Synthesis and Thermolysis Behavior of Monoethylpalladium Complexes, $EtPd(X)(PMe_3)_2$ (X = Electronegative Ligands)

Futoshi Kawataka, Yoshihito Kayaki, Isao Shimizu, and Akio Yamamoto*

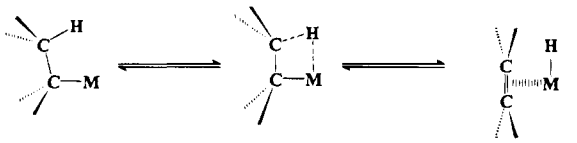
Department of Applied Chemistry, School of Science and Engineering, Waseda University, Ohkubo, Shinjuku, Tokyo 169, Japan

Received February 25, 1994[⊗]

A series of monoethylpalladium complexes coordinated with various electronegative ligands, *trans*-[$PdEt(X)(PMe_3)_2$], where X = OPh (**2a**), O_2CCH_3 (**2b**), O_2CCH_2Cl (**2c**), O_2CCHCl_2 (**2d**), O_2CCCl_3 (**2e**), $O_2CCH_2CH{=}CH_2$ (**2f**), SPh (**2g**), $SCOCH_3$ (**2h**), Cl (**2i**), Br (**2j**), and I (**2k**) have been prepared by protonolysis of *trans*-$PdEt_2(PMe_3)_2$ with HX or by metathesis of the known monoethylpalladium acetate complex. These complexes were characterized by means of ^1H-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-NMR, IR, and elemental analysis. Complexes **2a** and **2b** are thermolyzed in solution with evolution of ethylene whereas complexes **2c–2e** and **2g–2k** are decomposed with evolution of ethylene and ethane. Kinetic studies on the thermolysis of the ethylpalladium complexes revealed that they decompose according to the first-order rate law in concentration of the palladium complexes. The thermolysis is hindered by addition of X^- to the solution. A detailed analysis of the thermolysis revealed that there are two thermolysis routes, one major route involving dissociation of the X ligand to generate an unstable cationic ethylpalladium species that is rapidly thermolyzed, evolving ethylene, and another minor route proceeding from the neutral complex without dissociation of the anionic ligand. Comparison of the rate constant k_1 for dissociation of the anionic ligand X from *trans*-$PdEt(X)(PMe_3)_2$ showed that k_1 is the smallest for the Cl^- ligand dissociation. Activation parameters for the dissociation of the acetate ligand from **2b** were found as follows: $\Delta H^{\ddagger} = 9.9(\pm 1)$ kcal/mol, $\Delta S^{\ddagger} = -41(\pm 2)$ cal/(K·mol). The large negative entropy is consistent with a mechanism where dissociation of X is assisted by solvent coordination to generate a solvent-coordinated cationic ethylpalladium complex susceptible to β-H elimination. In fact removal of the chloride ligand on treatment of *trans*-$PdEt(Cl)(PMe_3)_2$ with $AgBF_4$ gave a thermally unstable complex *trans*-$[PdEt(solvent)(PMe_3)_2]^+BF_4^-$ which is readily decomposed to liberate ethylene above −30 °C.

Introduction

β-Hydrogen elimination of transition metal alkyls is one of the most important elementary processes in organometallic chemistry. The susceptibility to β-hydrogen elimination determines the stability of some transition metal alkyls and dictates the reaction pattern of the alkyl complexes.[1,2] By blocking the β-hydrogen elimination pathway (eq 1) one can achieve, in certain



(1)

cases, stabilization of transition metal alkyls, and various β-elimination stabilized transition metal alkyls have been prepared by applications of the concept.[3] However, for transition metal complexes having two alkyl groups reductive elimination provides an alternative route leading to their decomposition.[4] Some group 10 transition metal alkyls display different behaviors depending on the metal, configuration, and the nature of the supporting ligands. For example, platinum *cis*-dialkyls with tertiary phosphines as supporting ligands undero β-hydrogen elimination preceded by partial dissociation of the phosphine ligand to liberate alkane and alkene,[5,6] whereas the corresponding palladium *cis*-dialkyls reductively eliminate alkanes following the dissociation of one of the phosphine ligands.[7] In contrast, *trans*-diethylpalladium complexes having two tertiary phosphine ligands liberate ethylene and ethane

⊗ Abstract published in *Advance ACS Abstracts,* July 15, 1994.

(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry,* 5th ed.; Wiley Interscience: New York, 1988. (b) Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds. *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982.

(2) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. F. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley Interscience: New York, 1988. (c) Yamamoto, A. *Organotransition Metal Chemistry, Fundamental Concepts and Applications*; Wiley Intescience: New York, 1986. (d) Salzer, U.; Eschenbroich, O. *Organometallics-A Concise Introduction,* 2nd revised ed.: VCH Publishers: New York, 1992.

(3) (a) Mowat, W.; Shortland, A.; Hill, N. J.; Yagupsky, M.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1972,** 533. (b) Wilkinson, G. *Chimia* **1973,** *27,* 165. (c) Wilkinson, G. *Science* **1974,** *185,* 109. (d) Mowat, W.; Wilkinson, G. *J. Organometal. Chem.* **1972,** *38,* C35. (e) Davidson, J. P.; Lappert, M. F.; Pearce, R. *Acc. Chem. Res.* **1974,** *7,* 209. (f) Davidson, J. P.; Lappert, M. F.; Pearce, R. *Chem. Rev.* **1976,** *76,* 219.

(4) For example, see ref 2c, pp 240–245.

(5) (a) Brainard, R. L.; Whitesides, G. M. *Organometallics* **1985,** *4,* 1550. (b) Whitesides, G. M. *Pure Appl. Chem.* **1981,** *53,* 287. (c) MacCarthy, T. J.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981,** *103,* 3396, 3404. (d) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972,** *94,* 5258.

(6) Komiya, S.; Morimoto, Y.; Yamamamoto, A.; Yamamoto, T. *Organometallics* **1982,** *1,* 1528.

