Formation of a Palladalactone Complex by C-O Bond Cleavage of Diketene Promoted by a Zerovalent Palladium Complex

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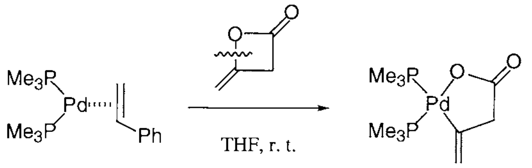
The reaction of diketene with $[Pd(PMe_3)_2(styrene)]$ **1** at room temperature gave $[Pd(OCOCH_2C{=}CH_2)(PMe_3)_2]$ **2** through cleavage of the C-O bond adjacent to the carbon bearing the exomethylene group. The structure of **2** was fully established by spectroscopic means, elemental analysis and single-crystal X-ray analysis. The reactivity of **2** has been investigated.

The C-O bonds in carboxylic esters and anhydrides can be cleaved on interaction with low valent transition metal complexes to give reactive organotransition metal complexes.[1] The organotransition metal complexes thus produced may be further subjected to the subsequent reactions to accomplish useful synthetic processes. A palladium-catalyzed direct hydrogenation of carboxylic acid to aldehydes recently developed illustrates an example of applications developed on the basis of the fundamental studies of oxidative additions of carboxylic acid derivatives with zero valent palladium complexes.[2]

Among carboxylic acid derivatives, diketene is considered to be a good candidate for examining its reactivity with transition metal complexes, since organotransition metal complexes derived thereof may provide opportunities of applications in organic synthesis. Diketene is commercially available and serves as a convenient starting material for preparation of a variety of useful intermediates in manufacturing important insecticides and pigments.[3] Its reactions with various nucleophiles with involvement of the ring cleavage between the carbonyl carbon and the oxetane oxygen have been extensively utilized in preparation of various compounds such as acetoacetic acid derivatives.[3,4] On the other hand, examples of the cleavage between the oxetane oxygen and the exomethylene-bearing carbon are quite limited.[5] Previously we have examined the C-O bond cleavage of diketene on reaction with a Ni(0) complex to generate propylene and CO_2, but the oxidative addition product of the diketene with the Ni(0) complex was not confirmed.[6] We now report the cleavage of the C-O bond in diketene on interaction with a Pd(0) complex to give a new palladacycle $[Pd(OCOCH_2C{=}CH_2)(PMe_3)_2]$, **2**. This is, to our knowledge, the first example of full characterization of the oxidative addition product of diketene with a transition metal complex with involvement of the C-O bond cleavage between the exomethylene-bearing carbon and the oxetane oxygen.

Treatment of *trans*-$[PdEt_2(PMe_3)_2]$[7a] with styrene gives a coordinatively unsaturated palladium(0) complex $[Pd(styrene)(PMe_3)_2]$ **1**.[7b] An equimolar amount of diketene was added to a THF solution containing **1** at room temperature. Immediate color change of the solution from yellow to red was observed with subsequent precipitation of a white solid from the reaction mixture. The white precipitate was filtered, washed with Et_2O, and recrystallized from acetone to give palladalactone complex **2** in 61% isolated yield. Characterization of the complex with spectroscopic means[8] and elemental analysis[9] indicated that the C-O bond adjacent to the carbon bearing the exomethylene group was cleaved to form a five-membered palladalactone **2** (Eq. 1).



(1)

1 **2**

Figure 1 shows the molecular structure of **2** determined by X-ray crystallography.[10] The palladalactone complex **2** was revealed to have a square-planar coordination around the palladium center. A significant deviation of the exomethylene unit from the square plane is noted. The two Pd-P bond distances showed a significant difference from each other due to the different trans influence of the coordinating carbon and oxygen atoms.[11,12]

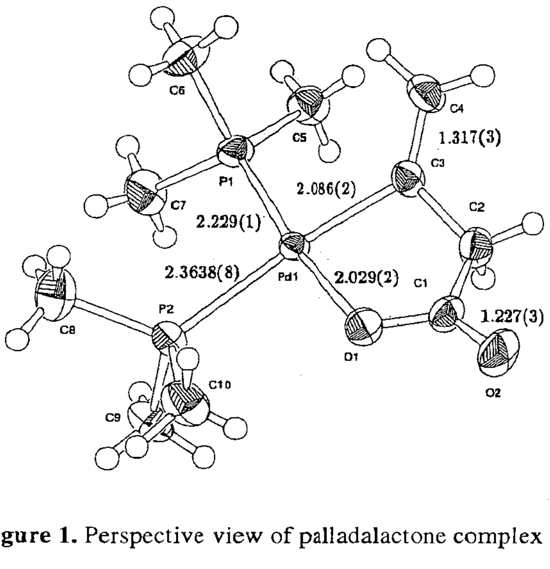


Figure 1. Perspective view of palladalactone complex **2**.

