the photolysis mixture showed the formation of **9b** (0.034 mmol, 19% yield) with 93% isomeric purity.

**Photolysis of 1 in the Presence of Vinyl Acetate.** A solution of 0.9797 g (3.02 mmol) of **1** and 2.3 g (27.2 mmol) of vinyl acetate in 100 mL of hexane was photolyzed for 2 h with ice cooling. The mixture was analyzed by GLC as being **11** (0.15 mmol, 6% yield) and unchanged **1** (17% yield). After addition of 1 mL of acetic acid to the photolysis mixture, the mixture was again analyzed by VPC. However, no change was observed. Pure **11** was isolated by preparative VPC. IR 1720, 1060 $cm^{-1}$; $^1H$ NMR $\delta$ 0.17 (9 H, s, $Me_3Si$), 2.10 (3 H, s, MeCO), 5.7–6.4 (3 H, m, $CH_2{=}CH$), 7.2–7.6 (5 H, m, ring protons). Exact mass. Calcd for $C_{13}H_{20}O_2Si_2$: 264.1022. Found: 264.0992.

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# Mechanisms of 1,1-Reductive Elimination from Palladium: Coupling of Styrylmethylpalladium Complexes

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**Abstract:** The complexes (*E*)- and (*Z*)-styrylbromobis(triphenylphosphine)palladium(II) [(*E*)- and (*Z*)-**1a**] react with methyllithium in benzene at ambient temperature to give (*E*)- and (*Z*)-propenylbenzene, respectively. A similar reaction at −78 °C afforded (*E*)- and (*Z*)-styrylmethylbis(diphenylmethylphosphine)palladium(II) [(*E*)- and (*Z*)-**2b**] as a cis–trans mixture. On raising the temperature of solutions of (*E*)- and (*Z*)-**2b**, (*E*)- and (*Z*)-propenylbenzenes are produced, respectively, and the intermediate olefin complexes (*E*)- and (*Z*)-propenylbenzenebis(diphenylmethylphosphine)palladium(0) [(*E*)- and (*Z*)-**3b**] can be observed by NMR. the reductive elimination reaction is intramolecular as determined by a crossover experiment and first order in dialkylpalladium(II) complex when diphenylmethylphosphine is present. The reaction of (*E*)-**2b** and trideuteriomethyl iodide gives some 3,3,3-trideuteriopropenylbenzene, again implicating a palladium(IV) intermediate as a possible reductive elimination intermediate in a catalytic coupling cycle.

The coupling of organic halides and organometallic reagents catalyzed by zero-valent nickel and palladium complexes provides a convenient low-energy path for carbon–carbon bond formation.[1-6] It is generally assumed that oxidative addition of the organic halide to the metal, metathesis of the halide by the organometallic reagent, and reductive elimination of the diorgano species are the key steps in the catalytic generation of a new carbon–carbon $\sigma$ bond.[2-9]

Although the oxidative addition step has been well studied,[10] the metathesis and reductive elimination steps are less well documented.[7] Possible modes of carbon–carbon $\sigma$ bond formation include 1,1-reductive elimination, dinuclear elimination, and radical pathways. Other competing decomposition modes include $\alpha$- and $\beta$-hydrogen elimination.[9,11-15]

The coupling of methyl to methyl,[16] methyl to fluorophenyl,[8] and methyl to benzyl[17] by the 1,1-reductive elimination from palladium has been reported. In the first two cases, coupling was followed by spectroscopic studies on the isolated diorganobis(phosphine)palladium species. In the 1,1-reductive elimination of methyl and benzyl groups, retention of configuration at the benzyl carbon was observed.[17]

For further exploration of the mechanism of 1,1-reductive elimination, particularly the stereochemistry, the coupling of methyl to a vinyl group was undertaken. The palladium-catalyzed coupling of $\beta$-bromostyrene and methylmagnesium bromide has been shown to proceed with retention of geometry at the double bond, (*Z*)-$\beta$-bromostyrene yielding (*Z*)-propenylbenzene.[6] The suggested mechanism included oxidative addition of (*Z*)-$\beta$-bromostyrene to yield (*Z*)-styrylbromobis(triphenylphosphine)palladium(II), bromide metathesis to give (*Z*)-styrylmethylbis(triphenylphosphine)palladium(II), and reductive elimination to produce (*Z*)-propenylbenzene.

This account reports the isolation of the unstable species (*E*)- and (*Z*)-styrylmethylbis(diphenylmethylphosphine)palladium(II) and the spectroscopic observation of styryl and methyl coupling.