0276-7333/94/2313-3517$04.50/0

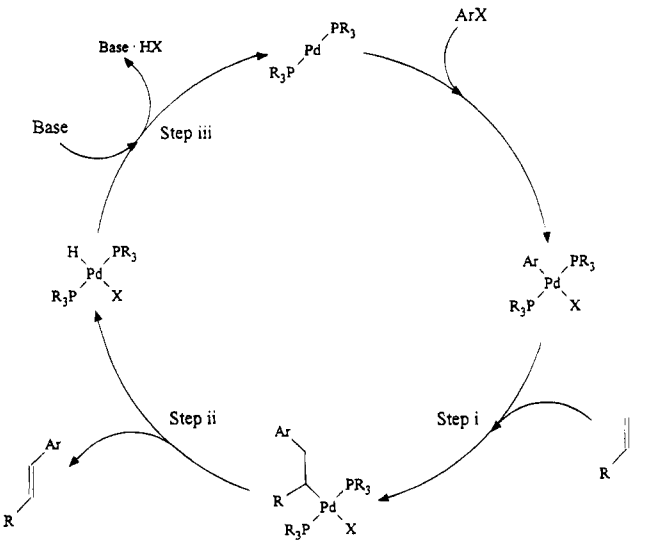
by the β-hydrogen elimination pathway without involving the phosphine dissociation.[8] Furthermore, nickel dialkyls having bipyridine as a ligand reductively eliminate alkane, the reaction being accelerated by addition of electronegative olefins.[9] The reason for the marked difference in the thermolysis courses of dialkyls of the same group 10 metals remains to be clarified.[10]

In the case of monoalkyltransition metal complexes, on the other hand, for which the reductive elimination pathway as in dialkyl transition metal complexes is lacking, β-hydrogen elimination or homolysis by a radical mechanism should constitute the dominant thermolysis route.[11] Thus study of the thermolysis mechanism of monoalkyl transition metal complexes having β-hydrogens should provide direct information on the factors determining the stability of transition metal monoalkyls and their chemical properties.[5,12,23]

Besides the fundamental problems regarding the stability of transition metal alkyls, study of the behavior of monoalkylpalladium complexes is pertinent to palladium-catalyzed organic synthesis. Among various palladium-catalyzed processes, arylation of olefins catalyzed by tertiary phosphine-coordinated complexes of palladium (Heck reaction)[13] has been extensively used in organic synthesis but there remain several problems concerning the mechanism.

In the Heck type reaction involving arylation of olefins the reaction course has been explained by the sequence of elementary steps in Scheme 1.[2,13] Among the elementary steps in the scheme, the oxidative addition of aryl halide to the Pd(0) complex to give arylpalladium halide has been extensively studied. The oxidative addition to a palladium(0) complex having monodentate tertiary phosphine ligands usually gives a phosphine-coordinated *trans*-arylpalladium halide complex.[2,3,14,15] The succeeding important key steps in the catalytic cycle are (i) insertion of an olefin into the arylpalladium bond to give a monoalkylpalladium halide, (ii) β-hydrogen elimination from the monoalkyl to liberate the arylated olefin, and (iii) subsequent removal of HX by a base to regenerate the Pd(0) species that oxidatively adds aryl halide to carry out the catalytic process. Much remains to be clarified on the factors determining the ease of olefin insertion into the Pd—aryl bond and the subsequent β-hydrogen elimination. As some valuable information has been provided previously by examination of the behavior of group 10 metal dialkyls, important information may be derived by examining the behavior of isolated monoalkyl complexes of group 10 metals having β-hydrogens in the alkyl group as a model of the catalytically active species.

Scheme 1. Mechanism of Heck Arylation



So far rather limited information is available on the properties of monoalkylpalladium complexes having β-hydrogens.[16] This is mainly due to the lack of isolable monoalkylpalladium complexes amenable for studying the behavior of these palladium alkyls.

In our previous studies on the reaction mechanisms of palladium-catalyzed single and double carbonylation reactions of aryl halides[17] and the synthesis of a palladacycloester[18] and of methylpalladium alkoxides,[16g,19] employment of trimethylphosphine proved to be quite useful in stabilizing the isolated complexes. The PMe_3 ligand, being compact and electron-donating, is less prone to dissociate from the metal center and thus blocks a coordination site required for decomposition to

(7) (a) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1868. (b) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.

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

(9) Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3350.

(10) (a) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857. (b) Tatsumi, K.; Nakamura, A.; Komiya, S.; Yamamoto, A.; Yamamoto, T. *J. Am. Chem. Soc.* **1984**, *106*, 8181. (c) Koga, N.; Morokuma, K.; *Chem. Rev.* **1991**, *91*, 823.

(11) The other possible decomposition route proceeding through α-hydrogen elimination is rare among group 10 metal alkyls.

(12) For studies on β-hydrogen elimination from monoalkylplatinum halide complexes, see: (a) Romeo, R.; Alibrandi, G.; Scolaro, L. M. *Inorg. Chem.* **1993**, *32*, 4688. (b) Romeo, R. *Comments Inorg. Chem.* **1990**, *11*, 21. (c) Alibrandi, G.; Scolaro, L. M.; Minniti, D.; Romeo, R. *Inorg. Chem.* **1990**, *29*, 3467. (d) Alibrandi, G.; Cusumano, M.; Minniti, D.; Scolaro, L. M.; Romeo, R. *Inorg. Chem.* **1989**, *28*, 342. (e) Alibrandi, G.; Minniti, D.; Romeo, R. *J. Organomet. Chem.* **1985**, *291*, 133. (f) Ermer, S. P.; Struck, G. E.; Bitler, S. P.; Richards, R.; Bau, R.; Flood, T. C. *Organometallics* **1993**, *12*, 2634. (g) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795. (h) Flood, T. C.; Bitler, S. P. *J. Am. Chem. Soc.* **1984**, *106*, 6076. (i) Brynza, H. E. *J. Chem. Soc., Chem. Commun.* **1985**, 1696. (j) Carr, N.; Mole, L.; Orpen, A. G. Spencer, J. L. *J. Chem. Soc., Dalton Trans.* **1992**, 2653.

(13) (a) Heck, R. F. *Org. React.* **1982**, *27*, 345. (b) Heck, R. F. *Pure Appl. Chem.* **1981**, *53*, 23. (c) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.

(14) (a) Ozawa, F.; Kurihara, K.; Fujimori, M.; Hidaka, T.; Toyoshima, T.; Yamamoto, A. *Organometallics* **1989** *8*, 180 and references therein. (b) Amatore, C.; Jutland, A.; Surarez A. *J. Am. Chem. Soc.* **1993**, *115*, 9531.

(15) However, the initial formation of the *cis* isomer followed by subsequent *cis*—*trans* ismomerization has been reported in ref 14b and in oxidative addition of iodouracil to Pd(0) and Pt(0) complexes: Urata, H.; Tanaka, M.; Fuchikami, T. *Chem. Lett.* **1987**, 751.

(16) (a) Zhang, L.; Zetterberg, K. *Organometallics* **1991**, *10*, 3806. (b) Arnek, R.; Zetterberg, K. *Organometallics* **1987**, *6*, 1230. (c) Reger, D. L.; Garza, D. G.; Baxter, J. C. *Organometallics* **1990**, *9*, 873. (d) Reger, D. L.; Garza, D. G. Lebioda, L. *Organometallics* **1991**, *10*, 902. (e) Reger, D. L.; Garza, D. G. *Organometallics* **1993**, *12*, 554. (f) Osakada, K.; Ozawa, Y.; Yamamoto, A. *J. Chem. Soc., Dalton Trans.* **1991**, 759. (g) Kim, Y.-J.; Osakada, K.; Takenaka, A.; Yamamoto, A. *J. Am. Chem. Soc.* **1990**, *112*, 1096.

