# Alteration of Reaction Course in Thermolysis of *cis*-Diethylbis(tertiary phosphine)palladium(II) from Reductive Elimination to β-Elimination Process Induced by Addition of Tertiary Phosphine Ligand

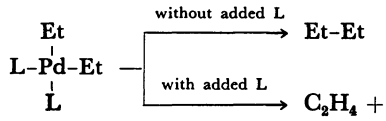
Fumiyuki OZAWA, Kunihiko KURIHARA, Takakazu YAMAMOTO, and Akio YAMAMOTO*
*Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227*
(Received August 20, 1984)

**Synopsis.** Addition of tertiary phosphine to a solution containing *cis*-diethylbis(tertiary phosphine)palladium(II) alters thermolysis course of the complex from reductive elimination process liberating butane to β-hydrogen elimination process in which ethane and ethylene are released. Study with a deuterium-labeled ethyl complex indicates involvement of an internal metalation process.

Studies on thermolysis mechanisms of isolated dialkylpalladium complexes provide essential information for understanding basic properties of organopalladium complexes. Two most important concerted thermolysis pathways of dialkylpalladium complexes relevant to organic synthesis are reductive elimination and β-elimination.[1] Thus, information concerning controlling factors of these two pathways is of crucial importance for designing selective organic reactions promoted by palladium complexes.

In the previous reports[2,3] we showed that thermolysis courses of diethylbis(tertiary phosphine)palladium(II) complexes were dictated by their configurations, cis or trans.

Trans isomers decompose through a clean β-elimination process to give ethylene and ethane in a 1:1 ratio, whereas cis isomers afford butane as the reductive elimination product. The β-elimination process of trans isomers is scarcely affected by addition of free tertiary phosphines to the systems and the reaction is assumed to proceed predominantly from four-coordinate species without predissociation of phosphine ligand.[3] In contrast, reductive elimination of the cis isomers is severely hindered by addition of phosphine ligands and a reaction mechanism proceeding through three-coordinate intermediates formed by partial dissociation of tertiary phosphine ligand has been proposed.[2,4] Further studies on the thermolysis reactions of *cis*-diethyl complexes revealed that addition of free phosphine ligands to the system not only retards the reductive elimination reaction but also forces to change the thermolysis course from the reductive elimination to the β-elimination process.




(L=$PMe_2Ph$, **1**; 1/2 $Ph_2P(CH_2)_2PPh_2$ (dppe), **2**; 1/2 $Ph_2P(CH_2)_3PPh_2$ (dppp), **3**; 1/2 $Ph_2P(CH_2)_4PPh_2$ (dppb), **4**)

TABLE 1. GASES EVOLVED ON THERMOLYSIS OF *cis*-$PdEt_2L_2$[a]

| Run | L | Additive (mol $dm^{-3}$) | Evolved gas ratio | | | Total amount[b] |
|---|---|---|---|---|---|---|
| | | | $C_2H_4$ | $C_2H_6$ | $C_4H_{10}$ | |
| 1 | $PMe_2Ph$ (**1**) | dmm (0.17) | 0.00 | 0.00 | *1.00* | 0.94 |
| 2 | $PMe_2Ph$ (**1**) | $PMe_2Ph$ (0.066) dmm (0.38) | 0.03 | 0.04 | *0.93* | 0.76 |
| 3 | $PMe_2Ph$ (**1**) | $PMe_2Ph$ (0.33) | *0.49* | *0.47* | 0.04 | 0.95 |
| 4 | $PMe_2Ph$ (**1**) | $PMe_2Ph$ (0.63) | *0.48* | *0.52* | 0.00 | 0.86 |
| 5 | 1/2dppe (**2**) | dmm (0.38) | 0.12 | 0.08 | *0.81* | 1.00 |
| 6 | 1/2dppe (**2**) | dppe (0.011) dmm (0.38) | *0.52* | *0.46* | 0.02 | 0.72 |
| 7 | 1/2dppp (**3**) | dmm (0.38) | 0.17 | 0.09 | *0.75* | 0.62 |
| 8 | 1/2dppp (**3**) | dppp (0.0087) dmm (0.38) | *0.47* | *0.50* | 0.04 | 0.90 |
| 9 | 1/2dppp (**3**) | dppp (0.036) | *0.50* | *0.47* | 0.04 | 0.89 |
| 10 | 1/2dppp (**3**) | dppp (0.26) | *0.50* | *0.48* | 0.03 | 0.94 |
| 11 | 1/2dppb (**4**) | dmm (0.38) | 0.17 | 0.09 | *0.75* | 0.62 |
| 12 | 1/2dppb (**4**) | dppb (0.12) | *0.48* | *0.50* | 0.02 | 0.93 |

