Organometallics **1982**, *1*, 1528–1536

reported by Seyferth and White[11] afforded XIV in 50–60% yield. XIV also was identified by comparison with an authentic sample.

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Thermolysis Mechanism of Symmetrical and Unsymmetrical Dialkylplatinum(II) Complexes with Tertiary Phosphine Ligands. Controlling Factors for β Elimination

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A series of symmetrical and unsymmetrical *cis*-dialkylplatinum(II) complexes with tertiary phosphine ligands *cis*-$Pt(R_a)(R_b)L_2$ (R_a, R_b = Me, Et, *n*-Pr, *i*-Pr, *n*-Pr, *i*-Bu, *n*-pentyl, C_2H_4Ph, $C_2H_4C_6H_4$-*p*-OMe; L_2 = $(PPh_3)_2$, $(PPhMe_2)_2$, dpe) has been prepared by reactions of $Pt(R_a)ClL_2$ with alkylating reagents such as R_bLi and R_bMgX. These complexes are characterized by elemental analyses and IR and NMR (^1H and $^{31}P\{^1H\}$) spectroscopy as well as by chemical reactions. Thermolysis of the dialkylplatinum complexes gives only the disproportionation products of the two alkyl groups via β elimination. A kinetic study of the thermolysis reveals the existence of the nondissociative path in addition to the dissociative one. In the presence of an excess of PPh_3, thermolysis proceeds mainly via a nondissociative path in which the liberation of olefin after facile reversible β elimination is probably rate determining. When the thermolysis of the unsymmetrical *cis*-$Pt(R_a)(R_b)L_2$ type complex is carried out in the absence of excess PPh_3, the relative rate of β elimination involving the R_a group to that involving the R_b group is proportional to the ratio of the number of β-hydrogen atoms in the R_a group to that in the R_b group.

Introduction

Transition-metal complexes having metal-to-carbon bonds play crucial roles in various organic reactions catalyzed by transition metals. Understanding the behavior of these transition-metal alkyl complexes is of fundamental importance in the elucidation of the metal-promoted catalytic processes. Recent studies on the thermal decomposition of isolated transition-metal alkyl complexes have shed some light for understanding the stability and reactivity of transition metal-to-carbon bond.[1] For transition-metal dialkyl complexes several thermolysis pathways are possible: (1) homolytic cleavage of the M–C bond (radical pathway); (2) reductive elimination (coupling reaction); (3) β elimination (disproportionation of two alkyl groups); (4) other pathways (α or γ elimination).

Among them, the β-elimination process is the most frequently observed thermolysis pathway. Clarification of the factors controlling the thermolysis pathway through β elimination is essential in understanding the mechanisms of the catalytic processes involving olefins and for design of organic syntheses utilizing transition-metal catalysts.

Dialkylplatinum(II) complexes, among other transition-metal alkyls, serve as excellent models for studying the β-elimination process since thermal decomposition of PtR_2L_2 results in the clean disproportionation liberating alkane, RH, and alkene, R(–H), in a 1:1 ratio.

$$PtR_2L_2 \xrightarrow{\Delta} RH + R(-H) + Pt(0) \text{ complexes}$$

Whitesides proposed a dissociative mechanism for the decomposition of $Pt(n\text{-}Bu)_2(PPh_3)_2$ and pointed out the importance of blocking the site for β elimination by the ligand in increasing the stability of the complex.[2] Reger also showed that an open coordination site on iron, formed by ligand dissociation, is required for β elimination from $Fe(Cp)(CO)(PPh_3)R$ to occur.[3] Recently, the steric influence of the ligands in *trans*-$PdEt_2L_2$ in the disproportionation reaction of the ethyl groups has been reported.[4] In this case, a thermolysis process involving ligand dissociation does not constitute the main decomposition pathway and the presence of bulky tertiary phosphine ligands in the undissociated *trans*-$PdEt_2L_2$ was found to facilitate the β-elimination process rather than to block it in contrast to the behavior of platinum dialkyls.

In order to obtain further insight into the β-elimination process, we have initiated a project to prepare and thermolyze a series of unsymmetrical dialkylplatinum(II) complexes, since the examination of products of the thermal decomposition was expected to afford direct information about the relative ease of β-hydrogen elimination from platinum alkyls. A part of the results have been

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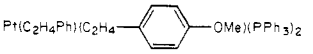
Table I. $^{31}P\{^1H\}$NMR Data of Dialkylplatinum(II) Complexes in CD_2Cl_2 [a]

compds ($Pt(R_a)(R_b)L_2$)	P_a, ppm	$J(P_a-P_b)$, Hz	$J(Pt-P_a)$, Hz	P_b, ppm	$J(Pt-P_b)$, Hz
2, $Pt(Et)(n\text{-}Pr)(PPh_3)_2$	32.7 d	5.9	1608	32.2 d	1640
9, $Pt(Et)(C_2H_4Ph)(PPh_3)_2$	32.6 d	7.8	1693	32.3 d	1824
10, $Pt(n\text{-}Pr)(C_2H_4Ph)(PPh_3)_2$	31.9 d	7.8	1681	32.3 d	1840
11, 	32.3 d	7.8	1781	32.3	1797
12, $Pt(Et)(n\text{-}Pr)(dpe)$	64.8 d	7.8	1609	64.5	1639
16, $Pt(Et)_2(PPh_3)_2$	32.5 s		1723		
17, $Pt(n\text{-}Pr)_2(PPh_3)_2$	32.4 s		1727		
18, $Pt(n\text{-}Bu)_2(PPh_3)_2$	32.4 s		1730		
19, $Pt(Et)_2(dpe)$	63.6 s		1617		
20, $Pt(n\text{-}Pr)_2(dpe)$	64.6 s		1627		

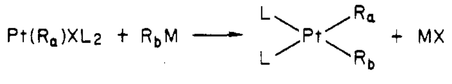
[a] P_a is trans to R_a; P_b is trans to R_b.

published previously in preliminary form.[5]

After the publication of the above communication Whitesides published the results of extensive studies on thermolysis of symmetrical dialkylplatinum complexes.[6] Our results reported herein on the unsymmetrical dialkylplatinum complexes provide complementary information to Whitesides' results.

Results

Preparation of Unsymmetrical Dialkylplatinum(II) Complexes. Alkylation of a monoalkylbis(tertiary phosphine)platinum(II) halide[6] with corresponding alkyllithium or Grignard reagent gave the following unsymmetrical *cis*-dialkylplatinum(II) complexes **1–15** in good yields.



(1)

1–15

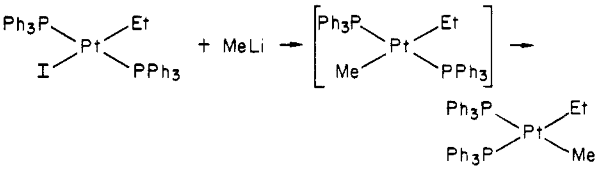
X, halogen
M, Li or Mg X
1, $Pt(Me)(Et)(PPh_3)_2$
2, $Pt(Et)(n\text{-}Pr)(PPh_3)_2$
3, $Pt(Et)(i\text{-}Pr)(PPh_3)_2$
4, $Pt(Et)(n\text{-}Bu)(PPh_3)_2$
5, $Pt(Et)(i\text{-}Bu)(PPh_3)_2$
6, $Pt(Et)(Ph)(PPh_3)_2$
7, $Pt(n\text{-}Pr)(n\text{-}Bu)(PPh_3)_2$
8, $Pt(i\text{-}Bu)(n\text{-}pentyl)(PPh_3)_2$
9, $Pt(Et)(C_2H_4Ph)(PPh_3)_2$
10, $Pt(n\text{-}Pr)(C_2H_4Ph)(PPh_3)_2$
11, $Pt(C_2H_4Ph)(C_2H_4C_6H_4\text{-}p\text{-}OMe)(PPh_3)_2$
12, $Pt(Et)(n\text{-}Pr)dpe$*
13, $Pt(Et)(n\text{-}Pr)(PPhMe_2)_2$
14, $Pt(CH_2CD_3)(n\text{-}Pr)(PPh_3)_2$
15, $Pt(CH_2CD_3)(C_2H_4Ph)(PPh_3)_2$
*dpe, 1,2-bis(diphenylphosphino)ethane