(17) (a) Ozawa, F.; Sugimoto, T.; Yuasa, Y.; Santra, M.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1984**, *3*, 683. (b) Ozawa, F.; Sugimoto, T.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1984**, *3*, 692. (c) Ozawa, F.; Soyama, H.; Yanagihara, H.; Aoyama, I.; Takino, H.; Izawa, K.; Yamamoto, T.; Yamamoto, A. *J. Am. Chem. Soc.* **1985**, *107*, 3235. (d) Ozawa, F.; Kawasaki, N.; Okamoto, H.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1987**, *6*, 1640. (e) Son, T.; Yanagihara, H.; Ozawa, F.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1251. (f) Huang, L.; Ozawa, F.; Yamamoto, A. *Organometallics* **1990**, *9*, 2603.

(18) Osakada, K.; Doh, M.-K.; Ozawa, F.; Yamamoto, A. *Organometallics* **1990**, *9*, 2197.

(19) (a) Kim, Y.-J.; Osakada, K.; Sugita, K.; Yamamoto, T.; Yamamoto, A. *Organometallics* **1988**, *7*, 2182. (b) Osakada, K.; Kim, Y.-J.; Yamamoto, A. *J. Organomet. Chem.* **1990**, *382*, 303. (c) Kim, Y.-J.; Tanaka, M.; Ishiguro, S.; Yamamoto, A. *Inorg. Chem.* **1991**, *30*, 197.

Table 1. ^{1}H-NMR (δ) of 2b−d[a]

	O_2CCH	PCH_3	$PdCH_2$	$PdCH_2CH_3$
2b	1.83 (3 H, s)	1.34 (18 H, t, J = 3.3 Hz)	1.01 (5 H[b] m)	
2c	3.80 (2 H, s)	1.29 (18 H, t, J = 3.3 Hz)	1.12 (2 H, m)	0.96 (3 H, m)
2d	5.95 (1 H, s)	1.34 (18 H, t, J = 3.3 Hz)	1.12 (2 H, m)	1.00 (3 H, m)
2e		1.35 (18 H, t, J = 3.3 Hz)	1.24 (2 H, m)	1.00 (3 H, m)

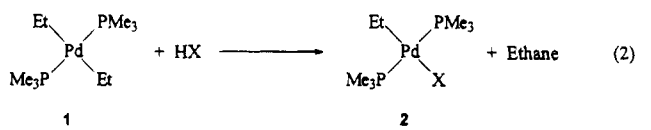
[a] Solvent = acetone-d_6, temperature = −20 °C. [b] Signals arising from protons of methylene and methyl groups are not separated.

occur. Another advantage of using the PMe_3 ligand is that the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of square planar complexes having PMe_3 ligands in mutually *trans* coordination sites show virtual coupling patterns and thus provide a readily noticeable clue regarding the retainment of the *trans* configuration.

Prior to this study we have prepared several *trans*-ethylpalladium complexes of the formula, *trans*-EtPd(X)$(PMe_3)_2$, where X are electronegative ligands, Cl, Br, I, and SAr.[16f,20] These complexes all proved thermally stable and easy to handle. In the present study we have extended the range of ethylpalladium complexes and prepared a variety of ethylpalladium complexes having various electronegative ligands. Here we wish to report the results of our study on the thermolysis behavior of these *trans*-ethylpalladium complexes undergoing the β-hydrogen elimination process to shed light on the β-hydrogen elimination pathway and the factors governing the process.

Results

Synthesis of Monoethylpalladium Complexes Having Various Electronegative Ligands. The *trans*-diethylpalladium(II) complex having trimethylphosphine ligands (**1**) serves as a convenient starting material to prepare various monoethylpalladium complexes (**2**) on reactions with various acidic reagents (eq 2).



(2)

1 2

X =			X =	
OPh	2a		SPh	2g
O_2CCH_3	2b		SAc	2h
O_2CCH_2Cl	2c		Cl	2i
O_2CCHCl_2	2d		Br	2j
O_2CCCl_3	2e		I	2k
O_2C	2f			

The protonolysis proceeds cleanly on treatment of the diethyl complex **1** with 1 equiv each of carboxylic acids such as acetic acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, 3-butenoic acid, and thioacetic acid with liberation of 1 equiv each of ethane, as confirmed by GLC analysis. Phenol and benzenethiol react with **1** in a similar way. The phenoxide complex **2a** and benzenethiolate complex **2g** have been previously prepared.[16f,g,20] Ethylpalladium halides having two PMe_3 ligands (**2i−2k**) can be prepared directly by treatment of **1** with HX (where X = Cl, Br, I) or

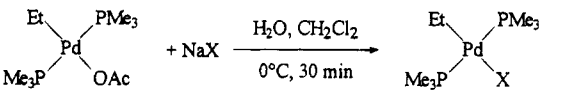
(20) Osakada, K.; Ozawa, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2002.

Table 2. ^{13}C-NMR (δ) of 2b−d

	O_2C	O_2C-C	$P-C$	$Pd-C-C$	$Pd-C$
2b[a]	175.9	24.4	12.8	16.4	2.6
2c[b]	170.5	45.1	12.7	16.4	3.3
2d[b]	167.2	70.5	12.7	16.3	4.1
2e[b]	163.4	97.4	12.5	16.4	5.1

[a] Solvent = THF-d_8. [b] Solvent = acetone-d_6.

alternatively through a metathesis reaction by treating methylene chloride solutions of the monoethylpalladium acetate complex **2b**, prepared in situ by eq 2, with aqueous solutions of alkali metal halides (eq 3).

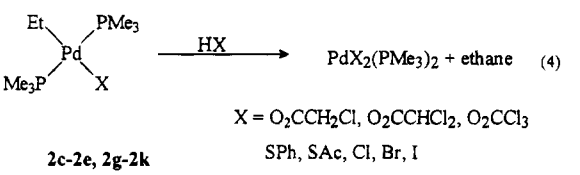


(3)

2b X = Cl (**2i**), Br (**2j**), I (**2k**)

Tables 1 and 2 summarize the NMR data of the newly isolated *trans*-monoethylpalladium complexes. All the complexes show the virtual triplet signals of the PMe_3 ligands in their ^{1}H NMR, indicating that the *trans* configuration is retained. On replacement of the acetate ligand with the more electronegative chloroacetate ligands the downfield shift of the methylene proton resonance is observed with very little shift of the methyl protons. A similar downfield shift of the methylene resonance is observed in the $^{13}C\{^1H\}$-NMR. The IR spectra of these *trans*-ethylpalladium complexes having mutually *trans* trimethylphosphine ligands show a single absorption near 950 cm^{-1}, in agreement with the *trans* configuration.

