sodium chloride solution (20 mL), and extracted with ether (50 mL × 3). The organic layer was filtered and dried over anhydrous magnesium sulfate. Distillation gave 1.38 g (92%) of phenyl(trimethylsilyl)carbinol (7):[7] 60-MHz ^1H NMR ($CDCl_3$) δ 0.00 (s, 9, $SiCH_3$), 1.85 (s, 1, OH), 4.42 (s, 1, CH), 7.15 (s, 5, C_6H_5); $[\alpha]^{24}_D$ −48.40° (*c* 1.78, toluene); $[\alpha]^{21}_D$ −39.56° (neat) [Lit.[7] $[\alpha]^{25}_D$ 93.0° (neat)].

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Stepwise Displacement of the Tertiary Phosphine Ligand in Square-Planar $[PdR_2L_2]$-Type Complexes by Organolithium Reagents with Stereochemical Retention Affording Organopalladate Complexes

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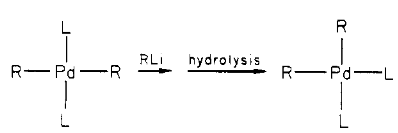
Reactions of *trans*- and *cis*-$[PdR_2L_2]$ (R = Me, Et, Ph; L = tertiary phosphine) with R′Li (R′ = Me, Ph) in ether or THF solution lead to stepwise displacement of L by R′ with stereochemical retention to afford alkylpalladate complexes $Li[PdR_2R'L]$ and $Li_2[PdR_2R'_2]$, as established by means of ^1H, ^{31}P, and ^{13}C NMR spectroscopy. The displacement of PEt_3 in *trans*-$[PdPh_2(PEt_3)_2]$ by MeLi is a slow process, and the rate is independent of the MeLi concentration with indication of a dissociative mechanism generating a three-coordinate, T-shaped intermediate, whereas the reaction of PdR_2L_2 (R = Me, Et) with MeLi is much faster. Displacement of PEt_2Ph in $Li[PdMe_3(PEt_2Ph)]$ by MeLi is a slow process and first order in concentrations of the complex and MeLi and independent of L. An associative mechanism involving a five-coordinate intermediate is proposed for the second displacement to account for the stereochemical retention. Factors influencing the ^1H and ^{13}C NMR chemical shifts of the neutral and palladate complexes are discussed.

Introduction

In contrast to the well-known anionic transition-metal complexes having π-acceptor ligands such as CO, examples of more electron-rich anionic organotransition-metal complexes are still limited[1] except for the conspicuously well-utilized alkylcuprate complexes[2a] and recently developed alkali-metal–transition-metal π complexes.[2b] For palladium, which ranks among the most frequently employed transition metals for organic synthesis,[1,3] the chemistry of organopalladate complexes has been very poorly exploited.[4] In some cases, where palladium compounds are used in combination with alkylating or arylating agents such as alkyl- (aryl-) lithium or magnesium compounds, particularly when the alkylating agent is used in excess to the palladium complexes, the possibility of formation of alkylpalladate complexes is considered not at all negligible, although generally neutral or cationic organopalladium complexes have been postulated in most cases.[3,5]

In the course of our studies on the preparation of dialkylpalladium complexes having two tertiary phosphine ligands,[6,7] we have observed that *trans*-$[PdR_2L_2]$ (R = alkyl group; L = monodentate tertiary phosphine) can be prepared by the reaction of bis(acetylacetonato)palladium with an alkylaluminum in the presence of L, whereas *cis*-$[PdR_2L_2]$ can be synthesized by treating bis(tertiary phosphine)palladium dihalides with an excess of an alkyllithium followed by hydrolysis of the unreacted alkyllithium. Examination of the cause of this puzzling effect of the nature of the alkylating agent on the configuration of the final product led us to the finding that the isomerization of *trans*-$[PdR_2L_2]$ to the cis isomer was promoted by addition of alkyllithium to the system.



In order to account for the trans to cis isomerization, we

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(1) For example: Heck, R. F. "Organotransition Metal Chemistry"; Academic Press: New York, 1974. Collman, J. P.; Hegedus, L. S. "Principles and Application of Organotransition Metal Chemistry"; University Science Book: Mill Valley, CA 1980. Tsuji, J. "Organic Synthesis by Means of Transition Metal Complexes"; Springer-Verlag: Berlin, 1975. Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

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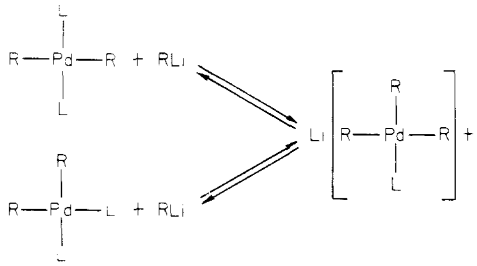
previously proposed a mechanism involving a trialkylpalladate intermediate on the basis of the observation of alkyl group scrambling in $[PdR_2L_2]$ with the alkyllithium in a study using deuterium-labeled methyllithium (eq 1).[7]

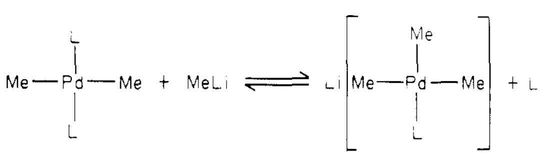


$$\left.\begin{array}{l}\mathrm{R-\underset{L}{\overset{L}{Pd}}-R + RLi}\\ \mathrm{R-\underset{L}{\overset{R}{Pd}}-L + RLi}\end{array}\right\} \rightleftharpoons \mathrm{Li}\left[\mathrm{R-\underset{L}{\overset{R}{Pd}}-R}\right] + \mathrm{L} \qquad (1)$$

Further spectroscopic study of the system revealed in fact the formation of the trialkylpalladate species and, furthermore, its conversion to a tetraalkylpalladate complex. We now report here the results of spectroscopic studies which reveal that the conversion of the dialkyl species to the trialkylpalladate proceeds by a dissociative process, whereas the transformation of the trialkylpalladate to the tetraalkylpalladate proceeds by an associative mechanism with stereochemical retention in the square-planar geometry of Pd(II) complexes.

Results

Reaction of $[PdMe_2L_2]$ (1) with MeLi. On addition of 2 mol of methyllithium per mol of *trans*-$[PdMe_2(PEt_2Ph)_2]$, *trans*-**1a**, in diethyl ether at room temperature, the initial triplet ^1H NMR signal of the palladium-bonded methyl groups is instantly transformed to two sets of doublets in a 1:2 intensity ratio at −0.30 and −0.79 ppm (upfield from tetramethylsilane, Me_4Si) as shown in Figure 1A. The other singlet at −1.97 ppm in Figure 1A arises from unreacted MeLi. The doublets collapse to singlets on irradiation of the sample solution with the resonance frequency for phosphorus. On the other hand, the $^{31}P\{^1H\}$ NMR spectrum of the same solution indicates the spectral change of the initial $^{31}P\{^1H\}$ NMR spectrum of *trans*-**1a** having a single peak at 31.8 ppm (downfield from PPh_3 added as an external reference) to the spectrum having a new singlet at 24.6 ppm ascribed to the coordinated phosphine ligand in the newly formed complex and another singlet at −10.9 ppm (upfield from PPh_3) arising from the PEt_2Ph ligand liberated from **1a**. The spectral change suggests the rapid conversion of *trans*-$[PdMe_2L_2]$ to Li-$[PdMe_3L]$ with release of PEt_2Ph on addition of MeLi to **1a** (eq 2).



$$\mathrm{Me-\underset{L}{\overset{L}{Pd}}-Me + MeLi} \rightleftharpoons \mathrm{Li}\left[\mathrm{Me-\underset{L}{\overset{Me}{Pd}}-Me}\right] + \mathrm{L} \qquad (2)$$

trans-1
1a, L = PEt_2Ph

2
2a, L = PEt_2Ph

The exactly same pattern of the ^1H and $^{31}P\{^1H\}$ NMR are observed when *cis*-**1a** instead of *trans*-**1a** was used, supporting the formation of the trialkyl(tertiary phosphine)palladate **2** in the reaction starting either from *trans*-**1a** or *cis*-**1a**, in agreement with our previous proposal as expressed by eq 1. In the ^1H NMR spectra, the doublet at lower field can be assigned to the methyl group trans to the phosphine ligand and the doublet at higher field with twice the intensity can be ascribed to the methyl groups cis to the phosphine ligand.

