  Bull. Chem. Soc. Jpn., 54, 1868—1880 (1981) [Vol. 54, No. 6

Mechanisms of Thermal Decomposition of *trans*- and *cis*-Dialkylbis-(tertiary phosphine)palladium(II). Reductive Elimination and *trans* to *cis* Isomerization

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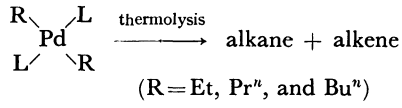
(Received August 30, 1980)

Series of *trans*- and *cis*-dialkylpalladium(II) complexes having tertiary phosphine ligands (L) of various basicities and bulkiness have been prepared and their thermolysis and isomerization mechanisms in solution have been studied. Examination of the cause of selective formation of *cis*-dialkyl isomers by using alkyllithium revealed a new type of *trans* to *cis* isomerization promoted by the alkyllithium. A process involving the formation of a trialkylpalladate intermediate is proposed as a mechanism for the *trans* to *cis* isomerization. Evidence to support the mechanism has been obtained by experiments using $LiCD_3$. Thermolysis of *cis*-PdR_2L_2 has been demonstrated to proceed through a unimolecular process initiated by a rate-determining dissociation of L to produce a three-coordinate "*cis*-PdR_2L" which reductively eliminates the R groups. Addition of free ligand to the system containing *cis*-$PdMe_2L_2$ effectively blocks the reductive elimination pathway thus forcing the complex to be thermolyzed by a route involving liberation of methane. The second, novel type of *trans* to *cis* isomerization reaction proceeding *via* an intermolecular methyl transfer process has been discovered. As the crucial intermediate in the process a methyl-bridged complex formed between the partly dissociated three-coordinate species and undissociated complex has been postulated. Thermolysis of *trans*-$PdMe_2L_2$ has been found to proceed *via* initial isomerization to the *cis* form followed by reductive elimination. The *trans-cis* isomerization equilibrium greatly favors the *cis* form for complexes having phenyl-substituted phosphines. For the PEt_3-coordinated palladium dimethyl, however, an equilibrium *trans*/*cis* ratio of 1.2 is reached at 39 °C. Factors influencing the stability of the palladium alkyls having the tertiary phosphine ligand are discussed on the basis of the present results as well as comparison of the thermolysis behavior of *trans*-$PdEt_2L_2$ and other transition metal alkyls. The presence of an energy barrier between the dissociated T-shaped intermediates *trans*-$PdMe_2L$ and *cis*-$PdMe_2L$ has been assumed. A unimolecular reductive elimination pathway proceeding from the T-shaped *cis*-$PdMe_2L$ intermediate through a Y-shaped transition state consistently accounts for the thermolysis as well as isomerization behavior of the *trans*- and *cis*-$PdMe_2L_2$.

Despite the abundance of organic reactions promoted by palladium and its compounds,[1] the fundamental studies on the behavior of alkylpalladium compounds, which may be regarded as key compounds in the Pd-promoted reactions, are still scarce.[2,3] By studying the decomposition mechanisms of palladium alkyls having stabilizing ligands such as tertiary phosphines, one can expect to get important information concerning the factors controlling the cleavage of the Pd–C bond and the subsequent C–C coupling reactions of the alkylpalladium complexes coordinated with the stabilizing ligands. The recent study by Stille and co-workers contributed to unveil part of the decomposition mechanisms of dialkylpalladium complexes having tertiary phosphine ligands,[2] but obviously more studies are required for understanding fundamental properties of the palladium alkyls.

As continuation of our effort to clarify the behavior of various transition metal alkyls,[4] we have prepared series of *cis*- and *trans*-dialkylbis(tertiary phosphine)-palladium(II) and have studied the chemical properties of these complexes. Examination of the thermolysis mechanisms of these isolated *cis* and *trans* complexes provides us a rare opportunity to study the crucial roles of the tertiary phosphine ligands in enhancing the stability of transition metal alkyls, affecting the thermolysis pathways, and determining the configurations of these complexes. In the previous paper we confirmed that *trans*-PdR_2L_2 (R=Et, Pr^n, and Bu^n; L=various tertiary phosphines) is thermolyzed through clean β-elimination pathways, liberating 1 : 1 mixtures of alkane and alkene. The reactions were shown to proceed predominantly from undissociated four-coordinate



(R=Et, Pr^n, and Bu^n)

species.[5] It was noted that the presence of the free tertiary phosphine ligands had small effect in hindering the thermolysis, and we proposed a thermolysis mechanism involving distortion from the square-planar configuration to facilitate the β-hydrogen elimination.

In the present paper we report the results of our mechanistic studies on thermolysis of *cis*- and *trans*-$PdMe_2L_2$, and of *cis*-$PdEt_2L_2$ and on *trans-cis* isomerization of the dimethylpalladium complexes. In contrast to the minor inhibition effect of tertiary phosphine ligands on β-elimination reaction of *trans*-PdR_2L_2 (R=Et, Pr^n, Bu^n), a pronounced inhibition effect of tertiary phosphine ligands on reductive elimination of the alkyl groups from *cis*-PdR_2L_2 type complexes was revealed. Two new types of *trans-cis* isomerization reactions were discovered. The behavior of these palladium alkyls was found to have some similarities with that of AuR_3L type complexes[6] which liberate the coordinated tertiary phosphine ligand in order to initiate reductive elimina-

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tion of the alkyl groups and isomerization between trialkylgold isomers having different alkyl groups.

Results and Discussion

Preparation of cis- *and* trans-*PdR_2L_2*. Employment of suitable synthetic methods has been found to lead to selective production of *cis*- and *trans*-PdR_2L_2. The *trans* isomers can be conveniently prepared by treating $Pd(acac)_2$ (acac=2,4-pentanedionato ligand) with $AlR_2(OEt)$ (R=Me, Et, Pr^n, Bu^n), or more preferably with $Al_2R_3(OEt)_3$, in the presence of tertiary phosphines (Method A, Eq. 1).[3,5] The *trans* isomers obtained by Method A are sometimes contaminated with *cis* isomers which may be removed by recrystallization. The *cis* isomers are prepared by alkylating $PdCl_2L_2$ with alkyllithium (Method B, Eq. 2).[7] For some complexes having basic tertiary phosphines such as PEt_3 where the preparation of a *cis* isomer by Method B is not suitable, a ligand exchange reaction of PEt_3 with another *cis* isomer provides an indirect route to selectively prepare the *cis* isomer (Method C, Eq. 3, Scheme 1).

Method A

$$Pd(acac)_2 + \text{excess } AlR_2(OEt) \text{ or } Al_2R_3(OEt)_3 + 2L \xrightarrow[-70 \text{ to } 0\,^\circ C]{Et_2O} \underset{(I—V)}{trans\text{-}PdR_2L_2}(+cis\text{-}PdR_2L_2) \quad (1)$$

(R=Me, Et, Pr^n, Bu^n; L=PEt_3, PMe_2Ph, PEt_2Ph, $PMePh_2$, $PEtPh_2$)

Method B

$$PdCl_2L_2 + \text{excess LiR} \xrightarrow[0\,^\circ C \text{ to room temp}]{Et_2O} \underset{(\mathbf{2}—\mathbf{5})}{cis\text{-}PdR_2L_2} \quad (2)$$

(R=Me, Et; L=PMe_2Ph, PEt_2Ph, $PMePh_2$, $PEtPh_2$)

Method C

$$cis\text{-}PdMe_2(PMePh_2)_2 + PEt_3 \quad (\mathbf{4a}) \xrightarrow[\text{room temp}]{Et_2O} \underset{(\mathbf{1a})}{cis\text{-}PdMe_2(PEt_3)_2} \quad (3)$$

Scheme 1.

Employment of the chelating diphenylphosphinoethane (dpe) ligand gives the *cis* isomers by the spatial constraint posed by the chelating ligand even by using Method A. The isolated dialkylpalladium complexes are listed in Table 1 with reference to the preparative methods. For differentiation of the isomers we use the Roman letters for describing the *trans* isomers and gothic Arabic numbers for representing the *cis* isomers.

Characterization of the complexes has been made on the basis of elemental analysis and IR and NMR spectroscopy. The characteristic IR and ^1H NMR data of the dimethyl- and diethylpalladium complexes are given in Table 2 (for further details of characterization, see Experimental part).

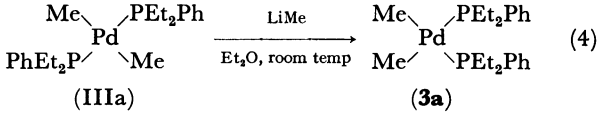
The trans-cis *Isomerization of $PdMe_2L_2$ Promoted by Alkyllithium.* Examination of the cause of the selective production of the *cis* and *trans* isomers by using different experimental methods led us to the discovery of a new type of isomerization reaction. The ethyl as well as the methyl complexes show similar behavior. Here we deal mainly with the *trans-cis* isomerization of the methyl complexes, since the isomerization of the ethyl complexes are essentially similar but complicated by their thermal instability.

Table 1. List of isolated PdR_2L_2

Compound				Method[a]
Configuration	R	L		
trans	Me	PEt_3	Ia	A
		PEt_2Ph	IIIa	A
		$PMePh_2$	IVa	A
		$PEtPh_2$	Va	A
	Et	PEt_3	Ib	A
		PMe_2Ph	IIb	A
		PEt_2Ph	IIIb	A
		$PMePh_2$	IVb	A
		$PEtPh_2$	Vb	A
	n-Pr	PEt_3	Ic	A
		PMe_2Ph	IIc	A
		$PMePh_2$	IVc	A
	n-Bu	PMe_2Ph	IId	A
cis	Me	PEt_3	**1a**	C
		PEt_2Ph	**3a**	B
		$PMePh_2$	**4a**	A, B
		$PEtPh_2$	**5a**	B
	Et	PMe_2Ph	**2b**	B
		PEt_2Ph	**3b**	B
	Me	dpe[b]	**6a**	A
	Et	dpe[b]	**6b**	A
	n-Pr	dpe[b]	**6c**	A

a) See Scheme 1. b) dpe=$Ph_2PCH_2CH_2PPh_2$.

