. **6a**: ^1H NMR ($CDCl_3$) δ 1.90−2.10 (m, 4H), 2.12 (m, 2H), 4.68 (m, 2H), 4.83 (dt, J = 3.0, 1.4 Hz, 2H), 5.24 (t, J = 3.0 Hz, 1H), 5.75 (s, 5H).

Generation of $[Pd(\eta^3\text{-}CH_2C(CH_2C_5H_5)CH_2)(\eta^5\text{-}C_5H_5)]$ (5a). Mixing **1a** with TlC_5H_5 (2.2 equiv) in CD_3NO_2 generated **5a** rapidly. **5a**: ^1H NMR (CD_3NO_2) δ 2.24 (s, 2H), 2.28 (d, J = 5.9 Hz, 2H), 3.16 (br t, J = 5.9 Hz, 1H), 3.63 (s, 2H), 5.75 (s, 5H), 6.45 (br d, J = 4.9 Hz, 2H), 6.50 (br d, J = 4.9 Hz, 2H).

Rearrangement of 2b to [Pd(η^3-$CH_2C(CMe_2C_5H_5)CH_2$)Cl]$_2$ (3b), [Pd(η^3-$CH_2C(CH_2C_5H_5)CMe_2$)Cl]$_2$ (3c), and (6,6-Dimethyl-7-methylenebicyclo[3.3.0]oct-2-ene-4-yl)(chloro)palladium (4b). **3b** and **3c** were formed instantaneously by dissolving **2b** (0.023 mmol) in CD_3NO_2 (0.6 mL). ^{1}H NMR (CD_3NO_2): **3b** δ 1.33 (s, 6H), 2.63 (s, 2H), 3.10 (br s, 1H), 3.97 (s, 2H), 6.48 (br s, 2H), 6.60 (br s, 2H); **3c** δ 1.24 (s, 3H), 1.41 (s, 3H), 2.28 (dd, J = 13.5, 7.6 Hz, 1H), 2.83 (dd, J = 13.5, 7.6 Hz, 1H), 3.18 (s, 1H), 3.28 (dd, J = 7.6, 7.6 Hz, 1H), 3.70 (s, 1H), 6.48 (br s, 2H), 6.60 (br s, 2H). On prolonged reaction time, **3b** and **3c** disappeared to give a complicated mixture. For isolation of the products, a CH_2Cl_2 solution (10 mL) of **2b** (299 mg, 1.00 mmol) was stirred at room temperature for 6 h. The color of the solution changed from red to yellow. The yellow solution was concentrated, and residues were subjected to flash column chromatography, yielding a yellow oily mixture (R_f = 0.56), whose ^{1}H NMR spectra was too complicated to allow assignments, and **4b** (R_f = 0.51) as a yellow solid. **4b**: Yield 112 mg (38%); mp 146 °C. ^{1}H NMR ($CDCl_3$): δ 0.95 (s, 3H), 1.26 (dd, J = 5.7, 1.9 Hz), 1.42 (s, 3H), 1.71 (m, 1H), 2.51 (d, J = 15.1 Hz, 1H), 2.63 (m, 1H), 4.87 (s, 1H), 4.99 (s, 1H), 5.29 (s, 1H), 5.41 (s, 1H), 5.75 (s, 1H). Anal. Calcd for $C_{11}H_{15}ClPd$: C, 45.70; H, 5.23. Found: C, 46.11; H, 5.34. MW calcd for the dimer: 578. Found: 598 at a concentration of 1.00×10^{-2} M.

Synthesis of 3b-PPh$_3$ and 3c-PPh$_3$. To a CH_3NO_2 solution (10 mL) of **3b** and **3c** generated from 200 mg of **2b** (0.69 mmol) was added PPh_3 (240 mg, 0.92 mmol). Purification by flash column chromatography (CH_2Cl_2/ethyl acetate = 90/10) gave a mixture of the PPh_3 adducts of **3b** and **3c** (R_f = 0.83) as a yellow solid whose ratio was 22:78 judging from the integral value of the ^{31}P NMR signals. Yield: 68 mg (18%). Anal. Calcd for $C_{29}H_{30}ClPPd$: C, 63.17; H, 5.48. Found: C, 62.35; H, 5.17. **3b**-PPh_3: ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 3H), 1.31 (s, 3H), 1.36 (s, 3H), 1.40 (s, 3H), 2.6−3.1 (m, 6H), 3.22 (s, 1H), 3.25 (s, 1H), 3.4−3.7 (m, 2H), 4,59 (m, 1H), 4.68 (m, 1H), 6.02 (m, 1H), 6.07 (m, 1H), 6.20 (m, 1H), 6.32 (m, 1H), 6.47 (m, 1H), 6.68 (m, 1H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −121.18 (s), −121.23 (s). **3c**-PPh_3: ^{1}H NMR ($CDCl_3$) δ 1.53 (d, J_{HP} = 5.6 Hz, 3H), 1.54 (d, J_{HP} = 5.6 Hz, 3H), 1.88 (d, J_{HP} = 8.4 Hz, 3H), 1.90 (d, J_{HP} = 8.8 Hz, 3H), 2.6−3.1 (m, 8H), 3.4−3.7 (m, 4H), 5.99 (s, 1H), 6.12 (s, 1H), 6.20 (m, 1H), 6.35 (m, 1H), 6.41 (m, 1H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ −116.83 (s).