## Results and Discussion

**Synthesis of Styrylbromobis(phosphine)palladium(II) Complexes.** Styrylbromobis(phosphine)palladium(II) complexes were synthesized by oxidative addition of (*E*)- or (*Z*)-$\beta$-bromostyrene (or (*E*)-*p*-chloro-$\beta$-bromostyrene) to tetrakis(phosphine)palladium(0) complexes (Figure 1). As found for similar oxidative addition reactions, the styrylbromopalladium complexes were trans and the reaction proceeded with net retention of the double bond geometry.[18-21]

**Coupling Reactions of Styrylbromobis(phosphine)palladium(II) Complexes and Methyllithium.** The coupling of styryl and methyl

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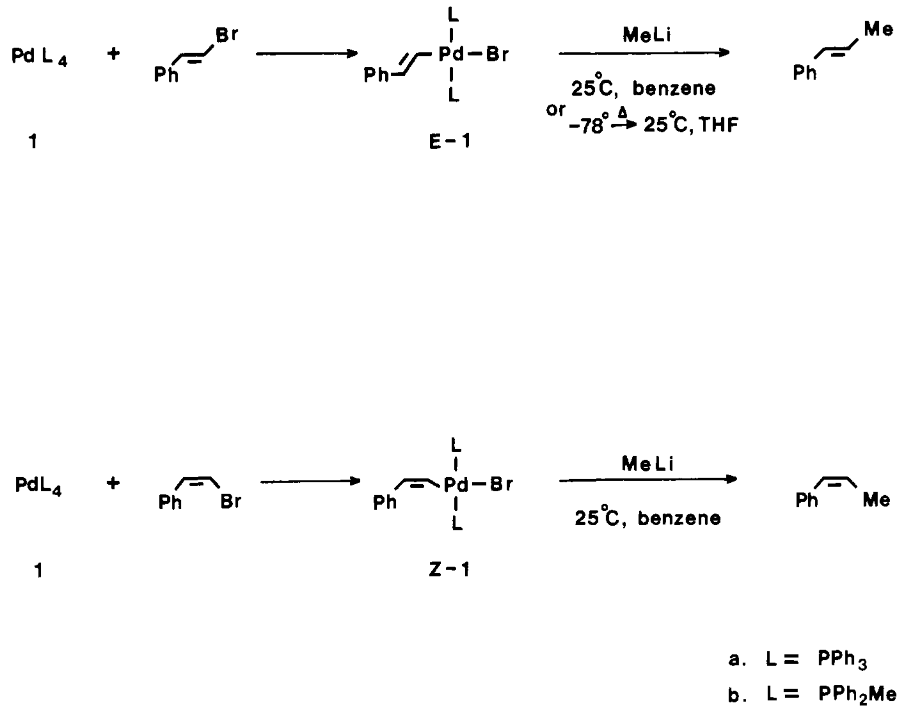


**Figure 1.** Synthesis of styrylbromopalladium complexes and reactions with methyllithium.

groups by reaction of (*E*)-**1a** and (*Z*)-**1a** with methyllithium in benzene at room temperature gave (*E*)- and (*Z*)-propenylbenzene, respectively, in high (>98%) yields. Reaction of (*E*)-**1b** with methyllithium at −78 °C in THF followed by warm-up to room temperature produced (*E*)-propenylbenzene in 82% yield (Figure 1). Small amounts of styrene were also produced.

The styrene could have been generated by $\alpha$ elimination of a methyl hydrogen in an intermediate styrylmethylpalladium complex. Alternative pathways include quenching of the styryl–palladium bond by a trace contaminant, i.e., water, or metathesis of the styryl group by methyllithium, forming styryllithium, which was quenched to give styrene.[22]

**Isolation of (*E*)- and (*Z*)-Styrylmethylbis(diphenylmethylphosphine)palladium(II) [(*E*)- and (*Z*)-2b].** The reaction of (*E*)-**1b** or (*Z*)-**1b** with 1 equiv of methyllithium in THF at −78 °C followed by low-temperature workup provided the thermally sensitive cis–trans mixture of (*E*)-**2b** or cis–trans mixture of (*Z*)-**2b**. These reaction products were also observed by $^{31}$P NMR in THF without isolation. In either case, a mixture of about 50% cis and 50% trans was observed for (*E*)-**2b**, and a mixture of about 70% cis and 30% trans was found for (*Z*)-**2b** (Figure 2, Table I). An analogous experiment on the triphenylphosphine derivatives was not carried out due to the low solubility of these complexes in THF.

Addition of 2 equiv of diphenylmethylphosphine to a mixture of *cis*- and *trans*-(*E*)-**2b** in THF or toluene, or to a mixture of *cis*- and *trans*-(*Z*)-**2b** in THF ([$PPh_2Me$] = 2[$Pd_{total}$]), caused the trans isomer to immediately isomerize to cis.