a) [Complex] = 0.05—0.10 mol $dm^{-3}$. Solvent: toluene (run 1), $Ph_2CH_2$ (runs 2—12). Thermolysis temp (°C): r.t. (run 1), 70 (runs 2—12). b) Total amounts (mol/mol of complex) = $\{(1/2)(C_2H_4+C_2H_6)+C_4H_{10}\}$/(complex).

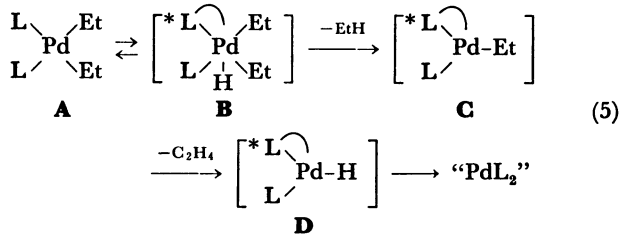
Table 1 summarizes distributions of hydrocarbons produced on thermolysis of four kinds of *cis*-diethyl complexes in solution in the presence and absence of free tertiary phosphines. Most of these reactions were carried out in the presence of dimethyl maleate (dmm). As previously mentioned,[2,3] dmm serves to trap $Pd(0)L_2$ species formed in thermolysis preventing decomposition of the $Pd(0)L_2$ species but does not affect the thermolysis of *cis*-$PdEt_2L_2$. The results in Table 1 clearly indicate that thermolysis course is effectively altered from the reductive elimination to the $\beta$-elimination pathway on addition of free phosphine ligands. Diphosphine coordinated compelexes **2—4** are more sensitive to addition of phosphines than complex **1** having monodentate ligand. Thermolysis rates in the systems with added phosphines were much slower than those without added phosphines. For example, complex **1** readily decomposes at room temperature to yield butane, while thermolysis of **1** (0.17 mol $dm^{-3}$) in $Ph_2CH_2$ containing 0.70 mol $dm^{-3}$ of $PMe_2Ph$ does not proceed at room temperature and takes place only at 60 °C. The reaction obeys the first order kinetics with respect to diethylpalladium concentration ($k_{obsd}=3.0\times10^{-5}$ $s^{-1}$) and liberates ethylene and ethane in a 1:1 ratio.

Examination of the thermolysis products of *cis*-$Pd(CH_2CD_3)_2(PMe_2Ph)_2$ (**5**) provides further information on the thermolysis mechanisms of *cis*-diethyl complexes. Thermolysis of **5** in solution without added $PMe_2Ph$ affords an almost quantitative yield of $CD_3CH_2CH_2CD_3$ as reported previously.[2] On the other hand, thermolysis of **5** in $Ph_2CH_2$ or $C_6D_6$ containing a ten fold excess amount of $PMe_2Ph$ per palladium liberates a quantitative yield of $CD_3CH_3$, instead of $CD_3CH_2D$, together with a quantitative amount of $CD_2{=}CH_2$.

$$cis\text{-}Pd(CH_2CD_3)_2(PMe_2Ph)_2 \xrightarrow{\text{with } PMe_2Ph} CD_3CH_3 + CD_2{=}CH_2 \quad (4)$$

Evidently no H-D scrambling in the ethyl groups is involved in these reductive elimination and $\beta$-hydrogen elimination processes. Furthermore, the ethane formation in thermolysis of the cis isomer arises by abstraction of hydrogen not from disproportionation of the two ethyl groups or from solvent but from the $PMe_2Ph$ ligand. A similar hydrogen abstraction process from phosphine ligand has been suggested in thermolysis of *cis*-$Pt(CH_2CD_3)_2(Me_2P(CH_2)_2PMe_2)$ producing $CD_3CH_3$ and $CH_2{=}CD_2$.[5]