These *trans*-ethylpalladium complexes **2a−2k** are stable in water and ethanol but are further decomposed by treatment with stronger protic acids with evolution of ethane to give dicarboxylates, dihalides, and dithiolates (eq 4).

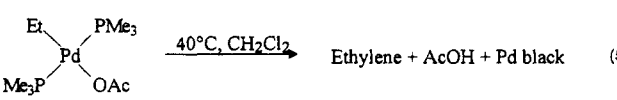


(4)

2c-2e, 2g-2k

An exception to the above reaction is the behavior of the acetate complex **2b** which forms a hydrogen-bonded adduct with the added acetic acid but resists further decomposition. The adduct formation is reflected by a stepwise shift of the acetate proton signal on addition of increasing amounts of acetic acid to the CD_2Cl_2 solution of **2b** at −20 °C from δ 1.73 of **2b** first to 1.82 and then to 1.89 with a concomitant shift of the PMe_3 triplet signals. The behavior is reminiscent of the formation of the hydrogen-bonded phenol adduct of *trans*-methylpalladium phenoxide having PMe_3 ligands on treatment with additional phenol.[16g,19]

Thermolysis of EtPd(X)$(PMe_3)_2$. The PMe_3-coordinated monoethylpalladium complexes are thermally moderately stable but can be readily thermolyzed on warming the solutions. The ethylpalladium acetate complex **2b** generates ethylene, acetic acid, and palladium black on thermolysis in dichloromethane (eq 5).



(5)

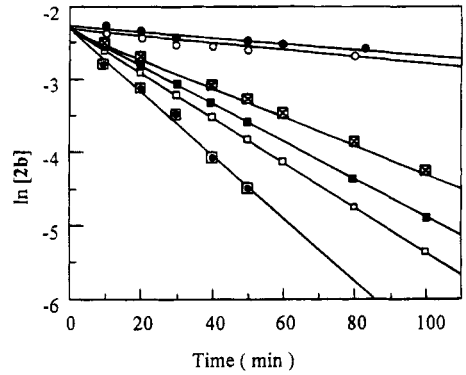


Figure 1. Time course of decrease in the concentration of *trans*-$PdEt(OAc)(PMe_3)_2$ (**2b**). $[\mathbf{2b}]_{t=0} = 0.1$ mol/L, in CH_2Cl_2 at 40 °C. Concentration of AcOH added: ⊡ = 0 mol/L, □ = 0.1 mol/L, ■ = 0.2 mol/L, × = 0.4 mol/L, ○ = 6.4 mol/L, ● = 12.8 mol/L. Concentrations of **2b** are in mol/L.

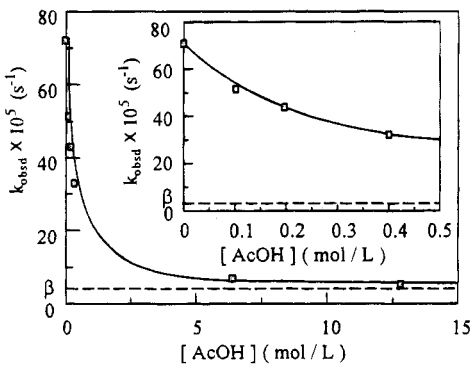


Figure 2. Dependence of the observed first-order rate constant, k_{obsd}, in the thermolysis of **2b** in CH_2Cl_2 at 40 °C on the concentration of added acetic acid.

The kinetics of the thermolysis of **2b** in dichloromethane in the presence and absence of additives was studied by following the rates of formation of ethylene by gas chromatography and by following the decrease in the concentration of the starting ethylpalladium complex by NMR spectroscopy. Both rates are in agreement with the first-order kinetics in **2b**, as expressed by eq 6.

$$-\frac{d[\mathbf{2b}]}{dt} = \frac{d[\text{ethylene}]}{dt} = k_{obsd}[\mathbf{2b}] \qquad (6)$$

The thermolysis of **2b** is suppressed by added acetic acid, as shown in Figure 1.

Figure 2 shows the decrease in the first-order thermolysis rate constants of **2b** on an increase in the concentration of the added acetic acid. It can be seen that the k_{obsd} value approaches a constant value of β on an increase in the concentration of acetic acid. A similar inhibition effect in the thermolysis of the ethylpalladium complex is observed on addition of alkali metal salts of acetic acid in the thermolysis of **2b** in ethanol, which is employed to increase the solubility of the acetate salts.

Figure 3 shows the linear relationship between the reciprocal of the value $(k_{obsd} - \beta)$ and the concentration of the added acetic acid with a small intercept γ.

Table 3 compares the observed first-order rate constants of the thermolysis of ethylpalladium acetate **2b** in various solvents. It is seen that k_{obsd} is greater in methyl acrylate and toluene, whereas in neat acetic acid the thermolysis is hindered. Although the reason for

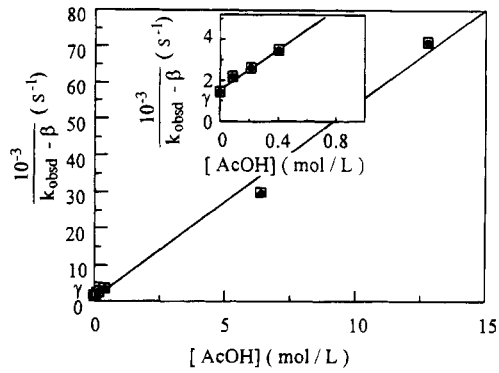


Figure 3. Plot of the value $10^{-3}/(k_{obsd} - \beta)$ vs the concentration of added acetic acid in the thermolysis of **2b** in CH_2Cl_2 at 40 °C.

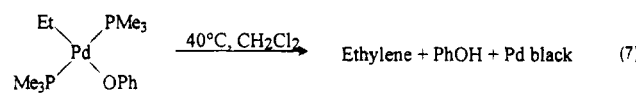
Table 3. Thermolysis of 2b in Various Solvents[a]

solvent	$10^4 k_{obsd}$ (s^{-1})	solvent	$10^4 k_{obsd}$ (s^{-1})
methyl acrylate	29(±1)	PMe_3	8.6(±0.4)
toluene	26(±1)	pyridine	5.3(±0.3)
THF	15(±1)	CH_3CN	4.7(±0.3)
acetone	14(±1)	DMF	3.1(±0.2)
EtOH	12(±1)	AcOH	0.95(±0.05)
CH_2Cl_2	10(±1)		

[a] Temperature = 40 °C. $[\mathbf{2b}]_{t=0} = 0.1$ mol/L.

variation of k_{obsd} in other solvents is not clear, k_{obsd} seems to be smaller in the strongly coordinating solvents.