Isomerization induced by added phosphine or polar solvents in similar complexes is well-known.[23-27] It has been postulated that the isomerization takes place via a five-coordinate intermediate that undergoes pseudorotation and then dissociates a phosphine ligand,[27] thus accounting for the isomerized product.

**Kinetics of the Decomposition of (*E*)- and (*Z*)-Styrylmethylbis(diphenylmethylphosphine)palladium(II) [(*E*)- and (*Z*)-2b].** Warming solutions of isolated (*E*)-**2b** or (*Z*)-**2b** in deuteriochloroform in 10 °C intervals produced no appreciable differences in $^1$H NMR spectra between −60 and −30 °C. At −20 °C a decrease in the concentration of the cis isomers was observed, whereas at −10 °C complete decomposition of the cis complex occurred. An appreciable amount of trans isomer was still present under the same conditions. At 20 °C the complete disappearance of the trans isomers took place. These reactions gave (*E*)-propenylbenzene for complex (*E*)-**2b** and (*Z*)-propenylbenzene for (*Z*)-**2b**.

Increasing the temperature of THF solutions of *cis*- and *trans*-(*E*)-**2b** or -(*Z*)-**2b** generated in situ resulted in an appreciable decrease in the concentration of the cis isomer between −30 and −20 °C. The trans isomer rapidly disappeared between −20 and −10 °C (Figure 3).

At −20 °C, two broad singlets ($^{31}$P NMR) resulted from the disappearance of the cis isomer of (*E*)-**2b** and (*Z*)-**2b**. The upfield singlet at −1.5 ppm was present in both the *E* and *Z* reaction products, whereas the broad downfield singlet appeared at 2.0 ppm for the product from the *E* isomer and at 1.3 ppm for the product from the *Z* isomer (Table I). After the trans isomer disappeared, the relative amounts of singlets at 1.3 or 2.0 ppm increased.

Cooling a sample of the *E* reaction product to −35 °C soon after the disappearance of both the cis and trans isomers caused the singlet at 2.0 ppm to form a broad doublet. At −68 °C, this resonance appeared as an AB quartet for both the *E* and *Z* reaction products, whereas the singlet at −1.5 ppm split into two singlets at −1.0 and −5.8 ppm in a ratio of about 5:1. Additional reaction at 25 °C caused the species at −1.0, 1.3, and 2.0 ppm to decrease in concentration, leaving the species at −5.8 ppm as the predominant product. Addition of 2 equiv of diphenylmethylphosphine to a solution containing the species responsible for the AB quartet and singlets at −1.0 and −5.8 at −78 °C caused the immediate disappearance of the AB quartet and singlet at −1.0 and clearly produced the species at −5.8 ppm.

Thus, the singlet at −5.8 ppm was assigned to tetrakis(diphenylmethylphosphine)palladium(0) by comparison to an authentic sample, whereas the singlet at −1.0 ppm was assigned to tris(diphenylmethylphosphine)palladium(0).[28] The appearance

(22) The latter mechanisms were further indicated when the reactions of *E*-**1b** or *Z*-**1b** and methyllithium were followed by $^{31}$P NMR by the formation of small amounts of methylbromobis(diphenylmethylphosphine)palladium(II).