Following the instantaneous conversion of **1a** to **2a**, a slow reaction ensues as observed in the ^1H NMR spectrum by the decrease of the two sets of doublets and of the singlet at −1.97 ppm and the growing of a new singlet at −0.82 ppm which overlaps with one of the doublet peaks of the methyl groups Figure 1A(c). The reaction reaches an equilibrium in several hours at room temperature. Absence of coupling to phosphorus in the new species suggests the formation of a methylpalladium complex without a coordinated tertiary phosphine. The most likely candidate is $Li_2[PdMe_4]$, **3a**, produced by the displacement of the tertiary phosphine ligand by MeLi as shown in eq 3. A related palladate complex with pentafluorophenyl groups has been recently prepared by Uson.[4]

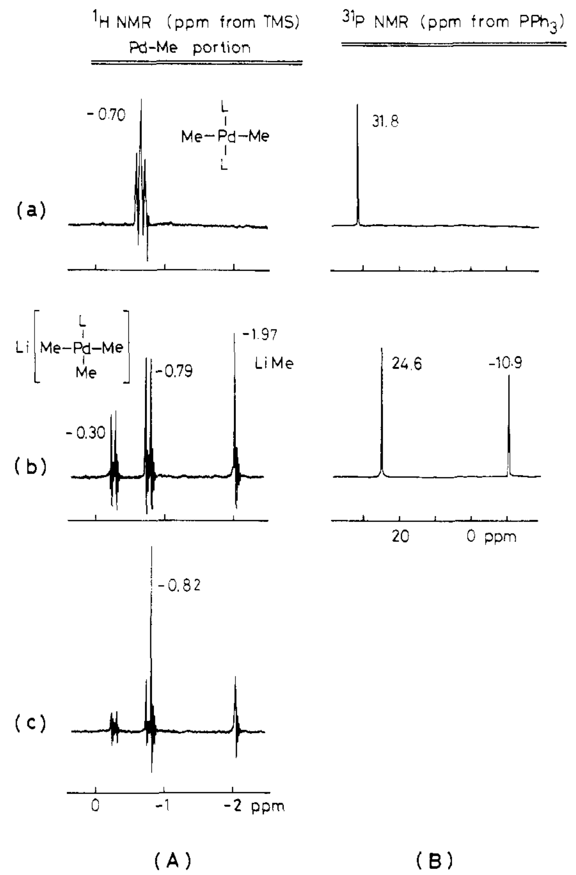
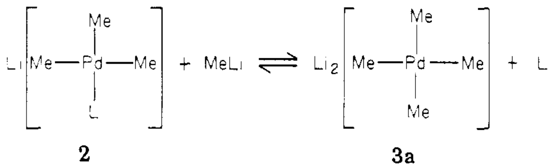


Figure 1. (A) ^1H NMR spectra in the Pd-*Me* portion (parts per million from Me_4Si, downfield positive) and (B) $^{31}P\{^1H\}$ NMR spectra (parts per million from PPh_3, downfield positive), in Et_2O at room temperature: (a) *trans*-$[PdMe_2(PEt_2Ph)_2]$, *trans*-**1a**; (b) immediately after the treatment of *trans*-**1a** with LiMe in a 1:2 molar ratio, (c) after reaching an equilibrium for the solution of b.



$$\mathrm{Li}\left[\mathrm{Me-\underset{L}{\overset{Me}{Pd}}-Me}\right] + \mathrm{MeLi} \rightleftharpoons \mathrm{Li_2}\left[\mathrm{Me-\underset{Me}{\overset{Me}{Pd}}-Me}\right] + \mathrm{L} \qquad (3)$$

2

3a

To substantiate the equilibrium as expressed by eq 3, the intensity change of the peaks due to the methyl group trans to the phosphine in **2** and the free MeLi as well as the new singlet peak at −0.82 ppm was plotted in Figure 2. It can be seen from Figure 2 that the intensities of the methyl group trans to L and of the free MeLi decrease with time in exactly the same manner, whereas the new peak at −0.82 ppm develops quite rapidly. It was confirmed from comparison of the peak intensity data that the new species having four methyl groups was generated at the cost of one equivalent each of MeLi and **2** in support of eq 3.

Table I. ^1H NMR Data of $[PdR_2L_2]$, $Li[PdR_2R'L]$, and $Li_2[PdR_2R'_2]$[a]

complex	Pd-R	chem shift,[b] ppm from Me_4Si in Et_2O	chem shift,[b] ppm from Me_4Si in THF
trans-**1a**, *trans*-$[PdMe_2(PEt_2Ph)_2]$	$Pd-CH_3$	−0.70 (t,[c] J = 5.0[d])	−0.67 (t, J = 5.0)
cis-**1a**, *cis*-$[PdMe_2(PEt_2Ph)_2]$	$Pd-CH_3$	+0.11 (q)	+0.08
cis-**1b**, *cis*-$[PdMe_2(PEt_3)_2]$	$Pd-CH_3$	−0.03 (q)	
trans-**1c**, *trans*-$[PdEt_2(PMe_2Ph)_2]$	$Pd-CH_2-CH_3$		+0.95 (t, J = 7.5)
	$Pd-CH_2-CH_3$		+0.41 (sex., J = 8.0)
$[PdMe_2(tmed)]$[e]	$Pd-CH_3$	−0.30 (s)	
2a, $Li[PdMe_3(PEt_2Ph)]$	$Pd-CH_3$ trans to L	−0.30 (d)	−0.26 (d, J = 5.6)
	$Pd-CH_3$ cis to L	−0.79 (d)	−0.76 (d, J = 6.2)
2b, $Li[PdMe_3(PEt_3)]$	$Pd-CH_3$ trans to L	−0.45 (d, J = 5.0)	
	$Pd-CH_3$ cis to L	−0.85 (d, J = 6.5)	
trans-**2e**, *trans*-$Li[PdPh_2Me(PEt_2Ph)]$	$Pd-CH_3$	−0.13 (d)	−0.18 (d)
trans-**2d**, *trans*-$Li[PdPh_2Me(PEt_3)]$	$Pd-CH_3$	−0.15 (d)	−0.27 (d, J = 6.1)
trans-**2c**, *trans*-$Li[PdEt_2Me(PMe_2Ph)]$	$Pd-CH_2-CH_3$		+1.09 (t, J = 7.5)
	$Pd-CH_2-CH_3$		+0.05 (qui., J = 8.2)
	$Pd-CH_3$		−0.24 (d, J = 6.5)
trans-**2f**, *trans*-$Li[PdPhMe_2(PEt_2Ph)]$	$Pd-CH_3$		−0.67 (d, J = 6.4)
cis-**2f**, *cis*-$Li[PdPhMe_2(PEt_2Ph)]$	$Pd-CH_3$ trans to L		−0.26 (d, J = 6.0)
	$Pd-CH_3$ cis to L		−0.68 (d, J = 6.0)
3a, $Li_2[PdMe_4]$	$Pd-CH_3$	−0.82 (s)	−0.79 (s)
trans-**3d**, *trans*-$Li_2[PdPh_2Me_2]$	$Pd-CH_3$	−0.52 (s)	−0.63 (s)
cis-**3d**, *cis*-$Li_2[PdPh_2Me_2]$	$Pd-CH_3$		−0.68 (s)
LiMe		−1.97 (s)	−2.06 (s)

[a] R and R′ represent alkyl and/or aryl group(s) and L stands for tertiary phosphine. [b] Downfield positive. [c] Abbreviation: s, singlet; d, doublet; t, triplet; q, quartet; qui, quintet; sex., sextet. [d] J means $^3J(H-P)$, values in hertz. Since the related sign has not been determined, the absolute value is presented. [e] tmed stands for *N*,*N*,*N*′,*N*′-tetramethylethylenediamine.

Table II. ^{31}P NMR Data of $[PdR_2L_2]$ and $Li[PdR_2R'L]$[a]

complex	chem shifts,[b] ppm from PPh_3 in Et_2O	chem shifts,[b] ppm from PPh_3 in THF
trans-**1a**, *trans*-$[PdMe_2(PEt_2Ph)_2]$	31.8	31.8
cis-**1a**, *cis*-$[PdMe_2(PEt_2Ph)_2]$	16.6	17.1
trans-**1e**, *trans*-$[PdPh_2(PEt_2Ph)_2]$		20.3
trans-**1d**, *trans*-$[PdPh_2(PEt_3)_2]$	17.2	17.3
2a, $Li[PdMe_3(PEt_2Ph)]$	24.6	24.6
trans-**2e**, *trans*-$Li[PdPh_2Me(PEt_2Ph)]$		16.1
trans-**2d**, *trans*-$Li[PdPh_2Me(PEt_3)]$		16.2
PEt_2Ph	−10.9	−10.7
PEt_3	−13.8	−13.8

[a] R and R′ represent alkyl and/or aryl group(s) and L stands for tertiary phosphine. [b] Down field positive.

It is thus indicated that the reaction of *trans*- or *cis*-$[PdMe_2L_2]$ with MeLi is a two-step equilibrium process as summarized by eq 4.

$$\underset{\mathbf{1}}{\textit{trans-}\text{ or }\textit{cis-}[PdMe_2L_2]} \underset{}{\overset{+MeLi,\ -L}{\rightleftharpoons}} \underset{\mathbf{2}}{Li[PdMe_3L]} \overset{+MeLi,\ -L}{\rightleftharpoons} \underset{\mathbf{3}}{Li_2[PdMe_4]} \quad (4)$$

When an appropriate amount of the phosphine is added to the equilibrium system of eq 4, an increase in the amount of **1** and a decrease in the amount of **3** are observed, the fact implying an equilibrium shift from right to left in eq 4. Because of these equilibria, attempts to isolate **2** and **3** were unsuccessful. The ^1H and $^{31}P\{^1H\}$ NMR data of the palladate complexes **2** and **3** are summarized, together with spectroscopic data of other complexes, in Table I and II.

