*Journal of Organometallic Chemistry*, 175 (1979) 143—155


# π-ALLYLMETAL CHEMISTRY 8*. UNCATALYZED CIS-TRANS ISOMERIZATION OF $\eta^3$-ALLYL(PENTACHLOROPHENYL)PALLADIUM(II) COMPLEX

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(Received February 13th, 1979)

Summary

Two geometrical isomers of an $\eta^3$-crotylpalladium(II) complex, $Pd(\eta^3\text{-crotyl})(C_6Cl_5)(PPh_3)$ have been found to undergo uncatalyzed mutual interconversion in benzene above room temperature. The rate constants of the isomerization have been determined by the $^1H$ NMR method at 45-67°C, and thermodynamic data calculated. The large decrease of the rate on adding free triphenylphosphine ligand is attributed to occurrence of a dissociative isomerization path involving a 3-coordinate intermediate. Reductive elimination of the complex takes place at much slower rates than the isomerization to afford $MeCH{=}CHCH_2C_6Cl_5$ selectively.

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Cis-trans isomerization of square-planar $d^8$ metal complexes including $^1H$ NMR site-exchange in $\eta^3$-allylpalladium(II) complexes[2] (eq. 1) is usually catalyzed by an added free ligand

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*Part 7, ref. 1.

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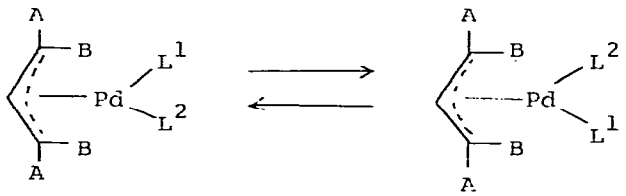
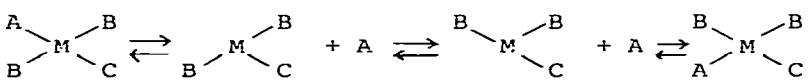


(1)

which is capable of forming 5-coordinate and/or ionic complexes as intermediates or in the transition state[3]. In recent years, uncatalyzed isomerization of different reactivity pattern[4-6], besides photochemical processes[7], has received increasing attention. Thus, it has been suggested by kinetic studies that the isomerization of organometallic complexes, Pt(aryl)Br-$(PEt_3)_2$[4] and $AuMe_2Et(PPh_3)$[5] proceeds through an unusual 14-electron, 3-coordinate intermediate having stereochemical integrity (eq. 2, A= $Br^-$ or $PPh_3$). Particularly notable in



(2)

this case is great retardation of the isomerization rate in the presence of added free ligand, A. We report here on the uncatalyzed cis-trans isomerization of an organo($\eta^3$-allyl)-palladium(II) complex, Pd($\eta^3$-MeCHCHCH$_2$)($C_6Cl_5$)($PPh_3$), $\underset{\sim}{1}$, the rate of which is similarly reduced to a great extent by free $PPh_3$. This isomerization also has relevance to the mode of regioselective reductive elimination of polychlorophenyl and allylic groups from $\underset{\sim}{1}$ as well as related $\eta^3$-crotyl(tetrachloro-phenyl)palladium(II) complexes[8].

## Results and Discussion

### Uncatalyzed cis-trans isomerization

Treatment of Pd($\eta^3$-MeCHCHCH$_2$)Cl($PPh_3$) with $C_6Cl_5Li$ in tetrahydrofuran gave the thermally stable complex, $\underset{\sim}{1}$, in good yield. The isomer ratio ($\underset{\sim}{1}$a/$\underset{\sim}{1}$b) of this complex before