These complexes were purified by recrystallization from suitable solvents and characterized by elemental analyses and IR and NMR spectra as well as by chemical reactions (see Experimental Section). Complexes **1–15** are stable in air at room temperature. The IR spectra of these complexes showed characteristic bands at 2800–3000 and 1180–1190 cm^{-1} attributable to ν(C–H) and δ(CH), respectively.[8] Acidolysis of these complexes with dry HCl liberated alkanes quantitatively, confirming that two alkyl groups are attached to Pt(II).

$$Pt(R_a)(R_b)L_2 + 2HCl \rightarrow R_aH + R_bH + PtCl_2L_2 \quad (2)$$

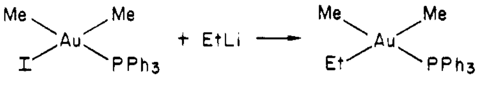
The ^{1}H NMR spectra of the unsymmetrical dialkylplatinum(II) complexes show complicated signals for the alkyl groups attached to Pt(II) due to coupling of protons to neighboring protons as well as to ^{31}P and ^{195}Pt nuclei. However, the doublet of doublets for Pt–Me in **1** and for $PPhMe_2$ in **13** (each with satellites due to coupling to ^{195}Pt) in the ^{1}H NMR spectrum suggest that these complexes have the cis configuration. The cis configuration of the unsymmetrical dialkylplatinum(II) complexes is further supported by the $^{31}P\{^1H\}$ NMR spectra of **2**, **10**, **11**, and **12** which show AB quartets having ^{195}Pt satellites (Table I). Absence of the other singlet excluded the possibility of the presence of the symmetrical alkyls. Coupling constants between ^{31}P and ^{195}Pt in the symmetrical alkyls increase in the order of diethyl-, di-*n*-propyl-, and di-*n*-butylplatinum(II) complexes, reflecting the decrease in trans influence of these alkyl groups.[9] Coupling constants of ^{195}Pt to ^{31}P trans to the phenethyl groups in **9**, **10**, and **11** are considerably larger than those in the aliphatic alkyls.

Alkylation of *trans*-$PtEtI(PPh_3)_2$ with MeLi gave only *cis*-$PtMeEt(PPh_3)_2$ which may have been formed by the spontaneous isomerization of the initially formed *trans*-$PtMeEt(PPh_3)_2$. The preference of the cis configuration rather than trans for these platinum dialkyl complexes probably arises not from kinetic but thermodynamic reasons.



(3)

In contrast, the alkylation of isoelectronic *cis*-$Au^{III}Me_2I(PPh_3)$ by EtLi is known to selectively afford *cis*-$Au^{III}Me_2Et(PPh_3)$ which slowly isomerizes to the trans isomer.[10]



(4)

Thermal Decomposition of Unsymmetrical Dialkylplatinum(II) Complexes. Thermolysis of series of unsymmetrical dialkylplatinum(II) complexes both in the solid state and in solution gave quantitative yields of the corresponding alkanes and alkenes, similar to the thermolysis of symmetrical dialkylplatinum(II) complexes.[2]

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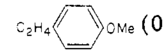
Table II. Gaseous Product Distribution in the Thermolysis of $Pt(R_a)(R_b)L_2$ without Solvent and in CH_2Ph_2 in the Absence of Added Ligand[f]

	compds (mmol)[c]		gases evolved, mmol						
	R_a	R_b	R_aH	R_a(-H)	R_bH	R_b(-H)	total yield (%)	R_a/ R_a(-H)	R_b(-H)/ R_bH
1	Et	Me (0.078)[a]	0	0.076	0.077	0	0.153 (98)	0	0
2	Et	*n*-Pr (0.060)[a]	0.022	0.036	0.034	0.023	0.155 (96)	0.61	0.68
2	Et	*n*-Pr (0.029)[b]	0.009	0.014	0.014	0.009	0.047 (81)	0.64	0.64
3	Et	*i*-Pr (0.031)[a]	0.012	0.016	0.016	0.014	0.058 (93)	0.75	0.88
4	Et	*n*-Bu (0.088)[a]	0.029	0.043	0.048	0.034	0.154 (87)	0.67	0.71
5	Et	*i*-Bu (0.039)[a]	0.007	0.030	0.024	0.007	0.068 (86)	0.23	0.29
6	Et	Ph (0.051)[a]	0	0.043	0.056	0	0.099 (96)	0	0
7	*n*-Pr	*n*-Bu (0.043)[a]	0.018	0.019	0.011	0.012	0.060 (70)	0.95	1.1
8	*i*-Bu	*n*-C_5H_{11} (0.022)[a]	0.007	0.013	0.007	0.004	0.031 (70)	0.54	0.57
9	Et	C_2H_4Ph (0.027)[b]	0.016	0.006	0.008	0.020	0.050 (93)	2.7	2.5
10	*n*-Pr	C_2H_4Ph (0.089)[b]	0.058	0.025	0.030	0.060	0.173 (97)	2.3	2.0
11	C_2H_4Ph	 (0.087)[b]	0.045	0.049	0.041	0.040	0.175 (99)	0.92	1.0
12[d]	Et	*n*-Pr (0.039)[a]	0.022	0.018	0.016	0.021	0.077 (99)	1.2	1.3
13[e]	Et	*n*-Pr (0.035)[a]	0.011	0.015	0.016	0.014	0.057 (81)	0.73	0.87
14	CH_2CD_3	*n*-Pr (0.449)[b]	0.156	0.241	0.233	0.154	0.784 (87)	0.65	0.66
15	CH_2CD_3	C_2H_4Ph (0.361)[b]	0.263	0.087	0.088	0.259	0.697 (97)	3.0	2.9

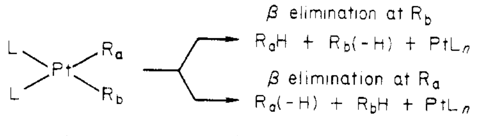
[a] Without solvent. [b] In CH_2Ph_2. [c] L = PPh_3. [d] L_2 = 1,2-bis(diphenylphosphino)ethane. [e] L = $PPhMe_2$. [f] Pt complexes were decomposed at 100–150 °C for 4 h both in the solid state and in CH_2Ph_2.

Table III. Gaseous Product Distribution in the Thermolysis of $Pt(R_a)(R_b)(PPh_3)_2$ in the Presence of Added PPh_3 in CH_2Ph_2[a]

	compds (mmol)		gases evolved, mmol						
	R_a	R_b	R_aH	R_a(-H)	R_bH	R_b(-H)	total yield (%)	R_aH/ R_a(-H)	R_b(-H)/ R_bH
2	Et	*n*-Pr (0.030)	0.021	0.009	0.008	0.022	0.060 (100)	2.3	2.7
4	Et	*n*-Bu (0.029)	0.019	0.008	0.008	0.018	0.053 (91)	2.4	2.3
7	*n*-Pr	*n*-Bu (0.029)	0.015	0.014	0.011	0.013	0.053 (91)	1.1	1.2
9	Et	C_2H_4Ph (0.030)	0.020	0.006	0.006	0.021	0.053 (88)	3.3	3.5
10	*n*-Pr	C_2H_4Ph (0.031)	0.015	0.014	0.014	0.016	0.059 (95)	1.0	1.1
11	C_2H_4Ph	 (0.050)	0.020	0.021	0.018	0.019	0.078 (78)	0.95	1.1
14	CH_2CD_3	*n*-Pr (0.029)	0.018	0.007	0.006	0.017	0.048 (83)	2.6	2.8
15	CH_2CD_3	C_2H_4Ph (0.031)	0.025	0.007	0.006	0.024	0.062 (100)	3.6	4.0

[a] Thermolysis temperature = 100 °C. [PPh_3] = 0.57–0.59 M.

Tables II and III summarize the results of thermolysis under various conditions. A fairly good material balance for the alkyl groups indicates the occurrence of a clean disproportionation of the two alkyl groups, both in the solid state as well as in solution. No coupling products were obtained. The thermolysis residue in the absence of PPh_3 has been stated to be a polymeric platinum(0) phosphine complex,[2,11] whereas PtL_3 becomes a final product in the presence of ligand. The following two disproportionation pathways are involved in the thermolysis of the unsymmetrical dialkylplatinum(II) complexes.



