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# Synthesis and β-Hydrogen Elimination of Water-Soluble Dialkylplatinum(II) Complexes in Water

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Water-soluble *cis*-dialkylplatinum(II) complexes *cis*-[$PtR_2L_2$] ($L_2$ = 2 TPPTS, 2 THMP, DHMPE; R = Me, Et, Ph) have been prepared by ligand displacement reactions of [$PtR_2$(1,5-COD)] with $L_2$. They are stable in water; the diethylplatinum(II) complexes *cis*-[$PtEt_2(TPPTS)_2$] undergo preferential disproportionation of the ethyl groups in water, giving ethylene and ethane in 1:1 ratio via β-hydrogen elimination in preference to protonolysis at 80 °C. A retardation effect of added free TPPTS on the reaction rate and a deuterium labelling study suggest a mechanism involving prior dissociation of TPPTS for reversible β-hydrogen elimination.

Many transition metal-mediated reactions and catalyses try to avoid moisture, because putative organometallic intermediates are believed to be easily hydrolyzed under the reaction conditions. Despite this consideration, organometallic reactions in water are becoming one of the promising areas of environmentally benign reaction systems,[1] since water is regarded as one of the most safe solvents and water/organic solvent biphasic catalysis can provide easy separation of hydrophobic organic products in industrial applications. In addition, many useful and well-established transition metal-mediated chemical transformations, which had been extensively developed in recent years, can be extended to the reactions of hydrophobic compounds in aqueous media. Thus, fundamental understanding of aqueous organometallic reactions has intrinsic importance in order to develop new transition metal-promoted chemical processes in water. To date, however, very limited water-soluble complexes having metal–carbon σ-bonds are known. Although methyliridium(I) complex *trans*-[IrMe(CO)(TPPMS)$_2$] (TPPMS = diphenylphosphinobenzene-3-sulfonic acid sodium salt) is known as one of the water-soluble organometallic compounds (Chart 1), its Ir–C bond was immediately hydrolyzed in water to form the corresponding hydroxoiridium(I) complex.[2] Pringle and co-workers[3] also reported *cis*-[$PtMe_2(THMP)_2$] and *cis*- and *trans*-[$PtMeX(THMP)_2$] [THMP = tris(hydroxymethyl)phosphine] with insufficient characterization due to facile decomposition during the isolation processes. We now describe the synthesis and thermal stability of water-soluble diorganoplatinum(II) complexes *cis*-[$PtR_2L_2$] with TPPTS [TPPTS = 3,3′,3″-phosphinidynetris(benzenesulfonic acid) trisodium salt], THMP, or DHMPE {1,2-bis[di(hydroxymethyl)phosphino]ethane} ligands by ligand substitution reactions of *cis*-[$PtR_2$(1,5-COD)] (COD = cyclooctadiene). Among them, diethylplatinum(II) complexes undergo smooth and selective disproportionation of the ethyl groups via β-hydrogen elimination even in water. A part of the results has been published in a preliminary form.[4]

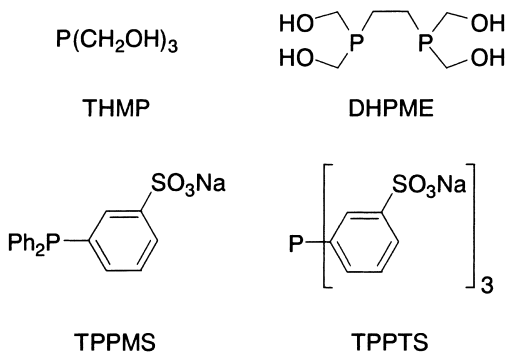



Chart 1.

## Experimental

All manipulations were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques. Water was purified by simple distillation, and other solvents were dried over and distilled from appropriate drying agents under $N_2$ and were stored under nitrogen before use. [$PtR_2$(1,5-COD)] were prepared according to the literature methods.[5] [$Pt(CH_2CD_3)_2$(1,5-COD)] (D content at the methyl group was estimated as 89%) was prepared by the reaction of [$PtI_2$(1,5-COD)] with ($CD_3CH_2$)MgBr. TPPTS was purchased from Aldrich and used as received. THMP and DHPME were prepared according to the literature methods.[6] IR spectra were measured on a JASCO FT/IR-410 spectrometer. NMR spectra were obtained on a JEOL LA-300 ($^1$H 300.4 MHz) spectrometer. Chemical shifts were relative to DSS ($^1$H) and 85% $H_3PO_4$ ($^{31}$P). Elemental analyses were performed with a Perkin-Elmer 2400 series II CHN analyzer. Gases were quantitatively analyzed by gas chromatography (Shimadzu GC-8A) using the internal standard method.