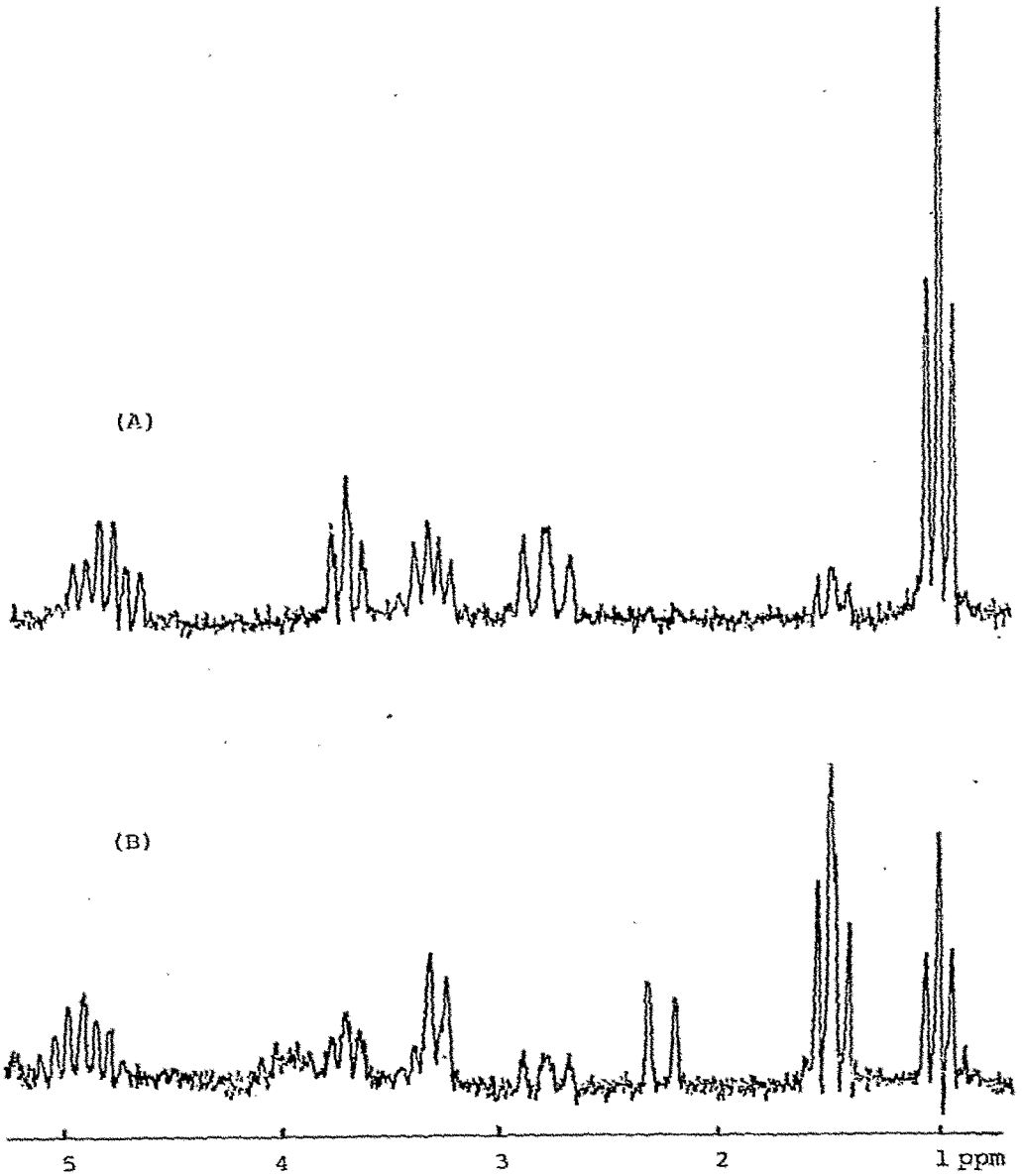
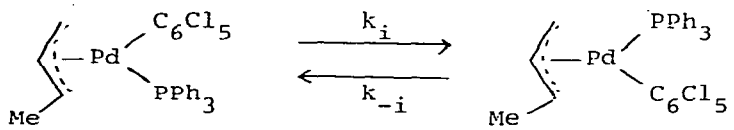



Fig. 1. $^{1}H$ NMR Spectra of Pd($^{3}$-crotyl)($C_6Cl_5$)($PPh_3$) 1.
A: Enriched in the isomer, 1a. B: After heating (A) at 51°C for 60 Min. For assignments see Experimental.