(5a)

(5b)

Product Analysis. In the Absence of PPh_3. As we noted in a preliminary form,[5] the ratios of $R_aH/R_a(-H)$ and $R_b(-H)/R_bH$ (cf. eq 6) are identical with the ratio of numbers of β-hydrogens in the two alkyl groups (R_a and R_b) when complexes of type *cis*-$Pt(R_a)(R_b)(PPh_3)_2$ are thermolyzed in the absence of added PPh_3 or in the solid state (Figure 1). For example, the ratios of ethane to ethylene and of propylene to propane in the thermolysis of 2 in diphenylmethane were 0.64 and 0.60, respectively, which are approximately equal to the ratio of the number of β-hydrogens in the propyl group to that in the ethyl group (0.67). When one of the alkyl groups (R_b) has no β-hydrogens as in the Me and Ph groups (1 and 6), only R_bH and R_a(-H) are formed. The results shown in Figure 1 indicate that the following relationship exists in the thermolysis of dialkylplatinum complexes

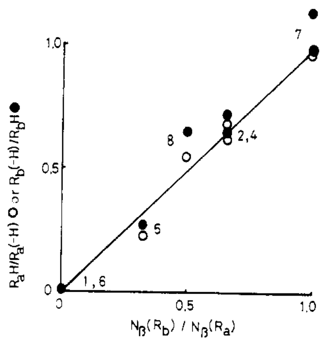


Figure 1. Relation between $N_β(R_b)/N_β(R_a)$ and $R_aH/R_a(-H)$ (or $R_b(-H)/R_bH$) in thermolysis of $Pt(R_a)(R_b)(PPh_3)_2$ performed in the solid state.

$$\frac{N_β(R_b)}{N_β(R_a)} = \frac{R_aH}{R_a(-H)} = \frac{R_b(-H)}{R_bH} \tag{6}$$

where $N_β(R_a)$ and $N_β(R_b)$ represent the numbers of β-hy-

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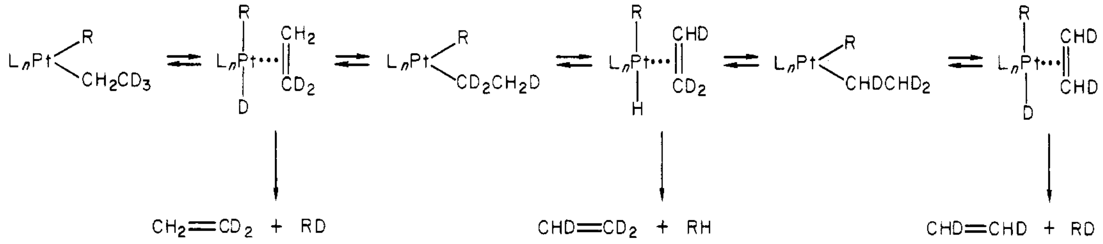
Scheme I. A Mechanism of H–D Scrambling in Ethylenes Formed in the Thermolysis of $PtR(CH_2CD_3)(R)(PPh_3)_2$



drogens in R_a and R_b, respectively. The results indicate that the relative ease of β-hydrogen elimination from the alkylplatinum complex is primarily determined by the numbers of hydrogens in the alkyl groups. Thermolysis of the ethylpropylplatinum(II) complex, **13**, having other monodentate ligands, PMe_2Ph, also gave similar results. In contrast to the linear relationship, as shown in Figure 1 and eq 6, observed for the simple dialkyl complexes, a considerably different tendency for the ease of β elimination has been observed for the alkyl aryl complexes **9** and **10**. The ratio of ethane to ethylene (or styrene to ethylbenzene) in thermolysis of **9** is significantly larger than the $N_\beta(R_a)/N_\beta(R_a)$ ratio which is 0.67 in this case. Similar deviation is also found in the thermolysis of propyl phenethyl complex **10**. The results indicate that hydrogens in the phenethyl group are more easily abstracted than those in the ethyl or propyl group. This is probably because the β-hydrogens in the phenethyl group are activated by the electron-withdrawing phenyl group. Substitution of the para hydrogen in the phenethyl group by a MeO group showed little influence on the relative ease of β elimination. Thus thermolysis of $Pt(C_2H_4Ph)(C_2H_4\text{-}p\text{-}C_6H_4OMe)(PPh_3)_2$ (**11**) gave a 1:1 mixture of styrene and ethylbenzene (and a 1:1 mixture of 4-(methoxyethyl)benzene and 4-methoxystyrene). The effect of the para-substituent in the phenethyl group may be too indirect to affect the thermolysis, or a steric effect of the phenyl group on the thermolysis may be involved. Thermolysis of complex **12**, having a bidentate dpe ligand, also gave different results from those expected from eq 6. The ratios of C_2H_6 to C_2H_4 and of C_3H_6 to C_3H_8 in thermolysis of **12** in the solid state are 1.2 and 1.3, respectively, showing that β-hydrogen abstraction takes place more easily from the *n*-Pr than from the Et group, although the *n*-Pr group has less β-hydrogens than the Et group. The other notable deviation from the relationship shown in eq 6 was observed in the thermolysis of complexes having branched alkyl groups. Thermolysis of ethylisopropylplatinum(II) complex **3** afforded gases having similar composition (a $R_a/R_a(-H)$ ratio of ca. 0.7) to those obtained in the case of thermolysis of ethyl*n*-propylplatinum(II) complex **2** rather than the ratio of 2.0 expected for the thermolysis of the CH_2CH_3 and $CH(CH_3)_2$. The result can be accounted for by skeletal isomerization from isopropyl- to *n*-propylplatinum species prior to the thermal decomposition (vide infra).[12]

In the Presence of PPh_3. The gaseous product ratios are dramatically changed in the thermolysis of unsymmetrical dialkylplatinum(II) complexes in solution on adding tertiary phosphine as shown in Table III. Thus, the amount of ethane (or propylene) evolved in the thermolysis of the ethylpropylplatinum **2** is larger than that of ethylene (or propane). In the presence of excess PPh_3 the β-hydrogen abstraction from the *n*-Pr group in **2** appears to be more facile than that from the ethyl group, although the former possesses fewer hydrogens than the latter. Under these conditions, the apparent ease of β-hydrogen elimination is in the order *n*-BuPt ≥ *n*-PrPt > EtPt.

H–D Exchange in the Alkyl Group. Facile H–D scrambling in the alkyl chain of $Pt(n\text{-Bu-}2,2\text{-}d_2)_2(PPh_3)_2$ during thermolysis has been reported by Whitesides et al.[2,6] In order to obtain further insight into the H–D scrambling, we performed thermolysis of specifically deuterated complexes **14** and **15**. In the thermolysis of $Pt(CH_2CD_3)(n\text{-}C_3H_7)(PPh_3)_2$ (**14**) in the absence and in the presence of added PPh_3, the ethylene liberated contained only *cis*- and *trans*-CHD=CHD, *cis*- and *trans*-CH_2=CD_2, and *cis*- and *trans*-CHD=CD_2 but no CH_2=CHD, C_2D_4, and C_2H_4. A mixture of deuterated ethanes, which contained no more than three deuteriums, was obtained as revealed by mass spectroscopy. No deuterium was found in the propylene, while propane evolved consisted of C_3H_8 and C_3H_7D. Thermolysis of $Pt(CH_2CD_3)(C_2H_4Ph)(PPh_3)_2$ (**15**) gave similar results (the products are CHD=CHD, CH_2=CD_2, CHD=CD_2, ethane-d_3, PhCH=CH_2, ethylbenzene-d_0 and -d_1). These results clearly exclude an intermolecular exchange mechanism and support a mechanism involving a 1,2-hydrogen shift in the same ethyl group. The following mechanism (Scheme I) involving β elimination and insertion into the Pt–H bond in one alkyl group without participation of the other alkyl group in the exchange process is compatible with the present results. For further information to be obtained regarding the extent of H–D exchange in the ethyl group, acidolysis by dry HCl of **14** recovered after partial thermolysis in the absence of added PPh_3 was performed. The ethane thus obtained from the acidolysis contained only CH_3CD_3, as confirmed by mass spectral analysis, indicating that the H–D exchange occurs only during the event of decomposition of the ethyl group in an activated state leaving the remaining ethyl and propyl groups intact. In contrast, similar acidolysis experiment carried out on a sample partly thermolyzed in the presence of excess PPh_3 afforded a mixture of CH_3CD_3 and CHD_2CH_2D.