**Synthesis of Water-Soluble *cis*-Dialkylplatinum(II) Complexes.** A typical procedure for [$PtMe_2(TPPTS)_2$] (**1a**) is given. To an ethanol solution (2 mL) of [$PtMe_2$(1,5-COD)] (22.8 mg, 0.0685 mmol) was added TPPTS (74.0 mg, 0.130 mmol) in water (1 mL). Stirring at room temperature for several minutes gave a colorless solution. Addition of acetone to the concentrated solu-

tion of the reaction mixture gave white powder, which was washed with hexane and dried under vacuum. Recrystallization from water with acetone gave white powder of **1a**·4$H_2O$ (80.1 mg, 80%). Anal. Found: C, 31.89; H, 2.92%. Calcd for $C_{38}H_{38}Na_6O_{22}P_2PtS_6$: C, 31.83; H, 2.62%. 1,5-COD liberated (95%). IR (KBr): 3331 ($\nu$OH), 1194 ($\nu_{as}$S=O), 1039 $cm^{-1}$ ($\nu_s$S=O). $^1H$ NMR ($D_2O$) $\delta$ 0.42 (m, $^2J_{H\text{-}Pt}$ = 69 Hz, 6H, Pt-$CH_3$), 7.39 (t, $^3J_{H\text{-}H}$ = 8 Hz, 6H, 5-CH of aryl), 7.53 (t, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}P}$ = 8 Hz, 6H, 6-CH of aryl), 7.76 (d, $^3J_{H\text{-}H}$ = 8 Hz, 6H, 4-CH of aryl), 7.79 (d, $^3J_{H\text{-}P}$ = 8 Hz, 6H, 2-CH of aryl). $^{31}P\{^1H\}$ NMR ($D_2O$) $\delta$ 29.3 (s, $^1J_{P\text{-}Pt}$ = 1855 Hz). Mp 186–190 °C (dec.).

[$PtEt_2$(TPPTS)$_2$] (**1b**)·4$H_2O$: Colorless powder from water/acetone. Yield 95.3 mg (72%). Anal. Found: C, 32.82; H, 3.19%. Calcd for $C_{40}H_{42}Na_6O_{22}P_2PtS_6$: C, 32.86; H, 2.90%. 1,5-COD liberated (101%). IR (KBr): 3442 ($\nu$OH), 1191 ($\nu_{as}$S=O), 1038 $cm^{-1}$ ($\nu_s$S=O). $^1H$ NMR ($D_2O$): $\delta$ 0.77 (m, $^3J_{H\text{-}Pt}$ = 74 Hz, 6H, Pt-$CH_2CH_3$), 1.13 (m, $^2J_{H\text{-}Pt}$ = 70 Hz, 4H, Pt-$CH_2CH_3$), 7.39 (t, $^3J_{H\text{-}H}$ = 8 Hz, 6H, 5-CH of aryl), 7.52 (t, $^3J_{H\text{-}H}$ = $^3J_{H\text{-}P}$ = 8 Hz, 6H, 6-CH of aryl), 7.71 (d, $^3J_{H\text{-}H}$ = 8 Hz, 6H, 4-CH of aryl), 7.85 (d, $^3J_{H\text{-}P}$ = 8 Hz, 6H, 2-CH of aryl). $^{31}P\{^1H\}$ NMR ($D_2O$) $\delta$ 29.0 (s, $^1J_{P\text{-}Pt}$ = 1677 Hz). Mp 158–164 °C (dec.).

[$PtMe_2$(THMP)$_2$] (**2a**): The compound was not isolated in a pure form and the yield was estimated by NMR in DMSO-$d_6$ as 82%. 1,5-COD liberated (93%). $^1H$ NMR (DMSO-$d_6$/$D_2O$ = 1/5 (v/v)): $\delta$ 0.49 (brs, $^2J_{H\text{-}Pt}$ = 66 Hz, 6H, Pt-$CH_3$), 4.29 (br, 12H, P$CH_2$OH). $^{31}P\{^1H\}$ NMR (DMSO-$d_6$/$D_2O$ = 1/5 (v/v)) $\delta$ 13.2 (s, $^1J_{P\text{-}Pt}$ = 1700 Hz).

[$PtEt_2$(THMP)$_2$] (**2b**): The compound was not isolated in a pure form and the yield estimated by NMR in DMSO-$d_6$ was 86% . 1,5-COD liberated (96%). $^1H$ NMR (DMSO-$d_6$/$D_2O$ = 1/5 (v/v)): $\delta$ 1.14 (m, 6H, Pt-$CH_2CH_3$), 1.2 (q, $^3J_{H\text{-}H}$ = 8 Hz, $^2J_{H\text{-}Pt}$ = 129 Hz, 4H, Pt-$CH_2CH_3$), 4.33 (brs, 12H, P$CH_2$OH). $^{31}P\{^1H\}$ NMR (DMSO-$d_6$/$D_2O$ = 1/5 (v/v)) $\delta$ 8.9 (s, $^1J_{P\text{-}Pt}$ = 1470 Hz).