recrystallization was ca 1. The $^1$H NMR spectral assignment of each isomer (see Fig. 1) was made on the basis of the




1a 1b (3)

preferential spin-spin coupling between the $^{31}$P nucleus and the allylic protons located trans to the phosphine, as in the case of Pd($\eta^3$-crotyl)(2,3,5,6-$C_6HCl_4$)L 2 (L= $PPh_3$)[8]. Repeated, fractional recrystallizations from benzene/n-hexane solutions at or below room temperature yielded samples which consisted of isomer 1a predominantly. Samples rich in 1b remained in the solution. Heating benzene solutions of 1a-rich samples above room temperature resulted in equilibration of the two isomers with 1b dominating under these conditions.

The equilibrium constants, $k_i/k_{-i}$ were measured from the $^1$H NMR intensities after sufficiently long reaction periods. The process leading to the equilibrium starting from 1a-rich samples could be followed by $^1$H NMR spectroscopy at 45-67°C. The kinetics obeyed a first-order dependence of the value, $[1a]_t-[1a]_{eq}$ over the period of 3 half-lives to give the values, $k_i + k_{-i}$. Hence, by combining these with the equilibrium constants, $k_i$ and $k_{-i}$ were obtained separately (Table 1). Thermodynamic data for the isomerization were calculated by the Arrhenius treatment; at 51°C, $\Delta H_i^{\ddagger}$ = 21.4 ± 1.8 Kcal/mol, $\Delta S_i^{\ddagger}$ = -8.0 ± 5.6 e.u., $\Delta H_{-i}^{\ddagger}$= 19.9 ± 1.4 Kcal/mol, $\Delta S_{-i}^{\ddagger}$= -14.5 ± 4.3 e.u., $\Delta H_{eq}^{o}$= 1.9 ± 0.6 Kcal/mol, $\Delta S_{eq}^{o}$= 7.4 ± 1.9 e.u. (the last two from the equilibrium constants). Interestingly, 1a has an enthalpy comparable to, or is even a little more stable than 1b, while the parent complex, Pd($\eta^3$-crotyl)Cl($PPh_3$), as well as the platinum analog,

Table 1. Equilibrium and Rate Constants for Isomerization,

$$\underset{\sim}{1a} \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} \underset{\sim}{1b}$$

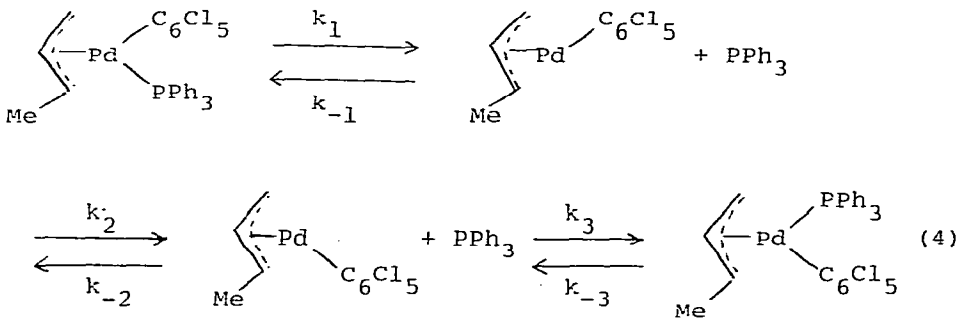
| Temp. (°C) | $k_i/k_{-i}$ | $10^4 k_i$ ($sec^{-1}$) | $10^4 k_{-i}$ ($sec^{-1}$) |
|---|---|---|---|
| 45 | 2.33 ± 0.14 | 2.5 ± 0.2 | 1.1 ± 0.1 |
| 51 | 2.33 ± 0.12 | 4.3 ± 0.3 | 1.8 ± 0.1 |
| 61 | 2.70 ± 0.27 | 15.4 ± 2.2 | 5.7 ± 0.8 |
| 67 | 2.85 ± 0.32 | 23.4 ± 3.6 | 8.2 ± 1.3 |