The *trans*-$PdMe_2(PEt_2Ph)_2$ (IIIa) was found to isomerize readily to the *cis* isomer (**3a**) in high yield on treatment with two equivalents of LiMe in ether for 2 h at room temperature. The LiMe was removed by hydrolysis after the isomerization was complete. Treatment of the *trans* isomer (IIIa) with 1.5 equivalents of $AlMe_2(OEt)$ under similar conditions did not give any *cis* isomer and the unreacted IIIa was recovered. It was further established that treatment of *trans*-$Pd(CH_3)_2(PEt_2Ph)_2$ (IIIa) with an equimolar amount of $LiCD_3$ in ether at room temperature gave the *cis* isomer (**3a'**) containing the CD_3 group after removal of the methyllithium by hydrolysis. Thermolysis of **3a'** at 60 °C in toluene containing dimethyl maleate, the presence of which serves to cause the clean thermolysis of the dialkyl complexes (*vide infra* and Ref. 5), released CD_3CD_3, CH_3CD_3, and CH_3CH_3 in a molar ratio of 0.18; 0.48: 0.34. Methyl scrambling was also observed in the reaction of *cis*-$Pd(CH_3)_2(PEt_2Ph)_2$ with an



(IIIa) (**3a**) (4)

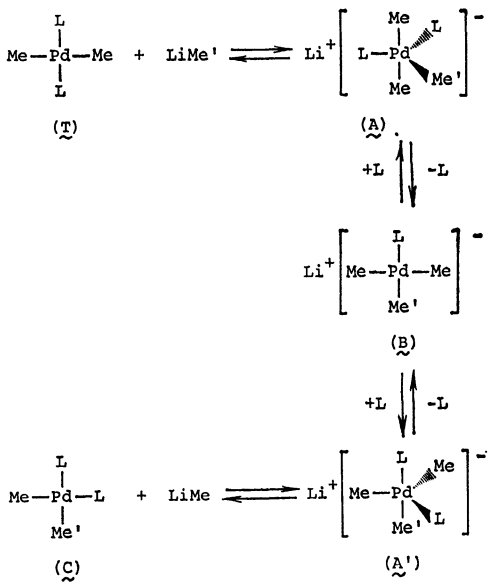
Table 2. IR[a] and ^{1}H NMR[b] data of PdR_2L_2 (R=Me, Et)

	Compound R	L		IR Data: Pd–R group δ(C–H)	IR Data: Pd–R group ν(Pd–C)	^{1}H NMR Data[c]: Pd–R –CH$_3$	^{1}H NMR Data[c]: Pd–R –CH$_2$–	^{1}H NMR Data[c]: P–R –CH$_3$	^{1}H NMR Data[c]: P–R –CH$_2$–
trans	Me	PEt_3	Ia	1130	455	−0.61(t)[d]	—	1.10(qui)[g]	1.75(m)
		PEt_2Ph	IIIa	1135	462	−0.55(t)[e]	—	1.17(qui)[g]	2.17(m)
		$PMePh_2$	IVa	1140	460	−0.91(t)[f]	—	1.92(t)[h]	—
		$PEtPh_2$	Va	1140	450	−0.82(t)[e]	—	1.13(qui)[g]	2.31(m)
	Et	PEt_3	Ib	1145, 1360	455	—[i]	0.33(q)[g]	1.12(qui)[g]	1.82(m)
		PMe_2Ph	IIb	1135, 1350	452	0.92(t)[g]	0.36(q)[g]	1.68(t)[h]	—
		PEt_2Ph	IIIb	1135, 1350	440	1.31(t)[g]	0.71(q)[g]	0.92(qui)[g]	1.92(m)
		$PMePh_2$	IVb	1140, 1355	455	0.41(t)[k]	0.05(q)[k]	1.99(t)[k]	—
		$PEtPh_2$	Vb	1140, 1355	455	0.55(t)[k]	0.17(q)[k]	1.23(qui)[k]	2.41(m)
cis	Me	PEt_3	**1a**	1120	465, 487	0.07(q)[j]	—	1.16(dt)[i]	1.79(m)
		PEt_2Ph	**3a**	1120	478, 505	0.17(q)[j]	—	1.04(dt)[i]	1.89(m)
		$PMePh_2$	**4a**	1125	475, 510	0.10(q)[j]	—	1.58(d)[e]	—
		$PEtPh_2$	**5a**	1123	470, 515	0.15(q)[j]	—	1.09(dt)[i]	1.81(m)
	Et	PMe_2Ph	**2b**[m]	1130, 1150, 1355	475, 490	1.20(br)[k]	1.02(br)[k]	1.38(d)[f]	—
		PEt_2Ph	**3b**[m]	1130, 1148, 1352	470, 505	1.15(t)[k]	0.99(br)[k]	0.88(dt)[k]	1.80(m)

a) KBr disc, in cm^{-1}. b) 100 MHz, chemical shifts are in δ values (ppm) with respect to Me_4Si as an external or internal standard (down field positive). Solvent: acetone-d_6 (Ia, IIIa, Ib, IIb, **1a**, **3a**, **4a**, **5a**, **2b**, **3b**); toluene-d_8 (IIIb); CD_2Cl_2 (IVa, Va, IVb, Vb). Temp (°C): 25 (Ia, IIIa, Ib, **1a**, **3a**, **4a**); −20 (IIb, IIIb, **5a**), −40 (IVa, Va, IVb, Vb, **2b**, **3b**). c) Multiplicity abbreviations are: d, doublet; t, triplet; q, quartet; qui, quintet; m, multiplet; dt, doublet of triplets. Coupling constants in Hz: d) 5.5. e) 5. f) 6. g) 8. h) 2. i) ^3J(HH)=7, ^3J(PH)=14. j) Abnormal quartet, see Ref. 3. k) Coupling constants are obscured due to broadening. e) Chemical shift is obscured due to the signals of P–C–CH$_3$ protons. m) Chemical shifts of these complex were determined by using ^{1}H-{^{31}P} NMR.

equimolar amount of $LiCD_3$. Thermolysis of the isolated *cis*-$PdMe_2(PEt_2Ph)_2$ containing the CD_3 group librated CD_3CD_3, CD_3CH_3, and CH_3CH_3 in a molar ratio of 0.13: 0.40: 0.47. Since the calculated ratio of the deuterated and undeuterated ethanes expected on the assumption of random scrambling of the methyl groups in the 1: 1 mixture of the methylpalladium and the trideuterio methyllithium is 0.11: 0.45: 0.45, and the separate experiment has established that the thermolysis of **3a** proceeds *via* a unimolecular process as discussed later, the results indicate that complete intermolecular scrambling of the methyl groups takes place on treatment of the *trans*- or *cis*-$PdMe_2(PEt_2Ph)_2$ with methyllithium.

Based on these results, we propose the following isomerization mechanism, which accounts for the predominant formation of the *cis* isomers when alkyllithiums are employed as the alkylating agent for preparation of the palladium alkyls. In this scheme, approach of the methyl anion toward the square-planar complex, forming an ionic penta-coordinated species (**A**) from which the tertiary phosphine ligand is displaced to give a square-planar trimethylpalladate intermediate, (**B**) seems to be a reasonable assumption.[8] Ensuing coordination of the phosphine ligand to the square-planar intermediate would displace one of the methyl groups, reforming a square-planar dimethyl complex. If the displacement reaction by L dispels the methyl group situated at the *cis* position to the remaining L, the regenerated complex formed through the intermediate (**A'**) in Scheme 2 would have the *cis* configuration, whereas displacement of the methyl



Scheme 2. Proposed mechanism for the *trans-cis* isomerization of $PdMe_2L_2$ promoted by methyllithium.

group (Me') *trans* to the remaining L in (**B**) would revert the square-planar intermediate back to the initial *trans* configuration. If one assumes that the *trans* effect of the methyl group in the intermediate (**B**) is greater than that of L, the preferential formation of the *cis* configuration may be reasonably explained. An alternative scheme involving a trigonal-bipyramid containing the phosphine ligands in axial positions as an

intermediate corresponding to (**A**) is also conceivable, although in that case pseudo rotation by a Berry mechanism should be invoked to account for the *trans-cis* isomerization and consequently the mechanism is less straightforward than the one proposed in Scheme 2. The proposed mechanism is reminiscent of the isomerization mechanism of $MCl_2(PR_3)_2$ (M=Pd, Pt) promoted by PR_3.[9] Although there has been no report on preparation of alkylpalladate type complexes, the assumption of the intermediate alkylpalladate does not seem unreasonable in view of the reported examples of the corresponding alkyl analogs of nickel, platinum, and gold.[10]

Table 3. Gases evolved on thermolysis of PdR_2L_2 (R=Me, Et)[a]

Run	Compound	Evolved gas ratio				Total[b] amounts
		R(-H)	RH	RR	Others	
1	*trans*-$PdMe_2(PEt_2Ph)_2$(IIIa)	—	0.04	0.96	c)	0.98
2	*trans*-$PdMe_2(PMePh_2)_2$(IVa)	—	0.08	0.92	c)	0.86
3	*trans*-$PdMe_2(PEtPh_2)_2$(Va)	—	0.05	0.95	c)	0.83
4	*cis*-$PdMe_2(PEt_2Ph)_2$(**3a**)	—	0.01	0.99	c)	0.96
5	*cis*-$PdMe_2(PMePh_2)_2$(**4a**)	—	0.04	0.96	c)	0.96
6	*cis*-$PdMe_2(PEtPh_2)_2$(**5a**)	—	0.01	0.99	c)	0.91
7	*cis*-$PdMe_2$(dpe)(**6a**)	—	0.02	0.98	c)	0.86
8	*trans*-$PdEt_2(PMe_2Ph)_2$(IIb)	0.49	0.51	—	—	0.95
9	*trans*-$PdEt_2(PEt_2Ph)_2$(IIIb)	0.49	0.49	0.02	—	1.03
10	*cis*-$PdEt_2(PMe_2Ph)_2$(**2b**)	trace	trace	1.00	—	0.94
11	*cis*-$PdEt_2(PEt_2Ph)_2$(**3b**)	trace	trace	1.00	—	0.85
12	*cis*-$PdEt_2$(dpe)(**6a**)	0.41	0.41	0.18	—	0.90

a) [Complex]≈0.05 mol/l. Solvent; benzene (Runs 1, 3, and 4); toluene (Runs 2 and 5—12). Additive; dmm (0.17 mol/l). Thermolysis temp (°C); 60 (Runs 1—7 and 12); 55 (Run 8); r.t. (Runs 9—11). b) Total amounts (mol/mol of complex)=[(1/2){R-(-H)+R(H)}+RR]/(complex). c) Evolution of a trace amount of C_2H_4 was observed.