[$PtPh_2$(THMP)$_2$] (**2c**): Colorless powder from ethanol/hexane. Yield 78.7 mg (58%). Anal. Found: C, 36.46; H, 4.50%. Calcd for $C_{18}H_{28}O_6P_2Pt$: C, 36.19; H, 4.72%. 1,5-COD liberated (92%). $^1H$ NMR ($D_2O$) $\delta$ 4.06 (s, $^2J_{H\text{-}Pt}$ = 11 Hz, 12H, P$CH_2$OH), 6.79 (t, $^3J_{H\text{-}H}$ = 7 Hz, 2H, *p*-Ph), 7.01 (t, $^3J_{H\text{-}H}$ = 7 Hz, 4H, *m*-Ph), 7.41 (d, $^3J_{H\text{-}H}$ = 7 Hz, $^3J_{H\text{-}Pt}$ = 57 Hz, 4H, *o*-Ph). $^{31}P\{^1H\}$ NMR ($D_2O$) $\delta$ 4.5 (s, $^1J_{P\text{-}Pt}$ = 1660 Hz).

[$PtMe_2$(DHMPE)] (**3a**): Colorless powder from ethanol/hexane. Yield 39.9 mg (63%). Anal. Found: C, 21.05; H, 4.66%. Calcd for $C_8H_{22}O_4P_2Pt$: C, 21.87; H, 5.05%. 1,5-COD liberated (100%). $^1H$ NMR ($D_2O$) $\delta$ 0.50 (t, $^3J_{H\text{-}P}$ = 7 Hz, $^2J_{H\text{-}Pt}$ = 69 Hz, 6H, Pt-Me), 1.96 (m, 4H, P$C_2H_4$), 4.14 (dd, $^2J_{H\text{-}H}$ = 14 Hz, $^2J_{H\text{-}P}$ = 2.1 Hz, 4H, P$CH_2$OH), 4.25 (d, $^2J_{H\text{-}H}$ = 14 Hz, $^3J_{H\text{-}Pt}$ = 12 Hz, 4H, P$CH_2$OH). $^{31}P\{^1H\}$ NMR ($D_2O$) $\delta$ 49.3 (s, $^1J_{P\text{-}Pt}$ = 1640 Hz).

[$PtEt_2$(DHMPE)] (**3b**): The compound was not isolated in a pure form and the yield estimated by NMR in DMSO-$d_6$ was 91%. 1,5-COD liberated (94%). $^1H$ NMR (DMSO-$d_6$/$D_2O$ = 1/5 (v/v)) $\delta$ 1.25 (q, $^3J_{H\text{-}H}$ = 8 Hz, $^2J_{H\text{-}Pt}$ = 71 Hz, 4H, Pt-$CH_2CH_3$), 1.26 (m, 6H, Pt-$CH_2CH_3$), 1.88 (m, 4H, P$C_2H_4$), 4.09 (dd, $^2J_{H\text{-}H}$ = 14 Hz, $^2J_{H\text{-}P}$ = 3 Hz, 4H, P$CH_2$OH), 4.22 (d, $^2J_{H\text{-}H}$ = 14 Hz, $^2J_{H\text{-}Pt}$ = 11 Hz, 4H, P$CH_2$OH). $^{31}P\{^1H\}$ NMR (DMSO-$d_6$/$D_2O$ = 1/5 (v/v)) $\delta$ 48.3 (s, $^1J_{P\text{-}Pt}$ = 1460 Hz).

[$PtPh_2$(DHMPE)] (**3c**): Colorless powder from ethanol/hexane. Yield 54.2 mg (64%). Anal. Found: C, 38.38; H, 4.81%. Calcd for $C_{18}H_{26}O_4P_2Pt$: C, 38.37; H, 4.65%. $^1H$ NMR ($D_2O$) $\delta$ 2.10 (m, 4H, P$C_2H_4$), 4.11 (m, 8H, P$CH_2$OH), 6.85 (t, $^3J_{H\text{-}H}$ = 7 Hz, 2H, *p*-Ph), 7.08 (t, $^3J_{H\text{-}H}$ = 7 Hz, 4H, *m*-Ph), 7.46 (t, $^3J_{H\text{-}H}$ = $^4J_{H\text{-}P}$ = 7 Hz, $^3J_{H\text{-}Pt}$ = 52 Hz, 4H, *o*-Ph). $^{31}P\{^1H\}$ NMR ($D_2O$) $\delta$ 43.9 (s, $^1J_{P\text{-}Pt}$ = 1600 Hz).