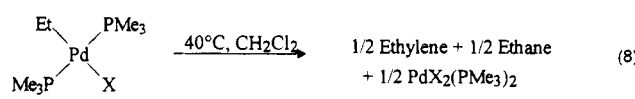
The other monoethylpalladium complex having the phenoxide ligand, **2a**, is thermolyzed in a similar fashion with liberation of ethylene and phenol together with formation of palladium black.



2a

Ethylpalladium 3-butenoate complex **2f** decomposes similarly with liberation of ethylene, 3-butenoic acid, and palladium black.

On the other hand, in the thermolysis of ethylpalladium dichloroacetate complex **2d**, evolution of a 1:1 mixture of ethylene and ethane is observed together with formation of the bis(dichloroacetate) complex and some palladium black (eq 8).

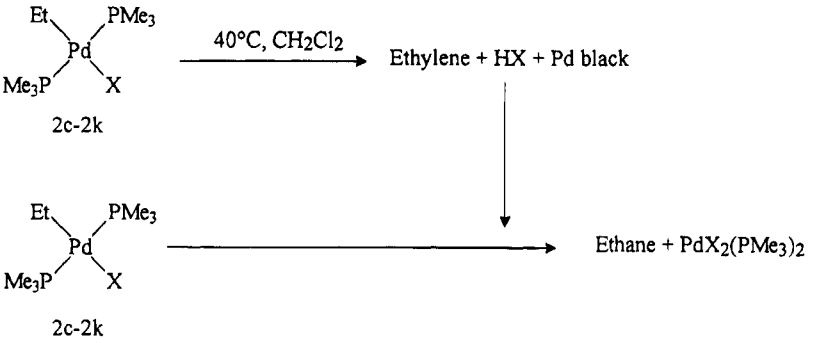


2c -2e, 2g -2k

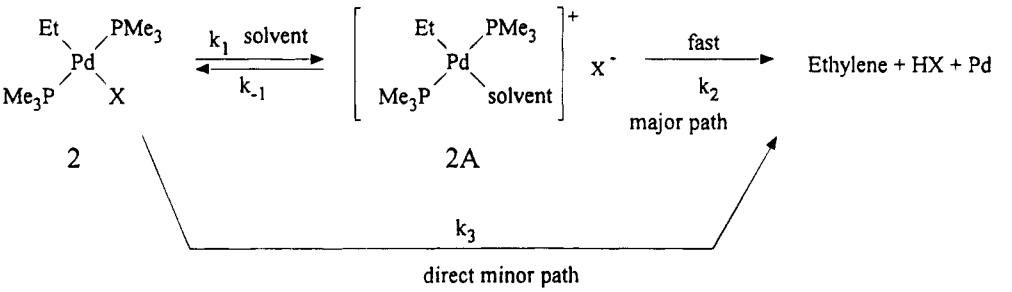
Formation of ethane may have been caused by attack of the dichloroacetic acid liberated in thermolysis of **2d** on the remaining ethylpalladium complex. Furthermore thermolysis of **2d** at 40 °C in pyridine solution, where the liberated dichloroacetic acid will be neutralized, gives only ethylene and palladium black. Other ethylpalladium complexes with chloroacetate (**2c**) and trichloroacetate (**2e**) ligands are also decomposed in a manner similar to the thermolysis of **2d** with liberation of ethylene and ethane.

Thus thermolysis of these ethylpalladium complexes having anionic ligands of strong protic acids can be

Scheme 2



Scheme 3



expressed by Scheme 2 in which 2 equiv of *trans*-PdEt(X)$(PMe_3)_2$ are thermolyzed by a process initiated by β-hydrogen elimination. The ethylpalladium halide (**2i**–**2k**) complexes also are decomposed similarly.

The thermolyses of these ethylpalladium complexes all obey first-order thermolysis kinetics. The inhibition effect of alkali metal salts of these anions (X) on the thermolysis of the *trans*-EtPd(X)$(PMe_3)_2$ type complexes was observed. Thus the thermolyses of these monoethylpalladium complexes **2a** to **2k** all conform to a similar pattern, as represented by Figures 1–3.

Thus the relationship of the value $1/(k_{obsd} - \beta)$ versus the concentration of the alkali metal salt of the anion added to EtPd(X)$(PMe_3)_2$ can be expressed by eq 9.

$$\frac{1}{k_{obsd} - \beta} = \alpha[\text{inhibitor}] + \gamma \qquad (9)$$

α = slope of the curve in Figure 3

β = asymptote of the curve in Figure 2

γ = intercept of the curve in Figure 3

Equation 9 can be transformed to eq 10.

$$k_{obsd} = \frac{1}{\alpha[\text{inhibitor}] + \gamma} + \beta \qquad (10)$$

Discussion

The monoethylpalladium complexes, **2a**–**2k**, with various electronegative ligands have been found isolable as moderately stable complexes when they are coordinated with PMe_3 ligands. On thermolysis of the EtPd(X)$(PMe_3)_2$ type complexes, where X is an anionic ligand of a relatively weak acid HX such as acetic acid and phenol, they are cleanly decomposed in solution via the β-hydroben elimination pathway with liberation of ethylene and protic acid formed by abstraction of a β-hydrogen from the ethyl group. In contrast, in thermolysis of EtPd(X)L_2, where X is an anion of a strong protic acid, ethane is evolved together with ethylene. The formation of ethane can be accounted for by attack of the protic acid liberated by β-hydrogen elimination on the remaining ethylpalladium complex. These results are consistent with the utility of nitrogen bases in Heck type olefin arylation, where HX is trapped by the base employed.

The results of kinetic study on the thermolysis of the ethylpalladium complexes to liberate ethylene suggest the involvement of two thermolysis routes, one minor process proceeding directly from the starting ethylpalladium complex and the other major pathway involving the dissociation of the anionic ligand from the starting complex, as shown in Scheme 3. The clear inhibition effect of the added anion X^- on thermolysis suggests formation of an ionic ethylpalladium intermediate **2A** which is subsequently decomposed by a rapid β-hydrogen elimination process. The inhibition effect of the added anion on the thermolysis of the EtPd(X)$(PMe_3)_2$ type complexes **2** has been observed for the phenoxide, monochloroacetate, dichloroacetate, and chloride complexes as well.

Assumption of the mechanism as shown in Scheme 3 with a steady state approximation for the concentration of the intermediate ethylpalladium–trimethylphosphine complex **2A** leads to first-order kinetics with k_{obsd} as expressed by eq 11. The expression is in agreement with

$$k_{obsd} = \frac{k_1 k_2}{k_{-1}[X] + k_2} + k_3 \qquad (11)$$

[X] = concentration of the anion added

the results expressed by eq 10, where α corresponds to k_{-1}/k_1k_2, β to k_3, and γ to $1/k_1$, respectively. The rate constants thus derived graphically from the figures are summarized in Table 4.