Thermolysis Mechanism of PdR_2L_2. In the previous papers thermolysis of PdR_2L_2 in the solid state[3] and of *trans*-PdR_2L_2 (R=Et, Pr^n, Bu^n), in solution[5] has been reported. Having established procedures for selective synthesis of the *cis*- and *trans*-alkyls, we now examine the thermolysis behavior of these complexes in solutions. Table 3 summarizes the distribution of hydrocarbons produced in thermolysis of various palladium methyls and ethyls. For obtaining quantitative data regarding the thermolysis of palladium alkyls it is essential to carry out the thermolysis under conditions which allow the complete liberation of the alkyl groups and prevent the precipitation of palladium metal in the reaction system. Otherwise, accurate measurement of the amounts of the liberated hydrocarbon products is hindered and release of the tertiary phosphine by decomposition of the phosphine-coordinated palladium complexes prevents the thermolysis of the remaining palladium alkyls and may severely distort the thermolysis kinetics. As it has been proved quite useful in the thermolysis study of *trans*-PdR_2L_2,[5] addition of dimethyl maleate (dmm) into the system containing the palladium alkyl under investigation serves quite satisfactorily to trap the $L_2Pd(0)$ complexes displacing all of the olefin produced by β-elimination and prevents the undesirable side reactions which may liberate the tertiary phosphine ligand to affect the thermolysis course. It has been confirmed that addition of dmm did not alter the rate of thermolysis of the palladium alkyls. Table 3 indicates that thermolysis of *trans*- and *cis*-$PdMe_2L_2$ liberates cleanly almost all of the methyl groups as ethane accompanied by formation of a small amount of methane and a negligible amount of ethylene (Runs 1—7). When the *trans*- or

$$\underset{\text{(}trans\text{ and }cis\text{)}}{PdMe_2L_2} \xrightarrow[\text{dmm}]{\text{thermolysis}} Pd(dmm)L_2 + \underset{(>0.95)}{CH_3CH_3} + \underset{(<0.05)}{CH_4} + \underset{(\approx 0)}{CH_2CH_2} \quad (5)$$

cis-$PdMe_2L_2$ were thermolyzed in the presence of free tertiary phosphines, the thermolysis course releasing ethane was severely hindered, making methane the main thermolysis product, albeit in small quantities as shown in Table 4. Thermolysis of *cis*-$Pd(CD_3)_2(PMePh_2)_2$ in C_6D_6 at 60 °C in the presence of 0.25 mol/l of $PMePh_2$ liberated methane composed of 98% of CD_3H and 2% of CD_4. The results suggest that the hydrogen abstraction is taking place probably *via* a process involving an orthometallated intermediate when the *cis*-dimethyl complex is thermolyzed in the presence of free phosphine.

In contrast to the liberation of ethane and ethylene in a 1:1 ratio on thermolysis of *trans*-$PdEt_2(PMe_2Ph)_2$

Table 4. The effects of addition of *t*-phosphines on the thermolysis of $PdMe_2L_2$[a]

Run	Compound[b]	Additive[c] (mol/l)	$\frac{[PR_3]}{[Complex]}$	$\frac{CH_4}{C_2H_6}$
1	**4a**	dmm (0.052)	0	0
2	**4a**	$PMePh_2$(0.025)	0.5	39
3	**4a**	$PMePh_2$(0.050)	1.1	72
4	**4a**	$PMePh_2$(0.125)	2.8	231
5	**4a**	$PMePh_2$(0.250)	5.8	838
6	Va	dmm (0.052)	0	0
7	Va	$PEtPh_2$(0.047)	1.0	3.2
8	Va	$PEtPh_2$(0.117)	1.2	5.3
9	Va	$PEtPh_2$(0.140)	2.8	8.1
10	Va	$PEtPh_2$(0.234)	3.1	10.1

a) Total amounts of evolved gases were below 5% except for Runs 1 and 6. b) **4a**, *cis*-$PdMe_2(PMePh_2)_2$; Va, *trans*-$PdMe_2(PEtPh_2)_2$. c) dmm, dimethyl maleate.

(IIb) and *trans*-$PdEt_2(PEt_2Ph)_2$ (IIIb) (Runs 8 and 9 in Table 3 and Ref. 5), thermolysis of *cis*-$PdEt_2(PMe_2Ph)_2$ (**2a**) and *cis*-$PdEt_2(PEt_2Ph)_2$ (**3b**) in toluene containing dmm (Runs 10 and 11 in Table 3) gave almost quantitative amounts of butane, the reductive elimination product of the palladium diethyls. The dichotomy

$$\begin{array}{l} \mathrm{L\text{–}Pd\text{–}Et} \xrightarrow{\text{thermolysis}} \mathrm{Et\text{–}Et} \\ \quad\mathrm{L} \\ \quad (\mathrm{L}=\mathrm{PMe_2Ph},\ \mathrm{PEt_2Ph}) \end{array} \qquad (6)$$

$$\begin{array}{l} \mathrm{L\text{–}Pd\text{–}L} \xrightarrow{\text{thermolysis}} \mathrm{C_2H_6} + \mathrm{C_2H_4} \\ \quad\mathrm{Et} \\ (\mathrm{L}=\mathrm{PMe_2Ph},\ \mathrm{PEt_3},\ \mathrm{PEt_2Ph},\ \mathrm{PMePh_2},\ \mathrm{PEtPh_2}) \end{array}$$

of the thermolysis products of the palladium diethyls depending on the configuration of the isomer is intriguing. The fact that the reductive elimination of the *cis*-alkyls is hindered whereas the β-elimination pathway of the *trans*-alkyls is not hindered by addition of free phosphines suggests that the tertiary phosphine ligand is serving to stabilize the *cis*-dialkyls by blocking the route leading to the three-coordinate species, whereas the phosphine does not block the site for β-elimination of *trans*-$PdEt_2L_2$ to take place. The results are in conflict with the generally held view that the tertiary phosphine's role is merely to block the site for the β-elimination to take place.[11]

In contrast to the occurrence of reductive elimination of the ethyl groups from *cis*-$PdEt_2L_2$ having the monodentate phosphine ligands, the thermolysis of *cis*-$PdEt_2$(dpe) having the bidentate ligand (**6b**, Run 12 in Table 3) liberated ethane and ethylene together with butane, indicating that both β-elimination and reductive elimination pathways are operative. Thermolysis of *cis*-$PdMe_2$(dpe), however, gave ethane, the reductive elimination product. The reason for the different thermolysis behavior of **6b** is not clear.

The occurrence of the reductive elimination of ethyl groups from *cis*-$Pd(CH_2CD_3)_2(PMe_2Ph)_2$ without involvement of H–D scrambling in the deuterated ethyl groups was confirmed by examination of the ^1H NMR of the deuterated butane formed on thermolysis. It was revealed that the proton content in the methyl and methylene groups in the butane produced on thermolysis was 7 and 93% respectively.

Kinetic Study of Thermolysis of cis-$PdMe_2(PMePh_2)_2$ (**4a**). In order to obtain further information on the thermolysis mechanism of the *cis*-dialkyl isomers, the thermolysis of *cis*-$PdMe_2(PMePh_2)_2$ (**4a**) was followed by measuring the evolved amount of ethane produced on thermolysis of **4a** in diphenylmethane containing dmm. Complex **4a** was chosen because of the stability of the *cis* isomer concerning the isomerization to the *trans* isomer as well as the convenient temperature range where the thermolysis proceeds at reasonable rates for the kinetic measurement. The thermolysis is first order in the palladium dimethyl concentration up to the decomposition of 80—90% of the complex (Fig. 1). The thermolysis is severely hindered by addition of small amounts of free $PMePh_2$

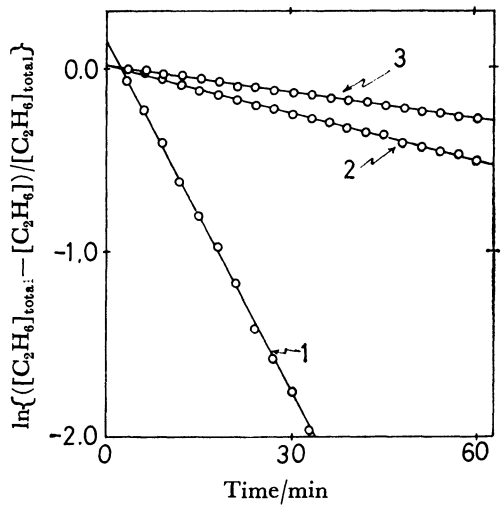


Fig. 1. Pseudo-first order plots for thermolysis of *cis*-$PdMe_2(PMePh_2)_2$ in Ph_2CH_2 containing 0.087 mol/l of dmm at 45.0 °C. [Complex]≈0.025 mol/l. Additive ($PMePh_2$, mol/l): 1) 0.00; 2) 1.25×10^{-3}; 3) 2.50×10^{-3}.

Table 5. The effects of addition of various ligands on thermolysis rates of *cis*-$PdMe_2(PMePh_2)_2$ (**4a**)

Run	Additive (mol/l)	$10^3\ k_{obsd}/s^{-1}$
1	dmm (0.087)	1.1
2	dmm (0.17)	1.1
3	dmm (0.35)	1.2
4	dmm (0.087) $PMePh_2$ (0.75×10^{-3})	0.21
5	dmm (0.087) $PMePh_2$ (1.25×10^{-3})	0.15
6	dmm (0.087) $PMePh_2$ (2.50×10^{-3})	0.08
7	dmm (0.087) Pyridine (0.15)	0.59
8	dmm (0.087) $AsPh_3$ (0.033)	0.37

a) [Complex]≈0.025 mol/l, at 45.0 °C, in Ph_2CH_2.

to the system. The pseudo-first-order rate constant k_{obsd} of thermolysis of **4a** under various experimental conditions are summarized in Table 5. As can be seen from Table 5 the thermolysis rate was not affected by the amount of dmm added to the system, whereas the addition of $PMePh_2$, pyridine, and $AsPh_3$ suppressed the thermolysis. The retardation effect of pyridine and $AsPh_3$ was smaller than that of $PMePh_2$. Plotting of the $1/k_{obsd}$ value *vs.* the concentration of $PMePh_2$ added to the system gave a straight line (Fig. 2). The results suggest that the thermolysis proceeds through a dissociative pathway involving the three-coordinate intermediate formed on partial dissociation of the phosphine ligand from *cis*-$PdMe_2(PMePh_2)_2$ as represented in Scheme 3. Assumptions of the ligand

$$\mathrm{L\text{–}Pd(Me)_2} \underset{+\mathrm{L},\ k_{-1}}{\overset{-\mathrm{L},\ k_1}{\rightleftharpoons}} \left[\mathrm{L\text{–}Pd(Me)_2}\right] \xrightarrow{k_2} \mathrm{C_2H_6}$$

Scheme 3. Theromlysis mechanism of *cis*-$PdMe_2L_2$ (L=$PMePh_2$).

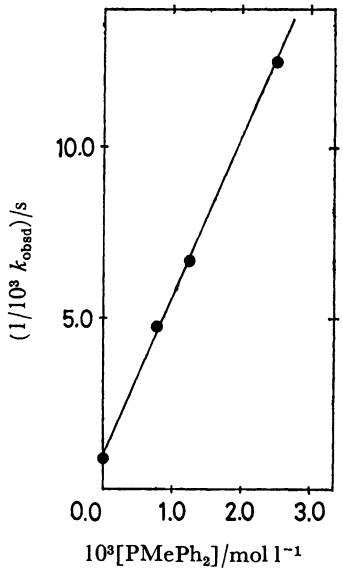


Fig. 2. Plots of $1/k_{obsd}$ *vs.* [$PMePh_2$] in thermolysis of *cis*-$PdMe_2(PMePh_2)_2$ (**4a**) in Ph_2CH_2 containing 0.087 mol/l of dmm at 45.0 °C. [**4a**]≈0.025 mol/l.

dissociation as the rate-determining process and of the steady-state approximation for the concentration of the three coordinate intermediate in Scheme 3 leads to the kinetic equations (7) and (8) which are in agreement with the experimental results as shown in Figs. 1 and 2.

$$-\frac{d[cis\text{-}PdMe_2L_2]}{dt} = \frac{k_1k_2}{k_{-1}[L]+k_2}[cis\text{-}PdMe_2L_2] \quad (7)$$

$$\frac{1}{k_{obsd}} = \frac{k_{-1}}{k_1k_2}[L] + \frac{1}{k_1} \quad (8)$$

Retardation effect of $AsPh_3$ and pyridine is also accommodated by the mechanism shown in Scheme 3. The corresponding *cis*-diethyl analog (**2b**) behaved similarly. An almost quantitative amount of butane was liberated on thermolysis of 0.077 mol/l of **2b** at 55 °C for 5 h in toluene containing dmm. The thermolysis was severely hindered in the presence of 0.17 mol/l of PMe_2Ph under otherwise the same conditions and only *ca.* 2% of butane per complex was released.