$Pt(\eta^3\text{-crotyl})(C_6HCl_4)(PPh_3)$, exist exclusively in the isomeric form with $PPh_3$ trans to the methyl group[9]. In a series of $Pd(\eta^3\text{-crotyl})X(L)$ complexes (X= Cl, Br; L= substituted pyridines), the relative stability of cis and trans isomers was discussed in terms of relative degree of steric interaction of the methyl group with the halide and the pyridines[10]. However, molecular models suggest the much severer steric repulsion between the methyl and $PPh_3$ in $\underset{\sim}{1a}$ than that between the methyl and $C_6Cl_5$ in $\underset{\sim}{1b}$, with the difference in the degrees of these two repulsions appearing almost as much as that between the Me-$PPh_3$ and Me-Cl repulsions in the corresponding isomers of $Pd(\eta^3\text{-crotyl})Cl(PPh_3)$. Yet it seems difficult to explain, at the moment, how electronic nature of the polychlorophenyl groups and metals contributes to determining the energy of the stereoisomers in $\eta^3$-crotyl(polychlorophenyl)metal complexes. It is also uncertain if the other isomer of $Pt(\eta^3\text{-crotyl})(C_6HCl_4)(PPh_3)$ is kinetically inaccessible.

It is remarkable that free $PPh_3$ added to the solution of

$\underset{\sim}{1}$ did not enhance the rate of isomerization, but rather retarded it considerably. Because of such retardation, as well as of the small increase in the rate of the concurrent decomposition path (see later) in the presence of added $PPh_3$, the effect of the latter path on the kinetic measurements was no longer negligible, so that reliable rate constants for the isomerization could not be obtained. However, occurrence of such suppressed isomerization is apparent from qualitative examination. Thus, at 51 °C after 20 min, which is nearly the half-life in the absence of $PPh_3$, the extent of isomerization was only 18, 16 and 16 % in the presence of $[PPh_3] = 2.7 \times 10^{-2}$, $6.4 \times 10^{-2}$ and $9.2 \times 10^{-2}$ mol/l, respectively. At this stage of isomerization the decomposition apparently was not yet significant, and if first-order kinetics are assumed to be valid for these runs too, then $k_i(PPh_3\ \text{free})/k_i(PPh_3) \simeq [\log(1/0.5)]/[\log(1/0.84)] \simeq 4$ is estimated. Further analysis was difficult as described above. On adding $PPh_3$ in up to $10^{-1}$ mol/l at the other temperatures, the initial rates were similarly reduced to approximately 1/3 − 1/4 of those in the absence of added $PPh_3$.

Since the addition of excess $PPh_3$ to $\underset{\sim}{1}$ under the kinetic conditions did not cause any appreciable change in the aspects of the $^1H$ NMR spectra of $\underset{\sim}{1}$, it is not likely that there exists any association product between $\underset{\sim}{1}$ and $PPh_3$ in concentrations sufficient to account for the retardation of isomerization by added $PPh_3$. Nor does a rapid dissociative equilibrium of $\underset{\sim}{1}$ generating free $PPh_3$ seem to be significant enough to induce a great decrease of the rate on adding $PPh_3$. We assume that the isomerization of $\underset{\sim}{1}$ shown in eq. 3 in the absence of added $PPh_3$ mostly proceeds after slow dissociation of $PPh_3$ (eq.4), in a manner similar to eq. 2.

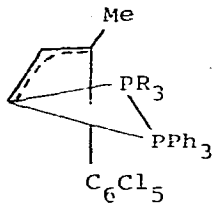


It is possible that, in the range of $[PPh_3] \geq 2.7 \times 10^{-2}$ mol/l, $k_{-1}[PPh_3]$ (or $k_3[PPh_3]$) is so large compared to $k_1$ and $k_2$ (or $k_{-3}$ and $k_{-2}$) that the isomerization through path 4 now becomes almost insignificant. The residual isomerization under these conditions, though its magnitude could not be determined definitively, might be attributed to a $PPh_3$-independent, intramolecular pathway. A similar dissociative cis-trans isomerization mechanism of $\eta^3$-allylmetal complexes has been described to occur, without proof, in epimerization of $Ni(\eta^3\text{-MeCHCHCHMe})Me(NH_2CHMePh)$[11]. Interestingly, both this complex and 1 contain poorly ionizable carbanion ligands which would make the $S_N2$-ionic consecutive mechanism a very high energy process.