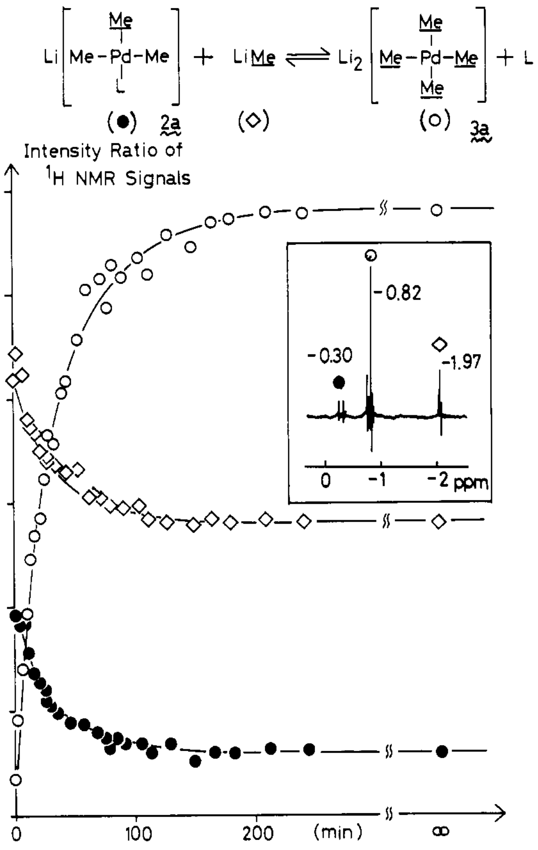


Figure 2. Time course of relative intensity of ^1H NMR signals on the reaction of $Li[PdMe_3(PEt_2Ph)]$, **2a**, with LiMe in Et_2O at 21.7 °C affording $Li_2[PdMe_4]$, **3a**: ●, the doublet at −0.30 ppm due to the methyl group trans to the phosphine ligand in **2a**; ○, the singlet at −0.82 ppm due to **3a**; ◇, the singlet at −1.97 ppm due to LiMe.

The ^{13}C NMR spectra in tetrahydrofuran (THF) solution also support the formation of trimethylpalladate **2**, and tetramethylpalladate **3** (see Table III). In the system of *trans*-**1a**–MeLi mixed in a 1:2 ratio, two sets of doublets at 0.4 and −5.2 ppm (downfield positive from the external reference of Me_4Si) were observed together with a triplet at −6.0 ppm ascribed to the methyl carbons of the starting complex *trans*-**1a** and a singlet at −15.5 ppm assigned to the methyl carbon of unreacted MeLi. The doublet at 0.4 ppm can be ascribed to the methyl carbon trans to the phosphine and the doublet at −5.2 ppm to the methyl carbons cis to the phosphine of **2a**. After the solution was

Table III. ^{13}C NMR Data of [PdR$_2$L$_2$], Li[PdR$_2$R′L], and Li$_2$[PdR$_2$R′$_2$][a]

			ethyl		phenyl			
complex		methyl, CH$_3$	CH$_2$-CH$_3$	-CH$_2$-CH$_3$	C$_b$[b]	C$_o$	C$_m$	C$_p$
trans-[PdMe$_2$(PEt$_2$Ph)$_2$], *trans*-**1a**	R	−6.0 (t, *J* = 10)						
	L		17.6 (t, *J* = 12)	9.1 (s)	135.0 (t, *J* = 20)	133.5 (t, *J* = 6)	128.4 (t, *J* = 4)	129.7 (s)
cis-[PdMe$_2$(PEt$_2$Ph)$_2$], *cis*-**1a**	R	+5.5 (dd, *J* = 110, *J* = 16)						
	L		17.7 (t, *J* = 10)	8.8 (s)	137.4 (t, *J* = 14)	132.7 (t, *J* = 5)	128.5 (t, *J* = 4)	129.4 (s)
trans-[PdPh$_2$(PEt$_3$)$_2$], *trans*-**1d**	R				169.2 (t, *J* = 13)	139.5 (s)	126.9 (s)	122.1 (s)
	L		15.2 (t, *J* = 13)	8.3 (s)				
trans-[PdPh$_2$(PEt$_2$Ph)$_2$], *trans*-**1e**	R				167.6 (t, *J* = 12)	139.7 (t, *J* = 2)	126.6 (s)	122.1 (s)
	L		16.2 (t, *J* = 13)	10.1 (d, *J* = 15)	133.8 (t, *J* = 20)	132.4 (t, *J* = 5)	129.5 (s)	128.5 (s)
Li[PdMe$_3$(PEt$_2$Ph)], **2a**	R	+0.4 (d, *J* = 123) −5.2 (d, *J* = 10)	[trans to L] [cis to L]					
	L		17.6 (d, *J* = 17)	8.2 (s)	138.1 (d, *J* = 23)	133.0 (d, *J* = 11)	128.0 (d, *J* = 9)	128.5 (s)
trans-Li[PdPh$_2$Me(PEt$_2$Ph)], *trans*-**2e**	R	+2.9 (d, *J* = 112)			179.6 (d, *J* = 13)	140.7 (d, *J* = 2)	125.6 (s)	120.3 (s)
	L		17.1 (d, *J* = 17)	7.9 (s)	138.0 (d, *J* = 23)	132.6 (d, *J* = 10)	128.0 (s)	127.7 (s)
trans-Li[PdPh$_2$Me(PEt$_3$)], *trans*-**2d**	R	+2.2 (d, *J* = 114)			180.0 (d, *J* = 12)	140.7 (d, *J* = 4)	125.8 (s)	120.3 (s)
	L		16.2 (d, *J* = 17)	8.3 (s)				
Li$_2$[PdMe$_4$], **3a**	R	−8.3 (s)						
trans-Li$_2$[PdPh$_2$Me$_2$], *trans*-**3d**	R	+1.2 (s)			159.0 (s)	141.8 (s)	125.8 (s)	121.4 (s)
LiMe		−15.5 (s)						
PEt$_3$			19.4 (d, *J* = 56)	9.9 (d, *J* = 15)				
PEt$_2$Ph			20.9 (d, *J* = 12)	10.2 (d, *J* = 15)	139.7 (d, *J* = 18)	312.9 (d, *J* = 18)	129.1 (d, *J* = 4)	128.7 (s)

[a] R and R′ represent alkyl and/or aryl group(s) and L stands for tertiary phosphine. In THF at room temperature. Chemical shift: ppm from Me$_4$Si (downfield positive). Coupling constant: Hz, coupling between C and P. Since the relative sign has not been determined, the absolute value is represented. Abbreviation: s, singlet; d, doublet; t, triplet; dd, doublet of doublets. [b] C$_b$, Pd- or P-bonded carbon.

allowed to stand for several hours at room temperature, a singlet corresponding to the methyl carbons in **3a** was observed at −8.3 ppm.

A comparison of the coupling constant ^3J(H–P) with ^2J(C–P) of **2a** in THF is of interest. The coupling constant between the phosphorus atom in phosphine ligand and the methyl protons trans to it (^3J(trans-H–P) = 5.6 Hz) is less than that between phosphorus in the phosphine ligand and the methyl protons cis to it (^3J(cis-H–P) = 6.2 Hz), whereas the coupling constant between the phosphine P and the methyl carbon trans to it (^2J(trans-C–P) = 123 Hz) is greater than that between P in the phosphine and the methyl carbons cis to it (^2J(cis-C–P) = 10 Hz).

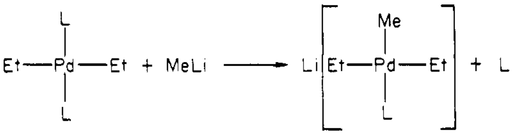
The reaction of Na$_2$PdCl$_4$ or Pd(OAc)$_2$ suspended in Et$_2$O solution with MeLi led to deposition of palladium metal without affording **3**. Thus the presence of the tertiary phosphine serves to stabilize the dimethyl and trimethyl complexes **1** and **2** and helps to stabilize the whole system in equilibria. In fact, it is not necessary to start from the isolated dimethylpalladium complex **1** in order to produce **2** and **3** in situ. Addition of PEt$_2$Ph to a heterogeneous ether solution of Na$_2$PdCl$_4$ yields a yellow precipitate of PdCl$_2$(PEt$_2$Ph)$_2$. Treatment of the system with an ether solution of MeLi at room temperature converts it into a colorless solution containing the white powder LiCl. The ^{1}H NMR spectrum of the supernatant solution shows the existence of *cis*-**1a**, *trans*-**2a**, and **3a**.