In order to see the effect of tertiary phosphine on the stability of the palladium dimethyls having various tertiary phosphine ligands, pseudo-first-order rate constant was measured for each complex in the absence of the added phosphine. The results summarized in Table 6 reflect both electronic and steric effects of the phosphine ligands on stability of the palladium dimethyls. Comparison of the thermolysis rate constants

Table 6. Thermolysis rates of *cis*-$PdMe_2L_2$[a)]

L	θ/°[b)]	pK_a[c)]	$10^3\ k_{obsd}/s^{-1}$
PEt_3	132	8.65	0.42
PEt_2Ph	136	6.78	0.53
$PMePh_2$	136	4.65	1.1
$PEtPh_2$	140	4.91	2.0

a) [Complex]≈0.025 mol/l, at 45.0 °C, in Ph_2CH_2 containing 0.087 mol/l of dmm. b) See Ref. 20. c) See Ref. 21.

of **3a** and **4a** having the phosphine ligands of similar cone angles but different basicities indicate that the more basic ligand is more strongly attached to the methyl complex giving rise to a slower thermolysis rate. On the other hand, the $PEtPh_2$-coordinated complex (**5a**) having a larger cone angle than $PMePh_2$ but a similar basicity is thermolyzed at a higher rate than the $PMePh_2$-coordinated complex (**4a**) as a consequence of the steric bulkiness. The PPh_3-coordinated complex is more unstable than **5a** and the thermolysis rate measurement was not attempted. The PEt_3-coordinated complex is much more stable as expected from its high basicity and low steric bulkiness than the complexes coordinated by phenyl-substituted phosphines. Comparison of the thermolysis rate constant of the PEt_3-coordinated complex with thermolysis rate of other complexes, however, was not feasible because of the considerably high rate of the *cis-trans* isomerization occurring concurrently with the thermolysis (*vide infra*). The thermolysis of $PdMe_2$(dpe) (**6a**) at 80 °C in diphenylmethane was almost completely suppressed by addition of about 2 equivalents of dpe. Since the dpe ligand usually serves as a better coordinating ligand than the mono phosphines, the previously mentioned formation of ethane and ethylene and not of butane as the main thermolysis product of $PdEt_2$(dpe) (**6b**) may be partly due to reluctance of the partial dissociation of the dpe ligand from **6b**. Thermolysis without partial dissociation of the ligand may force the complex decomposed by another route. It is noteworthy that addition of the phosphine ligand in thermolysis of $NiMe_2$(dpe)[12] showed no inhibition effect, suggesting a difference in the thermolysis mechanisms of the nickel and palladium congeners.

The unimolecular thermolysis pathway of the *cis* palladium alkyls was further supported by examining the thermolysis product of a mixture of *cis*-$Pd(CH_3)_2$-$(PMePh_2)_2$ (**4a**) and *cis*-$Pd(CD_3)_2$ $(PMePh_2)_2$ in a molar ratio of 0.90: 1.00. The ethane formed on thermolysis of the mixture contained CD_3CD_3, CD_3CH_3, and CH_3CH_3 in a ratio of 0.47: 0.05: 0.48, indicating that scrambling of the methyl groups constitutes only a minor process in thermolysis of **4a**. Stille and coworkers have obtained evidence supporting the involvement of the methyl group in $PMePh_2$ in thermolysis of **4a**.[13] The formation of the minor amount of CD_3CH_3 may have arisen from such a process since thermolysis of *cis*-$Pd(CD_3)_2(PMePh_2)_2$ evolved about 5% of CH_3-CD_3 but the thermolysis result of the mixed CH_3- and CD_3-complexes clearly indicates intramolecular coupling of the *cis* dimethyl groups as the main process. Further support of the unimolecular process in thermolysis of *cis*-PdR_2L_2 was provided by the negligible formation of propane on thermolyses of mixtures of *cis*-$PdMe_2$-$(PMePh_2)_2$ and *cis*-$PdEt_2(PMe_2Ph)_2$.

trans-cis *Isomerization of* $PdMe_2L_2$ *and Mechanism of Thermolysis of* trans-$PdMe_2L_2$. In contrast to the thermolysis behavior of *cis*-$PdMe_2L_2$ which is decomposed by a unimolecular reductive elimination mechanism, the thermolysis of *trans*-$PdMe_2L_2$ deviates from the first-order rate law and shows a marked acceleration in the thermolysis rate as the thermolysis proceeds.

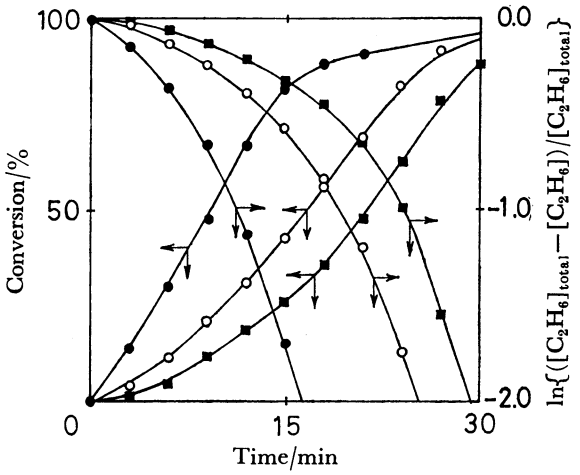


Fig. 3. Time-conversion curves and pseudo-first order plots for thermolysis of *trans*-$PdMe_2L_2$ in Ph_2CH_2 containing 0.087 mol/l of dmm at 62.0 °C. L=PEt_2Ph (IIIa, —■—), $PMePh_2$ (IVa, —○—), $PEtPh_2$ (Va, —●—).

Fig. 4. ^1H NMR spectral change of *trans* to *cis* isomerization of $PdMe_2(PMePh_2)_2$ in CD_2Cl_2 at 36.0 °C.

This indicates the presence of an autocatalytic thermolysis process. The typical time-conversion curves of thermolysis of *trans*-$PdMe_2L_2$ (IIIa, IVa, and Va) are shown in Fig. 3. Further examination of the thermolysis reactions of the *trans*-$PdMe_2L_2$ type complexes revealed the initial isomerization of the *trans* isomer to the *cis* isomer from which the reductive elimination proceeds. By selecting the proper complex and suitable reaction conditions the thermolysis of the palladium dimethyl can be kept minimal and the *trans-cis* isomerization can be conveniently observed. Figure 4 illustrates the typical change of the ^1H NMR spectrum of *trans*-$PdMe_2(PMePh_2)_2$ (IVa) to *cis*-$PdMe_2(PMePh_2)_2$ (**4a**) at 36 °C in CD_2Cl_2. The initial NMR spectrum shows the Pd–Me as well as the methyl signals of $PMePh_2$ as singlets, suggesting exchange between the phosphine ligand liberated from the *trans*-$PdMe_2(PMePh_2)_2$ and the phosphine ligand coordinated to palladium. The liberation and recoordination of the phosphine ligand is a reversible process at this stage, retaining the *trans* configuration since cooling of the solution gives a triplet pattern for the methyl signals of the methyl groups bonded to palladium in the *trans* form. When the solution is kept at 36 °C the signals due to the *trans* isomer decrease. This is accompanied by increase of the signals characteristic of the *cis* isomer. During the isomerization process no change of the chemical shifts of the signals due to the *trans* and *cis* isomers was observed. The isomerization was free of thermolysis up to the 80% conversion. Beyond that stage, formation of ethane in a minor amount was noticed, revealing the occurrence of a slow thermolysis.

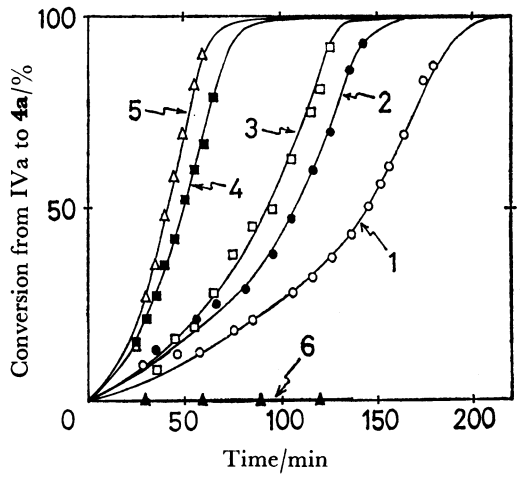


Fig. 5. Time-conversion curves of isomerization of *trans*-$PdMe_2(PMePh_2)_2$ (IVa) to *cis*-$PdMe_2(PMePh_2)_2$ (**4a**) in CD_2Cl_2 at 36.0 °C.

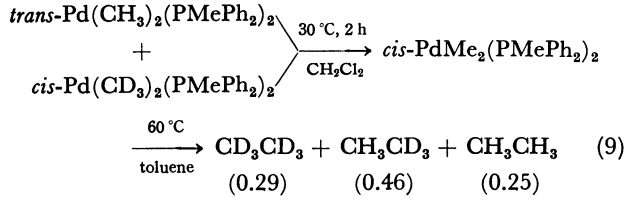
Initial concentration/mol l^{-1}

Run	IVa	Additive	
		4a	$PMePh_2$
1	0.067	0	0
2	0.107	0	0
3	0.064	0.027	0
4	0.069	0.059	0
5	0.071	0.114	0
6	0.090	0	0.050

For the $PMePh_2$-coordinated dimethylpalladium complex the equilibrium lies on the side of the *cis* form. Leaving the acetone-d_6 solution containing the *cis*-$PdMe_2(PMePh_2)_2$ (**4a**) at room temperature for one week led only to the slow decomposition of **4a** without any sign of *cis-trans* isomerization. With increasing replacement of the phenyl groups in the tertiary phosphine ligand by alkyl groups a noticeable effect on the *cis-trans* equilibrium becomes apparent. Although the equilibrium for the $PdMe_2(PMePh_2)_2$ type complex lies far on the side of the *cis* form in CD_2Cl_2 and in acetone-d_6, the PEt_3-coordinated dimethylpalladium complex undergoes *cis-trans* and *trans-cis* isomerization slowly reaching an equilibrium of *trans*/*cis*=1.2 after a few days at room temperature. For **3a** having the less basic and more bulky PEt_2Ph ligand than PEt_3, *cis-trans* isomerization was also observed with an quilibrium *trans*/*cis* ratio of 0.20 at room temperature in acetone-d_6. Apparently both steric and electric factors are involved to determine the *cis-trans* equilibrium, but the electronic factor may be dominant in influencing the equilibrium, as judged from the higher *trans* ratio at equilibrium of the PEt_2Ph-coordinated complex than that of the $PMePh_2$-coordinated complex, both phosphines having the same cone angle.