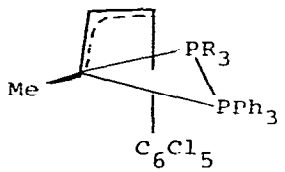
A different type of dissociative cis-trans isomerization in $Pd(\eta^3\text{-crotyl})Cl(amine)$[10] deserves comments. NMR double-resonance techniques indicated[10] dissociation of the amine ligand and the involvement of the dimer, $[Pd(\eta^3\text{-crotyl})Cl]_2$ as an intermediate during the cis-trans isomerization. In the present case, however, an analogous formation of the dimeric intermediate from the 3-coordinate complex shown in eq. 4 must be highly unfavorable, though not totally impossible, compared to the chloride bridging.

Another reason of the failure of 1 to undergo $PPh_3$-promoted isomerization is possibly of steric origin. Thus,

intramolecular movements of 5-coordinate intermediates such as 3a or 3b ($PR_3$= $PPh_3$)* leading to cis-trans isomerization[2,3] must be again quite high energy processes owing to the relatively large steric bulk of all the ligands involved therein. As




3a




3b

for the 5-coordinate intermediates, we assume that they can actually be formed with considerable ease, for we have found that an apparently ligand-dependent substitution of $PPh_3$ in 1 for $P(C_6H_4OMe\text{-}p)_3$ with complete retention of stereochemistry takes place under much milder conditions than the isomerization. For example, addition of $P(C_6H_4OMe\text{-}p)_3$ to 1 at 23°C resulted in very rapid disappearance of the NMR resonances of 1b and appearance of those of 4b (see Experimental), while analogous exchange of the phosphines in 1a was somewhat slower with the apparent half-life of this process being approximately 200 and 30 min for $[P(C_6H_4OMe\text{-}p)_3]= 8.7 \times 10^{-2}$ and $5.96 \times 10^{-1}$ mol/l, respectively. The greater rate of the substitution with retention than that of the isomerization was previously reported for $Pt(aryl)Br(PEt_3)_2$[4], $AuMe_2Et(PPh_3)$[5] and $PtCl_2(R_2SO)_2$[6], and thus seems to be common in the complexes undergoing uncatalyzed cis-trans isomerization. The different reactivity of 1a and 1b in the substitution is also interesting.

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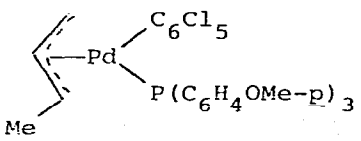
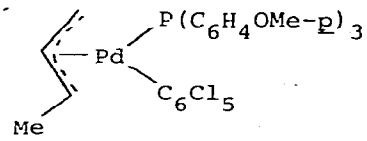
*Those configurations which contain the $\eta^3$-crotyl group in two equatorial positions would be very unstable due to unfitting bond angles, though the trigonal bipyramidal model may be an oversimplification.

Molecular models indicate that greater steric repulsion is present between the crotyl methyl and the phosphines in 3a than in 3b ($PR_3$= $P(C_6H_4OMe\text{-}p)_3$), this perhaps being responsible, in part, for the slower substitution rate of 1a.