Similar displacement of the tertiary phosphine ligands in [PdR$_2$L$_2$] by the methyl group in MeLi is observed also in a dimethylpalladium complex with triethylphosphine ligands (see Table I and II). The A$_3$XX′A′$_3$ pattern of the ^{1}H NMR signal due to the Pd-bonded methyl groups in *cis*-**1b** disappeared with increase of the two sets of doublets in a 1:2 intensity ratio at −0.45 and −0.85 ppm, suggesting the formation of Li[PdMe$_3$(PEt$_3$)], **2b**. The former doublets are assigned to the Pd-bonded methyl groups trans to the triethylphosphine and the latter to the two methyl groups cis to the triethylphosphine. As in the PEt$_2$Ph-containing complex **2a**, the ^3J(H–P) coupling constant due to the trans phosphine was slightly smaller than the coupling constant due to the cis phosphine. Following the formation of **2b**, growth of the singlet at −0.82 ppm due to Li$_2$[PdMe$_4$] is observed.

Reaction of [PdEt$_2$L$_2$] with MeLi. The ^{1}H NMR spectrum of *trans*-[PdEt$_2$(PMe$_2$Ph)$_2$], *trans*-**1c**, in THF solution exhibits a triplet at 0.95 ppm due to the methyl and a sextet at 0.41 ppm due to the methylene in the Pd-bonded ethyl groups.

In the reaction of *trans*-**1c** with an equimolar amount of MeLi in THF at room temperature, a doublet ^{1}H NMR signal at −0.24 ppm, a quintet at 0.05 ppm, and a triplet at 1.09 ppm arise at the expense of the signals due to the starting complex *trans*-**1c**. The spectrum also shows the doublet signal assigned to the methyl protons of the liberated PMe_2Ph in addition to the doublet ascribed to the methyl protons of the coordinated PMe_2Ph ligand in approximately 1:1 ratio.

These ^1H NMR data indicate the formation of Li[$PdEt_2Me(PMe_2Ph)$], **2c**, by the reaction of *trans*-**1c** with MeLi. The doublet at −0.24 ppm is assigned to the methyl protons of the Pd-bonded methyl group, the quintet at 0.05 ppm to the methylene protons, and the triplet at 1.09 ppm to the methyl protons of the Pd-bonded ethyl groups. If the palladate complex **2c** has a cis configuration, two ethyl groups directly bonded to palladium would be magnetically different. The ^1H NMR spectrum, however, shows the existence of only one kind of the ethyl groups, indicating that the complex **2c** produced in the reaction of *trans*-**1c** with MeLi has a trans configuration.



(5)

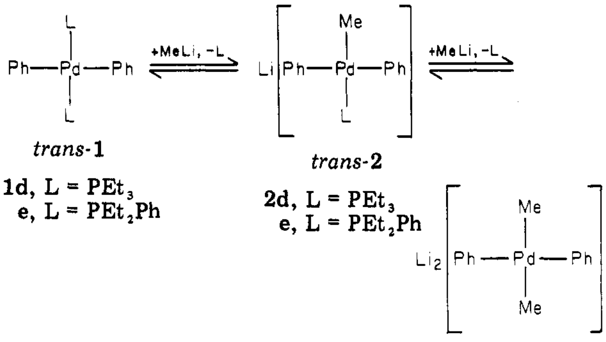
trans-**1c** *trans*-**2c**

L = PMe_2Ph

The result shows that the tertiary phosphine trans to the other phosphine ligand has been displaced by the methyl group from MeLi with *retention* of the stereochemistry. Study of the reaction of the dimethylpalladium complexes with ethyllithium was not feasible because of the instability of ethyllithium in THF.

Allowing the reaction mixture of *trans*-**1c** with methyllithium to stand for a longer period of several hours caused further reaction as reflected by the development of a complicated NMR spectrum that suggests the occurrence of isomerization of *trans*-**2c** to *cis*-Li[$PdMe_2EtL$], *trans*-Li[$PdMe_2EtL$], Li[$PdMe_3L$], and other species accompanied by the evolution of ethane. Because of the decomposition of the resulting complexes and of the complexity of the spectrum, no further study was attempted.

Reaction of [$PdPh_2L_2$] with MeLi. For obtaining information regarding the stereochemistry of the ligand displacement reaction of [PdR_2L_2] by alkyllithium, the reaction of *trans*-[$PdPh_2(PEt_3)_2$], *trans*-**1d**, with MeLi was examined. The result can be expressed by eq 6, representing the stereospecific stepwise displacement of the tertiary phosphine ligand by the methyl group in MeLi with retention of the original configuration in **1d**.



trans-**1**
1d, L = PEt_3
e, L = PEt_2Ph

trans-**2**
2d, L = PEt_3
e, L = PEt_2Ph

(6)

trans-**3d**

The ^1H NMR spectrum of the THF solution of *trans*-[$PdPh_2(PEt_3)_2$], *trans*-**1d**, after its treatment with an equimolar amount of MeLi shows a slow conversion of *trans*-**1d** to *trans*-**2d** as indicated by development of a doublet at −0.27 ppm arising from the methyl group in addition to the singlet peak at −2.06 ppm due to the remaining MeLi. When *trans*-**1d** was mixed with more than an equimolar amount of MeLi, a further spectral change was observed: a singlet developed at −0.63 ppm at the expense of the doublet at −0.27 ppm and of the singlet at −2.06 ppm (Figure 3), suggesting the occurrence of the stepwise reactions represented by eq 6.

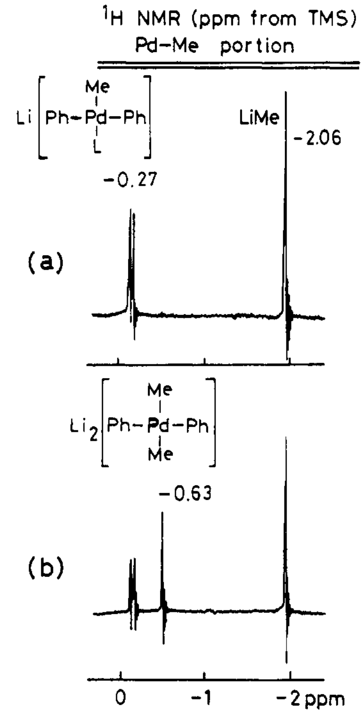


Figure 3. ^1H NMR spectra in the Pd–Me portion (parts per million from Me_4Si) in THF at room temperature: 3 h (a) and 9 days (b) after the treatment of *trans*-[$PdPh_2(PEt_3)_2$], *trans*-**1d**, with LiMe in 1:1 (a) and 1:2 (b) molar ratios at room temperature.

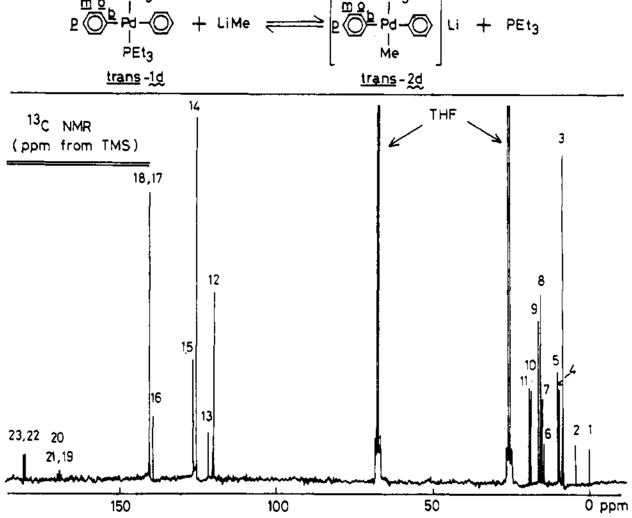


Figure 4. ^{13}C NMR spectrum (parts per million from Me_4Si, downfield positive) in THF at room temperature 1 h after *trans*-[$PdPh_2(PEt_3)_2$] was mixed with MeLi in a 1:1 molar ratio.