For the dimethylpalladium complex coordinated with $PMePh_2$, kinetic studies concerning the *trans* to *cis* isomerization have been made by pursuing the decrease of the Pd–Me signal in the ^1H NMR spectra of the *trans* form IVa measured in CD_2Cl_2 at 36.0 °C. This system is free from the reverse, *cis* to *trans* isomerization and the time-conversion curves, as reproduced in Fig. 5, shows a typical autocatalytic acceleration effect. The *trans-cis* isomerization rate is increased with increase of the initial concentration of the *trans* form IVa (Runs 1 and 2 in Fig. 5) and the rate is particularly enhanced on addition of the increasing amount of the *cis* form (**4a**) to the system (Runs 3, 4, and 5). The isomerization was markedly suppressed by adding free $PMePh_2$ to the system (Run 6).

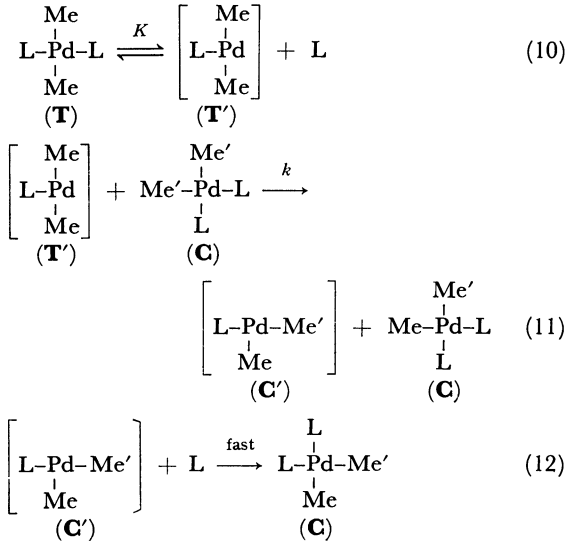
Further examination of the *trans-cis* isomerization using the deuterated dimethylpalladium complex revealed scrambling of the methyl groups during the isomerization process. Examination of the thermolysis product liberated from *cis*-$PdMe_2(PMePh_2)_2$, derived by isomerization of *trans*-$Pd(CH_3)_2(PMePh_2)_2$ in CH_2Cl_2 at 30 °C for 2 h in the presence of an equilmolar amount of *cis*-$Pd(CD_3)_2(PMePh_2)_2$, revealed that the ratio of CD_3CD_3: CH_3CD_3: CH_3CH_3 in the evolved ethane was 0.29: 0.46: 0.25, indicating the complete scrambling of the methyl groups. Since it has been already



(9)

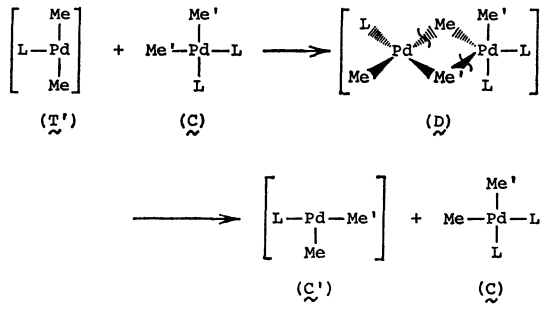
confirmed that the thermolysis of the mixture of *cis*-$Pd(CH_3)_2(PMePh_2)_2$ and *cis*-$Pd(CD_3)_2(PMePh_2)_2$ predominantly gives CD_3CD_3 and CH_3CH_3, the above result clearly indicates the involvement of an intermolecular process causing the exchange of the methyl groups. Since it has been established on the basis of ^1H NMR spectrum that *trans*-$PdMe_2(PMePh_2)_2$ is partly dissociated with retention of the "*trans*" configuration in solution without rapid transformation into the *cis* configuration, it is reasonable to assume the presence of an energy barrier between the three-coordinate species having the methyl groups at mutually *trans* positions (**T′** form in the following equations) and another three-coordinated species having the methyl groups at mutually *cis* positions (**C′**). Our next task is to find a reasonable mechanism which allows the complex led to the *cis* form with the assistance of the *cis*-$PdMe_2L_2$ or *trans*-$PdMe_2L_2$ with involvement of the methyl scrambling.

Since there is no precedent of the *trans-cis* isomerization proceeding by an intermolecular mechanism to our knowledge, examination of various isomerization models merits the consideration. In the first place, the intramolecular isomerization mechanism is excluded on the basis of the kinetic results and the intermolecular scrambling experiment. Secondly, inhibition of the isomerization by addition of free phosphine supports a mechanism involving the partial dissociation of the phosphine ligand from the square-planar complex with exclusion of other mechanisms involving association of non-dissociated four coordinate species. Thirdly, a bimolecular mechanism between two three-coordinated species formed by the ligand dissociation is unlikely on the ground of kinetic results. After exclusion of these other possible mechanisms we are left with the following mechanism to account for the isomerization of *trans*-$PdMe_2L_2$ promoted by *cis*-$PdMe'_2L_2$. As the inter-



Scheme 4. Proposed mechanism for *trans-cis* isomerization of *trans*-$PdMe_2L_2$ promoted by *cis*-$PdMe_2L_2$.

mediate in the crucial intermolecular reaction (11) we postulate the formation of the following methyl bridged species, which on cleavage of the original methyl–palladium bonds may give the dissociated (**C′**) and undissociated *cis*-dimethyl (**C**) complexes. Rapid coordination of the free phosphine ligand to the unsaturat-



(13)

ed species (**C**′) completes the isomerization, giving the product *cis*-PdMeMe′L_2 (Eq. 12). Retention of the *cis* configuration of the added *cis* isomer after departure from the bridged species (**D**), in which a trigonal bipyramidal structure is assumed, is in agreement with the generally observed retention of configuration in the other isomerization reactions of square-planar transition metal complexes.[8] Since the methyl group has a greater *trans* effect than the tertiary phosphine, cleavage of the methyl group in the position *trans* to the terminal methyl group as shown in **D** is reasonable. The rapid coordination of the free phosphine to the split-out species (**C**′) leading to the square-planar *cis*-$PdMe_2L_2$ (Eq. 12) is a likely process in view of the absence of broadening of the ^1H NMR signal of the palladium bonded methyl groups in *cis*-$PdMe_2L_2$.

The *trans-cis* isomerization strongly favors the *cis* form for complexes having phosphines with the phenyl groups as discussed previously. For these cases assumption of Scheme 4, in which rapid equilibrium for Eq. 10, the rate determining step for Eq. 11 and the subsequent rapid trapping of the (**C**′) in Eq. 12 are involved, leads to the kinetic expression given by Eq. 14.

$$-\frac{d[\mathbf{T}]}{dt} = k[\mathbf{T}'][\mathbf{C}] \tag{14}$$

Since $[\mathbf{T}]_0+[\mathbf{C}]_0=[\mathrm{T}]+[\mathbf{C}]$, where $[\mathbf{T}]_0$ and $[\mathbf{C}]_0$ stand for the initial concentrations of the *trans* and *cis* isomers and [**T**] and [**C**] the concentrations of the isomers at time *t*, [**C**] may be expressed as

$$[\mathbf{C}] = [\mathbf{T}]_0 + [\mathbf{C}]_0 - [\mathbf{T}]. \tag{15}$$

From Eq. 10 it follows

$$K = [\mathbf{T}'][\mathrm{L}]/[\mathbf{T}] \quad \text{where } [\mathbf{T}'] = [\mathrm{L}] \text{ and}$$
$$[\mathbf{T}'] = \sqrt{K[\mathbf{T}]}. \tag{16}$$

From Eqs. 14, 15, and 16

$$-\frac{d[\mathbf{T}]}{dt} = k\sqrt{K}\sqrt{[\mathbf{T}]}([\mathbf{T}]_0+[\mathbf{C}]_0-[\mathbf{T}]) \tag{17}$$

$$\int_{[\mathbf{T}]_0}^{[\mathbf{T}]} \frac{d[\mathbf{T}]}{\sqrt{[\mathbf{T}]}([\mathbf{T}]_0+[\mathbf{C}]_0-[\mathbf{T}])} = -\int_0^t k\sqrt{K}\,dt. \tag{18}$$

From Eq. 18 the following equation is derived:

$$\ln\frac{(\sqrt{[\mathbf{T}]_0+[\mathbf{C}]_0}+\sqrt{[\mathbf{T}]})^2}{[\mathbf{C}]} = -k\sqrt{K}\sqrt{[\mathbf{T}]_0+[\mathbf{C}]_0}\cdot t + \ln\frac{(\sqrt{[\mathbf{T}]_0+[\mathbf{C}]_0}+\sqrt{[\mathbf{T}]_0})^2}{[\mathbf{C}]_0}. \tag{19}$$

Plots of $\ln(\sqrt{[\mathbf{T}]_0+[\mathbf{C}]_0}+\sqrt{[\mathbf{T}]})^2/[\mathbf{C}]$ *vs.* *t* as computed from the time-conversion curves shown in Fig. 5 are straight lines as shown in Fig. 6 up to about 60—

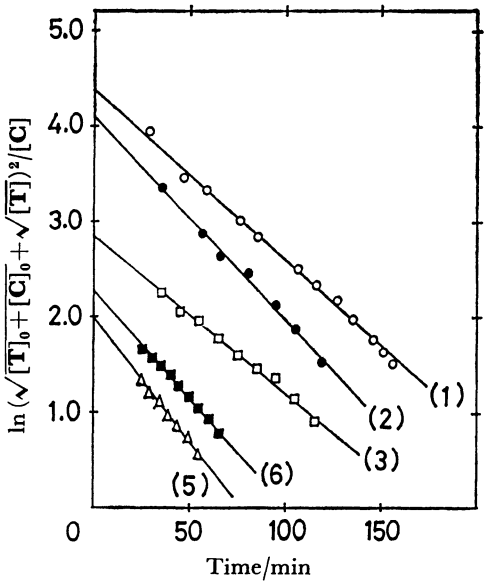
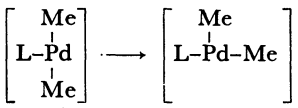


Fig. 6. Plots of $\ln(\sqrt{[\mathbf{T}]_0+[\mathbf{C}]_0}+\sqrt{[\mathbf{T}]})^2/[\mathbf{C}]$ *vs.* *t* in *trans* to *cis* isomerization of $PdMe_2(PMePh_2)_2$.