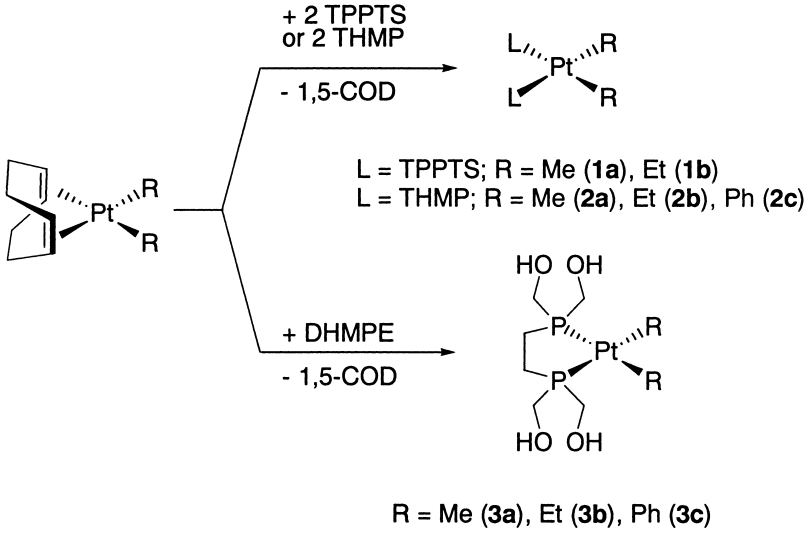
**Thermolysis of Water-Soluble *cis*-Dialkylplatinum(II) Complexes.** Thermolysis reactions were carried out in glass bottles (10 mL) under reduced pressure. Typically, **2b** (21.0 mg, 0.0144 mmol) was placed in a glass bottle with a serum cap and the system was evacuated. Water (2.0 mL) was then added through the serum cap by using a hypodermic syringe. Methane (1.19 mL) was added by using a calibrated hypodermic syringe as an internal standard. The solution was heated to 80 °C and the aliquots (20 μL) of the gas phase were periodically taken with a gas-tight microsyringe for quantitative GC analysis (Porapak Q column).

**Protonolysis of Water-Soluble *cis*-Dialkylplatinum(II) Complexes.** Protonolysis of **1a** is given as a typical example. **1a** (14.3 mg, 0.0194 mmol) was placed in a glass bottle (10 mL) with a serum cap and the system was degassed. A large excess of 12 M hydrochloric acid was added by using a hypodermic syringe, liberating only methane. Ethane (1.19 mL) was added as an internal standard and methane (184%/Pt) was detected by GC method. For **1b** (17.1 mg, 0.0123 mmol), the yield of ethane liberated was 166%/Pt. For **3a** (10.8 mg, 0.0246 mmol), the yield of methane liberated was 201%/Pt. Protonolysis of other *cis*-dialkylplatinum(II) complexes with THMP or DHMPE ligands (**2a**–**b**, **3b**) were performed by using in-situ prepared samples in DMSO. A typical procedure for **2a** is given. The DMSO solution (200 μL) of **2a** was prepared in situ from [$PtMe_2$(1,5-COD)] (5.0 mg, 0.015 mmol) and THMP (3.9 mg, 0.032 mmol) in a glass bottle (10 mL) with a serum cap and the system was degassed. Dry ether solution of hydrogen chloride (0.38 M, 1 mL) was added by using a hypodermic syringe at room temperature. Ethane (0.113 mL) was added as an internal standard. Methane (203%/Pt) was detected by GC. For **2b** and **3b**, 208%/Pt and 154%/Pt of ethane were detected.

**Deuterium Labeling Study.** [$Pt(CH_2CD_3)_2$(TPPTS)$_2$] was prepared by the reaction of [$Pt(CH_2CD_3)_2$(1,5-COD)] (24.1 mg, 0.0668 mmol) with two equivalents of TPPTS (72.0 mg, 0.127 mmol). Yield 90.3 mg (88%). The deuterium NMR spectrum indicates no incorporation of D in the methylene group and the D content in the methyl group was estimated as 89% by $^1H$ NMR. [$Pt(CH_2CD_3)_2$(TPPTS)$_2$] (69.1 mg, 0.0471 mmol) in water (2.0 mL) was heated to 80 °C for 2 h. The evolved gases were collected by using a Toepler pump through the cold trap (−40 °C) and the IR spectrum of the gas was measured using a gas-cell with KRS-5 windows. The following bands ($cm^{-1}$) were observed: 1387 ($CH_2$=$CD_2$), 1339 (*cis*-CHD=CHD), 1301 (*trans*-CHD=CHD), 987 (*trans*-CHD=CHD), 943 ($CH_2$=$CD_2$), 918 (CHD=$CD_2$), 842 (*cis*-CHD=CHD), 764 (CHD=$CD_2$), 751 ($CH_2$=$CD_2$), 725 (CHD=$CD_2$, *trans*-CHD=CHD). No characteristic bands for $C_2H_4$, $C_2H_3D$, and $C_2D_4$ were observed.[7]

