Carbon-carbon Bond Forming Reactions of μ-Vinylcarbenedipalladium Complexes

Sensuke Ogoshi,* Ken Tsutsumi,† Tsutomu Shinagawa, Kiyomi Kakiuchi,† and Hideo Kurosawa*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565-0871
†*Graduate School of Material Science, Nara Institute of Science and Technology, Ikoma, Nara 630-0101*

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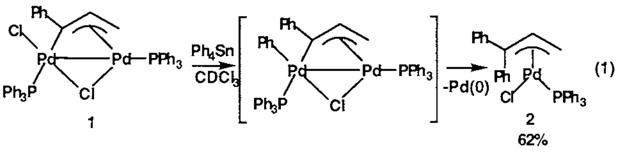
μ-η^3-Vinyl(phenyl)carbenedipalladium complex reacted with tetraphenyltin to give a η^3-diphenylallylpalladium complex through reductive elimination, and with internal alkynes to give μ-η^2:η^3-dienylcarbene complexes through migratory insertion.

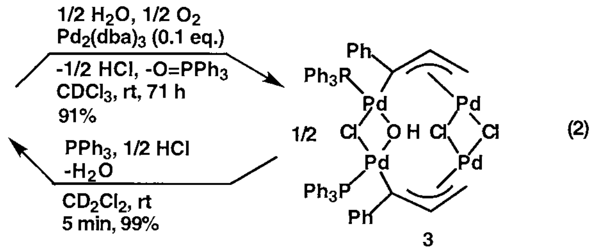
Although vinylcarbene complexes of transition metals including mononuclear and binuclear centers are becoming more common and their synthetic application has attracted increasing attention,[1] no precedent of the reaction of vinylcarbenepalladium or even carbenepalladium complexes has been reported.[2] Recently, we have reported the high yield synthesis of μ-η^3-vinylcarbenedipalladium (**1**), the first example of vinylcarbene complexes of palladium,[3] by the reaction of μ-η^3-propagyldipalladium complex with HCl. We report herein C-C bond formation using reductive elimination and migratory insertion of **1** and its analog.

In a sealed glass tube, a $CDCl_3$ solution of **1** and $SnPh_4$ was heated at 40 °C for 45 h to give η^3-1,1-diphenylallylpalladium complex (**2**) (eq 1).[4] This complex might be generated by the reductive elimination from a phenylated dipalladium intermediate. The C-C bond coupling at dinuclear center could be a nice model for the reaction on the metal surface.[5] Mononuclear vinylcarbene complexes also react with nucleophiles to give η^3-allyl complexes.[6]



(1)

In the presence of a catalytic amount of $Pd_2(dba)_3$ (dba =dibenzylideneacetone), the complex **1** reacted with H_2O and O_2 to give hydroxo bridged μ-η^3-vinylcarbenedipalladium dimer (**3**) in an excellent yield (eq 2).[7] The structure of the complex **3** was determined by X-ray diffraction analysis (Figure 1).[8] This complex has a unique structure in which one of four bridging ligands is OH group. The coordination mode and geometry of μ-η^3-vinylcarbene group in **3** are quite similar to those in **1**. However, the Pd-Pd distance in **3** (3.17 Å) is somewhat longer than in **1** (2.87 Å), possibly reflecting the absence, in the former, of the Cl bridge on the Pd-Pd opposite to the vinylcarbene bridge. The transformation shown in eq 2 did not work well without $Pd_2(dba)_3$ which might have a role of oxidizing PPh_3 to O=PPh_3, which was confirmed by ^{31}P NMR spectra. Treatment of **3** with PPh_3 and HCl regenerated the dinuclear complex **1** quantitatively.