Rearrangement of the Alkyl Group. Attempts to prepare a *sec*-butylethylplatinum(II) complex having PPh_3 ligands from *sec*-BuLi according to eq 1 failed. Instead, pure *n*-butylethylplatinum(II) complex **4** was isolated from the reaction mixture of $PtEtCl(PPh_3)_2$ and *sec*-BuLi. The observation indicates the occurrence of the rearrangement of the secondary alkyl group to the primary alkyl group during the preparation. In the case of alkylation of $PtEtCl(PPh_3)_2$ with *i*-PrLi a mixture of $Pt(Et)(i\text{-Pr})(PPh_3)_2$ and $Pt(Et)(n\text{-Pr})(PPh_3)_2$ in about a 1:1 ratio was obtained. The isolated $Pt(Et)(i\text{-Pr})(PPh_3)_2$ was slowly isomerized to $Pt(Et)(n\text{-Pr})(PPh_3)_2$ in CD_2Cl_2 at room temperature.[12] No large effect of added PPh_3 on the isomerization rate was observed.

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[12] Similar rearrangement of alkyl groups have been reported: (a) Reger, D. L.; Culbertson, E. C. *Inorg. Chem.* **1977**, *16*, 3104. (b) Tamaki, A.; Mageniss, S. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 6. (c) Bennett, M. A.; Charles, R. *Ibid.* **1972**, *94*, 666. (d) Arnold, D. P.; Bennett, M. A.; Crisp, G. T.; Jeffery, J. C. "Catalytic Aspects of Metal Phosphine Complexes" Alyea, E. C., Meek, D. W., Eds.; American Chemical Society: Washington, D.C. 1982; *Adv. Chem. Ser. No. 196*, p 195.

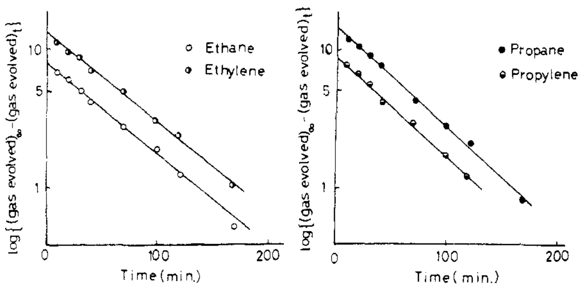

Figure 2. First-order plot for thermolysis of Pt(Et)(*n*-Pr)$(PPh_3)_2$ in the presence of ethyl methacrylate in CH_2Ph_2 at 60.0 °C: [Pt(Et)(*n*-Pr)$(PPh_3)_2$] = 0.028 M; [ethyl methacrylate] = 0.280 M.

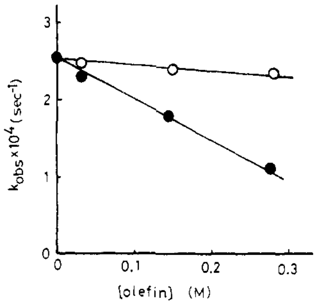

Figure 3. Effect of added olefins on k_{obsd} in CH_2Ph_2 at 60.0 °C ([Pt(Et)(*n*-Pr)$(PPh_3)_2$] = 0.028–0.030 M): ●, dimethyl maleate; ○, ethyl methacrylate.

Kinetics. The rates of evolution of ethane, ethylene, propane, and propylene were followed by measuring the amounts of the gases evolved in the thermolysis of *cis*-Pt(Et)(*n*-Pr)$(PPh_3)_2$, **2**, in diphenylmethane which was chosen for its thermal stability and chemical inertness to the platinum complexes. In the absence of added PPh_3 the composition of gases evolved during the thermolysis gradually changed. Although the relative ratio of C_2H_6:C_3H_8:C_3H_6 did not change throughout the kinetic experiment, the ratio of ethylene to these gases increased continuously with time. This seems to be due to delayed release of C_2H_4 trapped by PtL_2 formed by the thermolysis.[13] When olefins such as ethyl methacrylate and dimethyl maleate were added, trapped C_2H_4 was liberated and the composition of the gas evolved became invariant throughout the thermolysis. Similar kinetic behavior (trapping of C_2H_4 by a complex formed by thermolysis and liberation of C_2H_4 by added olefins) has been found in the thermolysis of $PdEt_2L_2$.[4] When the thermolysis reaction was studied in CH_2Ph_2 solutions containing the olefin at 60 °C by following the rate of evolution of each gas (C_2H_4, C_2H_6, C_3H_6, and C_3H_8), the thermolysis reaction was found to obey first-order kinetics with the rate constant k_{obsd} (Figure 2).

$$\text{rate} = -\frac{d}{dt}[\text{Pt(Et)}(n\text{-Pr})L_2] = k_{obsd}[\text{Pt(Et)}(n\text{-Pr})L_2] \quad (7)$$

Thermolysis of other dialkyl complexes also shows a similar first-order kinetics.

$$\text{rate} = -\frac{d}{dt}[\text{Pt}(R_a)(R_b)L_2] = k_{obsd}[\text{Pt}(R_a)(R_b)L_2] \quad (8)$$

Dependences of k_{obsd} on the concentration of added ethyl methacrylate and dimethyl maleate in the thermolysis of **2** are shown in Figure 3. Rate constants k_{obsd} slightly decreases with increase in the concentration of the olefins.

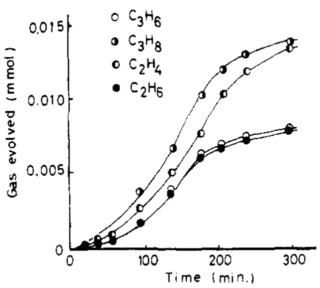

Figure 4. Thermolysis of Pt(Et)(*n*-Pr)$(PPh_3)_2$ in the presence of PPh_3 in CH_2Ph_2 at 60.0 °C: [Pt(Et)(*n*-Pr)$(PPh_3)_2$] = 0.0304 M; [PPh_3] = 0.061 M.

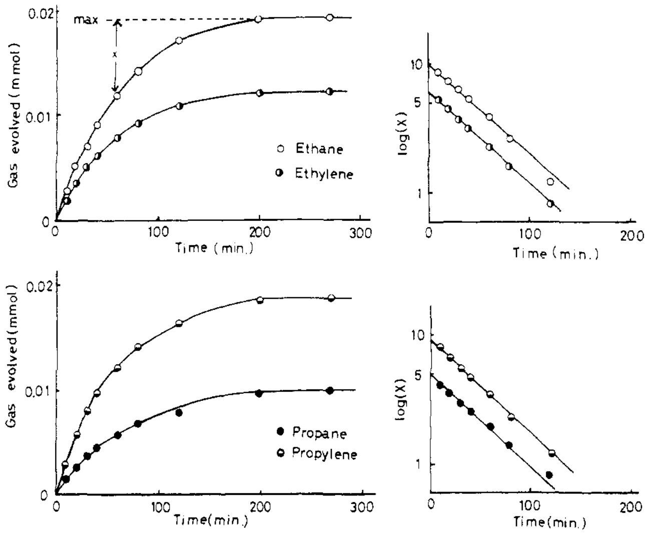

Figure 5. Time courses and first-order plot for thermolysis of Pt(Et)(*n*-Pr)$(PPh_3)_2$ carried out in the presence of added PPh_3 in CH_2Ph_2 at 100 °C. [Pt(Et)(*n*-Pr)$(PPh_3)_2$] = 0.0287 M and [PPh_3] = 0.286 M.

A more electronegative olefin such as dimethyl maleate has a larger inhibition effect in the decomposition. The result is in contrast to the slight acceleration of thermolysis of *trans*-$PdEt_2L_2$ by addition of electronegative olefins.

Addition of only a small amount of PPh_3 strongly suppresses the rate of thermolysis of **2** in CH_2Ph_2 in accordance with Whitesides and co-workers' previous observation concerning the thermolysis of Pt(*n*-Bu)$_2$$(PPh_3)_2$.[2] The first-order kinetics does not hold when the concentration of added PPh_3 is small (below ca. 0.1 M), and the time course of the evolution of gas shows an S-shaped profile as shown in Figure 4. Therefore no further kinetic investigation was attempted for the system containing a relatively low concentration of PPh_3 because of the ambiguity in the estimation of rate constants.

On the other hand, in the presence of excess of PPh_3 (0.2–1.0 M) the thermolysis is strongly suppressed to such an extent that the rate of the thermal decomposition of **2** is too slow to follow at 60 °C. The thermolysis of **2** carried out at higher temperatures revealed that the reaction obeyed the first-order kinetics. The composition of the released gases was invariable throughout the thermolysis (Figure 5). As shown in Figure 6, the rate of decomposition sharply falls with increasing concentration of added PPh_3, reaching a constant value in a higher PPh_3 concentration range of 0.4–1.0 M in accordance with Whitesides' results.[6]

These results suggest the presence of at least two thermolysis pathways. One pathway involves a three-coordinate intermediate formed by partial dissociation of L from *cis*-Pt(R_a)(R_b)L_2. Thermolysis through this coordinatively unsaturated intermediate is more facile than the

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[13] (a) Cook, C. D.; Jauhal, G. S. *Can. J. Chem.* **1967**, *45*, 301. (b) Cook, C. D.; Jauhal, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 1464. (c) Birk, J. P.; Halpern, J.; Pickard, A. L. *Ibid.* **1968**, *90*, 4491.