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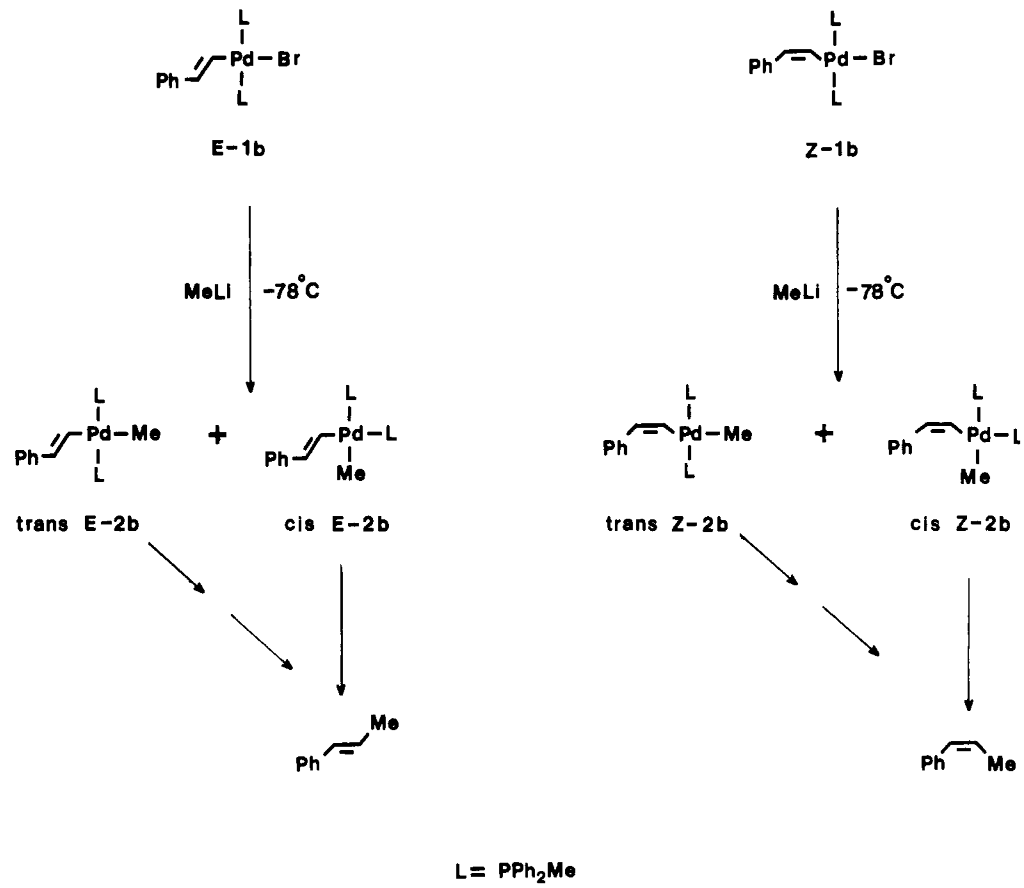



**Figure 2.** Synthesis, isomerization, and reductive elimination reactions of styrylmethylbis(diphenylmethylphosphine)palladium(II) complexes.

of one resonance at higher temperatures indicates a rapid exchange of phosphine ligands (eq 1). At −68 °C, the rate of exchange is slowed, allowing the observation of both species.

$$Pd(PPh_2Me)_3 \underset{-\,PPh_2Me}{\overset{+\,PPh_2Me}{\rightleftharpoons}} Pd(PPh_2Me)_4 \qquad (1)$$

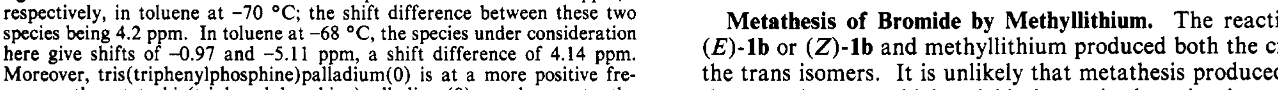
The species responsible for the broad singlets at 1.3 and 2.0 ppm at −20 °C and doublet of doublets at −68 °C were assigned to the $\pi$ complexes (*E*)- and (*Z*)-propenylbenzenebis(diphenylmethylphosphine)palladium(0). The equivalency of the phosphorus nuclei at higher temperatures has recently been described as a result of a rapid equilibrium between complexed and free olefin (eq 2).[29]

$$(PhCH{=}CHCH_3)Pd(PPh_2Me)_2 \rightleftharpoons PhCH{=}CHCH_3 + Pd(PPh_2Me)_2 \qquad (2)$$

The coupling of *cis*-(*E*)-**2b** was followed in the presence of 2 equiv of diphenylmethylphosphine. In this case, coupling occurred between −20 and −10 °C, rather than −30 and −20 °C, and **1b** was the only observable product. When the disappearance of *cis*- and *trans*-(*E*)-**2b** was followed in the presence of 8.4 equiv of (*E*)-propenylbenzene, the appearance of tris(diphenylmethylphosphine)palladium(0) was suppressed.

The kinetics were obtained by following the disappearance of *cis*-(*E*)-**2b** at −30 °C. The concentration of *trans*-(*E*)-**2b** remained constant at this temperature; however, a temperature of −20 °C provided a convenient rate of disappearance of the trans species. The decomposition of both the *cis*- and *trans*-(*E*)-**2b** showed a positive deviation from first-order kinetics, indicating an autocatalytic mode of decomposition. The presence of 1.95 equiv of (*E*)-propenylbenzene significantly decreased the autocatalysis for the disappearance of *trans*-(*E*)-**2b** and gave a slower reaction, whereas 1.95 equiv of (*E*)-propenylbenzene did not appreciably affect the rate of disappearance of *cis*-(*E*)-**2b**. However, in the presence of 1.74 equiv of diphenylmethylphosphine, the disappearance of *cis*-(*E*)-**2b** was strictly first order ($k = 1.28 \times 10^{-4}$ $s^{-1}$) and no longer autocatalytic (Figure 4).