To our knowledge this is the first clear demonstration that the dissociation of an anionic ligand from a neutral alkylpalladium complex promotes the β-hydrogen elimi-

Table 4. Rate Constants in the Thermolysis 10^4 of $PdEt(X)(PMe_3)_2$[a,b]

complexes	solvent	additive	temp (°C)	10^4k_1 (s^{-1})	k_2/k_{-1} (mol/L)	10^5k_3 (s^{-1})
2a	EtOH	PhOH	40	5.5(±0.2)	0.12(±0.01)	3.3(±0.1)
2b	CH_2Cl_2	AcOH	40	1.2(±0.5)	1.6(±0.1)	2.8(±0.1)
	EtOH	NaOAc	30	4.1(±0.2)	0.35(±0.04)	2.6(±0.5)
	EtOH	NaOAc	40	9.8(±0.5)	0.57(±0.06)	3.5(±0.4)
	EtOH	NaOAc	50	15(±1)	0.83(±0.08)	7.2(±0.3)
	EtOH	NaOAc	60	20(±1)	1.2(±0.1)	26(±1)
2c	EtOH	NaO_2CCH_2Cl	40	6.4(±0.3)	2.0(±0.2)	2.7(±0.1)
2d	EtOH	NaO_2CCHCl_2	40	4.1(±0.2)	6.0(±0.6)	3.0(±0.1)
2i	EtOH	NaCl	40	1.3(±0.1)	71(±7)	2.0(±0.2)
2j	EtOH	NaBr	40	*c*	*c*	5.3[c](±0.3)

[a] The values of k_{obsd} were obtained by GLC determination of the ethylene evolved. [b] $[2]_{t=0} = 0.1$ mol/L. [c] Inhibition by NaBr was not observed. The k_{obsd} value is regarded as k_3.

Scheme 4

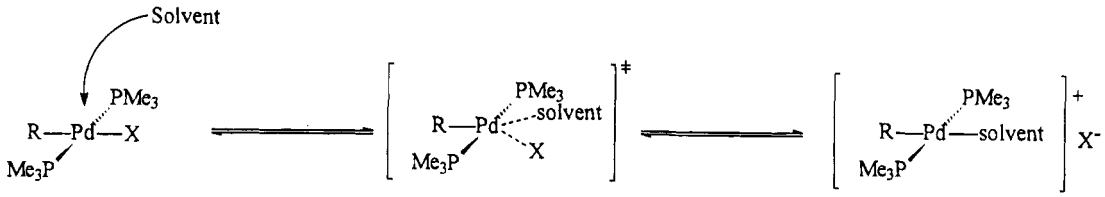


Table 5. Activation Parameters for Thermolysis of 2b

rate constants	E_a (kcal/mol)	$\Delta H^‡$ (kcal/mol)	$\Delta S^‡$ [cal/(K·mol)]
k_1	11 ± 1	9.9 ± 1	−41 ± 2
k_2/k_{-1}	8.1 ± 0.1	8.1 ± 0.1	−34 ± 1
k_3	17 ± 1	16 ± 1	−25 ± 1

nation. Table 4 shows that the influence of the anionic ligand in **2** on thermolysis constant k_3 corresponding to the undissociative route is small.

Comparison of the k_1 value of the ethylpalladium chloride complex **2i** at 40 °C with the k_1 values of the phenoxide (**2a**) and carboxylate complexes (**2b–2d**) indicates that the k_1 value for **2i** is smaller than those for other carboxylate ligands. It is also noted that the k_2/k_{-1} value for the chloride complex is much larger than the values for the other complexes. The results suggest that the Cl^- ligand dissociation takes place less readily than the other electronegative ligands such as phenoxide and carboxylate. Since the k_2 values should be independent of X^-, the large value of k_2/k_{-1} implies that once dissociated, the cationic ethylpalladium complex will decompose rather than recoordinate the chloride ion.

For the ethylpalladium acetate complex **2b** the rate constants at temperatures of 30–60 °C were determined as shown in Table 4. The activation parameters for k_1,k_2/k_{-1}, and k_3 are summarized in Table 5.

The large negative value for the $\Delta S^‡$ in dissociation of OAc^- from $EtPd(OAc)(PMe_3)_2$ suggests that the dissociation of the acetate is assisted by solvent coordination, as shown in Scheme 4.

Similar negative entropy values were observed in the substitution reaction of platinum complexes[21] and in *trans*–*cis* isomerization of *cis*-[Pt(neopentyl)(Cl)$(PEt_3)_2$.[22] In these cases solvent-assisted replacement of the chloride ligand was assumed.

In the direct β-H elimination of *trans*-$EtPd(OAc)(PMe_3)_2$ without OAc dissociation, the entropy change was also negative. This may reflect a constrained transition state such that involves an agostic interaction.[23] However, because of the relatively large error value involved, we refrain from detailed discussions.

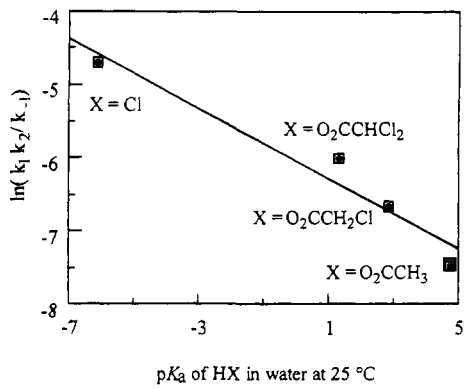


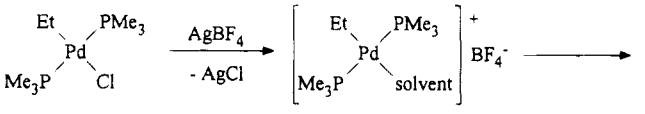
Figure 4. Correlation of k_1k_2/k_{-1} and pK_a of HX in water at 25 °C. Values of k_1k_2/k_{-1} are in mol/(L·s).

Figure 4 shows the correlation of the k_1k_2/k_{-1} value in the thermolysis of the various *trans*-$EtPd(X)(PMe_3)_2$ type complexes with the pK_a of HX in water at 25 °C. The results indicate the presence of a roughly linear relationship between the $\log(k_2k_1/k_{-1})$ value and pK_a. This is understandable since k_2 should be independent of the X ligand if Scheme 3 is valid. Then there should be a linear relationship between the pK_a value and the tendency of dissociation of the X anion in solution from the $EtPd(X)(PMe_3)_2$ complex.