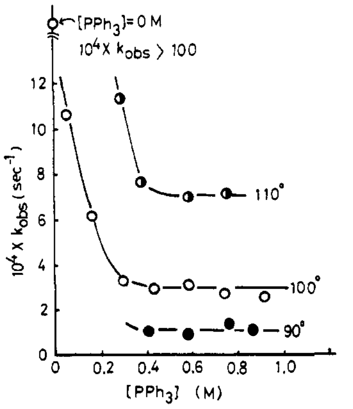
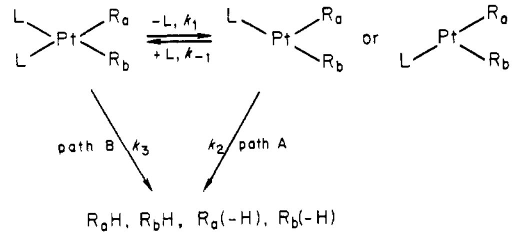


Figure 6. Effect of PPh_3 concentration on k_{obsd} of Pt(Et)(*n*-Pr)$(PPh_3)_2$ in CH_2Ph_2. [Pt(Et)(*n*-Pr)$(PPh_3)_2$] = 0.029 M.

Scheme II. Thermolysis Mechanism of *cis*-$Pt(R_a)(R_b)L_2$



other route. The thermolysis of $Pt(R_a)(R_b)L_2$ in the presence of added L proceeds without involvement of the partly dissociated three-coordinate species. Scheme II shows the thermolysis mechanism proceeding through these two routes (path A and path B). The assumption of the parallel decomposition pathways from the undissociated four-coordinate and the dissociated three-coordinate species and of the steady-state approximation for the concentration of the three-coordinate species gives the following rate equation

$$-\frac{d}{dt}[PtR_2L_2] = \left(k_3 + \frac{k_1k_2}{k_{-1}[L] + k_2}\right)[PtR_2L_2] = k_{obsd}[PtR_2L_2] \qquad (9)$$

The rate constant at higher concentration of added PPh_3 corresponds to k_3 which is the rate constant for direct decomposition without dissociation. The values of k_3 for the thermolysis of various unsymmetrical and symmetrical dialkylplatinum(II) complexes are shown in Table IV. For symmetrical dialkyl complexes the rate constant k_3 increases in the order Et_2Pt < $(n\text{-}Pr)_2Pt$ < $(n\text{-}Bu)_2Pt$ complexes. An unsymmetrical dialkylplatinum(II) complex, $Pt(R_a)(R_b)L_2$, has a k_3 value which is approximately the average of those of the corresponding symmetrical dialkylplatinum(II) complexes $Pt(R_a)_2L_2$ and $Pt(R_b)_2L_2$.

Deuterium kinetic isotope effects were obtained by comparing the rates of decomposition of $Pt(CH_2CD_3)$(*n*-Pr)$(PPh_3)_2$, 14, and $Pt(CH_2CH_3)$(*n*-Pr)$(PPh_3)_2$, 2 (Table IV). The $k_3(2)/k_3(14)$ value was 1.01, indicating a negligible kinetic isotope effect on the rate-determining step. A similar value of $k_3(9)/k_3(15)$ = 0.94 was also obtained.

Kinetic activation parameters at 100 °C in the thermolysis of 2 were obtained from the temperature dependence of k_3: $\Delta H^{\ddagger} = -28$ kcal/mol, $\Delta S^{\ddagger} = 1.2$ eu, and $\Delta G^{\ddagger} = 29$ kcal/mol.

Discussion

In the thermolysis of square planar four-coordinate dialkylmetal (d^8) complexes, MR_2L_2, which release disproportionation products of the two alkyl groups, the following three pathways of thermal decomposition are conceivable.

Table IV. k_3 Values in Thermal Decomposition of $Pt(R_a)(R_b)(PPh_3)_2$ [a]

compds	10^4k_3, s^{-1}
Pt(Et)(*n*-Pr)$(PPh_3)_2$	2.84
$Pt(CH_2CD_3)$(*n*-Pr)$(PPh_3)_2$	2.81
Pt(Et)(*n*-Bu)$(PPh_3)_2$	3.92
Pt(*n*-Pr)(*n*-Bu)$(PPh_3)_2$	4.52
$Pt(Et)(C_2H_4Ph)(PPh_3)_2$	3.40
$Pt(CH_2CD_3)(C_2H_4Ph)(PPh_3)_2$	3.60
Pt(*n*-Pr)$(C_2H_4Ph)(PPh_3)_2$	4.81
$Pt(Et)_2(PPh_3)_2$	1.77
Pt(*n*-Pr)$_2(PPh_3)_2$	4.15
Pt(*n*-Bu)$_2(PPh_3)_2$	6.55

[a] In CH_2Ph_2 at 100 °C. [PPh_3] = 0.57-0.59 M.

(A) dissociative path

$$MR_2L_2 \xrightarrow{-L} MR_2L \rightarrow \text{decomposition}$$

(B) nondissociative path

$$MR_2L_2 \rightarrow \text{decomposition}$$

(C) associative path

$$MR_2L_2 + L \rightarrow MR_2L_3 \rightarrow \text{decomposition}$$

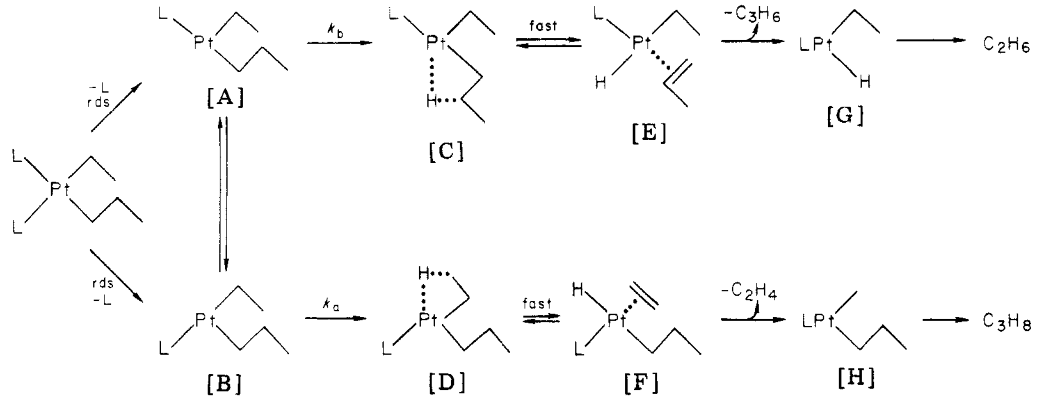
Path A is observed in thermolysis of platinum(II) dialkyls in the absence of added ligands and involves slow preliminary ligand dissociation to give an unstable three-coordinate intermediate from which facile disproportionation of the two alkyl groups takes place. Path B proceeds without dissociation of ligand. *trans*-$PdEt_2L_2$, whose thermolysis affords clean disproportionation products, is the typical example which involves path B.[4] Recent kinetic investigation of the thermolysis of *cis*-$PtEt_2(PEt_3)_2$ by Whitesides also pointed out the existence of path B in addition to path A.[6] Path C with L equal to a tertiary phosphine is rare for β elimination, since the five-coordinate complex is coordinatively saturated to undergo the β elimination. The thermolysis behavior of the complexes studied here involves paths A and B whose mechanistic consideration will be separately discussed below.

Thermal Decomposition through a Three-Coordinate Intermediate (Path A). In the absence of PPh_3 a major thermolysis pathway involves the three-coordinate species as suggested by the kinetic study. Dissociation of PPh_3 from $PtR_2(PPh_3)_2$ is considered to be the rate-determining step as Whitesides reported. In his mechanism, a facile disproportionation of two alkyl groups is considered to take place from an unstable coordinatively unsaturated T-shaped intermediate[6,10b] $^{31}P\{^1H\}$ NMR spectra of 2 both in the presence and in the absence of PPh_3 do not show the existence of the associated or dissociated species but only the four-coordinate species in accordance to the mechanism.