## Results and Discussion

**Synthesis of Water-Soluble Diorganoplatinum(II) Complexes.** When (1,5-cyclooctadiene)dimethylplatinum(II), [$PtMe_2$(1,5-COD)] was treated with two equivalents of TPPTS in ethanol/$H_2O$ (ca. 2:1) at room temperature, immediate ligand displacement took place to give *cis*-dimethylbis(TPPTS)platinum(II), *cis*-[$PtMe_2$(TPPTS)$_2$] (**1a**) in 80% yield with liberation of 1,5-COD (95%) (Scheme 1). Addition of excess acetone to the concentrated aqueous solution gave analytically pure colorless powder of **1a**. The diethylplatinum(II) analog **1b** was also prepared in a similar manner in 72% yield.




Scheme 1.

They are soluble in water and thermally stable at room temperature, but started to darken above 150 °C without melting in the solid state.

$^{31}P\{^{1}H\}$ NMR spectrum of **1a** in $D_2O$ shows a singlet at $\delta$ 29.3 with $^{195}Pt$ satellites. The $^{1}J_{Pt\text{-}P}$ value of 1855 Hz is relatively small, suggesting that two phosphorus nuclei are placed *trans* to the methyl ligands with strong *trans* influence, as would be consistent with the square planar *cis* configuration of **1a**.[8] The $^{1}H$ NMR displays a characteristic second order $A_3XX'A'_3$ multiplet centered at $\delta$ 0.42 due to the Pt-Me groups of *cis*-$[PtMe_2(PR_3)_2]$ with $^{195}Pt$ satellites ($^{2}J_{H\text{-}Pt}$ = 69 Hz).[9] **1b** also shows two multiplets having $^{195}Pt$ satellites centered at $\delta$ 0.77 ($^{3}J_{H\text{-}Pt}$ = 74 Hz) and 1.13 ($^{2}J_{H\text{-}Pt}$ = 70 Hz) assignable to methyl and methylene protons of the Et groups. The $^{31}P\{^{1}H\}$ NMR spectrum of **1b** in $D_2O$ shows a singlet at $\delta$ 29.0 with $^{195}Pt$ satellites ($^{1}J_{P\text{-}Pt}$ = 1677 Hz). Addition of free TPPTS to a $D_2O$ solution of **1b** did not cause any apparent line broadening or chemical shift change of the signals of the coordinated and uncoordinated TPPTS in the $^{31}P\{^{1}H\}$ NMR, implying that fast phosphine ligand exchange process does not take place on the NMR time scale.

Dimethyl-, diethyl-, and diphenylplatinum(II) derivatives with THMP or DHMPE ligands were similarly prepared [$PtR_2L_2$: L = THMP, R = Me (**2a**), Et (**2b**), Ph (**2c**); $L_2$ = DHMPE, R = Me (**3a**), Et (**3b**), Ph (**3c**)]. The $^{1}H$ NMR of dimethylplatinum(II) complexes **2a** and **3a** displays a triplet at $\delta$ 0.49 and 0.50 with $^{195}Pt$ satellites assignable to the Pt-Me. For **3a** a characteristic second-order multiplet at $\delta$ 1.96 ($AX_2X'_2A'$) assignable to the bridging methylene protons of the DHMPE ligand was observed. Consistently, diastereotopic methylene protons of $CH_2OH$ groups in the coordinated DHMPE ligand in **3a** appear as an AB quartet at $\delta$ 4.14 and 4.25: the latter involves Pt satellites, suggesting chelation of the DHMPE ligand. Diphenyl derivatives **2c** and **3c** with THMP or DHMPE ligands were also isolated and show the *ortho*-H protons of the phenyl groups with $^{195}Pt$ satellites. Diethylplatinum(II) analogues *cis*-$[PtEt_2L_2]$ with these ligands ($L_2$ = 2 THMP (**2b**), DHMPE (**3b**)) were difficult to be isolated in a pure form, but the formation was unambiguously determined by the $^{1}H$ and $^{31}P\{^{1}H\}$ NMR. Signals due to methylene and methyl protons of the ethyl groups in **2b** and **3b** are very close to each other giving a complicated multiplet at $\delta$ 1.1–1.2 with distinct $^{195}Pt$ satellites of only the methylene quartet signal. The phosphorus ligands in **2a–c** are also considered to occupy positions *trans* to the ethyl ligand, similar to other dialkylplatinum(II) complexes, because the $J_{P\text{-}Pt}$ values are relatively small (1700 Hz for **2a**, 1470 Hz for **2b**, 1660 Hz for **2c**).