In order to determine the configurations of *trans*-**2d** and *trans*-**3d**, the $^{13}C\{^1H\}$ NMR spectrum of *trans*-**1d** in THF after it was mixed with an equimolar amount of MeLi in THF was observed after 1 day (Figure 4). The spectrum of the reaction mixture is considerably complicated but can be accounted for in terms of a mixture of *trans*-**1d**, *trans*-**2d**, and liberated PEt_3 by comparison with the $^{13}C\{^1H\}$ NMR spectra of *trans*-**1d** and free PEt_3. Each peak in Figure 4 is numbered from the high field to the lower field except for the strong peaks centered at 26.3 and 68.1 ppm due to THF. The two doublets [4, 5] and [10, 11] are due to the methyl and methylene carbons coupled to phosphorus in free PEt_3 released from **1d** on reaction with MeLi. Each counterpart of the doublet [4, 5] splits to a quartet and each counterpart of the doublet [10, 11] splits to a triplet in the nondecoupled spectrum, supporting the assignment of the signals to the methyl and methylene groups in free PEt_3, respectively. The $^{13}C\{^1H\}$ NMR signals of the starting complex *trans*-**1d** are observed as follows. The signal [3] is due to the methyl carbons in the PEt_3 ligands. The signals [6, 7, 8] are triplets arising from the methylene carbons in the coordinated PEt_3 split by virtual coupling to two mutually trans-situated phosphorus nuclei. The peak [8] overlaps with a part of the doublet [8, 9] due to *trans*-**2d**. The peaks [13], [15], [16], and [19, 20, 21] are assigned to the phenyl carbons bonded to Pd in the starting complex *trans*-**1d**. They are respectively assigned in the order to the C_p (para), C_m (meta), C_o (ortho), and C_b (Pd-bonded) carbons of the phenyl groups. The triplet [19, 20, 21] indicates the trans configuration of the starting complex **1d**. The rest of the signals can be assigned to *trans*-**2d** existing as the sole anionic species. The peaks [1, 2] are the doublet due to the methyl carbon in the methyl group bonded to Pd in *trans*-**2d** coupled to the phosphorus in the PEt_3 ligand. The singlet [3] is due to the methyl carbons in the coordinated PEt_3 ligand in *trans*-**2d** overalpped with the signal of methyl carbons in the coordinated PEt_3 in *trans*-**1d**. The doublet [8, 9] is due to the methylene carbons in the coordinated PEt_3 in *trans*-**2d** partly overlapped with the triplet of the coordinated PEt_3 in *trans*-**1d**. Signals [12], [14], [17, 18], and [22, 23] in the lower field arise from the phenyl carbons in the palladate complex *trans*-**2d**. They are assigned in turn to the C'_p C'_m C'_o, and C'_b (Pd-bonded) carbons in the phenyl groups in *trans*-**2d**. If the palladate complex should have phenyl groups situated in mutually cis positions, the phenyl groups whould be magnetically nonequivalent. The presence of only one kind of the phenyl groups strongly suggests the trans isomer existing as the sole diphenylmonomethylpalladate species. The splitting to doublets of the carbon signals [1, 2], [8, 9], [17, 18], and [22, 23] by coupling to the phosphorus in the coordinated mono tertiary phosphine ligand supports the formulation of the palladate complex as *trans*-**2d** shown in eq 6 and Figure 4.

The ^{31}P NMR spectrum of the THF solution of *trans*-**1d** after its treatment with an equimolar amount of MeLi also supports the formation of *trans*-**2d**. A singlet at 16.2 ppm appears together with a singlet at −13.8 ppm due to free PEt_3 liberated from *trans*-**1d** at the expense of a singlet at 17.3 ppm due to the starting complex *trans*-**1d** (see Table II).

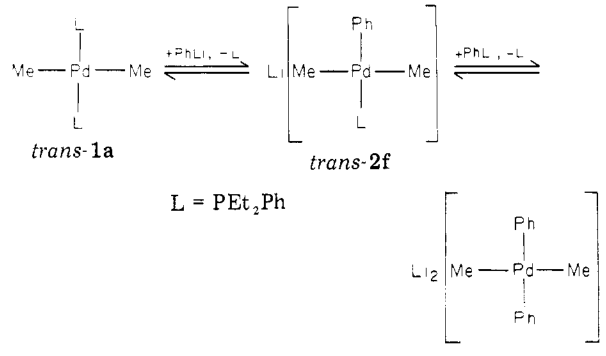
The ^1H NMR spectrum of the THF solution containing *trans*-**1d** mixed with more than an equimolar amount of MeLi shows a singlet at −0.63 ppm in addition to the doublet at −0.27 ppm arising from the methyl protons of the Pd-bonded methyl group in *trans*-**2d** and a singlet at −2.06 ppm due to free MeLi. The ^{13}C NMR spectrum of the same solution exhibits a singlet at 1.2 ppm arising from Pd-bonded methyl groups and singlets at 121.4, 125.8, 141.8, and 159.0 ppm due, in turn, to the C''_p, C''_m, C''_o, and C''_b carbons in the phenyl groups bonded to palladium, together with signals due to *trans*-**2d**, free PEt_3, and MeLi. The ^1H and ^{13}C NMR spectra suggest the formation of the dianionic palladate $Li_2[PdPh_2Me_2]$, **3d**. Since **3d** is formed from *trans*-**2d**, it probably has a trans configuration. The trans geometry of $Li_2[PdPh_2Me_2]$ (**3d**) is further supported by the appearance of a singlet at −0.63 ppm in ^1H NMR spectrum when *trans*-$[PdMe_2(PEt_2Ph)_2]$ is treated with LiPh in THF solution (vide infra).

A completely analogous spectroscopic pattern is observed when PEt_2Ph-coordinated complex *trans*-$[PdPh_2(PEt_2Ph)_2]$, *trans*-**1e**, is treated with MeLi. The spectroscopic change is consistent with the slow formation of *trans*-$Li[PdPh_2Me(PEt_2Ph)]$, *trans*-**2e**, followed by its slow conversion into *trans*-$Li_2[PdPh_2Me_2]$, *trans*-**3d**.

Thus the stepwise displacement of the tertiary phosphine ligands in *trans*-**1** by the methyl groups of MeLi with *retention* of the trans geometry has been confirmed.

Hydrolysis of the equilibrium system containing *trans*-$Li[PdPh_2MeL]$ and *trans*-$Li_2[PdPh_2Me_2]$ reveals the formation of only *trans*-$[PdPh_2L_2]$. The formation of the *trans*-diphenyl complex by hydrolysis is in contrast to the formation of the *cis*-dimethyl complex when the solution containing $Li[PdMe_3L]$ and $Li_2[PdMe_4]$ was hydrolyzed. The $[PdPh_2L_2]$-type complex seems to have a strong inclination to take the trans geometry.

Reaction of *trans*- and *cis*-$[PdMe_2(PEt_2Ph)_2]$ (1a) with PhLi. For an examination of the stereospecific displacement reaction in the square-planar palladium complexes, the reaction of $[PdMe_2L_2]$ with PhLi was studied. The reaction of *trans*-**1a** with an equimolar amount of PhLi in THF gives instantly a doublet at −0.67 ppm in the ^1H NMR spectrum, suggesting the formation of *trans*-$Li[PdPhMe_2(PEt_2Ph)]$, *trans*-**2f**. The ^1H NMR spectrum changes further when the reaction mixture is left standing for a few minutes at room temperature with the growth of a singlet at −0.63 ppm. The chemical shift of the singlet is identical with that of *trans*-$Li_2[PdPh_2Me_2]$, *trans*-**3d**, previously obtained by the reaction of *trans*-$[PdPh_2(PEt_2Ph)_2]$, *trans*-**1e**, with MeLi. Thus the displacement of the tertiary phosphine ligand in *trans*-**1** by LiPh proceeds by stereochemical retention in two steps as expressed by eq 7.



trans-1a

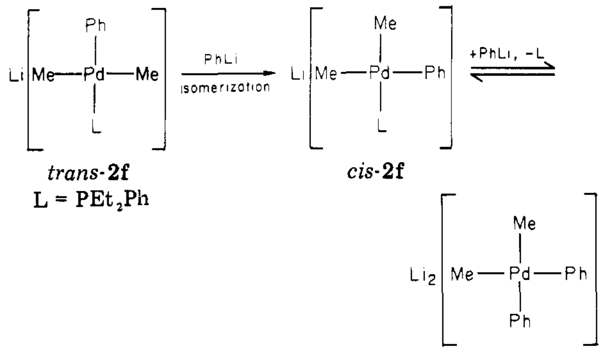
trans-2f

L = PEt_2Ph

(7)

When the reaction system is left standing for several days, the other types of reactions take place as observed by appearance of a set of two doublets at −0.26 and −0.68 ppm with an equal intensity. The two doublets are due to *cis*-$Li[PdPhMe_2(PEt_2Ph)]$, *cis*-**2f**, formed by isomerization of *trans*-**2f** (vide infra). The ^1H NMR of the reaction system shows the formation of still another species as a singlet at −0.68 ppm, which is tentatively assigned to *cis*-$Li_2[PdMe_2Ph_2]$, *cis*-**3d**, because the same resonance is observed on treatment of *cis*-$[PdMe_2L_2]$ with PhLi (vide infra). The reactions may be expressed as shown in eq 8.