For the sake of simplicity, let us discuss the thermolysis of $Pt(C_2H_5)(n\text{-}C_3H_7)(PPh_3)_2$, 2, in the absence of PPh_3. The following experimental facts should be accommodated in the thermolysis mechanism involving the three-coordinate intermediate: (a) the number of β-hydrogens dictates the relative ease of the β elimination; (b) the deuteriums in the ethyl group of 14 recovered after partial thermolysis are not scrambled; (c) the H–D scrambling in the ethyl group takes place within the ethyl group without participation of the propyl group which remains as a "spectator".

The mechanism shown in Scheme III is compatible with these experimental findings. In this scheme one of the

Scheme III. A Thermolysis Mechanism of *cis*-Pt(Et)(*n*-Pr)(PPh$_3$)$_2$ in the Absence of Added PPh$_3$ Ligand



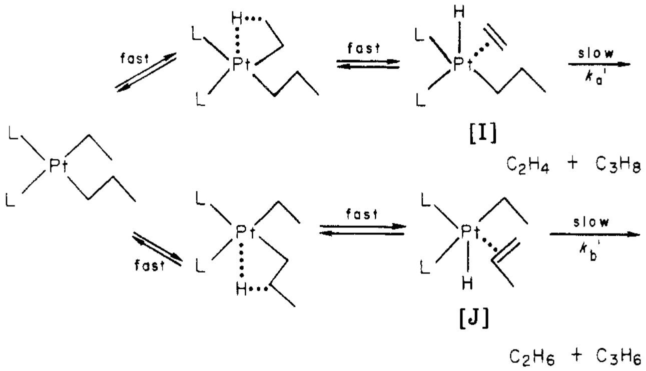
tertiary phosphine ligands dissociates first as the rate-determining step to form the three-coordinate species [A] or [B] having a vacant site for β-hydrogen elimination. The polytopal, side-to-side "windshield wiper"-type rearrangement between the three-coordinate species [A] and [B] is assumed to be a rapid process in agreement with Whitesides' results. For the intermediate [A] to be thermolyzed an activation process with a rate constant k_b may be involved to give [C] in which a β-hydrogen in the propyl group interacts with platinum. The corresponding activation from [B] gives [D] in which a β-hydrogen in the ethyl group interacts with platinum.

In the freely rotating alkyl groups the spatial requirement for the maximum interaction of the β-hydrogens with the metal may not differ from that of the ethyl to the propyl group. Thus the ratio of rate constants k_a/k_b may be determined primarily by the number of β-hydrogens. The β-hydrogen elimination process in the activated states, [C] and [D], gives [E] and [F], respectively. Since H–D scrambling takes place only in the activated state, β elimination and its reverse process ([E] → [C] or [F] → [D]) must be a rapid process.

On β-hydrogen abstraction of [C] a four-coordinate species, [E], may be produced which is to be decomposed further by reductive elimination of ethane and liberation of propylene. The species [D] may be likewise decomposed through the β-elimination process followed by reductive elimination of propane and release of ethylene. It is not to be experimentally verified whether the liberation of propylene precedes the reductive elimination of ethane as shown in Scheme III ([E] to [G]) or ethane may be first reductively eliminated followed by propylene liberation. However, if the β-hydrogen elimination takes place as shown in Scheme III by a hydrogen migration mechanism to give [E], which has trans hydrido and ethyl ligands, the configuration is not favorable for the reductive elimination to take place first. Thus we prefer to depict the reaction course as shown in Scheme III where propylene is liberated first followed by reductive elimination of ethane.

Thermal Decomposition from a Four-Coordinate Intermediate (Path B). In the presence of a large excess of added PPh$_3$, the thermolysis proceeds without ligand dissociation. Since a deuterium labeling experiment shows that H–D exchange along the ethyl group takes place prior to the rate-determining step, the following mechanism involving a five-coordinate intermediate is consistent with the experimental facts (Scheme IV). In this scheme, the facile reversible β elimination to give the five-coordinate species [I] or [J] is assumed as the pre-rate-determining step to account for the H–D exchange in the ethyl group. This scheme can accommodate also the facile skeletal isomerization of the branched to linear alkyl group, a process which is not inhibited by addition of the tertiary phosphine. The intermediate [I] or [J] may be further decomposed through a rate-determining process which may be either alkane reductive elimination or olefin liberation. Although Whitesides favored the reductive elimination of ethane as the rate-determining step in the thermolysis of PtEt$_2$(PEt$_3$)$_2$ in the presence of added PEt$_3$, we prefer the olefin loss as the rate-determining step. This mechanism is consistent with the mechanism presented to account for the thermolysis of Pt(R$_a$)(R$_b$)(PPh$_3$)$_2$ in the absence of added PPh$_3$. We believe that this mechanism is reasonable on the basis of the following observations.

Scheme IV. A Thermolysis Mechanism of *cis*-Pt(Et)(*n*-Pr)(PPh$_3$)$_2$ in the Presence of Excess of PPh$_3$ Ligand



Thermolysis of the deuterium-labeled ethylplatinum complexes showed the absence of a kinetic isotope effect, while a k_H/k_D of 3.3 was observed for the rate-determining reductive elimination of methane (D) from Pt(CH$_3$)(H,D)(PPh$_3$)$_2$ by Halpern.[14] Whitesides observed the k_H/k_D ratio of 1.4–1.7 in the thermolysis of PtEt$_2$(PEt$_3$)$_2$ in the presence of 1.64 M PEt$_3$ and favored the reductive elimination of alkane as the rate-determining step. The reason for this discrepancy of our result from that of Whitesides is not clear. The k_H/k_D ratio of 1.4–1.7 observed by Whitesides is still within the range which accommodates the olefin loss as the overall rate-limiting step, if one takes into account a combination of secondary isotope effects as argued in the paper.[6]

The other support for olefin loss as the rate-determining step is found in comparison of the order of rates of thermolysis of series of PtR$_2$(PPh$_3$)$_2$ and gaseous thermolysis product distribution. The rate constant k_3 for the thermolysis through the four-coordinate species (path B) increases in the order PtEt$_2$ < PtEt(*n*-Pr) < PtEt(*n*-Bu) < Pt(*n*-Pr)$_2$ < Pt(*n*-Pr)(*n*-Bu) < Pt(*n*-Bu)$_2$. If one can neglect the effect of the coordinated olefin on the reductive

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[14] Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915.

elimination of alkane[15] from species [I] or [J] in Scheme IV propane should be produced in preference to ethane from Pt(Et)(*n*-Pr)$(PPh_3)_2$ with reductive elimination of alkane as the rate-determining step. The actual product distribution with formation of more ethane than propane differs from this expectation. Thus, the liberation of olefin from intermediate [I] or [J] seems more plausible as the rate-determining step. This mechanism implies that the coordinating ability of the olefin produced on β-hydrogen elimination affects the rate of liberation of the olefin from [I] or [J]. The generally observed trend of the bonding ability of the olefin in transition-metal π complexes decreasing in the order ethylene > propylene > butene is compatible with the expected ease of olefin liberation from [I] or [J] in the order ethylene < propylene < butene. Thus the assumption of easier liberation of propylene from [J] than the loss of ethylene from [I] accounts for the greater thermolysis of the dipropylplatinum complexes than the diethylplatinum complexes and formation of larger amount of propylene than propane from the ethyl propyl complex **2** thermolyzed in the presence of added excess PPh_3. As a whole, the mechanism presented here is consistent with the experimental results.

In the study of thermolysis of $PtEt_2(PEt_3)_2$ Whitesides examined kinetics in the presence of 0.3 M PEt_3 and proposed a mechanism different from those for thermolysis in the absence of PEt_3 and in the presence of excess of PEt_3. Examination of the thermolysis kinetics of Pt(Et)(*n*-Pr)$(PPh_3)_2$ **2**, containing PPh_3 below 0.1 M revealed the feature as shown in Figure 4 having an S-shaped time–gas evolution curves. The initial stage of slow thermolysis may be ascribed to the retardation of thermolysis by the effect of added small amount of PPh_3. This inhibition may be removed as the thermolysis proceeds, since the small amount of added PPh_3 may be trapped by the coordinatively unsaturated $Pt(PPh_3)_2$ generated on thermolysis. Hence the thermolysis resumes the normal course as we observed in the absence of added PPh_3. The eventual ratios of propane/propylene and ethylene/ethane conform to eq 6 and differ from the corresponding ratios observed in thermolysis carried out in the presence of excess of PPh_3 as shown in Table III. Because of the presence of the somewhat abnormal kinetic data, we avoid to discuss the thermolysis results in the intermediate concentration range of the added PPh_3 (below 0.1 M).