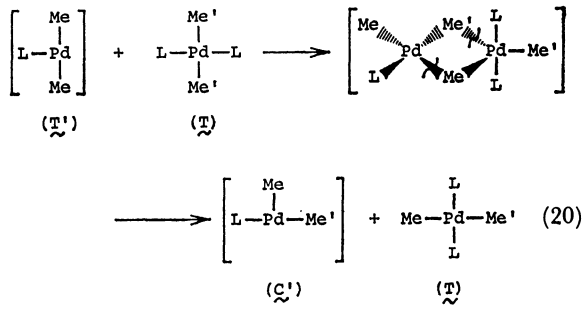
80% conversions. The values obtained by dividing the slopes of these lines in Fig. 6 by $-\sqrt{[\mathbf{T}]_0+[\mathbf{C}]_0}$ give a constant value $(1.0\pm0.1)\times10^{-3}$ s^{-1} $mol^{-1/2}$ $l^{-1/2}$ corresponding to $k\sqrt{k_1}$ in a reasonable agreement with each other value. Thus the isomerization of the *trans* isomer to the *cis* isomer catalyzed by the *cis* isomer can be explained by assuming the mechanism shown in Scheme 4, at least for the most part where the acceleration effect is observed.

The initial period of isomerization, however, where the *cis* isomer is not present, remains to be explained by the other mechanism than the one involving the *cis* isomer. If the slow isomerization of the three-coordinate **T**′ complex to **C**′ complex shown below is excluded



(19)

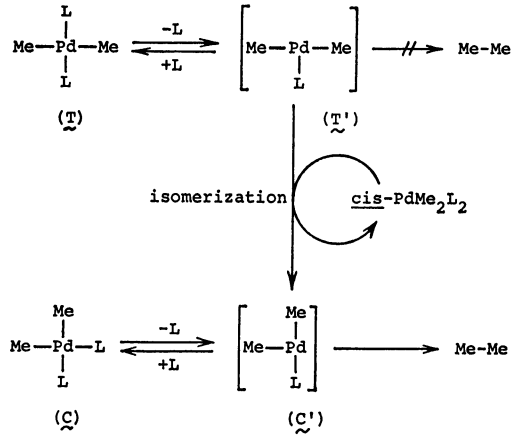
even in the initial period, the remaining reasonable mechanism to account for the isomerization in the initial period is the one assisted by the undissociated *trans* isomer itself. Experimentally it is difficult to get evidence to prove or disprove mechanisms given by Eq. 19 or Eq. 20 for the initial period where the isomerization rate is small. The acceleration effect observed by increasing the initial concentration of the



(20)

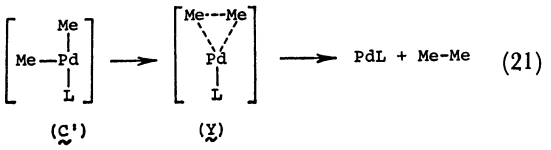
trans isomer suggests an intermolecular mechanism such as Eq. 20. The much enhanced acceleration of the isomerization by addition of the *cis* isomer (*e.g.* Run 3 in Fig. 5 in comparison with Run 2 in which the total concentration is higher than in Run 3) suggests that the reaction proceeds mainly by a mechanism involving acceleration by the *cis* isomer (*e.g.* Scheme 4). For the *cis* to *trans* isomerization, which was noticeable for the PEt_3-coordinated complex **1a** and to a lesser extent for the PEt_2Ph-coordinated complex **3a**, a mechanism following the reverse course of the *trans* to *cis* isomerization as expressed by Scheme 4 may be operative.

With the information concerning the *trans* to *cis* isomerization we are now in a situation to resume the discussion on the thermolysis behavior of the *trans* palladium dimethyls at elevated temperatures as shown in Fig. 3. As can been seen from the figure, the thermolysis rate is markedly accelerated as the reaction proceeds. These results combined with those on the thermolysis of *cis*-$PdMe_2L_2$ previously discussed suggest that the thermolysis of *trans*-$PdMe_2L_2$ proceeds after its isomerization to the (**C**′) type three-coordinate intermediate. This intermediate is also formed by partial dissociation of the ligand in thermolysis of *cis*-$PdMe_2L_2$ as shown in Scheme 5.



Scheme 5. Proposed mechanism of reductive elimination of methyl group from *trans*- and *cis*-$PdMe_2L_2$.

It is noteworthy that the three-coordinate "*cis*" type complex (**C**′) has a moderate stability without being immediately thermolyzed by a reductive elimination pathway. The results suggest intervention of another type of three-coordinate species connected with the transition state for the reductive elimination. A plausible candidate for the species formed by the rearrangement of configuration from the T-shaped species (**C**′) is a planar Y-shaped complex from which the alkyl groups are reductively eliminated. A similar intermediate has been invoked in explanation of the



(21)

thermolysis and isomerization behavior of AuR_3L type complexes.[6]

It is intriguing to note the similarity between thermolysis mechanisms of the alkyl complexes of Group I transition metal, AuR_3L, and of Group VIII transition metal, $PdMe_2L_2$. Furthermore, comparison of the thermolysis behavior of PdR_2L_2 with that of NiR_2L_2 and PtR_2L_2 reveals the contrasting difference in thermolyses of these three, Group VIII dialkyls. Pertinent characteristics in thermolysis patterns of the three dialkyls are as follows. (1) Reductive elimination of $NiMe_2(bpy)$[14] and $NiMe_2(dpe)$[12] is not hindered by the presence of free ligand. This suggests that the reductive elimination from the four-coordinate species can proceed without ligand liberation in contrast to the striking inhibition effect of the phosphine ligand on thermolysis of *cis*-PdR_2L_2. (2) Thermolysis of *cis*-PtR_2L_2 by a β-hydrogen elimination pathway is severely hindered by addition of a free phosphine,[15] whereas the thermolysis of *trans*-$PdEt_2L_2$ proceeding also through a β-hydrogen elimination pathway is not hindered by the presence of the free phosphine.[5]

Attempting to clarify the difference in the thermolysis behavior of *cis*-$PdMe_2L_2$ and *cis*-$NiMe_2L_2$, Tatsumi and Hoffmann recently performed extended HMO calculations.[16] Their results explain most of the thermolysis behavior of *cis*-$PdMe_2L_2$ and *cis*-$NiMe_2L_2$ and suggest the presence of an energy barrier between the T-shaped "*trans*" form (**T**′) and "*cis*" form (**C**′). Their calculation indicates that a lower energy barrier is found for reductive elimination *via* the Y-shaped species rather than directly from the undissociated complex or from **C**′ intermediate in the case of palladium dialkyls, whereas the reductive elimination from the undissociated $NiMe_2L_2$ complex may take place with a lower energy barrier than the case for *cis*-$PdMe_2L_2$.

On Factors Influencing the Stability of Palladium Alkyls.

In discussion of the factors influencing the stability of transition metal alkyls one of the most important information regarding the roles of the supporting ligands such as tertiary phosphines and organic nitrogen bases may be obtained by careful kinetic studies of the thermolysis mechanism of the isolated transition metal alkyls. It has been established in the previous report[5] that the tertiary phosphine ligand does not serve in blocking the β-hydrogen elimination pathway effectively in the thermolysis of *trans*-$PdEt_2L_2$ but rather the bulky ligands destabilize the Pd–Et bonds. The present study, however, indicates that thermolysis of the *cis*-dialkylpalladium complexes proceeding through a reductive elimination pathway can be severely hindered by the presence of free tertiary phosphines. In the thermolysis involving the ligand dissociation the nature of the ligands and that of the alkyl groups give mutual influence on the ease of cleavage of the Pd–PR_3 bond and Pd–alkyl bonds. Although the intrinsic bond strength of the Pd–Et bond may certainly differ from that of the Pd–Me bond, the principal factor in determining the stability of the phosphine-coordinated *cis*-palladium dialkyls, may be sought in the ease of release of the phosphine ligand. The ethyl group situated at the *trans* position to one of the phosphine ligands may

have greater *trans* labilizing effect than the methyl group in the rate-determining phosphine dissociating process. This would explain the greater stability of the dimethyl complexes than the corresponding diethyl complexes.

The results obtained in the present study as well as the previous one provide pertinent information not only about the factors concerning the stability of palladium alkyls but also regarding palladium-catalyzed reactions causing the C–C bond coupling. Although the actual catalyst systems, being constituted of a series of elementary steps, are much more complicated than the simple thermolysis of the isolated palladium dialkyls, part of the roles of the added ligands may be connected with the effect of the ligand on reductive elimination of dialkyls as discussed here.

Experimental

All manipulations were carried out under an atmosphere of nitrogen or argon, or *in vacuo*. Solvents were dried in the usual manner, distilled, and stored under a nitrogen atmosphere.

Infrared spectra were recorded on a Hitachi 295 spectrometer using KBr pellets. ^{1}H NMR spectra were measured on a JEOL PS-100, FX-100, and PMX-60 spectrometers. ^{1}H NMR signals are referred to Me_4Si as internal or external standard. Analysis of the gases evolved by the reactions was carried out by gas chromatography (Shimadzu GC-3BF) after collecting gases using a Toepler pump, by which the volumes of gases were also measured. Analysis of the gases dissolved in solution was also carried out by gas chromatography (Shimadzu GC-6A) after collecting the volatile matters in the reaction solution by a trap-to-trap distillation. Micro analyses (C and H) were carried by Mr. T. Saito of our laboratory using Yanagimoto CHN Autocorder Type MT-2. Analysis of the palladium content was performed by colorimetric method using 1-nitroso-2-naphthol as a color-producing reagent.[17] The complete ionization of the palladium in the complex was achieved by treating the sample with a hot aqua regia.