Measurement of the Reaction Rate. **2a** (2.3−11.5 mg, 0.0088−0.0440 mmol) in an NMR tube was dissolved in a deuterio solvent (0.6−1.2 mL) containing an internal standard (hexane 0.4−1.2 μL) at −78 °C. The tube was sealed and kept at −78 °C until it was put in an NMR spectrometer. We defined T = 0 as the time when the first measurement was finished and assayed the decay of **2** at regular intervals at 25 °C until 60−70% decay of **2a**. Plotting 1/[**2a**] against T gave straight lines, the slope of which corresponds to k ($-d[\mathbf{2a}]/dt = k[\mathbf{2a}]^2$). The initial concentration $[\mathbf{2a}]_0$ (M) and the second-order rate constant k ($M^{-1}s^{-1}$) (standard deviation σ) are as follows:

$CDCl_3$;

$[\mathbf{2a}]_0 = 6.20 \times 10^{-3}$, $k = 6.37 \times 10^{-4}$ ($\sigma = 0.996$)

$[\mathbf{2a}]_0 = 1.34 \times 10^{-2}$, $k = 6.12 \times 10^{-4}$ ($\sigma = 0.985$)

$[\mathbf{2a}]_0 = 2.91 \times 10^{-2}$, $k = 6.43 \times 10^{-4}$ ($\sigma = 0.969$)

$[\mathbf{2a}]_0 = 7.30 \times 10^{-2}$, $k = 6.02 \times 10^{-4}$ ($\sigma = 0.997$)

CD_2Cl_2;

$[\mathbf{2a}]_0 = 1.39 \times 10^{-2}$, $k = 1.13 \times 10^{-2}$ ($\sigma = 0.994$)

$[\mathbf{2a}]_0 = 2.10 \times 10^{-2}$, $k = 9.54 \times 10^{-3}$ ($\sigma = 0.997$)

The transformation of **2a** (1.66×10^{-2} M) with 10.4 equiv of **2d** was also carried out under the same procedure and conditions. The first-order rate constant was found to be $k' = 7.56 \times 10^{-5}$ ($\sigma = 0.997$).

Methanolysis of 2. Determination of the products **7a** and **7b** was carried out in CD_3OD in NMR tubes. Their ^{1}H NMR data were in accord with those of **7a** and **7b**, which were isolated as follows.

Synthesis of [Pd(η^3-$CH_2C(CH_2OMe)CH_2$)Cl]$_2$ (7a). To MeOH (300 mL) was added **2a** (146 mg, 0.631 mmol) at −78 °C, and then the mixture was warmed to room temperature. The solution was stirred for 1 h at room temperature. The solvent was evaporated under vacuum, and a residue was recrystallized with CH_2Cl_2−hexane to give a yellow crystal of **7a**. Yield 20 mg (47%); mp 132 °C. ^{1}H NMR ($CDCl_3$): δ 2.95 (s, 2H), 3.53 (s, 3H), 4.01 (s, 2H), 4.10 (s, 2H). Anal. Calcd for C_5H_9ClOPd: C, 26.46; H, 4.00. Found: C, 26.83; H, 3.96. MW calcd for the dimer: 454. Found: 421 at a concentration of 1.72×10^{-2} M.

Synthesis of [Pd(η^3-$CH_2C(CMe_2OMe)CH_2$)Cl]$_2$ (7b). A similar procedure as for the synthesis **2b** (311 mg, 1.20 mmol) in MeOH (100 mL) gave a yellow solid of **7b**. Yield 110 mg (36%); mp 124 °C. ^{1}H NMR ($CDCl_3$): δ 1.47 (s, 6H), 2.85 (s, 2H), 3.49 (s, 3H), 4.03 (s, 2H). Anal. Calcd for $C_7H_{13}ClOPd$: C, 32.96; H, 5.14. Found: C, 33.86; H, 5.11. MW calcd for the dimer: 510. Found: 501 at a concentration of 1.18×10^{-2} M.

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Supporting Information Available: Tables of positional parameters, thermal parameters, bond lengths, and bond angles and diagrams of orientation in the unit cell for **4a**-PPh_3 (18 pages). Ordering information is given on any current masthead page.

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