In the thermolysis of Pt(Et)(*n*-Pr)(dpe), **12**, we observed the higher ratio of ethane/ethylene and propylene/propane (Table II) than what we expect from eq 6. The employment of the bidentate tertiary phosphine ligand may make the dissociation of the phosphine more difficult, and the thermolysis may take the course which we observed in the presence of the added phosphine.

A small inhibition effect of added olefins such as ethyl methacrylate and dimethyl maleate on the thermolysis rate is noteworthy, since it is known that the electronegative olefins usually accelerate the thermolysis of transition-metal dialkyl complexes such as NiR_2bpy,[16] $PdEt_2L_2$,[4] and $PtEt_2bpy$.[17] In the present case, olefins may act as a ligand to occupy the vacant site for β elimination, so that the thermolysis rate decreases with increasing the concentration of olefins.

Concluding Remarks

Our results and mechanistic interpretation on thermolysis of unsymmetrical and symmetrical dialkylplatinum complexes having tertiary phosphine ligands are complementary to Whitesides' results. The presence of at least two thermolysis pathways with and without dissociation of the coordinated tertiary phosphine ligand as expressed in Schemes II–IV has been confirmed. With minor differences from the interpretation of Whitesides we favor olefin liberation as the rate-determining step in the thermolysis of $PtR_2(PPh_3)_2$ in the presence of PPh_3. The information derived here points to the importance of the added tertiary phosphine in affecting the thermolysis pathway. Interestingly, the behavior of the *cis*-PtR_2L_2 resembles that of the *trans*-$PdEt_2L_2$[4] but differs from that of *cis*-$PdEt_2L_2$.[18]

Experimental Section

General Procedure and Materials. Manipulation of complexes and reactions were carried out under deoxygenated nitrogen or argon or under vacuum. Solvents were dried by usual methods, distilled, and stored under nitrogen or argon before use. IR spectra were recorded on a Hitachi-295 spectrometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were measured by using JEOL-PMX-60 and FX-100 spectrometers. Data are reported as follows: chemical shift, multiplicity (b = broad, s = singlet, d = doublet, t = triplet, m = multiplet), integration, coupling constant (hertz), and assignment. Mass spectra were recorded on a Hitachi RMU-7M spectrometer. Elemental analyses were performed by Mr. Saito in our laboratory by using Yanagimoto CHN-autocorder type MT-2. Analyses of gases evolved in the thermolyses were carried out by gas chromatography after gases were collected by using a Toepler pump by which the volumes of gases were measured. Grignard reagents and alkyllithiums were prepared from alkyl halides and alkali metals by usual methods in suitable solvent under argon. PPh_3 was used as purchased. 1,2-Bis(diphenylphosphino)ethane (dpe) and dimethylphenylphosphine were prepared by the usual methods. MeO-*p*-$C_6H_4CH_2CH_2Br$ was synthesized by the literature method from MeO-*p*-$C_6H_4CH_2CH_2OH$ and PBr_3.[19] *cis*-$PtR_2(PPh_3)_2$ (R = Me, Et, *n*-Pr, *n*-Bu) was prepared by the reaction of *cis*-$PtCl_2(PPh_3)_2$ with corresponding alkyllithium or Grignard reagent. CD_3CH_2Li was prepared from Li and CD_3CH_2Br[20] in pentane.

$Pt(C_2H_4Ph)_2$(cod). To a suspension of PtI_2(cod) (2.45 g, 0.439 mmol) in Et_2O (20 mL) at 0 °C was added $PhCH_2CH_2MgCl$ (4.4 mmol) in Et_2O slowly to give a yellow-brown solution. After slow hydrolysis with water at 0 °C, the combined Et_2O layer and Et_2O extracts (3 × 20 mL) were separated and dried with Na_2SO_4. Evaporation of Et_2O in vacuo gave a yellow oil which was dissolved in pentane and was filtered. Complete removal of pentane afforded a yellow oil: 91%; ^1H NMR (acetone-d_6) δ 7.0–7.4 (m, 10, Ph), 4.7 (br, 4, J(Pt–H) = 40, =CH), 0.8–3.6 (m, 16, C_2H_4Ph and CH_2 of cod).

$Pt(C_2H_4Ph)Cl$(cod). Dry HCl in Et_2O (5.44 mmol) was added to an Et_2O solution of $Pt(C_2H_4Ph)_2$(cod) (2.81 g, 5.48 mmol) at 0 °C to give a white precipitate. After the mixture was stirred for 1 h, the white precipitate was filtered and recrystallized from acetone to afford white needles in 77% yield: ^1H NMR (acetone-d_6) δ 7.0–7.4 (m, 5, Ph), 5.4 (br, 2, J(Pt–H) = 40, =CH of cod trans to C_2H_4Ph), 4.2 (br, 2, J(Pt–H) = 72, =CH_2 of cod trans to Cl), 1.0–3.3 (m, 12, C_2H_4Ph and CH_2 of cod). Anal. Calcd for $C_{16}H_{21}ClPt$: C, 42.5; H, 4.7. Found: C, 43.3; H, 4.8.

$Pt(Et)(C_2H_4Ph)$(cod). The oily compound was prepared from $Pt(C_2H_4Ph)Cl$(cod) (607 mg, 1.37 mmol) and EtMgBr (1.5 mmol) in Et_2O (10 mL) at −10 to 0 °C, analogous to the preparation of $Pt(C_2H_4Ph)_2$(cod), in 84% yield. Oily Pt(*n*-Pr)(C_2H_4Ph)(cod) and $Pt(C_2H_4C_6H_4$-*p*-OMe)(C_2H_4Ph)(cod) were prepared analogously in 84 and 92% yields, respectively: ^1H NMR (acetone-d_6) $PtEt(C_2H_4Ph)$(cod), δ 7.0–7.4 (m, 5, Ph), 4.8 (br, 2 J(Pt–H) = 40,

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[15] We should note, however, that the absence of influence of the coordinated olefin on the reductive elimination of alkane from the intermediate [I] or [J] is an assumption not substantiated experimentally.

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=CH), 4.5 (br, 2, *J*(Pt–H) = 40, =CH), 0.6–3.3 (m, 12, C_2H_4Ph and CH of cod) Pt(*n*-Pr)(C_2H_4Ph)(cod), δ 7.0–7.4 (m, 5, Ph), 4.8 and 4.5 (br, 2 for each, *J*(Pt–H) = 40, =CH), 0.6–3.5 (m, 19, C_2H_4Ph, C_3H_7, and CH_2 of cod), Pt(C_2H_4Ph)($C_2H_4C_6H_4$-*p*-OCH_3)(cod), δ 6.8–7.4 (m, 9, Ph and C_6H_4), 4.7 (br, 4, *J*(Pt–H) = 40, =CH), 3.76 (s, 3, OCH_3), 1.0–3.3 (m, 16, $C_2\mathit{H}_4Ph$ and CH_2 of cod).