The palladalactone **2** shows high reactivity toward various compounds as summarized in Figure 2. Unsaturated compounds such as CO and isocyanides undergo insertion into the Pd-C bond followed by reductive elimination and proton migration to give cyclic anhydride derivatives **3** (84% yield), **4** (80%) and **5** (60%).[13] Methyl iodide attacks the ring oxygen as an electrophile to give an alkylpalladium iodide **6** (94%). Maleic anhydride and dimethyl acetylenedicarboxylate removed one of the two PMe_3 ligands to give a monophosphine coordinated palladalactone complex **7** in 53% isolated yield at room temperature.[14] Addition of an equimolar amount of PMe_3 to the monophosphine palladalactone complex **7** regenerated the bis-phosphine palladalactone complex **2**. The poor solubility of **7** in usual organic solvents suggests that the coordinatively unsaturated palladalactone entity forms an oligomeric complex where the palladium center is coordinated with the carbonyl group of the adjacent palladalactone entity. Formation of a nickel-containing tetramer with cyclic five-membered amide rings bonded with the adjacent entities through the carbonyl groups has been previously reported.[15] The tetramer was converted into a monomeric nickelalactam on treatment with PEt_3 to form a mononuclear bis-phosphine complex.

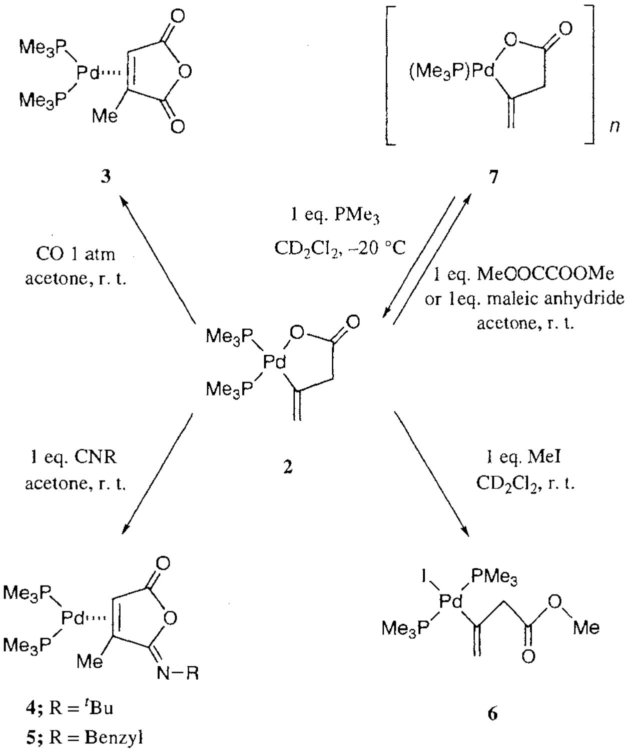


Figure 2. Reactivity of the palladalactone complex **2**.

The ease of the C-O bond cleavage in diketene promoted by the Pd(0) complex to form the palladalactone having high reactivity toward various reactants suggests the potential applicability of the C-O bond cleavage processes to organic synthesis which is presently examined.

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References and Notes

1 a) A. Yamamoto, *Adv. Organometal. Chem.*, **34**, 111 (1992). b) Y. -S. Lin, and A. Yamamoto, "Topics in Organometallic Chemistry," ed by S. Murai, Springer, Berlin (1999), Vol. 3, pp. 161-192.

2 a) K. Nagayama, F. Kawataka, M. Sakamoto, I. Shimizu, and A. Yamamoto, *Chem. Lett.*, **1995**, 367. b) K. Nagayama, I. Shimizu, and A. Yamamoto, *Chem. Lett.*, **1998**, 1143. c) K. Nagayama, F. Kawataka, M. Sakamoto, I. Shimizu, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **72**, 573 (1999). d) K. Nagayama, I. Shimizu, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **72**, 799 (1999).

3 R. J. Clemens, *Chem. Rev.*, **86**, 241 (1986).

4 a) C. E. Garrett and G. C. Fu, *J. Am. Chem. Soc.*, **120**, 7479 (1998). b) J. C. Ruble and G. C. Fu, *J. Org. Chem.*, **61**, 7230 (1996). c) I. Shibata, M. Nishio, A. Baba, and H. Matsuda, *J. Chem. Soc., Chem. Commun.*, **1993**, 1067. d) M. Hayashi, T. Inoue, and N. Oguni, *J. Chem. Soc., Chem. Commun.*, **1994**, 341. e) M. Hayashi, T. Inoue, Y. Miyamoto, and N. Oguni, *Tetrahedron*. **50**, 4385 (1994).

5 Y. Abe, M. Sato, H. Goto, R. Sugawara, E. Takahashi, and T. Kato, *Chem. Pharm. Bull.*, **31**, 4346 (1983). b) Y. Abe, H. Goto, M. Sato, and T. Kato, *Chem. Pharm. Bull.*, **31**, 1108 (1983). c) T. Fujisawa, T. Sato, Y. Gotoh, M. Kawashima, and T. Kawara, *Bull. Chem. Soc. Jpn.*, **55**, 3555 (1982). d) K. Itoh, M. Fukui, and Y. Kurachi, *J. Chem. Soc., Chem. Commun.*, **1977**, 500. e) K. Itoh, T. Yogo, and Y. Ishii, *Chem. Lett.*, **1977**, 103.