A mixture of *cis*-(*E*)-styrylperdeuteriomethylbis(diphenylmethylphosphine)palladium(II), *cis*-(*E*)-D-**2b**, and *cis*-(*E*)-*p*-chlorostyrylmethylbis(diphenylmethylphosphine)palladium(II), *cis*-(*E*)-Cl-**2**, was prepared at −78 °C and allowed to warm to 25 °C. GC/MS analysis of the product indicated the formation of 3,3,3-trideuteriopropenylbenzene and *p*-chloropropenylbenzene with little or no cross coupled product (eq 3).



(3)

**Metathesis of Bromide by Methyllithium.** The reaction of (*E*)-**1b** or (*Z*)-**1b** and methyllithium produced both the cis and the trans isomers. It is unlikely that metathesis produced only the trans isomers which quickly isomerized to cis, since *trans*-(*E*)-**2b** was shown to be very stable under the metathesis conditions at −68 °C and was, in fact, very stable even at −30 °C. Conversely, the cis isomer could not have been the exclusive metathesis product

(28) The assignment of the species producing a singlet at −1.0 ppm to tris(diphenylmethylphosphine)palladium(0) was made on the basis of the observed exchange with tetrakis(diphenylmethylphosphine)palladium(0) and its disappearance in the presence of added phosphine. Comparison to the shifts of tris- and tetrakis(triphenylphosphine)palladium(0) also supports this assignment. The shifts of the latter are reported at 22.6 and 18.4 ppm,[37] respectively, in toluene at −70 °C; the shift difference between these two species being 4.2 ppm. In toluene at −68 °C, the species under consideration here give shifts of −0.97 and −5.11 ppm, a shift difference of 4.14 ppm. Moreover, tris(triphenylphosphine)palladium(0) is at a more positive frequency than tetrakis(triphenylphosphine)palladium(0), analogous to the species at −0.97 ppm and tetrakis(diphenylmethylphosphine)palladium(0) at −5.11 ppm.

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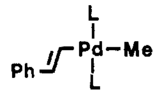
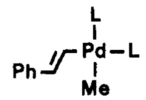
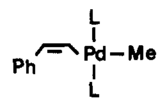
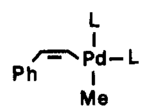
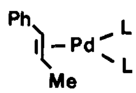
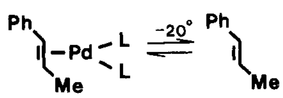
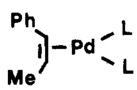
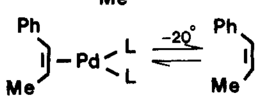
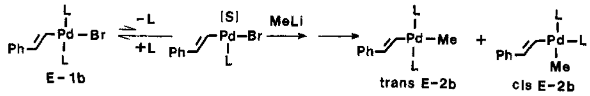
**Table I.** $^{31}$P NMR of (*E*)- and (*Z*)-Styrylmethylbis(diphenylmethylphosphine)palladium(II) and Decomposition Products[a]

| complex | | δ |
|---|---|---|
|  | | 14.2, 13.8[b] (s) |
|  | | 3.35, 2.84[b] (q), $J_{PP}$ = 23 |
|  | | 13.2, 13.0[c] (s) |
|  | | 2.26, 1.72[c] (q), $J_{PP}$ = 24 |
|  | | 2.42, 2.41[b] (q), $J_{PP}$ = 54 |
|  | + $PdL_2$ | 2.0, 2.3[b,d] (br s) |
|  | | 1.38 (q), $J_{PP}$ = 53 |
|  | + $PdL_2$ | 1.3 (br s)[d] |
| $PdL_3$ [e] | | −1.03, −0.97[b] (s) |
| $PdL_4$ [f] | | −5.78, −5.11[b] (s) |
| $PdL_3 \underset{-L}{\overset{-20°, +L}{\rightleftharpoons}} PdL_4$ | | −1.5, −1.3[b,d] (s) |

[a] Spectra were obtained in THF at −68 °C, except where otherwise indicated, relative to an external standard of 10% $Me_3PO_4$ in THF at −68 °C (at ambient temperature, when 85% $H_3PO_4$ = 0, $Me_3PO_4$ = 3.5 ppm); br s = broad singlet, q = quartet. [b] Obtained in toluene. [c] Obtained in deuteriochloroform. [d] Obtained immediately after the decomposition of the trans isomer. [e] See ref 28. [f] Assigned by comparison to authentic material.

which quickly isomerized to trans, because it was shown to be the thermodynamically more stable isomer.