(2)

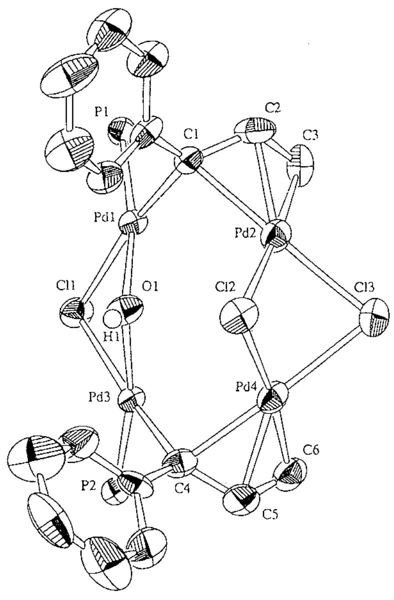


Figure 1. Structure of **3**.

In a sealed glass tube, a $CDCl_3$ solution of **3** and 2.2 equiv of internal alkynes was heated at 60 °C for 17 h. The ^{1}H NMR

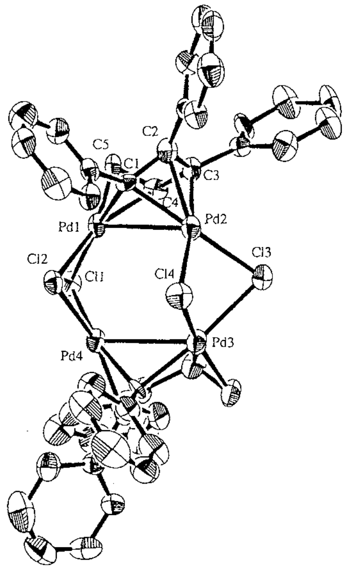
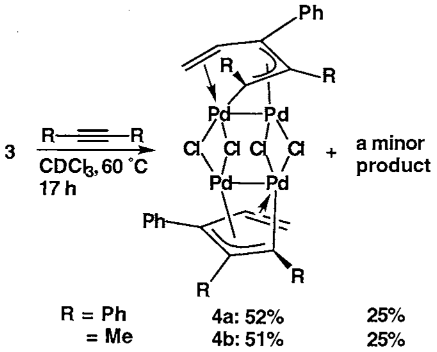


Figure 2. Structure of **4a**.

spectrum of a reaction mixture showed the presence of two sets of resonances (ca. 2:1) which are similar to each other.[9] The major product was separated by recrystallization from a yellow eluent of column chromatography to give a μ-η^2:η^3-dienylcarbene complex (**4a**, **4b**) (eq 3).[10] The structure of **4a** was determined by X-ray structure analysis,[11] revealing that alkynes have inserted into the palladium-carbene carbon bond to form a new μ-η^3-vinylcarbene moiety [12, 13] and OH group has been replaced by Cl in $CDCl_3$ (Figure 2). In fact the reaction of **3** with an alkyne in C_6D_6 did not proceed. The isolated **4a** was not transformed into the minor product in a solution, suggesting that there is no equilibrium between the two products.[9] The complex **1** also reacted with alkynes to give **4a**, albeit in low yield.



(3)

In summary, we demonstrated here the C-C bond formation reaction of μ-η^3-vinylcarbenedipalladium which is the first vinylcarbene complex of palladium. Further studies on the reaction of μ-η^3-vinylcarbenedipalladium are in progress.

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References and Notes

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

2 A review on palladium carbene complexes: P. M. Maitlis, P. Espinet, and M. J. H. Russell in "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, New York(1982), vol. 6, pp. 292-299.

3 S. Ogoshi, K. Tsutsumi, M. Ooi, and H. Kurosawa, *J. Am. Chem. Soc.* **117**, 10415 (1995).

4 Selected spectral data for **2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.76 (dd, J = 7.3, 2.2 Hz, 1H), 2.92 (dd, J = 12.5, 2.2 Hz, 1H), 5.83 (dd, J = 12.5, 7.3 Hz, 1H), 7.31-7.70 (m, 25H). ^{31}P NMR ($CDCl_3$, 162 MHz) δ 28.45 (s). : Anal. Found: C, 59.84; H, 4.47%. Calcd for $C_{33}H_{28}ClPPd \cdot CH_2Cl_2$: C, 59.85; H. 4.43%.