Preparation of Unsymmetrical Dialkylplatinum(II) Complexes Having Tertiary Phosphine Ligands. Pt(Et)(*n*-Pr)(PPh_3)$_2$, 2. An Et_2O suspension of PtEtCl(PPh_3)$_2$ (1030 mg, 1.31 mmol) was treated with a slight excess of *n*-PrLi (1.4 mL of 0.96 M solution in pentane) below 0 °C. After 3 h the mixture was hydrolyzed. The Et_2O layer and benzene extracts were collected, and the solvents were removed by evaporation. The resulted colorless solid was recrystallized from a benzene–pentane mixture; yield 700 mg (67%). Similarly 1 and **4–13** were obtained. Elemental analyses, yields, and decomposition points of these complexes except **1–8**, which have been reported elsewhere[5] are summarized. **Pt(Et)(C_2H_4Ph)(PPh_3)$_2$·0.5Et_2O, 9**: 92% recrystallized from a mixture of CH_2Cl_2 and Et_2O; dec pt 144–145 °C. Anal. Calcd for $C_{48}H_{49}O_{0.5}P_2Et$: C, 64.7; H, 5.2. Found: C, 64.3; H, 5.4. **Pt(*n*-Pr)(C_2H_4Ph)(PPh_3)$_2$·0.5toluene, 10**: 70% after recrystallization from a mixture of toluene and hexane; dec pt 130–131 °C. Anal. Calcd for $C_{50.5}H_{50}P_2Pt$: C, 66.4; H, 5.5. Found: C, 66.0; H, 5.5. **Pt(C_2H_4Ph)($C_2H_4C_6H_4$-*p*-OMe)(PPh_3)$_2$, 11**: 64% after recrystallization from a CH_2Cl_2–Et_2O mixture; dec pt 132–133 °C. Anal. Calcd for $C_{55}H_{55}O_{1.5}P_2Pt$: C, 66.3; H, 5.6. Found: C, 66.3; 5.4. **Pt(Et)(*n*-Pr)dpe, 13**: 75% (crude); the compound was recrystallized from a benzene–pentane mixture in 17% yield; dec pt 166–167 °C. Anal. Calcd for $C_{31}H_{36}P_2Pt$: C, 55.9; H, 5.5. Found: C, 56.3; H, 5.3. Complexes **9**, **10**, and **11** were also prepared by the ligand exchange reaction of Pt(R_a)(R_b)(cod) with L. For example, an Et_2O solution (5 mL) of Pt(Et)(C_2H_4Ph)(cod) (323 mg, 0.74 mmol) was treated with excess PPh_3 (580 mg, 2.21 mmol) at room temperature for 1 day. Evaporation of volatile matter in vacuo gave a white solid which was recrystallized from a CH_2Cl_2–Et_2O mixture (77% yield).

^1H NMR data are summarized: 1 (CD_2Cl_2), δ 0.40, (dd, 3, *J*(P–H) = 7 and 8, *J*(Pt–H) = 70, MeP), 0.5–1.7 (m, 5, EtPt), 7.0–7.5 (m, 30, PPh_3); **13** (CD_2Cl_2), δ 7.2–7.6 (m, 20, Ph), 2.4 (t of d, 4, *J*(H–H) = 0.5, *J*(P–H) = 2.0, CH_2 in dppe ligand), 0.5–1.8 (m, 12, Et and *n*-Pr); **12** (C_6D_6), 6.9–7.6 (m, 10, PPh*Me*$_2$), 1.0–2.5 (m, 12, Pt(*Et*)(*n-Pr*)L_2), 1.25 (d, 6, *J*(P–H) = 7, PPh*Me*$_2$), 1.24 (d, 6, *J*(P–H) = 7, PPh*Me*$_2$). ^1H NMR spectra of **2–11** showed complicated patterns for alkyl groups, but the relative ratio of integration of each group is consistent with its structure. $^{31}P\{^1H\}$ NMR spectral data of **2**, **9**, **10**, **11**, **12** as well as symmetrical dialkylplatinum(II) complexes are summarized in Table I.

Acidolysis of **9** (22.5 mg, 0.025 mmol) with dry HCl gave ethane (0.023 mmol, 91%) and ethylbenzene (0.022 mmol, 89%). Similarly **10** (21.0 mg, 0.023 mmol) liberated propane (0.019 mmol, 83%) and ethylbenzene (0.018 mmol, 78%), **13** (15.5 mg, 0.023 mmol) afforded ethane (0.021 mmol, 91%) and propane (0.020 mmol, 87%), and **2** (38.0 mg, 0.048 mmol) gave ethane (0.043 mmol, 90%) and propane (0.039 mmol, 81%), respectively, on acidolysis.

Kinetic Studies. Pt(R_a)(R_b)(PPh_3)$_2$ was placed in a round-bottomed flash equipped with a gas-tight rubber serum cap. CH_2Ph_2 was transferred by means of a hypodermic syringe, and the flask was placed in a thermostatted oil bath. Gas samples (less than 0.5% of the total volume) were removed periodically from the magnetically stirred flask and analyzed by gas chromatography. For systematic errors arising from the difference in solubilities of the gases in CH_2Ph_2 to be avoided, CH_4 was used as internal standard for gas chromatographic analysis after calibration.

Deuterium-Labeling Experiments. Pt(CH_2CD_3)(*n*-C_3H_7)(PPh_3)$_2$ (**14**) and Pt(CH_2CD_3)(C_2H_4Ph)(PPh_3)$_2$ (**15**) were analogously prepared by the reactions of Pt(CH_2CD_3)Cl(PPh_3)$_2$ with *n*-C_3H_7Li and PhC_2H_4MgBr in Et_2O, respectively: IR **14**, ν(C–D) 2190 (sh), 2160 (w), 2050 (m) cm^{-1}, δ (C–D) 840 (w) cm^{-1}, **15**, ν(C–D) 2180 (sh), 2150 (m), 2080 (w), 2040 (m) cm^{-1}, δ(C–D) 835 (w) cm^{-1}.

Thermolysis of 14 and 15 in the Absence of PPh$_3$. Complex **14** (357 mg, 0.449 mmol) dissolved in CH_2Ph_2 (3 mL) was heated at 100 °C for 3 h to give ethane (0.241 mmol), ethylene (0.156 mmol), propane (0.154 mmol), and propylene (0.233 mmol). These gases were separated by gas chromatography, and the deuterium contents in these gases were analyzed by IR and mass spectroscopy. Mass spectral analysis revealed that ethylene contained only $C_2H_2D_2$ and C_2HD_3 (ca. 1:1). IR spectrum of the mixture of deuterated ethylenes showed bands attributable to CHD=CD_2 (765, 920 cm^{-1}), CH_2=CD_2 (750, 945 cm^{-1}), *trans*-CHD=CHD (726, 989 cm^{-1}), and *cis*-CHD=CHD (842 cm^{-1}). Ethane was found to consist of a mixture of CH_3CD_3 and CH_2DCHD_2. The propyrene evolved contained solely C_3H_6, and propane was a mixture of C_3H_8 and C_3H_7D roughly in a 1:1 ratio. Thermolysis of **15** (309 mg, 0.361 mmol) in the absence of PPh_3 in CH_2Ph_2 (10 mL) liberated ethylene and ethane with similar compositions as mentioned above. Ethylbenzene contained a mixture of PhC_2H_4D and PhC_2H_5 (ca, 1:1); styrene was not deuterated.

Thermolysis of 14 in the Presence of PPh$_3$. Thermolysis of **14** (56.5 mg, 0.077 mmol) in the presence of PPh_3 (375.6 mg, 1.43 mmol) in CH_2Ph_2 (2 mL) gave almost the same results concerning deuterium contents in gases as described in the experiment carried out in the absence of PPh_3.

H–D Exchange in the Thermolysis of 14. Complex **14** (49.5 mg, 0.623 mmol) in CH_2Ph_2 (2 ml) was heated for 10 min to decompose 9% of **14**. Hydrolysis of the recovered **15** with dry HCl gave ethane and propane which were separately collected by GC. The mass spectrum of ethane was identical with that of authentic CH_3CD_3 which was obtained by hydrolysis of CD_3CH_2Li. Propylene consisted of only C_3H_8. Complex **14** (118.8 mg, 0.149 mmol) was thermolyzed at 100 °C for 40 min in the presence of PPh_3 (779 mg, 2.97 mmol) in CH_2Ph_2 (5 mL) (50% of **14** decomposed). Mass spectral analysis of ethane, which was liberated on hydrolysis of the recovered **14** with dry HCl, showed the formation of CH_3CD_3 and CHD_2CH_2D. Propane consisted of only C_3H_8.

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Registry No. 1, 69206-37-7; **2**, 69206-38-8; **3**, 69206-39-9; **4**, 69206-40-2; **5**, 69206-41-3; **6**, 69206-42-4; **7**, 69206-43-5; **8**, 83095-63-0; **9**, 83095-64-1; **10**, 83095-65-2; **11**, 83095-66-3; **12**, 83095-67-4; **13**, 83095-68-5; **14**, 83095-69-6; **15**, 83095-70-9; PPh_3, 603-35-0; Pt(C_2H_4Ph)$_2$(COD), 83095-71-0; PtI_2(COD), 12266-72-7; $PhCH_2CH_2Cl$, 622-24-2; Pt(C_2H_4Ph)Cl(COD), 83095-72-1; Pt(Et)(C_2H_4Ph)(COD), 83095-73-2; EtBr, 74-96-4; Pt(*n*-Pr)(C_2H_4Ph)(COD), 83095-74-3; Pt($C_2H_4C_6H_4$-*p*-OMe)(C_2H_4Ph)(COD), 83095-75-4; PtEtCl(PPh_3)$_2$, 69206-44-6; *n*-Pr-Li, 2417-93-8.