The results in the present study suggest that removal of the anionic ligand X from $EtPd(X)(PMe_3)_2$ leads to destabilization of the ethylpalladium complex inducing β-hydrogen elimination. In fact treatment of *trans*-$EtPdCl(PMe_3)_2$ with $AgBF_4$ in CD_2Cl_2 solution at −30 °C leads to the formation of a very unstable cationic ethylpalladium complex which is decomposed with evolution of ethylene at a much lower temperature than the neutral ethylpalladium complex. The NMR spectroscopic examination of the cationic complex revealed retention of the two PMe_3 ligands in mutually *trans*

(21) Belluco, U.; Ettore, R.; Basolo, F.; Pearson, R. G.; Turco, A. *Inorg. Chem.* **1966**, *5*, 591.
(22) Alibrandi, G.; Scolaro, L. M.; Minniti, D.; Romeo, R. *Inorg. Chem.* **1991**, *30*, 4007.
(23) (a) Brookhart, M.; Green, L. M. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Carr, N.; Dunne, B. J.; Orpen, A. G.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1988**, 926. (c) Mole, L.; Spencer, J. L.; Carr, N.; Orpen, A. G. *Organometallics* **1991**, *10*, 49.

positions for the cationic ethylpalladium complex produced by removal of the chloride ligand with the silver salt. The reaction may be represented by eq 12, where the site *trans* to the ethyl group is occupied by the solvent molecule or the fluoride ion in the BF_4 group.



Ethylene + HX + Pd (12)

We are presently characterizing the cationic alkylpalladium complexes and studying their behavior. The destabilization of the ethylpalladium complexes by removal of the halide ligand with generation of the cationic alkyl species may be relevant to the rate acceleration in the Heck type arylation of olefins in the presence of a silver salt.[24]

Experimental Section

General Procedure. All manipulations of the complexes were performed under argon by using Schlenk flasks. Chloroacetic acid, dichloroacetic acid, and trichloroacetic acid were purchased from Tokyo Kasei Co. Ltd. and used as received. PMe_3 was purchased from Aldrich Co. Ltd. Complexes **1**, **2a**, and **2g** were prepared respectively as reported in literature.[8,16f,g]

Elemental analyses were carried out by using a Yanako MT-3. NMR spectra were recorded on a JEOL EX-270 spectrometer (^1H, 270.166 MHz; ^{13}C, 67.936 MHz; ^{31}P, 109.381 MHz). ^1H and ^{13}C signals are referred to Me_4Si as an internal standard and ^{31}P NMR signals to 85% H_3PO_4 as an external reference. Since the ^1H and ^{13}C NMR data are summarized in Tables 1 and 2, these data are omitted in the Experimental Section. IR spectra were recorded on a Hitachi I-3000 spectrophotometer. Preparative methods of the new monoethylpalladium complexes are described below.

Preparation of *trans*-PdEt(OAc)(PMe_3)$_2$ (2b). Acetic acid (68.5 μL, 1.19 mmol) was added to a CH_2Cl_2 (12 mL) solution of *trans*-$PdEt_2(PMe_3)_2$ (378.6 mg, 1.19 mmol) at −30 °C. Stirring the reaction mixture for 30 min gave a colorless solution. Evaporation of the solvent left a white solid of *trans*-PdEt(OAc)(PMe_3)$_2$ which was recrystallized from Et_2O to afford 280 mg of crystals (0.808 mmol, 70.3% yield), mp 77−78 °C dec. Anal. Calcd for $C_{10}H_{26}O_2P_2Pd$: C, 34.6; H, 7.6. Found: C, 34.2; H, 7.6. ^{31}P-NMR (acetone-d_6): δ −13.2 (s). IR (KBr): 1560, 1416, 948 cm^{-1}.

Preparation of *trans*-PdEt(O_2CCH_2Cl)(PMe_3)$_2$ (2c). Chloroacetic acid (48.4 μL, 0.512 mmol) was added to a CH_2Cl_2 (5.1 mL) solution of *trans*-$PdEt_2(PMe_3)_2$ (162.1 mg, 0.512 mmol) at −30 °C. Stirring the reaction mixture for 30 min gave a colorless solution. Evaporation of the solvent left a white solid of *trans*-PdEt(O_2CCH_2Cl)(PMe_3)$_2$ which was recrystallized from Et_2O to afford 107.4 mg of crystals (0.281 mmol, 55.2% yield), mp 86−87 °C dec. Anal. Calcd for $C_{10}H_{25}ClO_2P_2Pd$: C, 31.5; H, 6.6. Found: C, 31.4; H, 6.5. ^{31}P-NMR (acetone-d_6): δ −13.1 (s). IR (KBr): 1602, 1532, 1420, 1400, 950 cm^{-1}.

Preparation of *trans*-PdEt(O_2CCHCl_2)(PMe_3)$_2$ (2d). Dichloroacetic acid (43 μL, 0.520 mmol) was added to a CH_2Cl_2 (5.2 mL) solution of *trans*-$PdEt_2(PMe_3)_2$ (164.8 mg, 0.520 mmol) at −30 °C. Stirring the reaction mixture for 30 min gave a colorless solution. Evaporation of the solvent left a white solid of *trans*-PdEt(O_2CCHCl_2)(PMe_3)$_2$ which was recrystallized from Et_2O to afford 138.5 mg of crystals (0.333 mmol, 62.5% yield), mp 83 °C dec. Anal. Calcd for $C_{10}H_{24}Cl_2O_2P_2Pd$: C, 28.9; H, 5.8. Found: C, 27.5; H, 5.9. ^{31}P-NMR (acetone-d_6): δ −13.3 (s). IR (KBr): 1634, 1596, 1536, 1384, 950 cm^{-1}.

Preparation of *trans*-PdEt(O_2CCCl_3)(PMe_3)$_2$ (2e). Trichloroacetic acid (182 mg, 1.11 mmol) was added to a CH_2Cl_2 (12 mL) solution of *trans*-$PdEt_2(PMe_3)_2$ (353.3 mg, 1.11 mmol) at −30 °C. Stirring the reaction mixture for 30 min gave a colorless solution. Evaporation of the solvent left a white solid of *trans*-PdEt(O_2CCCl_3)(PMe_3)$_2$ which was recrystallized from Et_2O to afford 371.8 mg of crystals (0.830 mmol, 74% yield), mp 46−48 °C dec. Anal. Calcd for $C_{10}H_{23}Cl_3O_2P_2Pd$: C, 26.7; H, 5.2. Found: C, 26.9; H, 5.2. ^{31}P-NMR (acetone-d_6): δ −13.4 (s). IR (KBr): 1680, 1420, 1338, 950 cm^{-1}.