The metathesis was slowed by free phosphine. When 1 equiv of methyllithium was added to a mixture of (*E*)-**1b** containing 2 equiv of diphenylmethylphosphine in THF at −78 °C, the first spectrum obtained within 10 min at −68 °C still showed the presence of (*E*)-**1b**. As the temperature was increased in 10 °C intervals, (*E*)-**2b** was formed at the expense of (*E*)-**1b**. The analogous experiment with no added diphenylmethylphosphine showed metathesis to be complete within 10 min at −68 °C. In the latter case, both *cis*- and *trans*-(*E*)-**2b** were formed, whereas in the former case only *cis*-(*E*)-**2b** was formed. This is not surprising because *trans*-()-**2b** was shown to rapidly isomerize to *cis*-(*E*)-**2b** in the presence of added diphenylmethylphosphine. The phosphine dependence can be explained by a prior ligand dissociation step (eq 4). It could also be explained by competition



(4)

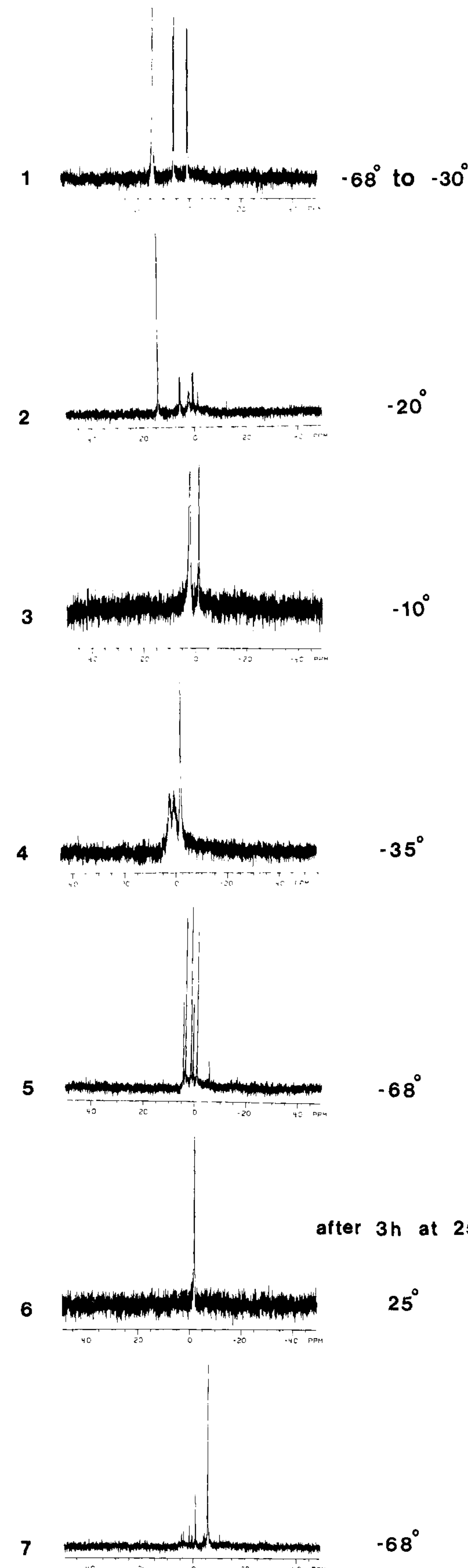
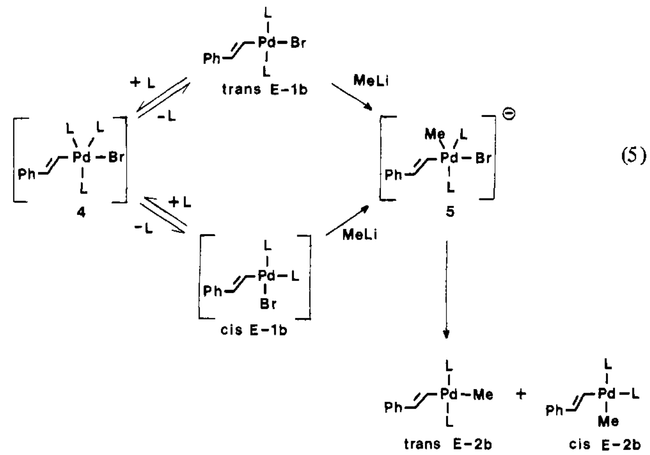



**Figure 3.** $^{31}$P NMR of the disappearance of *cis*- and *trans*-(*E*)-**2b** [shifts: Table I].

of free phosphine and methyllithium for the vacant coordination site on *trans*-(*E*)-**1b**, forming the five-coordinated species **4** and **5** (eq 5).