While dimethylplatinum(II) complex **1a** is also stable in water for more than two weeks at 50 °C, diethylplatinum(II) complex **1b** slowly decomposed under similar conditions to give a mixture of ethylene and ethane in a day at room temperature. However, when **1a** or **1b** was treated with concentrated hydrochloric acid, immediate protonolysis took place to evolve methane (184%/**1a**) or ethane (166%/**1b**). Protonolysis of **1a** with weaker acids such as acetic acid and formic acid proceeded much more slowly in water and dimethyl malonate did not react with **1a** at all at room temperature. On the other hand, dimethylplatinum(II) complexes **2a** or **3a** having THMP or DHMPE ligand are relatively unstable in water at room temperature in comparison with **1a**, slowly liberating methane. The fact suggests additional protonolysis pathways probably enhanced by THMP and DHMPE ligands, though the detailed mechanism is not clear at present. Protonolyses of **2a** and **3a** with strong acid such as HCl also immediately liberated quantitative amounts of methane (203%/**2a**, 160%/**3a**). Diphenylplatinum(II) complexes **2c** and **3c** are very stable even in water at room temperature and the aqueous solution stood without decomposition for a few days at room temperature. They are thermally more stable than dimethyl- or diethylplatinum(II) complexes in water. While **2a** completely decomposed at 50 °C in 7 h, **2c** slowly decomposed during seven days to give benzene (163%) under the same conditions.

**Thermolysis of *cis*-Diethylplatinum(II) Complexes in Water.** Of particular interest is the thermolysis of *cis*-diethylplatinum(II) complex **1b**, since it may undergo competing $\beta$-hydrogen elimination reaction and/or hydrolysis. Heating of

**1b** in water at 80 °C liberated ethylene and ethane in an approximately 1:1 ratio in 2 h, indicating that disproportionation of the ethyl groups preferentially took place over protonolysis even in water [Eq. 1]. Thermolyses of other diethylplatinum(II) complexes **2b** and **3b** in $D_2O$ at 80 °C for 30 min also liberated a mixture of ethylene and ethane, however, the ratios of ethylene to ethane were approximately 0.35 and 0.5 for **2b** and **3b**, respectively, indicating that concomitant protonolysis of the ethyl groups was also taking place simultaneously in addition to disproportionation of the ethyl groups. This protonolysis may also be enhanced by the hydroxy group in THMP or DHMPE ligands.

$$\mathbf{1b} \xrightarrow[H_2O]{80\ ^\circ C} \underset{94\%}{CH_2{=}CH_2} + \underset{90\%}{CH_3CH_3} \quad (1)$$

On the other hand, the ratio of ethylene to ethane was approximately constant during the thermolysis of **1b**, indicating occurrence of clean disproportionation of the ethyl groups. Figure 1 shows the time-yield curves of ethylene and ethane for the thermolysis of **1b** in $H_2O$. Platinum(0) product may be formed, as previously reported in the thermolysis of dialkylplatinum(II) complexes in aprotic solvents.[10] Such a clean disproportionation of the ethyl groups also excludes the possible free radical mechanism, since the ethyl radical is known to favor coupling rather than disproportionation.[11] Thus the concerted $\beta$-hydrogen elimination giving a ethyl(ethylene)hydridoplatinum(II) intermediate, followed by reductive elimination of ethane at Pt, would be the most plausible mechanism. In order to get more mechanistic insight of the $\beta$-hydrogen elimination process, the effect of added TPPTS on the time-course of thermolysis was examined (Fig. 1).

The thermolysis reactions were found to obey first-order kinetics with rate constant $k_{obsd}$.

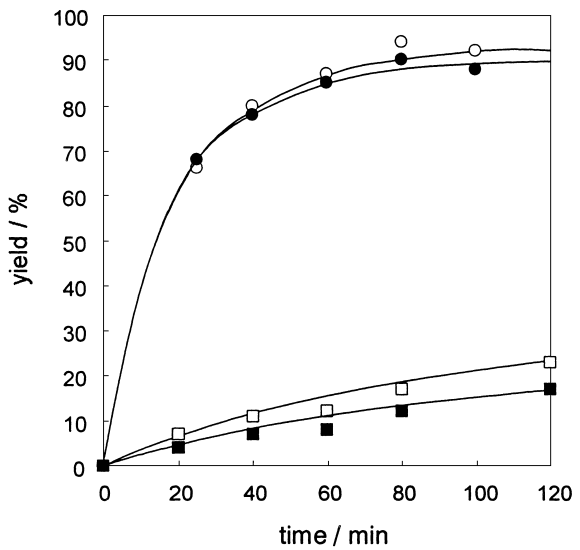
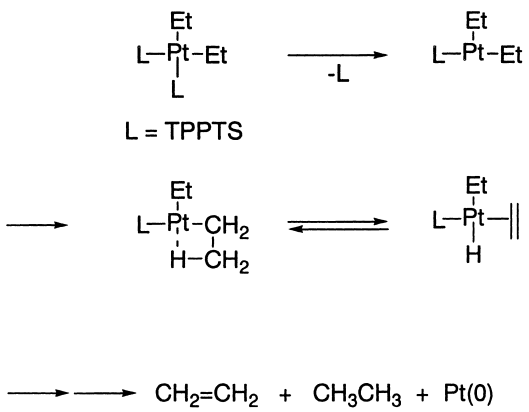