A similar experiment to eq 7 also was carried out by using *cis*-$[PdMe_2L_2]$ instead of *trans*-$[PdMe_2L_2]$ with PhLi in THF solution. When *cis*-$[PdMe_2(PEt_2Ph)_2]$ was mixed with an equimolar amount of PhLi in THF, an ^1H NMR spectrum showing two sets of doublets of equal intensity at −0.26 and −0.68 ppm was obtained. The spectral pattern



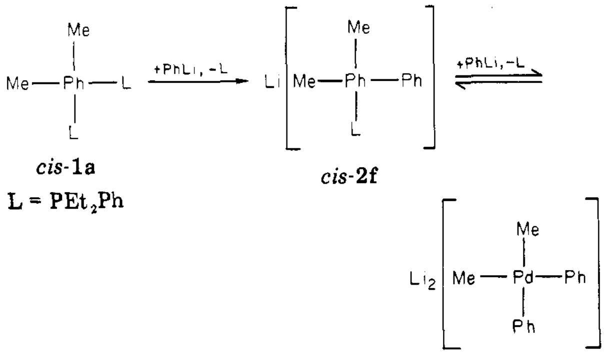
trans-**2f**
L = PEt$_2$Ph

cis-**2f**

(8)

cis-**3d**

and the chemical shifts agree well with those of the species formed by spontaneous isomerization of *trans*-**2f** and suggest the formation of *cis*-**2f**.



cis-**1a**
L = PEt$_2$Ph

cis-**2f**

(9)

cis-**3d**

By referring to the assignment of the chemical shift of the methyl groups in Li[PdMe$_3$(PEt$_2$Ph)], where the methyl signal at the lower field was assigned to the methyl group trans to L and the higher ones to the methyl groups cis to L, we ascribe the doublet at −0.26 ppm to the methyl group trans to L while the other doublet at −0.68 ppm to the methyl group cis to L. When the solution was allowed to stand for a few days, further complication of the ^{1}H NMR spectrum ensued with growth of a signal due to MeLi, the fact indicating the displacement of the Pd-bonded methyl group(s) by PhLi with the release of MeLi. The growing of a singlet at −0.68 ppm suggests the formation of *cis*-Li$_2$[PdPh$_2$Me$_2$], *cis*-**3d**.

Comparison of the reaction of *trans*-[PdPh$_2$L$_2$] with MeLi expressed by eq 6 with that of *trans*- and *cis*-[PdMe$_2$L$_2$] with PhLi represented by eq 7 and 8 shows the trend that *trans*-**2d** having two phenyl ligands in mutually trans positions is more reluctant to isomerize. The higher reactivity of *trans*-**2f** toward isomerization may be due to the greater trans effect of the methyl group than that of the phenyl group.

Reaction of [PdBr$_2$(tmed)] with MeLi. Treatment of [PdBr$_2$(tmed)] (tmed = *N,N,N′,N′*-tetramethylethylenediamine) with MeLi in a 1:5 molar ratio with Et$_2$O at 0 °C gives a colorless homogenous solution. The ^{1}H NMR spectrum of the solution exhibits two singlets at −0.82 and −0.30 ppm in a Pd-bonded methyl region in addition to a singlet at −1.97 ppm due to free MeLi. The signal at −0.82 ppm can be readily assigned to the methyl protons of Li$_2$[PdMe$_4$] (vide supra). Four signals that are ascribed to tmed are observed at 2.32, 2.39, 2.41, and 2.48 ppm. The first two singlets are identified with signals due to free tmed. The ^{1}H NMR data indicate the formation of [PdMe$_2$(tmed)] by the displacement of Br in [PdBr$_2$(tmed)] by the methyl groups. The signal at −0.30 ppm is assigned to the Pd-bonded methyl protons, and the two signals at 2.41 and 2.48 ppm are assigned to the methyl and methylene protons of the coordinated tmed, respectively. It is a general trend that signals due to tmed move to low field on coordination. Li$_2$[PdMe$_4$] is considered to be formed by the displacement of tmed in [PdMe$_2$(tmed)] by the methyl groups as follows.

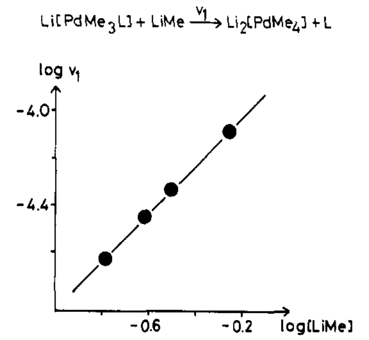
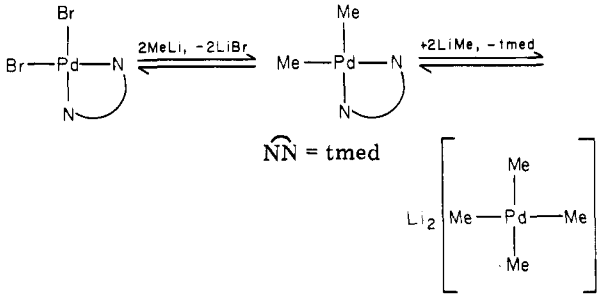


Figure 5. A plot of log v_1 vs. log [MeLi] in the reaction of Li[PdMe$_3$(PEt$_2$Ph)] with MeLi in Et$_2$O at 21.7 °C, where v_1 is the formation rate of Li$_2$[PdMe$_4$].



(10)

Thus a tetramethylpalladate complex can be prepared not only from the displacement reaction of tertiary phosphine in [PdMe$_2$L$_2$] by the methyl groups but also from the reaction of [PdBr$_2$(tmed)] with MeLi.

Kinetic Study of the Palladate Formation Reactions. After characterization of the palladate complexes, we examined the kinetics of the reactions of organopalladium complexes to find the considerable difference in reaction rates of the stepwise reactions depending on the nature of the starting diorganopalladium complexes. The difference in rates enabled us to study each reaction step under appropriate conditions. It was found that the second step in eq 4, namely, the reaction of trimethylpalladate to tetramethylpalladate, proceeds at a rate amenable to a kinetic study by means of ^{1}H NMR spectroscopy, whereas the first step involving the displacement of L by the methyl group to give **2** is completed within the time it takes to mix **1** with MeLi.

The initial rate of formation of **3a** from **2a** was observed by following the ^{1}H NMR spectral change of the methyl resonances at 21.7 °C. Analysis of the later stage of the reaction is hindered by occurrence of a reverse reaction from **3a** to **2a**. The results are summarized in Table IV which shows that the rate of reaction, v_1, increases with the increase in the MeLi concentration and also with the increase in the concentration of **2a**. As shown in Figure 5, the plot of log v_1 against log [LiMe] gives a straight line with the slope of unity. A similar plot of log v_1 against log [**2a**] gives also a straight line with the slope of unity. On the other hand, the comparison of runs 3, 8, and 9 reveals that the addition of PEt$_2$Ph to the system scarcely affects the reaction rate. Thus, the rate equation may be expressed as shown in eq 11.

$$v_1 = -\frac{d[2]}{dt} = \frac{d[3]}{dt} = k_1[2][\text{MeLi}] \qquad (11)$$

Table IV. Kinetic Data for the Reaction $Li[PdMe_3L] + MeLi \xrightarrow{v_1} Li_2[PdMe_4] + L$ (Where $L = PEt_2Ph$) in Et_2O at 21.7 °C

run	$Li[PdMe_3L]$, mol L^{-1}	MeLi, mol L^{-1}	L, mol L^{-1}	$10^5 v_1$,[a] mol L^{-1} s^{-1}	$10^4 k$,[b] mol^{-1} L s^{-1}
1	0.18	0.56	0	8.1	8.1
2	0.18	0.31	0	4.7	8.3
3	0.18	0.24	0	3.5	8.1
4	0.18	0.17	0	2.4	7.9
5	0.11	0.18	0	1.6	8.4
6	0.16	0.18	0	2.3	8.1
7	0.21	0.18	0	3.0	8.0
8	0.18	0.24	0.54	3.5	8.0
9	0.17	0.24	1.07	3.3	7.5
				av	8.0 ± 0.5

[a] Formation rate of $Li_2[PdMe_4]$. [b] Second-order rate constant.

Table V. Kinetic Data for the Reaction *trans*-$[PdPh_2L_2] + MeLi \xrightarrow{v_2} Li[PdPh_2MeL] + L$ (Where $L = PEt_3$) in THF at 21.7 °C

run	*trans*-$[PdPh_2L_2]$, mol L^{-1}	MeLi, mol L^{-1}	L, mol L^{-1}	$10^5 v_2$,[a] mol L^{-1} s^{-1}	$10^4 k$,[b] s^{-1}
1	0.18	0.27	0	1.9	1.1
2	0.18	0.46	0	2.1	1.2
3	0.18	0.69	0	2.0	1.1
4	0.12	0.69	0	1.4	1.2
5	0.24	0.69	0	2.7	1.1
6	0.18	0.69	0.18	1.9	1.1
7	0.18	0.69	0.90	2.1	1.2
				av	1.1 ± 0.1

[a] Formation rate of $Li[PdPh_2MeL]$. [b] First-order rate constant.