4a




4b

Regioselective coupling

We have shown before that a mixture of two geometrical isomers of 2 (L= $PPh_3$, $SbPh_3$) undergo a clean, regioselective reductive elimination at higher temperatures to give $MeCH{=}CHCH_2C_6HCl_4$[8], but the precise mode of the coupling consistent with the regiochemistry was not elucidated. A mixture of 1a and 1b similarly decomposed in benzene at 80°C, in 5 hr to afford $MeCH{=}CHCH_2C_6Cl_5$ in more than 90 % yield. Since the interconversion shown in eq. 3 is now found to be much faster than the decomposition path in the absence of added $PPh_3$, the regioselectivity may reasonably be explained by occurrence of a concerted cis-coupling of the two organic groups preferentially in the isomer 1a or the analogous isomers of 2. Accordingly, the isomer ratio of 1 recovered after partial thermolysis at 80°C in benzene remained nearly constant (1a/1b= 24/76), irrespective of the reaction time or the composition of the starting material.

On the other hand, the isomer distribution of the complex recovered during the thermolysis in the presence of a large excess of $PPh_3$ (more than $2.50 \times 10^{-1}$ mol/l) was time-dependent because the rate of the decomposition was apparently comparable to or even greater than that of the isomerization. Thus, as the decomposition proceeded, the ratio, 1a/1b

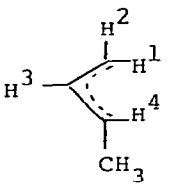
(initially $\geq 1$) gradually became smaller, and then crossed over the equilibrium point. For example, heating a benzene solution of an equilibrium mixture (1a/1b= 27/73) of 1 ($8.4 \times 10^{-2}$ mol/l) at [$PPh_3$]= $2.50 \times 10^{-1}$ mol/l at 61°C, 4 hr gave 63 % of $MeCH{=}CHCH_2C_6Cl_5$ with 1a/1b of the remaining complex found to be ca. 14/86. These facts may again support the preferential coupling in 1a. The small increase of the decomposition rate in the presence of added $PPh_3$, though observed only qualitatively, may or may not originate from interaction of 1a with $PPh_3$ as in 3a. A $PPh_3$-promoted reductive elimination of cis-Pt(aryl)$_2$($PPh_3$)$_2$ has been suggested to be attributable to a similar weak interaction of the complex with $PPh_3$ in the transition state[12].

## Experimental

$^1$H NMR spectra were measured on a Japan Electron Optics JNM-PS-100 spectrometer with tetramethylsilane as internal standard ($\delta$= 0.00). Probe temperatures (correct within $\pm$0.5°C) were checked before and after each kinetic run. Benzene used in kinetic measurements was of spectroscopy grade.

Preparation of 1. To a tetrahydrofuran solution (150 ml) of $C_6Cl_5Li$ which was prepared from $C_6Cl_6$ (2.05 g; 7.2 mmol) and equimolar amount of n-BuLi in n-hexane, was added dropwise Pd($\eta^3$-crotyl)Cl($PPh_3$) (3.20 g; 7.0 mmol) in tetrahydrofuran (250 ml) under nitrogen at -78°C. The reaction mixture was stirred for 1 hr, and then the temperature was gradually raised to 20°C. The solvent was removed under vacuum, and the residue was extracted with benzene (30 x 2 ml). The benzene solution was passed through a Florisil column, and the volume of the solution was reduced to ca. 10 ml under vacuum. To this solution was added sufficient methanol (10 ml) to cause precipitation of pale yellow solids (3.8 g). The $^1$H NMR spectrum in benzene (see below) of this material showed

the existence of approximately equal amounts of two isomers. Recrystallization from ca. 10 ml of benzene/n-hexane (1:1 by volume) in the refrigerator afforded colorless crystals (2.9 g) having a decomposition point above 130 °C (Found: C, 52.48; H, 3.78. Calcd. for $Pd(C_4H_7)(C_6Cl_5)P(C_6H_5)_3 \cdot 1/2C_6H_6$: C, 52.27; H, 3.54 %.) The presence of benzene of crystallization was confirmed by $^1H$ NMR intensities in $CDCl_3$. The same recrystallization procedure was repeated twice to give ca. 1.3 g of a crystalline sample whose $^1H$ NMR spectrum indicated the presence of 94 % of 1a and 6 % of 1b. Concentrating the combined mother liquor afforded a solid sample (1.0 g) having the ratio of 1a/1b = ca. 1/3. $^1H$ NMR (benzene):