Fig. 1. Time-courses of thermolysis of **1b** at 80 °C in water. Ethylene (○) and ethane (●) evolved in the absence of TPPTS ([**1b**] = 7.2 mmol/L); ethylene (□) and ethane (■) evolved in the presence of TPPTS ([**1b**] = 7.0 mmol/L, [TPPTS] = 34.8 mmol/L).

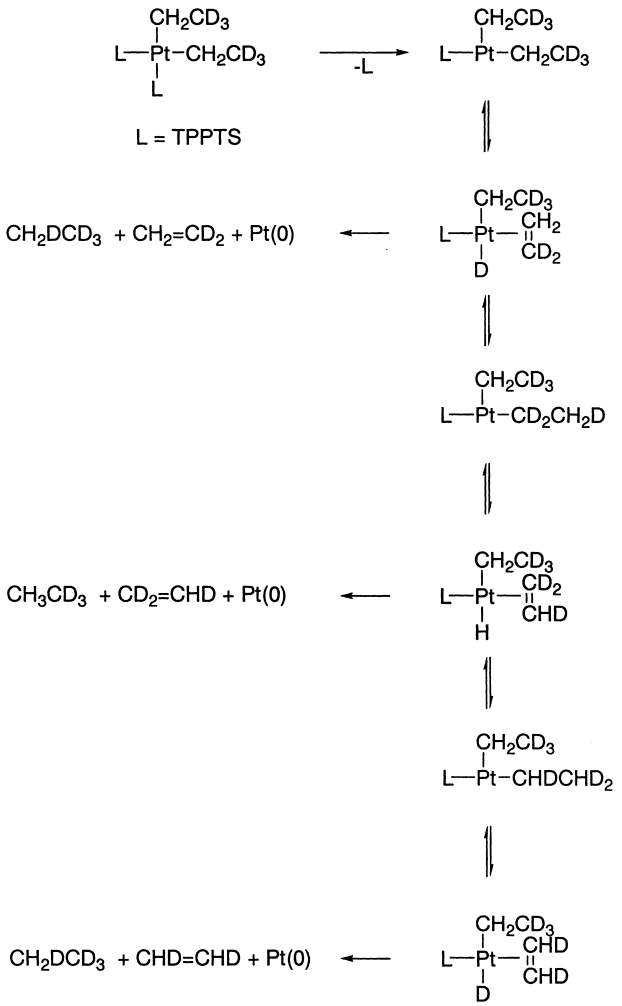
$$-\frac{d}{dt}[PtEt_2(TPPTS)_2] = k_{obsd}[PtEt_2(TPPTS)_2] \quad (2)$$

Estimated rates constants $k_{obsd}$ are $5.6 \times 10^{-4}$ $s^{-1}$ and $2.7 \times 10^{-5}$ $s^{-1}$ in the absence and presence of free TPPTS ([TPPTS] = 34.8 mmol/L), respectively. Addition of five equivalents of free TPPTS suppressed the reaction rate to ca. 1/20. Such retardation effect is considered to arise from the competitive coordination of TPPTS to **1b** to block the fifth coordination site at Pt for $\beta$-hydrogen elimination[12] and/or from preventing the prerequisite formation of 3-coordinate intermediate which would be formed by dissociation of one TPPTS ligand.[13] However, neither 3-coordinate species [$PtEt_2$(TPPTS)] nor 5-coordinate species [$PtEt_2(TPPTS)_3$] was detected by NMR in the presence or absence of added TPPTS, indicating that the complex **1b** always keeps its square planar 4-coordinate structure during the thermolysis. If the competitive association of TPPTS to 4-coordinate species is responsible for the retardation effect, a considerable amount of 5-coordinate species should be detected in the presence of TPPTS, and therefore the former associative mechanism is excluded. Thus, a reaction mechanism via rate limiting dissociation of TPPTS giving an unstable three coordinate T-shape intermediate is proposed, as previously described by Whitesides[10a,b] and us[10c] as shown in Scheme 2.