5 P. M. Maitlis, H. C. Long, R. Quyoum, M. L. Turner, and Z. -Q. Wang, *J. Chem. Soc., Chem. Commun.*, **1996**. 1.

6 T. Mitsudo, H. Watanabe, T. Sasaki, Y. Takegami, and Y. Watanabe, *Organometallics*, **8**, 368 (1989). K. E. Garrett, J. B. Sheriden, D. B. Pourreau, W. C. Feng, G. L. Geoffroy, D. L. Staley, and A. L. Rheingold, *J. Am. Chem. Soc.*, **111**, 8383 (1989).

7 Selected spectral data for **3**: ^{1}H NMR (400 MHz, $CDCl_3$) 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 (100 MHz, $CDCl_3$) δ 57.68, 112.68 (J_{CP} = 9.3 Hz), 122.83. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.85 (s): Anal. Found: C, 49.44; H, 3.82%. Calcd for $C_{54}H_{47}Cl_3OP_2Pd_4$: C, 49.66; H. 3.63%.

8 Crystal data for **3**: $C_{54}H_{43}P_2OCl_3Pd_4 \cdot 4(H_2O) \cdot CHCl_3$ triclinic, $P\bar{1}$(*No.2*), a = 15.276(5) Å, b = 16.798(4) Å, c = 15.080(4) Å, α = 112.20(2)°, β = 119.30(2)°, γ = 68.64(2)°, Z = 2, Dcalc = 1.63 g/cm^3, R = 0.083, Rw = 0.119.

9 Athough we were unable to determine the full structure of the minor product, it might also include the same μ-η^2:η^3-dienylcarbene group because of the similarity of ^{1}H NMR spectra of **4** to those of the minor product.

10 Selected spectral data for **4a**: (48%: isolated yield by recrystallization) ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.68 (dd, J = 13.2, 1.6 Hz, 2H), 5.09 (dd, J = 7.3, 1.6 Hz, 2H), 6.47 (dd, J = 13.2, 7.3 Hz, 2H), 6.80-7.50 (m, 60H): Anal. Found: C, 45.40; H, 3.05%. Calcd for $C_{46}H_{36}Cl_4Pd_4 \cdot CH_2Cl_2$: C, 45.48; H. 3.09%. **4b**: (43%: isolated yield after recrystallization) ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.05 (s, 6H), 2.10 (s, 3H), 4.19 (dd, J = 13.2, 1.6 Hz, 2H), 4.83 (dd, J = 7.3, 1.6 Hz, 2H), 6.03 (dd, J = 13.2, 7.3 Hz, 2H), 7.20-7.80 (m, 20H): Anal. Found: C, 34.46; H, 3.09%. Calcd for $C_{26}H_{28}Cl_4Pd_4$: C, 34.39; H. 3.11%.

11 Crystal data for **4a** (recrystallized from a hexane-ethyl acetate solution): $C_{46}H_{36}Cl_4Pd_4 \cdot CH_3COOC_2H_5 \cdot C_6H_{14}$ monoclinic, $P2_1/c$ (*No.14*), a = 12.111(8) Å, b = 16.150(1) Å, c = 27.182(10) Å, β = 98.48(5)°, Z = 4, Dcalc = 1.68 g/cm^3, R = 0.058, Rw = 0.060.

12 μ-Vinylcarbene ruthenium complex reacts with alkynes to give similar μ-η^2:η^3-dienylcarbene complexes. P. Q. Adams, D. L. Davis, A. F. Dyke, S. A. R. Knox, K. A. Mead, and P. J. Woodward, *J. Chem. Soc., Chem. Commun.*, **1983**, 222.

13 μ-Carbene complexes react with alkynes to give μ-η^3-vinylcarbene complexes: see Ref. 1.