6 T. Yamamoto, J. Ishizu, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **55**, 623 (1982).

7 a) Y. -J. Kim, K. Osakada, A. Takenaka, and A. Yamamoto, *J. Am. Chem. Soc.*, **112**, 1096 (1990). b) K. Osakada, Y. Ozawa, and A. Yamamoto, *J. Organomet. Chem.*, **399**, 341 (1990).

8 **2**: ^{1}H NMR ($CDCl_3$, –20 °C, 500 MHz) δ 5.10 (dd, 1H, $^4J_{HP}$ = 26.5 Hz, $^4J_{HP}$ = 13.8 Hz, C=CH_2), 4.60 (dd, 1H, $^4J_{HP}$ = 11.6 Hz, $^4J_{HP}$ = 5.03 Hz, C=CH_2), 3.44 (dd, 2H, $^4J_{HP}$ = 7.69 Hz, $^4J_{HP}$ = 1.28 Hz, CH_2), 1.50 (dd, 9H, $^2J_{HP}$ = 9.25 Hz, $^4J_{HP}$ = 1.28 Hz, P(CH_3)$_3$), 1.34 (dd, 9H, $^2J_{HP}$ = 9.25 Hz, $^4J_{HP}$ = 1.28 Hz, P(CH_3)$_3$); ^{13}C{^{1}H} NMR ($CDCl_3$, –20 °C, 125.7 MHz) δ 184.2 (d, $^3J_{CP}$ = 7.3 Hz, *C*=O), 163.1 (d, $^2J_{CP}$ = 113.6 Hz, *C*=CH$_2$), 113.6 (s, C=*C*H$_2$), 54.7 (s, *C*H$_2$), 17.9 (d, $^1J_{CP}$ = 33.9 Hz, P(*C*H$_3$)$_3$), 14.8 (d, $^1J_{CP}$ = 20.2 Hz, P(*C*H$_3$)$_3$); ^{31}P{^{1}H} NMR ($CDCl_3$, –20 °C, 109.4 MHz) δ -5.67 (d, $^2J_{PP}$ = 38.2 Hz, *P*(CH$_3$)$_3$), -21.6 (d, $^2J_{PP}$ = 38.2 Hz, *P*(CH$_3$)$_3$); IR(KBr disc); ν(C-H) 2925, 2910, ν(C=O) 1632, ν(P-C) 975, 951 cm^{-1}.

9 Anal. Calcd for $C_{10}H_{22}O_2P_2Pd$: C, 35.05; H, 6.47%. Found: C, 35.18; H, 6.78%.

10 The single crystals suitable for crystallography were grown in dry acetone at -30 °C. Crystal data: $C_{10}H_{22}O_2P_2Pd$; Molecular weight = 342.63; triclinic; space group *P*1(#2); a = 9.481(6) Å, b = 9.986(6) Å, c = 9.323(6) Å, α = 101.89(6)°, β = 117.58(4)°, γ = 72.86(5)°, V = 745.2(8) Å^3; Z = 2; μ(Mo Kα) =14.43 cm^{-1} ; D_{calcd} = 1.527 g cm^{-3}; 3601 unique data, 3407 observed data ($F_0 > 3\sigma(F_0)$). A crystal with approximate dimensions of 0.20 x 0.20 x 0.15 mm was used for analysis. The structure was solved by direct methods (SIR 92) and refined by full-matrix least-squares calculations. Final R and R_w values were 0.020 and 0.025, respectively.

11 Reaction of 3-butenoic acid with an equimolar amount of [Pd(PMe$_3$)$_2$(styrene)] gives a five-membered palladalactone complex. The complex was characterized by single-crystal X-ray analysis. K. Osakada, M. -K. Doh, F. Ozawa, and A. Yamamoto, *Organometallics*, **9**, 2197 (1990).

12 Palladalactone complexes with four and six-membered rings have been prepared using ketene and their molecular structures have been determined by X-ray diffraction. S. Baba, T. Ogura, and S. Kawaguchi, *J. Chem. Soc., Chem. Commun.*, **1972**, 910.

13 Complexes **3** – **7** have been characterized by spectroscopic means and elemental analysis.

14 When palladalactone complex **2** and dimethyl acetylenedicarboxylate were mixed in acetone-d_6 at room temperature, the yellow solution immediately became red, and the white powder was precipitated from the reaction mixture. The starting material **2** disappeared, and the ^{31}P NMR spectrum displayed signals for remaining PMe_3 ligand. The result indicates that one of the two PMe_3 ligands in complex **2** was stripped away by action of dimethyl acetylenedicarboxylate to give monophosphine complex **7**.

15 T. Yamamoto, K. Sano, K. Osakada, S. Komiya, A. Yamamoto, Y. Kushi, and T. Tada, *Organometallics*, **9**, 2369 (1990)