The reversibility of the $\beta$-hydrogen elimination was also examined by the deuterium labeling experiment. **1b**-$d_6$, *cis*-[$Pt(CH_2CD_3)_2(TPPTS)_2$] was prepared and decomposed in water at 80 °C. The ethylene liberated in the thermolysis was analyzed by studying the IR spectrum of the gas and was found to consist of only $CH_2{=}CD_2$, *cis*- and *trans*-CHD=CHD, and $CD_2$=CHD, while no absorptions due to $C_2H_4$, $CH_2$=CHD, and $C_2D_4$ were detected. Deuterium scrambling in evolved ethylene and absence of ethylene-$d_0$, $d_1$, and $d_4$ clearly indicate that the facile H–D exchange was taking place within one ethyl ligand and the other ethyl group was not participate this H–D exchange process. The facile and reversible $\beta$-hydrogen elimination giving a ethyl(ethylene)hydridoplatinum(II) intermediate, followed by re-insertion into the Pt–H bond, is proposed as a mechanism as shown in Scheme 3. This process must take place after the prerequisite phosphine dissociation as well as before the reductive elimination of ethane. Such a dissociative




Scheme 2.




Scheme 3.

process is essentially the same as the mechanism established in the thermolysis of $[PtR_2(PPh_3)_2]$ in non-aqueous organic solvents.[10] It is interesting to note that the thermolysis of **1b** in water in the absence of excess phosphine proceeds slightly faster than that of triphenylphsophine analog $[PtEt_2(PPh_3)_2]$ in $CH_2Ph_2$. The effect of added phosphine ligand is less pronounced in water. This suggests that the phosphine dissociation of **1b** for $\beta$-hydrogen elimination in water is slower than that of $[PtEt_2(PPh_3)_2]$ in $CH_2CPh_2$, probably due to the weaker electron-donating ability of TPPTS than $PPh_3$, and/or that the rate of $\beta$-hydrogen elimination followed by elimination of ethylene and ethane and the rate of association of TPPTS to the 3-coordinate intermediate are in the same order.[13]

The present results display the intrinsic thermal stability of the Pt–C bond in water and the occurrence of a typical organometallic reaction such as $\beta$-hydrogen elimination in preference to hydrolysis even in water, suggesting that transition metal-mediated organic transformations and catalyses via organometallic intermediates, which are frequently performed in aprotic solvents, can be extended to the reactions in aqueous medium.

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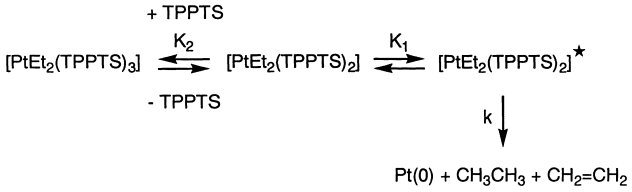
11 Disproportionation-combination rate constant ratio is 0.14 for Et radical and the value is relatively invariable in various solvents: "Free Radicals," ed by J. K. Kochi, Wiley-Interscience Publication, New York (1973), Vol 1, p. 11.

12 If the competitive coordination of TPPTS to **1b** to block the fifth coordination site at Pt for $\beta$-hydrogen elimination is responsible for the retardation effect, the following rate equation is derived by assuming pre-equilibrium of competitive coordination of TPPTS and $\beta$-hydrogen to Pt. In order to obtain the present retardation effect of added TPPTS, a significant amount of $[PtR_2L_3]$ should be observed during the thermolysis. However, the complex **1b** always keeps its square planar 4-coordinate structure during

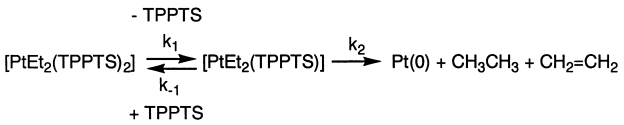
the thermolysis and the equilibrium constants $K_1$ and $K_2$[TPPTS] estimated by NMR were too small (at least smaller than 0.01) to show the effect, excluding the associative mechanism (Scheme 4 and Eq. 3).




Scheme 4.

$$-\frac{d}{dt}[PtEt_2]_{total} = \frac{kK_1}{1 + K_1 + K_2[TPPTS]}[PtEt_2]_{total} \quad (3)$$

13 The steady state approximation of the 3-coordinate intermediate, from which a facile reversible $\beta$-hydrogen elimination takes place followed by reductive elimination of ethane and liberation of ethylene, gives the following rate equation which is consistent with the experimental data with approximate values of $k_1$ and $k_{-1}/k_2$ are $5.6 \times 10^{-4}$ s$^{-1}$ and $5.7 \times 10^2$ L/mol. The observed weaker magnitude of the retardation effect of added TPPTS suggests the considerably smaller $1/k_2K$ value for **1b** than [$PtEt_2$-($PPh_3$)$_2$]. This may be due to larger phosphine dissociation constant and/or facile succeeding processes of **1b**.




Scheme 5.

$$-\frac{d}{dt}[PtEt_2(TPPTS)_2] = \frac{k_1k_2}{k_2 + k_{-1}[TPPTS]}[PtEt_2(TPPTS)_2] \quad (4)$$