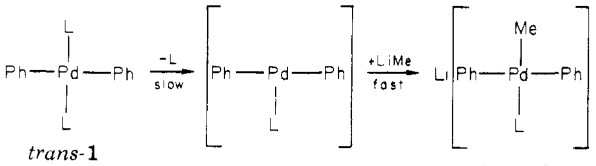
In contrast to the very rapid transformation of *trans*-$[PdMe_2(PEt_2Ph)_2]$, **1a**, on reaction with MeLi to form the trialkylpalladate complex **2a**, the reaction of *trans*-$[PdPh_2(PEt_3)_2]$ **1d** with MeLi to afford *trans*-**2d** is a slow process proceeding at a rate convenient to observe by means of ^1H NMR spectroscopy. The rates of formation of *trans*-**2d** in THF are summarized in Table V. It can be seen that the variation of MeLi concentration does not affect the reaction rate v_2, while the rate increases with increase in the concentration of **1d**. The addition of PEt_3 to the system does not affect the reaction rate. Thus, the rate equation may be expressed as shown in eq 12.

$$v_2 = d[\mathbf{2d}]/dt = k_2[\mathbf{1d}] \qquad (12)$$

The results suggest that the reaction of formation of **2d** proceeds through a dissociative pathway involving the partial dissociation of the PEt_3 ligand from **1d** followed by rapid reaction with MeLi.[8]

Discussion

As revealed unequivocally by NMR spectroscopy, *the displacement of the tertiary phosphine ligands in* $[PdR_2L_2]$*-type complexes by the alkyl group in RLi proceeds in two steps to afford triorganopalladate* **2** *and tetraorganopalladate* **3** *with retention of the original configuration.* Although there have been detailed studies on the mechanism of ligand displacement reactions in $[PdX_2L_2]$ (X = halogen),[9] precedents for studies on the ligand displacement reaction of the organopalladium complexes are extremely limited. It is noteworthy that the tertiary phosphine ligand displacement in *trans*-$[PdPh_2L_2]$ by the methyl groups of MeLi is a slow process proceeding by a dissociative mechanism, whereas the second displacement reaction proceeds by an associative mechanism, both with stereochemical retention of the geometry of the initial diorganopalladium complexes. The kinetic studies by Stille[5] and ourselves[7] demonstrated previously that the thermolysis of *cis*-$[PdMe_2L_2]$ proceeded by a dissociative mechanism through the intermediacy of the "T-shaped" cis isomer $[PdMe_2L]$ and there was a kinetic barrier between the T-shaped "cis" and "trans" $[PdR_2L]$ isomers. The formation of the T-shaped intermediate has been postulated in thermolysis of the dialkylplatinum[10] and trialkylgold[11] complexes and supported by molecular orbital calculations.[11,12] In one example, a T-shaped molecular structure has been established by X-ray crystallography for a three-coordinate cationic rhodium complex.[13] The results of the present study add another example supporting the intermediacy of a T-shaped species.



(13)

trans-**1**
1d, L = PEt_3
e, L = PEt_2Ph

trans-**2**
2d, L = PEt_3
e, L = PEt_2Ph

---

[8] Assumption of ligand dissociation as the rate-determining process and of the steady-state approximation for the concentration of the three-coordinate intermediate **4** in the following scheme leads to the kinetic equation eq 17.

$$\underset{\mathbf{1d}}{trans\text{-}[PdPh_2L_2]} \underset{+L,\,k_{-2}}{\overset{-L,\,k_2}{\rightleftarrows}} \underset{\mathbf{4}}{[PdPh_2L]} \xrightarrow{MeLi,\,k_3} \underset{\mathbf{2d}}{Li[PdPh_2MeL]} \qquad (16)$$

$$\frac{d[\mathbf{2d}]}{dt} = \frac{k_2k_3[MeLi][\mathbf{1d}]}{k_{-2}[L] + k_3[MeLi]} \qquad (17)$$

If $k_3[MeLi]$ is much greater than $k_{-2}[L]$, eq 17 can be approximated by eq 12.

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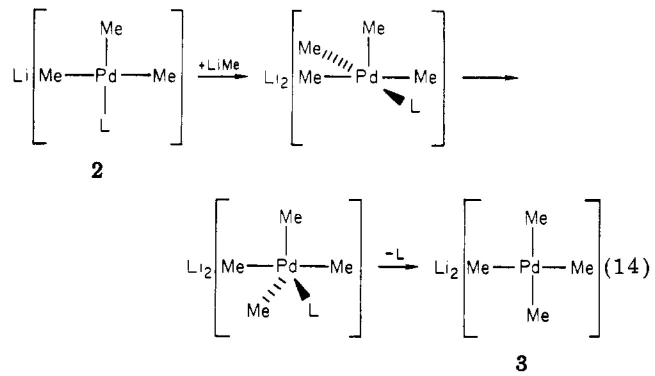
The dissociative mechanism through the T-shaped intermediate postulated for the reaction from *trans*-$[PdPh_2L_2]$ to *trans*-$Li[PdPh_2MeL]$ may be applied also to the reaction from *trans*-$[PdMe_2L_2]$ to $Li[PdMe_3L]$.[14]

The ligand displacement reaction of *trans*- or *cis*-$[PdMe_2L_2]$ by MeLi was revealed to be a rapid process, followed by a slow bimolecular displacement independent of the added phosphine concentration and dependent on the MeLi concentration. To account for the associative pathway, assumption of the mechanism involving the following five-coordinate intermediate(s) is reasonable and compatible with stereochemical retention in ligand placement of $Li[PdMe_3L]$ by MeLi.



2

3

(14)

The overall reactions of conversion of $[PdR_2L_2]$ to $Li_2[PdR_4]$ may be regarded as a nucleophilic ligand displacement by carbanionic alkyl or aryl groups making the palladate complex more electron rich. We can estimate indirectly to what extent the neutral $[PdEt_2L_2]$ becomes electron rich in its reaction with MeLi to produce *trans*-$[PdEt_2MeL]$ by observing the change in the chemical shift difference, Δ, between the CH_2 and CH_3 protons in the Pd-bonded ethyl groups (eq 5). It is known that there is a linear relationship between the chemical shift difference Δ and the electronegativity χ of the element attached to an ethyl group as shown in eq 15.[15,16]

$$\chi = 0.62\Delta + 2.07 \qquad (15)$$

The electronegativity values calculated by using the above equation and the observed chemical shift difference of the methyl and methylene protons in the ethyl groups in *trans*-$[PdEt_2(PMe_2Ph)_2]$ and *trans*-$Li[PdEt_2Me(PMe_2Ph)]$ were 1.74 and 1.43, respectively.[17] Thus a considerable decrease in the electronegativity of the entity bound to the ethyl groups is indicated. This result explains reasonably well that the nucleophilic attack by the methyl group on the palladium complex is slower in the second step starting from $Li[PdR_3L]$ than in the first step where the neutral diorganopalladium is attacked.

We have here three groups of methylpalladium complexes of neutral, monoanionic, and dianionic types with and without the tertiary phosphine ligand and phenyl groups. As Figure 6 shows, the ^1H chemical shift of the methyl group is observed in THF in approximately the same region, *independent* of the charge on the complex and *dependent* on the nature of the ligand trans to the methyl group. For example, the methyl group resonating in the region of −0.6 to −0.8 ppm has a methyl or phenyl group trans to the methyl group referred to, irrespective of the charge on the complex. On the other hand, the resonance of the methyl group trans to the phosphine is observed at the lower field of −0.18 to −0.26 ppm for the triorganopalladate complexes and +0.08 ppm for neutral dimethylpalladium complex. The methyl proton resonances of other $[PdMe_2L_2]$-type complexes having a tertiary phosphine ligand other than PEt_2Ph and of *trans*-$Li[PdEt_2Me(PMe_2Ph)]$ (not shown in Figure 6) are also observed in a similar region.

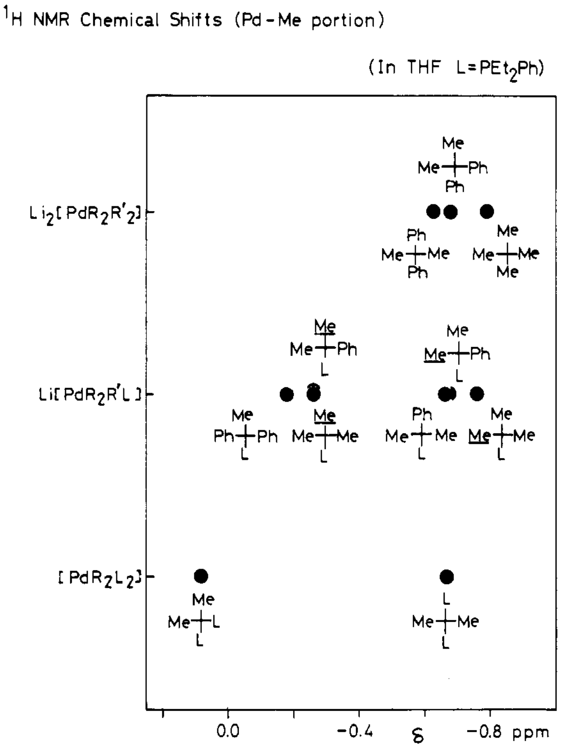


Figure 6. ^{13}C NMR chemical shifts of the methyl portion for a series of $Li_n[PdMe_2R_n(PEt_2Ph)_{2-n}]$ in THF at room temperature, where R stands for the methyl or phenyl group.

The implication of this trend is the importance of the ligand trans to the methyl group rather than the charge on the complex in determining the chemical shift of the methyl group. The tertiary phosphine appears to have a higher ability to deshield the methyl group trans to the phosphine than the methyl or phenyl group.