Preparation of *trans*-PdEt(O_2C−CH_2−CH=CH_2)(PMe_3)$_2$ (2f). 3-Butenoic acid (37 μL, 0.44 mmol) was added to an acetone (1 mL) solution of *trans*-$PdEt_2(PMe_3)_2$ (138.7 mg, 0.438 mmol) at −30 °C. Stirring the reaction mixture for 30 min gave a colorless solution. Evaporation of the solvent left a white solid of *trans*-PdEt(O_2C−CH_2−CH=CH_2)(PMe_3)$_2$ which was recrystallized from Et_2O to afford 74.2 mg of product (0.199 mmol, 45.5% yield), mp 114−116 °C dec. ^1H-NMR (CD_2Cl_2): δ 1.00 (m, 5 H, PdCH_2CH_3), 1.29 (vt, J = 3.0 Hz, 18 H, PCH_3), 2.90 (d, J = 7.0 Hz, 2 H, O_2CCH_2), 4.90 (brd, 1 H, *trans*-CHH=CHCH_2), 5.00 (d, J = 4.3 Hz, 1 H, *cis*-CHH=CHCH_2), 6.00 (m, 1 H, O_2CCH_2CH). ^{31}P-NMR (CD_2Cl_2): δ −14.5 (s). IR (KBr): 1576, 1410, 1396, 950 cm^{-1}.

Preparation of *trans*-PdEt($SCOCH_3$)(PMe_3)$_2$ (2h). Thioacetic acid (130 μL, 0.234 mmol) was added to a dichloromethane (15 mL) solution of *trans*-$PdEt_2(PMe_3)_2$ (580 mg, 0.234 mmol) at −50 °C. Stirring the reaction mixture for 1 h gave a colorless solution. Evaporation of the solvent left a white solid of *trans*-PdEt($SCOCH_3$)(PMe_3)$_2$ which was washed with pentane and ether several times and recrystallized from acetone to afford 437 mg of crystals (0.121 mmol, 66% yield), mp 60−62 °C dec. Anal. Calcd for $C_{10}H_{26}SOP_2Pd$: C, 33.1; H, 7.2. Found: C, 33.0; H, 7.4. ^1H-NMR (acetone-d_6): δ 1.07 (t, J = 6.4 Hz, 3 H, PdCH$_2$CH_3), 1.16 (m, 2 H, PdCH_2), 1.39 (brs, 18 H, PCH_3), 2.20 (s, 3 H, SCOCH_3). ^{31}P-NMR (acetone-d_6): δ −13.0 (s). ^{13}C-NMR (acetone-d_6): δ 10.1 (s, PdCH$_2$CH$_3$), 13.7 (vt, J = 14.0 Hz, PCH$_3$), 17.1 (s, PdCH$_2$), 36.6 (s, SCOCH$_3$), 206.6 (s, PdSCO). IR (KBr): 1604, 1420, 950 cm^{-1}.

***trans*-PdEt(X)(PMe_3)$_2$ (X = Cl (2i), Br (2j), I (2k).** An aqueous sodium halide solution was added to a CH_2Cl_2 solution of *trans*-PdEt(OAc)(PMe_3)$_2$ (0.1 mol/L) at 0 °C. Stirring the reaction mixture for 30 min gave a yellow (**2i**), orange (**2j**), and red (**2k**) solution, respectively. Evaporation of the CH_2Cl_2 layer left solids of *trans*-PdEt(X)(PMe_3)$_2$ which were recrystallized from Et_2O (50−70% yield). These complexes were prepared by a different method.[16f]

Estimation of the Rate Constants of the Thermolysis of *trans*-PdEt(X)(PMe_3)$_2$. Method A. NMR samples containing a fixed concentration (0.1 or 0.08 mol/L) of *trans*-PdEt(X)(PMe_3)$_2$ and various concentrations of additives were prepared. ^1H-NMR spectra of the samples were periodically measured at several preset temperatures. The k_{obsd} value was determined by following the decrease of *trans*-PdEt(X)(PMe_3)$_2$ with time by NMR.

Method B. Samples containing *trans*-PdEt(X)(PMe_3)$_2$ (0.1 or 0.08 mol/L) and additives in various concentrations were prepared. The yields of ethylene were periodically measured

(24) (a) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1989**, *53*, 4909. (b) Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1986**, *51*, 5286. (c) Karabelas, K.; Westerlund, C.; Hallberg, A. *J. Org. Chem.* **1985**, *50*, 3896. (d) Anderson, C.-M.; Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1985**, *50*, 3890. (e) Abelman, M. M.; Overman, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 2328. (f) Abelman, M. M.; Oh, T.; Overman, L. E. *J. Org. Chem.* **1987**, *52*, 4130. (g) Jeffery, T. *Tetrahedron Lett.* **1992**, *33*, 1989. (h) Larock, R. C.; Gong, W. H. *J. Org. Chem.* **1989**, *54*, 2047. (i) Cabri, W.; Candiani, I.; Bedeschi, A.; Penco, S.; Santi, R. *J. Org. Chem.* **1992**, *57*, 1481. (j) Grigg, R.; Loganathan, V.; Santhakumar, V.; Sridhavan, V.; Teasdale, A. *Tetrahedron Lett.* **1991**, *32*, 687. (k) Sato, Y.; Watanabe, S.; Shibasaki, M. *Tetrahedron Lett.* **1992**, *33*, 2589, 2593. (l) Albeniz, A. C.; Espinet, P.; Foces, C.; Cano, F. H. *Organometallics* **1990**, *9*, 1079.

at several preset temperatures by GLC analysis. The k_{obsd} value was determined by observing the amount of ethylene produced.

For the cases where ethylene and ethane were produced on thermolysis, the thermolysis rate constant was derived by assuming that two molecules of the ethylpalladium complex were decomposed by a single β-hydrogen elimination process.

Removal of Chloride from 2i. Silver tetrafluoroborate (21.0 mg, 0.107 mmol) was added to an acetone-d_6 (0.3 mL) solution of *trans*-PdEt(Cl)(PMe_3)$_2$ (34.8 mg, 0.108 mmol) at −30 °C. Only one kind of species was observed by ^{1}H-, ^{13}C-, and ^{31}P-NMR. ^{1}H-NMR (acetone-d_6): δ 1.03 (tt, J = 4.0, 7.3 Hz, 3 H, $PdCH_2CH_3$), 1.38 (vt, 3.3 Hz, 18 H, PCH_3), 1.45−1.62 (m, 2 H, $PdCH_2$). ^{13}C-NMR (acetone-d_6): δ 10.2 (s, $PdCH_2CH_3$), 12.6 (vt, J = 4.1 Hz, PCH_3), 16.5 (s, $PdCH_2$). ^{31}P-NMR (acetone-d_6): δ −14.3 (s).

OM940149H