For 1a, 1.01(t), $J_H4 = J_P = 6.0$ Hz ($CH_3$); 2.84(dd), $J_H3 = 12.0$ Hz, $J_P = 10.5$ Hz ($H^1$); 3.39(dq), $J_H3 = 12.0$ Hz ($H^4$); 3.78(t), $J_H3 = J_P = 7.5$ Hz ($H^2$); 4.91(dt) ($H^3$). For 1b, 1.49(dd), $J_H4 = 6.0$ Hz, $J_P = 7.5$ Hz ($CH_3$); 2.29(d), $J_H3 = 12.0$ Hz ($H^1$); 3.33(d), $J_H3 = 7.5$ Hz ($H^2$); 3.98(ddq), $J_H3 = 12.0$ Hz, $J_P = 10.0$ Hz ($H^4$); 4.97(dt) ($H^3$).

Equilibrium and kinetic measurements Solutions of the complex enriched in 1a in benzene ($9.4 \times 10^{-2}$ — $2.70 \times 10^{-1}$ mol/l) with or without known concentrations of free $PPh_3$ were prepared at room temperature. These solutions were sealed in conventional, thin-walled NMR tubes under vacuum (ca. 1 mmHg) after degassing several times by the freeze-thaw cycle. Equilibrium constants were calculated for the samples without free $PPh_3$ on the basis of the peak areas of the $H^1$ resonances after 7 or 8 half-lives, when formation of the coupling product (see below) in up to ca. 10 % yields caused contamination of the methyl resonance of 1b by that of the coupling product. Kinetic studies were performed by integrating the methyl as well as $H^1$ absorptions of 1a

and 1b at appropriate intervals. All plots of $\log\{[1a]_t-[1a]_{eq}\}$ against time gave straight lines for more than 3 half-lives except for the runs in the presence of added free $PPh_3$. The values, $k_i + k_{-i}$ were calculated from the slopes of these plots. In the presence of added $PPh_3$, occurrence of a concurrent decomposition path and, consequently, apparent formation of $Pd(PPh_3)_4$ in solution and often as precipitates hampered kinetic analysis.

Phosphine exchange Within 10 min after adding $P(C_6H_4OMe\text{-}p)_3$ ($8.7 \times 10^{-2}$ and $5.96 \times 10^{-1}$ mol/l) to a benzene solution of 1 ($8.7 \times 10^{-2}$ mol/l) with 1a/1b= 75/25 or 32/68 at 23°C, the $^1H$ NMR spectrum indicated complete disappearance of the peaks due to 1b, and new peaks attributable to 4b were observed; 1.60(dd) ($CH_3$), 2.42(d) ($H^1$), 3.50(d) ($H^2$), 4.12(ddq) ($H^4$), 5.13(dt) ($H^3$) with each coupling constant being almost identical with the corresponding value of 1b. The peaks due to 1a were gradually replaced by new peaks of 4a with the ratio, (1a + 4a)/4b invariably equal to 1a/1b of the original; 1.17(t) ($CH_3$), 2.93(dd) ($H^1$), 3.85(t) ($H^2$), 5.04(dt) ($H^3$). The resonance of $H^4$ of 4a overlapped with the OMe peak.

Reductive elimination Thermal decomposition of 1 was performed in benzene at 80°C, 5 hr in a manner essentially similar to that already described for 2 (L= $PPh_3$)[8]. The yield of $MeCH{=}CHCH_2C_6Cl_5$ was determined to be more than 90 % by $^1H$ NMR spectroscopy using methyl β-naphthyl ether as internal standard; 1.49(d), $J_H$= 5.5 Hz ($CH_3$); 3.34(d), $J_H$= 5.5 Hz ($CH_2$); 5.2-5.5(m) (-CH=CH-). The compound was also analyzed by mass spectroscopy as in the case of $MeCH{=}CHCH_2C_6HCl_4$[8].

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