Triethylphosphine (Strem) was used as purchased. Dimethylphenylphosphine, diethylphenylphosphine, diphenylmethylphosphine, and diphenylethylphosphine were prepared by the reactions of $PPhCl_2$ and PPh_2Cl, respectively, with RMgX (R=Me, X=I; R=Et, X=Br). 1,2-Bis(diphenylphosphino)ethane (dpe) was prepared by the literature method starting from PPh_3.[18]

trans-$PdMe_2(PEt_3)_2$ (Ia), *cis*-$PdMe_2$(dpe) (**6a**), *cis*-$PdEt_2$(dpe) (**6b**), and *cis*-$PdPr^n_2$ (dpe) (**6c**) were prepared by the reactions of $Pd(acac)_2$, $AlR_2(OEt)$ (R=Me, Et, Pr^n), and tertiary phosphines according to the method described previously.[3] A series of *trans*-PdR_2L_2 (R=Et, L=PEt_3 (Ib), PMe_2Ph (IIb), PEt_2Ph (IIIb), $PMePh_2$ (IVb), $PEtPh_2$ (Vb); R=Pr^n, L=PEt_3 (Ic), PMe_2Ph (IIc), $PMePh_2$ (IVc); R=Bu^n, L=PMe_2Ph (IId)) were also prepared by the reactions of $Pd(acac)_2$, $AlR_2(OEt)$, and tertiary phosphines.[3,5]

Preparation of trans-*PdMe$_2$(PEt$_2$Ph)$_2$ (IIIa) (Method A).* To the heterogeneous red mixture of $Pd(acac)_2$ (2 g, 6.6 mmol), PEt_2Ph (3 ml, 17.1 mmol) and Et_2O (40 ml) cooled to −70 °C, a hexane solution of $AlMe_2(OEt)$ (5 ml, 19 mmol) was added dropwise. On raising the temperature of the mixture gradually, it became homogeneous at −30 °C. The solution was stirred for several hours at 0 °C. After concentrating the solution to *ca.* 10 ml, the solution was cooled to −70 °C overnight to yield a white precipitate of *trans*-$PdMe_2(PEt_2Ph)_2$ (IIIa), which was filtered, washed with a small amount of Et_2O at the same temperature and dried *in vacuo*. It was confirmed that the crude product of complex IIIa contained only *trans* isomer by means of IR spectroscopy. The product was recrystallized from acetone to yield white crystals of IIIa (1.5 g, 49%). Similarly obtained was *trans*-$PdMe_2(PEtPh_2)_2$ (Va) by using $PEtPh_2$ in place of PEt_2Ph. Complex Va was recrystallized from THF–CH_2Cl_2 (yield, 65%).

trans-$PdMe_2(PMePh_2)_2$ (IVa) was also prepared in a similar way from $Pd(acac)_2$, $PMePh_2$, and $AlMe_2(OEt)$. The crude complex first isolated from the reaction system, however, was a mixture of *trans* isomer (IVa) and *cis* isomer (**4a**). These two isomers were separated by extraction with acetone, in which the *cis* isomer is readily dissolved. The *trans* isomer (IVa) and the *cis* isomer (**4a**) were recrysrallized from THF–CH_2Cl_2 and acetone, respectively (yield; IVa, 14%; **4a**, 32%).

Characterization of these complexes was carried out by means of IR and ^{1}H NMR spectroscopy, and elemental analysis. Anal. (IIIa) Found: C, 56.3; H, 8.2%. Calcd for $C_{22}H_{36}P_2Pd$: C, 56.4; H, 7.7%. (IVa) Found: C, 62.1; H, 5.9%. Calcd for $C_{28}H_{32}P_2Pd$: C, 62.6; H, 6.0%. (Va) Found: C, 64.0; H, 6.5%. Calcd for $C_{30}H_{36}P_2Pd$: C, 63.8; H, 6.4%. (**4a**) Found: C, 63.2; H, 6.5%. Calcd for $C_{28}H_{32}P_2Pd$: C, 62.6; H, 6.0%.

Preparation of cis-*PdMe$_2$(PEt$_2$Ph)$_2$ (3a) (Method B).* To the heterogeneous yellow mixture of *trans*-$PdCl_2(PEt_2Ph)_2$ (3.5 g, 6.8 mmol) and Et_2O (40 ml) containing a small amount of PEt_2Ph (*ca*, 0.2 ml), Et_2O solution of MeLi (*ca.* 60 mmol) was added at −30 °C. The system was stirred at room temperature to give a heterogeneous pale yellow mixture containing a white precipitate of LiCl. Stirring was continued for 2 h. Evaporation (by pumping) of the ether phase, after hydrolysis at 0 °C, afforded a crude product of *cis*-$PdMe_2(PEt_2Ph)_2$ (**3a**) as confirmed by IR spectroscopy. The crude product was recrystallized from Et_2O to yield white crystals of **3a** (2.7 g, 85%). Similarly obtained by Method B was *cis*-$PdMe_2(PMePh_2)_2$ (**4a**) and *cis*-$PdMe_2(PEtPh_2)_2$ (**5a**). These complexes (**4a** and **5a**) were recrystallized from acetone (yield; **4a**, 48%; **5a**, 71%).

Characterization of **4a** was carried out by means of IR spectroscopy. Characterizations of **3a** and **5a** were carried out by means of IR and ^{1}H NMR spectroscopy, and elemental analysis. Anal. (**3a**) Found: C, 56.2; H, 8.0%. Calcd for $C_{22}H_{36}P_2Pd$: C, 56.4; H, 7.7%. (**5a**) Found: C, 63.5; H, 6.5%. Calcd for $C_{30}H_{36}P_2Pd$: C, 63.8; H, 6.4%.

Preparation of cis-*PdMe$_2$(PEt$_3$)$_2$ (1a) by the Ligand Exchange Reaction of* cis-*PdMe$_2$(PMePh$_2$)$_2$ (4a) with PEt$_3$ (Method C).* To a white heterogeneous mixture of *cis*-$PdMe_2(PMePh_2)_2$ (**4a**) (0.53 g, 0.99 mmol) and Et_2O (4 ml), PEt_3 (3.4 mmol) was added at room temperature to instantly yield a pale yellow clear solution. Evaporation of solvent by pumping afforded a pale yellow oil, which was washed with hexane at −70 °C to yield a white precipitate of *cis*-$PdMe_2(PEt_3)_2$ (**1a**). The product was filtered, washed with a small amount of Et_2O at −70 °C, and dried *in vacuo* (0.19 g, 52%). Characterization of **1a** was carried out by IR and ^{1}H NMR spectroscopy, and elemental analysis. Found: C, 45.7; H, 9.9%. Calcd for $C_{14}H_{36}P_2Pd$: C, 45.1; H, 9.7%.

Preparation of cis-*PdEt$_2$(PMe$_2$Ph)$_2$ (2b) (Method B).* To a Schlenk tube containing the mixture of $PdCl_2(PMe_2Ph)_2$ (1.6 g, 3.4 mmol) and EtLi (solid state) (0.28 g, 7.7 mmol) cooled at −70 °C, Et_2O (30 ml) containing a small amount of PMe_2Ph was added. On gradually raising the temperature the mixture became homogeneous at −20 °C. Stirring the solution at −20 °C for several hours yielded LiCl as a white precipitate, the amount of which increased gradually. After

concentration of the mixture to *ca.* 3 ml, hexane (30 ml) was added to the system at −10 °C. The solution was collected by filtration at the same temperature. Concentration of the filtrate to *ca.* 5 ml yielded a pale yellow precipitate, which was filtered, washed with a small amount of hexane at −70 °C and dried *in vacuo*. The product was recrystallized from cold Et_2O containing a small amount of PMe_2Ph to yield white crystals of *cis*-$PdEt_2(PMe_2Ph)_2$ (**2b**) (26%). Similarly obtained was *cis*-$PdEt_2(PEt_2Ph)_2$ (**3b**) by the use of $PdCl_2(PEt_2Ph)_2$ in place of $PdCl_2(PMe_2Ph)_2$ (13%). Since these complexes are too unstable for microanalysis, their characterization was carried out by means of IR and ^1H NMR spectroscopy, macroscopic analysis of Pd, and determination of the amount of ethane evolved on acidolysis with concd H_2SO_4. Anal. (**2b**) Found: Pd, 24.5%. Calcd for $C_{20}H_{32}P_2Pd$: Pd, 24.1%. (**3b**) Found: Pd, 21.1%. Calcd for $C_{24}H_{40}P_2Pd$: Pd, 21.4%. The amounts of ethane evolved by acidolysis with concd H_2SO_4 (mol/mol of complex): **2b**, 2.0; **3b**, 1.9.

Characterization of trans- *and* cis-*PdR_2L_2 by ^1H NMR and IR Spectroscopy (see also Table 2).* The ^1H NMR spectrum of *trans*-$PdMe_2L_2$ gives a triplet for the Pd–Me groups whereas that of *cis*-$PdMe_2L_2$ gives rise to a characteristic pattern of a distorted quartet ($A_3XX'A_3'$ pattern).[3] Other spectral patterns helping the assignment are a quintet pattern for the *trans* isomers and a doublet of triplets pattern for the *cis* isomers having tertiary phosphine ligands with ethyl group(s), and a triplet pattern for the *trans* isomers and a doublet for the *cis* isomers containing tertiary phosphine ligands with methyl group(s).

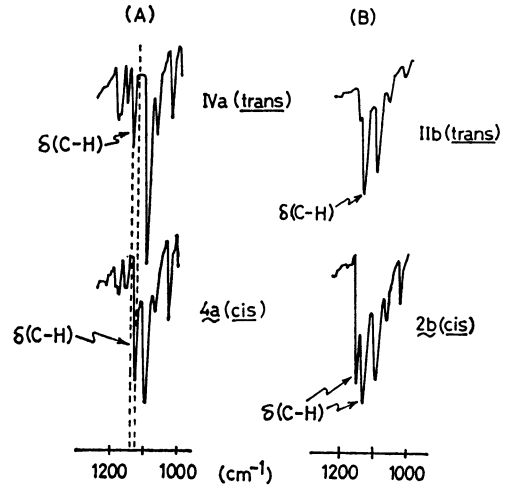


Fig. 7. Characteristic IR absorptions due to δ(C–H) of Pd–R groups of *trans*- and *cis*-PdR_2L_2 (KBr disc). (A) *trans*- and *cis*-$PdMe_2(PMePh_2)_2$. (B) *trans*- and *cis*-$PdEt_2(PMe_2Ph)_2$.

The IR spectra also serve in diagnosis of the isomers. The *trans* isomers show only one ν(Pd–C) band in the range of 455 to 462 cm^{-1} whereas the *cis* isomers give two ν(Pd–C) bands in the region of 465 to 515 cm^{-1}. Other characteristic bands helping to differentiate the *cis* and *trans* isomers are those arising from the C–H deformation of the Pd-bonded alkyl groups as shown in Fig. 7. The δ(C–H) vibration of the methylpalladium complexes gives a single absorption at 1120 cm^{-1} for the *cis* isomers and 1140 cm^{-1} for the *trans* isomers, whereas the δ(C–H) of the ethyl complexes gives two absorptions at 1130 and 1150 cm^{-1} for the *cis* isomers and a single band at 1140 cm^{-1} for the *trans* isomer. Since these absorptions are relatively unperturbed by the tertiary phosphine ligands, observation of these bands helps to determine the configuration of the isomers.

Mass Spectral Analysis of Deuterated Ethanes. Ethane produced by thermolysis was collected by using a Toepler pump through a dry ice–EtOH trap in order to avoid contamination by the solvent, and analyzed by mass spectrometer. To obtain accurate cracking patterns for each component, authentic samples of C_2D_6, CH_3CD_3, and C_2H_6 were prepared. CH_3CD_3 was prepared by the acidolysis of *trans*-$Pd(CH_2CD_3)_2(PMePh_2)_2$ (isotopic purity, 97%)[5] with concd H_2SO_4. CH_3CH_3 was used as purchased (Takachiho Chemical Industry). C_2D_6 was prepared by cracking *cis*-$Pd(CD_3)_2(PMePh_2)_2$ at 60 °C in toluene containing dmm. Since the deuterated ethane thus produced contains a small amount of CH_3CD_3, the true fragmentation pattern of CD_3CD_3 was obtained by subtracting the contribution of peaks due to CH_3CD_3 using the independently obtained fragmentation pattern of CH_3CD_3. The results of mass spectral analysis were reproducible within ±5%.