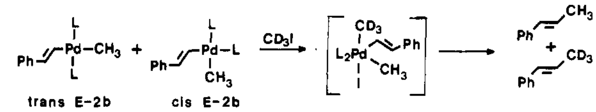

(5)

Evidence for **4** and *cis*-(*E*)-**1b** was obtained from the spectrum of (*E*)-**1b** in the presence of 2 equiv of diphenylmethylphosphine. The usual sharp singlets for *trans*-(*E*)-**1b** and diphenylmethylphosphine at 20 °C were not present in the mixture; instead, a very broad resonance appeared at −12.5 ppm, indicating a rapid phosphine exchange. At −100 °C, three broad resonances appeared at 6.3, 0.97, and −4.02 ppm in addition to a sharp resonance at −30.8 ppm. The resonance at 6.3 ppm is *trans*-(*E*)-**1b**, whereas that at −30.8 ppm is diphenylmethylphosphine. Resonance at 0.97 and −40.2 ppm could be species **4** and *cis*-(*E*)-**1b**.

**Mechanism of Reductive Elimination.** The greater thermal instability of *cis*-(*E*)-**2b** compared to *trans*-(*E*)-**2b** and the formation of olefin complex at the expense of *cis*-(*E*)-**2b** is consistent with a 1,1-reductive elimination reaction of *cis*(*E*)-**2b**. Although *trans*-(*E*)-**2b** also formed the olefin complex upon decomposition, the higher temperature required suggests that isomerization to *cis*-(*E*)-**2b** or to a cis three-coordinate species occurred. A number of pathways that involve complexes of various geometries and coordination numbers are possible for 1,1-reductive elimination.[16] In the case of the dimethylbis(phosphine)palladium complexes, it was shown that isomerization from *trans*- to *cis*-dimethylbis(phosphine)palladium occurred, followed by phosphine dissociation to form a three-coordinate intermediate, from which reductive elimination took place.[16] Extended Hückel calculations show that reductive elimination from a cis "T"-shaped intermediate represents the lowest energy pathway for a three-coordinate intermediate.[30] The rates of reductive elimination of ethane from the *cis*-dimethylpalladium(II) complexes are much slower, however, than the elimination of propenylbenzene from the *cis*-styrylmethylpalladium complexes. In the latter case, excess phosphine did not cause any change in the rate of coupling in the early stages of reaction, indicating coupling could be taking place directly from the square-planar cis complex (Figure 5). The coupling of a cis $d^8$ $L_2MR_2$ to a $d^{10}$ $L_2M$ and $R_2$ is symmetry allowed for a least-motion $C_{2v}$ departure.[30] However, the energy of the antisymmetric $b_2$ orbital involved is much higher for palladium than for nickel complexes, and the lowest energy reductive elimination pathway for nickel(II) complexes is that which originates directly from the four-coordinate square-planar geometry.[30] In the sytrylmethylpalladium complexes, the coupling is that of a cis $d^8$ $L_2MR_2$ to a $d^{10}$ $L_2M$ (olefin) complex. Thus, the energy of the $b_2$ orbital should be significantly lowered, allowing coupling from a square-planar four-coordinate complex to take over as the low-energy pathway in place of phosphine dissociation and coupling from a cis "T-shaped" complex. However, added phosphine did cause a retardation of the reaction rate in the latter stages of the reaction, indicating that dissociation of phosphine from *cis*-(*E*)-**2b** also occurred to form **8**. π complex (*E*)-**3b** can react with dissociated phosphine to form **3b**. Such scavenging of dissociated phsophine should shift the dissociation equilibrium (*cis*-(*E*)-**2b** ⇌ **8**, Figure 5) to the right and account for the autocatalysis observed. Once the dissociated phosphine is depleted, **9** can react with **3b** to account for the small amount of **1b** formed initially. Finally, **3b** and (*E*)-**3b** can decompose to account for the rest of **1b** formed after a prolonged reaction time at 25 °C.

Although the isomerization of *trans*-(*E*)-**2b** to *cis*-(*E*)-**2b** was very rapid at −68 °C in the presence of 2 equiv of diphenylmethylphosphine, the isomerization at −20 °C was slowed down by 2 equiv of propenylbenzene. This implies that a dissociative mechanism for trans to cis isomerization is occurring in the decomposition of *trans*-*E*-**2b** in the absence of added phosphine and added L (propenylbenzene) shifts the dissociative path to the left (*trans*-(*E*)-**2b** ⇌ **7**, Figure 5). The cause of autocatalysis is not certain although it also could be attributed to the scavenging of phosphine by the coordinatively unsaturated palladium(0) products.