It is known that the ^{13}C chemical shifts of the carbon directly bonded to platinum in the methyl- and phenylplatinum complexes are correlated with each other, and the shielding is determined by σ interaction in the Pt–C bond.[18] Inspection of the ^{13}C chemical shifts of the phenyl carbons in *trans*-$[PdPh_2L_2]$, *trans*-$Li[PdPh_2MeL]$, and *trans*-$Li_2[PdPh_2Me_2]$ reveals that the chemical shifts of the C_o, C_m, and C_p carbons are relatively invariant, while that of the quaternary carbon bonded to $Pd(C_b)$ shows a conspicuously irregular variation as shown in Table III, suggesting the dominant contribution of σ interaction in the phenyl–palladium bond. The ^{13}C chemical shift of the quaternary carbon observed at 167.6 ppm in *trans*-$[PdPh_2(PEt_2Ph)_2]$ (**1e**) moves downfield to 179.6 ppm in

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[14] Although a five-coordinate intermediate $Li[PdMe_3L_2]$ was proposed in our previous paper for the conversion of $[PdR_2L_2]$ to $Li[PdR_3L]$ during the trans–cis isomerization of $[PdMe_2L_2]$ promoted by MeLi,[7] the present study makes the associative mechanism unlikely, although the displacement of R in $Li[PdR_3L]$ by L to convert it into $[PdR_2L_2]$ may well proceed by an associative mechanism.

[15] Ham, N. S.; Mole, T. In "Progress in Nuclear Magnetic Resonance Spectroscopy"; Emsley, J. W., Feeney, F., Sutcliffe, L. H., Ed.; Pergamon Press: New York, 1969; Vol. 4, p 101.

[16] Narashimhan, P. T.; Rogers, M. T. *J. Chem. Soc., Dalton Trans.* **1960**, 5983.

[17] Because the both complexes have the ethyl groups in mutually trans positions, the trans influence of the ethyl groups may be cancelled and may not affect the following reasoning.

[18] Clark, H. C.; Ward, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 1741.

trans-Li[$PdPh_2Me(PEt_2Ph)$] (**2e**) by displacement of the tertiary phosphine ligand by the methyl group despite of the anionic nature of **2e**, whereas the further displacement of PEt_2Ph by the methyl group caused the upfield shift to 159.0 ppm. The PEt_3-coordinated complex *trans*-**1d** shows similar behavior in the stepwise displacement of PEt_3 by the methyl group. Displacement of the PEt_2Ph ligand in *trans*-[$PdMe_2(PEt_2Ph)_2$] by the methyl group shows a similar trend but in a less marked manner. The first displacement of PEt_2Ph by the methyl group causes the slight deshielding of the *trans*-methyl carbon from −6.0 to −5.2 ppm, followed by an upfield shift to −8.3 ppm on the second displacement of a PEt_2Ph ligand in *trans*-Li[$PdMe_3(PEt_2Ph)$] by the methyl group, giving $Li_2[PdMe_4]$. Since the ^{13}C chemical shift is expected to reflect the electron density of the carbon atom in question, it would be anticipated that the ^{13}C chemical shift of the Pd-bonded carbon moves upfield when the negative charge on palladium is increased, if the electronic factor alone should play the dominant role in determining the shielding at the Pd-bonded carbon. The observed anomaly in the ^{13}C chemical shift of the carbon bonded to palladium on displacement of the tertiary phosphine ligand in [PdR_2L_2] by the methyl group may be related to steric influence. However, we refrain from discussing this question further because of the limited NMR data on organopalladium complexes.

Experimental Section

All measurements 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.

^1H, ^{13}C, and ^{31}P NMR spectra were measured on JEOL PS-100 and FX-100 spectrometers at room temperature and at 21.7 °C in kinetic studies. ^1H and ^{13}C NMR signals are referred to Me_4Si and ^{31}P NMR signals to PPh_3. Elemental analyses were carried out by Mr. T. Saito of our laboratory using Yanagimoto CHN autocorder type MT-2. Methyllithium purchased from Alfa Products (low halide) was used after several recrystallizations. Phenyllithium was prepared prior to use from PhBr and Li wire by the literature method. The concentration was determined by acid/base titration after hydrolysis. *trans*-[$PdMe_2(PEt_2Ph)_2$] (*trans*-**1a**), *cis*-[$PdMe_2(PEt_2Ph)_2$] (*cis*-**1a**), *cis*-[$PdMe_2(PEt_3)_2$] (*cis*-**1b**), and *trans*-[$PdEt_2(PMe_2Ph)_2$] (*trans*-**1c**) were prepared according to the method described previously.[7] *trans*-[$PdPh_2(PEt_3)_2$] (*trans*-**1d**) was synthesized by the published procedure.[19]

Preparation of *trans*-[$PdPh_2(PEt_2Ph)_2$] (*trans*-1e). To the heterogeneous mixture of [$PdCl_2(PEt_2Ph)_2$] (1.32 g, 2.59 mmol) and Et_2O (36 mL) cooled to −75 °C was added carefully an ether solution of LiPh (1.04 g, 5.18 mmol). The reaction mixture was stirred for 40 min at −75 °C to give a white precipitate, which was filtered, washed with 20 mL of cold Et_2O, and recrystallized from 40 mL of acetone to yield pure crystals of *trans*-**1e** (0.62 g, 41%). Characterization of this complex was carried out by means of IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analysis. Anal. Calcd for $C_{32}H_{40}P_2Pd$: C, 64.8; H, 6.8. Found: C, 64.7; H, 6.9.

Characterization of *trans*-[$PdPh_2L_2$] (L = PEt_3 (*trans*-1d), PEt_2Ph (*trans*-1e)). In ^{13}C NMR spectra, the signals due to the quaternary carbons of coordinated phenyl groups were observed as a triplet at 169.2 (^2J(C–P) = 13 Hz) and 167.6 ppm (^2J(C–P) = 12 Hz) for *trans*-**1d** and *trans*-**1e**, respectively (see Table III).

In the ^1H NMR spectrum of *trans*-**1e** in CD_2Cl_2, the signal assigned to the methyl groups in PEt_2Ph ligands showed a quintet pattern characteristic of complexes having ethyl-substituted phosphines in mutually trans positions at +0.90 ppm (^4J(H–P) = 7.5 Hz), while the superposition of the methyl and methylene signals of the ethyl groups in the phosphine ligands for *trans*-**1d** prevented the measurement of the coupling constants. The ^{13}C and ^1H NMR data described above are typical for complexes having mutually trans phosphine groups.

Preparation of [$PdBr_2$(tmed)]. Addition of *N,N,N′,N′*-tetramethylethylenediamine (tmed) (1.0 mL, 6.77 mmol) to an aqueous solution containing $PdCl_2$ (1.0 g, 5.64 mmol) and KBr (5.37 g, 45 mmol) generated a yellowish orange precipitate of [$PdBr_2$(tmed)], which was filtered, washed with water and acetone, and dried in vacuo (yield 1.97 g, 91%). Anal. Calcd for $C_6H_{16}Br_2N_2Pd$: C, 18.8; H, 4.2; N, 7.3; Br, 41.8. Found: C, 18.9; H, 4.4; N, 7.4; Br, 41.1.

Reaction of *trans*-[PdR_2L_2] with MeLi or PhLi. To an Et_2O or THF solution of accurately weighed [PdR_2L_2] was added a calculated amount of Et_2O or THF solution of MeLi or PhLi at −75 °C. The resulting homogeneous solution was transferred to NMR sample tubes under a nitrogen atmosphere. The tubes, chilled in liquid nitrogen, were sealed under vacuum, and ^1H, ^{13}C, and ^{31}P NMR measurements were carried out at room temperature to observe the spectroscopic change of the solution.

Kinetic Studies of Palladate Formation Reactions. To a Schlenk tube containing a weighed amount of [PdR_2L_2] complex was added a calculated amount of Et_2O or THF solution of MeLi at −75 °C. The resulting homogeneous solution was transferred to NMR sample tubes under a nitrogen atmosphere. The sealed tube was placed in a thermostated NMR probe (±1.0 °C). The amounts of palladate complexes were determined by measuring the intensities of Pd–Me signals at suitable time intervals at 21.7 °C.

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Registry No. *trans*-**1a**, 77831-30-2; *cis*-**1a**, 77881-04-0; *cis*-**1b**, 65732-09-4; *trans*-**1c**, 75108-70-2; *trans*-**1d**, 83947-32-4; *trans*-**1e**, 83947-33-5; **2a**, 83947-24-4; **2b**, 83947-25-5; *trans*-**2c**, 83947-28-8; *trans*-**2d**, 83947-27-7; *trans*-**2e**, 83947-26-6; *trans*-**2f**, 83947-29-9; *cis*-**2f**, 83997-78-8; **3a**, 83947-30-2; *trans*-**3d**, 83947-31-3; *cis*-**3d**, 83997-79-9; $PdCl_2(PEt_2Ph)_2$, 29484-77-3; PhLi, 591-51-5; $PdBr_2$(tmed), 83947-34-6; $PdCl_2$, 7647-10-1; KBr, 7758-02-3; MeLi, 917-54-4.

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(19) Calvin, G.; Coates, G. E. *J. Chem. Soc.* **1960**, 2008.