Reactions of trans-*$PdMe_2(PEt_2Ph)_2$ (IIIa) with MeLi and $AlMe_2(OEt)$.* To a homogeneous Et_2O solution (4 ml) of *trans*-$PdMe_2(PEt_2Ph)_2$ (IIIa) (0.25 g, 0.53 mmol), an ether solution of MeLi (1.1 mmol) was added by means of a syringe at room temperature and the system was stirred for 2 h at the same temperature. After hydrolysis at 0 °C, the solvent was evaporated from the solution to leave a white precipitate, which was washed with a small amount of Et_2O and dried *in vacuo* (0.23 g, 93%). The product was identified as *cis*-$PdMe_2(PEt_2Ph)_2$ (**3a**) on the basis of the IR and ^1H NMR spectroscopy.

On the other hand, the reaction of IIIa (0.098 g, 0.21 mmol) with $AlMe_2(OEt)$ (0.39 mmol) in Et_2O (2 ml at room temperature for 2 h yielded only *trans*-$PdMe_2(PEt_2Ph)_2$ (0.090 g, 92%) after concentration of the solution, washing with hexane at −70 °C, and drying *in vacuo*. Characterization of the product was carried out by IR spectroscopy.

Reactions of trans-*$PdMe_2(PEt_2Ph)_2$ (IIIa) and* cis-*$PdMe_2(PEt_2Ph)_2$ (**3a**) with CD_3Li.* To a homogeneous Et_2O (2 ml) solution of *trans*-$PdMe_2(PEt_2Ph)_2$ (IIIa) (0.16 g, 0.34 mmol), CD_3Li (isotopic purity, 99%) (0.37 mmol) was added by means of a syringe at room temperature. The system was stirred for 2 h at the same temperature. After hydrolysis at 0 °C, the solvent was removed by pumping to yield a white precipitate (0.14 g). The precipitate was identified as *cis*-$PdMe_2(PEt_2Ph)_2$ containing CD_3 groups on the basis of the IR spectrum (ν(C–D) (KBr disc) = 2190, 2080, and 2030 cm^{-1}). Ethane evolved on thermolysis of the reaction product in toluene (2 ml) containing dmm (50 μl) at 60 °C was collected and analyzed by mass spectrometry, and the ratio of CD_3CD_3, CH_3CD_3, and CH_3CH_3 in the ethane was found to be 0.18: 0.48: 0.34.

On the other hand, the reaction of *cis*-$PdMe_2(PEt_2Ph)_2$ (**3a**) (0.15 g, 0.31 mmol) and CD_3Li (0.32 mmol) in ether (2 ml) at room temperature for 2 h also gave *cis*-$PdMe_2(PEt_2Ph)_2$ containing CD_3 groups as a white precipitate after hydrolysis at 0 °C (0.13 g). The ethane evolved on thermolysis of the reaction products in toluene (2 ml) containing dimethyl maleate (50 μl) at 60 °C was determined to be consisted of CD_3CD_3, CH_3CD_3, and CH_3CH_3 in a molar ratio of 0.13: 0.40: 0.47 as measured by mass spectrometry.

Preparation and Thermolysis Products of cis-*$Pd(CD_3)_2(PMePh_2)_2$.* *cis*-$Pd(CD_3)_2(PMePh_2)_2$ was prepared by the reaction of $PdCl_2(PMePh_2)_2$ and CD_3Li (isotopic purity, 99%) in a similar manner to the preparation of **4a** and was identified by means of IR and ^1H NMR spectroscopy: ν(C–D) (KBr disc) = 2200, 2090, and 2040 cm^{-1}. In ^1H NMR

spectrum (100 MHz, in acetone-d_6, at room temperature), the complete absence of the signal due to Pd–CH_3 was confirmed.

It was confirmed by mass spectrometry that ethane evolved on thermolysis of *cis*-$Pd(CD_3)_2(PMePh_2)_2$ at 60 °C in toluene (2 ml) containing dmm (50 μl) consisted of CD_3CD_3 and CH_3CD_3 in a molar ratio of 0.95: 0.05.

Thermolysis of the mixture of *cis*-$Pd(CD_3)_2(PMePh_2)_2$ (0.061 g, 0.11 mmol) and *cis*-$Pd(CH_3)_2(PMePh_2)_2$ (0.067 g, 0.12 mmol) in toluene (2 ml) containing dmm (50 μl) at 60 °C gave CD_3CD_3, CH_3CD_3, and CH_3CH_3 in a molar ratio of 0.47: 0.05: 0.48.

Preparation and Thermolysis Products of cis-*Pd(CH_2CD_3)$_2$(PMe_2Ph)$_2$*.* CD_3CH_2Li was prepared by the reaction of CD_3CH_2Br (isotopic purity, 97%)[19] with Li in pentane. *cis*-$Pd(CH_2CD_3)_2(PMe_2Ph)_2$ was prepared by the reaction of $PdCl_2(PMe_2Ph)_2$ and CD_3CH_2Li in a similar manner to the preparation of **2b** and was characterized by means of IR and ^1H NMR spectroscopy: ν(C–D) (KBr disc)=2170, 2145, 2095, and 2040 cm^{-1}. In ^1H NMR spectrum (100 MHz, in acetone-d_6, at −40 °C), only a signal due to Pd–CH_2 was observed as broad $A_2XX'A'_2$ pattern.

Butane produced by thermolysis of *cis*-$Pd(CH_2CD_3)_2(PMe_2Ph)_2$ in toluene containing dmm at room temperature was collected by means of GLC after collecting the volatile materials in thermolysis solution by the trap-to-trap distillation. In ^1H NMR spectrum (100 MHz, in C_6D_6, at room temperature) of collected butane, the ratio of methyl and methylene protons was 7: 93.

Kinetic Studies of Thermolysis of $PdMe_2L_2$*.* A 30 ml Schlenk tube containing a Ph_2CH_2 solution (4 ml) of the complex (about 0.05 g) and the additive (dmm or tertiary phosphine) was sealed with a gas-tight rubber serum cap and evacuated. The Schlenk tube was placed in a thermostatted bath (HAAKE F2) controlled to ±0.5 °C. The rate constants for thermolysis of the complex were obtained by measureing the amount of ethane evolved with time. The amount of ethane was confirmed by means of GLC using ethylene as an internal standard.

Kinetic Studies of trans *to* cis *Isomerization of* $PdMe_2(PMePh_2)_2$*.* The appropriate amount of *trans*-$PdMe_2(PMePh_2)_2$ (IVa) and and *cis*-$PdMe_2(PMePh_2)_2$ (**4a**) or $PMePh_2$ were placed in a weighed NMR tube and the tube was connected to a vacuum line with a Teflon joint. After evacuation, CD_2Cl_2 was transferred by the trap-to-trap distillation. The amount of transferred CD_2Cl_2 was determined by weighing, and concentrations of the complexes and $PMePh_2$ were determined by measuring the weight of CD_2Cl_2 added. The sealed tube was placed in a thermostatted NMR probe (±1.0 °C). The amount of IVa on isomerization was determined by measuring the ratio of the area of Pd–Me signals of IVa and **4a**.

Reaction of trans-*Pd(CH_3)$_2$($PMePh_2$)$_2$ and* cis-*Pd(CD_3)$_2$($PMePh_2$)$_2$.* To a Schlenk tube containing *trans*-$Pd(CH_3)_2(PMePh_2)_2$ (IVa) (0.072 g, 0.13 mmol) and *cis*-$Pd(CD_3)_2(PMePh_2)_2$ (0.076 g, 0.14 mmol), CH_2Cl_2 (2 ml) was added by means of a syringe to yield a clear pale yellow solution. After stirring the system for 2 h at 30 °C, the solvent was removed by pumping to yield a white precipitate of *cis*-$PdMe_2(PMePh_2)_2$ containing CD_3 groups (0.14 g). Identification of the product was carried out by IR spectroscopy. Thermolysis of the reaction product in toluene (2 ml) containing dmm (50 μl) at 60 °C liberated CD_3CD_3, CH_3CD_3, and CH_3CH_3 in a molar ratio of 0.29: 0.46: 0.25.

This work was supported by a Grant-in-Aid for Scientific Research No. 555340 from the Ministry of Education, Science and Culture.

References

1) For example; P. M. Maitlis, "The Organic Chemistry of Palladium," Academic Press, New York (1971), Vols. 1 and 2; J. Tsuji, "Advances in Organometallic Chemistry," Academic Press, New York (1979), Vol. 17, p. 141; R. F. Heck, "Organotransition Metal Chemistry," Academic Press, New York (1974).

2) D. Milstein and J. K. Stille, *J. Am. Chem. Soc.*, **101**, 4981 (1979).

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

4) A. Yamamoto and T. Yamamoto, a review paper in preparation.

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

6) S. Komiya, T. A. Albright, R. Hoffmann, and J. K. Kochi, *J. Am. Chem. Soc.*, **98**, 7255 (1976).

7) G. Calvin and G. E. Coates, *J. Chem. Soc.*, **1960**, 2008.

8) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reaction," 2nd ed, John Wiley and Sons Inc., New York (1967).

9) R. Romeo, P. Ugualiati, and V. Belluco, *J. Mol. Catal.*, **1**, 325 (1975/76), and references cited therein.

10) G. W. Rice and R. S. Tobias, *J. Am. Chem. Soc.*, **99**, 2141 (1977), and references cited therein.

11) W. Mowat, S. G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, **1972**, 533.

12) T. Kohara, T. Yamamoto, and A. Yamamoto, *J. Organomet. Chem.*, **192**, 265 (1980).

13) J. K. Stille, private communication.

14) T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **93**, 3350 and 3360 (1971).

15) S. Komiya, T. Yamamoto, and A. Yamamoto, *Chem. Lett.*, **1978**, 1273; G. M. Whitesides, J. F. Gaasch, and E. R. Stedronsku, *J. Am. Chem. Soc.*, **94**, 5258 (1972); J. X. McDermott, J. F. White, and G. M. Whitesides, *ibid.*, **98**, 6521 (1976).

16) K. Tatsumi, R. Hoffmann, A. Yamamoto, and J. K. Stille, *Bull. Chem. Soc. Jpn.*, **54**, 0000 (1981).

17) K. L. Cheng, *Anal. Chem.*, **26**, 1894 (1954).

18) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, **1962**, 1490.

19) T. Yamamoto, T. Saruyama, Y. Nakamura, and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, **49**, 589 (1976).

20) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).

21) G. M. Kosolapoff and L. Maier, "Organic Phosphorus Compounds," Wiley-Interscience, New York (1972), Vol. 1, p. 78.

22) **Note added in proof.** A related independent study to the present work dealing with the *trans-cis* isomerization and reductive elimination of ethane from $PdMe_2L_2$ was recently reported by Gillie and Stille.[22] Their results mostly agree with ours except for the *trans-cis* isomerization mechanism.

23) A. Gillie and J. K. Stille, *J. Am. Chem. Soc.*, **102**, 4933 (1980).