When the reductive elimination pathway is blocked in thermolysis of *cis*-$PdEt_2L_2$ by addition of tertiary phosphine ligand, the complex is forced to take another course. The most probable process suggested by the present study is internal ortho metalation of the starting *cis*-diethyl complex (**A**) involving C–H bond cleavage at the phenyl group in $PMe_2Ph$[6] to give **B**. The internally metalated diethyl(hydrido)palladium-(IV) species **B** then reductively eliminates ethane to give a monoethyl complex (**C**). Species **C** then undergoes $\beta$-elimination process liberating ethylene and forming a hydridopalladium complex (**D**), which is



(5)

spontaneously converted into Pd(0) complex.

## Experimental

All manipulations were carried out as reported previously.[2,3] Analysis of the gases evolved by thermolysis of *cis*-$Pd(CH_2CD_3)_2(PMe_2Ph)_2$ (**5**)[2] was carried out by GC-mass spectrometry (Hitachi M-80 spectrometer; column, Porapak Q; FD mass method). Structure of deuterated ethylene was confirmed by IR spectroscopy.[8] The rate constant for thermolysis of *cis*-$PdEt_2(PMe_2Ph)_2$ (0.17 mol $dm^{-3}$) in $Ph_2CH_2$ containing $PMe_2Ph$ (0.70 mol $dm^{-3}$) at 60 °C was obtained by measuring the amounts of ethylene and ethane evolved with time using a Toepler pump.

*Preparation of* cis-*PdEt*$_2$*(dppp) (3) and* cis-*PdEt*$_2$*(dppb) (4).* *Cis*-diethyl complexes **3** and **4** were prepared by the reactions of $Pd(acac)_2$, $Al_2Et_3(OEt)_3$, and corresponding phosphine ligands in a manner similar to the preparation of *cis*-$PdEt_2$(dppe) (**2**)[9] and were identified by means of elemental analysis and IR and $^1H$ and $^{13}C\{^1H\}$ NMR spectroscopy.

## References

1) J. K. Kochi, "Organometallic Mechanisms and Catalysts," Academic Press, New York (1978); J. Tsuji, "Organic Synthesis by Means of Transition Metal Complexes," Springer-Verlag, Berlin (1975); S. G. Davies, "Organotransition Metal Chemistry. Applications to Organic Synthesis," Pergamon Press, New York (1982); S. Murahashi, M. Yamamura, K. Yanagisawa, N. Mita, and K. Kudo, *J. Org. Chem.*, **44**, 2408 (1979); A. Sekiya and N. Ishikawa, *J. Organomet. Chem.*, **125**, 281 (1977) and **118**, 349 (1976); A. Minato, K. Tamao, T. Hayashi, K. Suzuki, and M. Kumada, *Tetrahedron Lett.*, **22**, 5319 (1981) and **21**, 845 (1980); T. Hayashi, M. Konishi, M. Fukushima, T. Mise, M. Kagotani, M. Tajika, and M. Kumada, *J. Am. Chem. Soc.*, **104**, 108 (1982); T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi, and K. Hirotsu, *ibid.*, **106**, 158 (1984).

2) F. Ozawa, T. Ito, Y. Nakamura, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **54**, 1868 (1981).

3) F. Ozawa, T. Ito, and A. Yamamoto, *J. Am. Chem. Soc.*, **102**, 6457 (1980).

4) A. Gille and J. K. Stille, *J. Am. Chem. Soc.*, **102**, 4933 (1980); A. Moravsky and J. K. Stille, *ibid.*, **103**, 4182 (1981).

5) T. J. McCarthy, R. G. Nuzzo, and G. M. Whitesides, *J. Am. Chem. Soc.*, **103**, 3396 (1981).

6) G. W. Parshall, *Acc. Chem. Res.*, **3**, 139 (1970) and **8**, 113 (1975).

7) K. Tatsumi, R. Hoffmann, A. Yamamoto, and J. K. Stille, *Bull. Chem. Soc. Jpn.*, **54**, 1857 (1981).

8) T. Ikariya and A. Yamamoto, *J. Organomet. Chem.*, **120**, 257 (1976).

9) T. Ito, H. Tsuchiya, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **50**, 1319 (1977).