**Effect of Methyl Iodide on the Decomposition of (*E*)-Styrylmethylbis(diphenylmethylphosphine)palladium(II).** That oxidative addition of methyl iodide to (*E*)-**2b** forming a palladium(IV) intermediate could occur was indicated by the formation of 3,3,3-trideuteriopropenylbenzene when a mixture of *cis*- and *trans*-(*E*)-**2b** (~1:1) was warmed from −78 to 25 °C in the presence of trideuteriomethyl iodide (eq 6). The relative amount




(6)

of undeuterated vs. deuterated product was approximately 4. Addition of 10.6 equiv of methyl iodide die not cause an immediate reaction at −30 °C. In fact, little *trans*-(*E*)-**2b** decomposed after 12.5 h at −30 °C, whereas the cis isomer decomposed within that time limit to form a red solution. It is most likely that the deuterated product was formed by oxidative addition to the more thermally stable trans isomer at a temperature above that which the cis isomer has already undergone 1,1-reductive elimination. Since oxidative addition of β-bromostyrene to $PdL_n$ and $PtL_n$ is known to occur 100 times faster than methyl iodide,[21] it is possible for Pd(IV) species to become involved in the β-bromostyrene–methylmagnesium bromide–$PdL_n$ catalytic cycle.

## Experimental Section

**General and Instrumental Information.** All manipulations involving air-sensitive compounds were carried out under an argon or a nitrogen atmosphere. Solvents were dried, distilled, and deoxygenated prior to use. Triphenylphosphine was recrystallized from ethanol, whereas diphenylmethylphosphine (Strem) was distilled from sodium prior to use. Pure (*Z*)-β-bromostyrene was prepared as described,[31,32] whereas pure (*E*)-β-bromostyrene was obtained by purification of commerical β-bromostyrene (Aldrich).[33] Deuteriomethyllithium was prepared similarly to that described.[16] The concentration of deuteriomethyllithium and methyllithium in ether (Aldrich) was determined by titration with 2-butanol in xylene with *o*-phenanthroline as indicator. Authentic (*E*)- and (*Z*)-propenylbenzene (ICN) were obtained commercially.

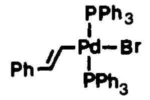
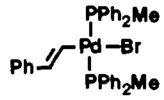
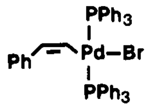
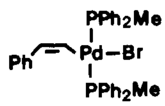
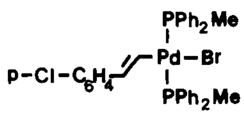
$^1$H NMR spectra were recorded on EM-360 or JEOL FX-100 spectrometers, whereas $^{31}$P NMR spectra were recorded on an NT-150 spectrometer. The JEOL FX-100 and NT-150 spectrometers were equipped with variable-temperature probes for low-temperature work. Toluene-$d_8$ (Stohler) and deuteriochloroform were deoxygenated by the freeze–pump–thaw method at −78 °C prior to use. When purified deuteriochloroform was required, it was passed through a column of basic alumina prior to deoxygenating. Toluene and THF used in $^{31}$P NMR work were distilled from sodium benzophenone prior to use. $Me_4Si$ was omitted as an internal $^1$H NMR reference for the styrylmethylpalladium complexes since it obscures the palladium methyl resonances: THF was used as a reference. An external reference of 10% trimethyl phosphate in THF at −68 °C was used in $^{31}$P NMR work.

GLC analyses were carried out by using a 0.375 in. × 10 ft 20% Carbowax 20 M on Chromosorb W 60/80 column or a 0.25 in. × 6 ft 3% SE-30 on Aeropak 30 100/120 column. Tetralin (Aldrich) was distilled before use as a GC standard. GC/MS data were obtained by using a Perkin Elmer Sigma-3 gas chromatograph equipped with a 50-m

(30) Tatsumi, K.; Hoffman, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.*, in press.

(31) Grovenstein, E. Jr.; Lee, D. E. *J. Am. Chem. Soc.* **1953**, *75*, 2639.
(32) Cristol, S. J.; Norris, W. P. *J. Am. Chem. Soc.* **1953**, *75*, 2645.
(33) Dolby, L. J.; Wilkins, C.; Frey, T. G. *J. Org. Chem.* **1966**, *31*, 1114.

**Table II.** $^1$H and $^{31}$P NMR of Styrylbromopalladium(II) Complexes, *trans*-($p$-X-$C_6H_4$-$CH_a$=$CH_b$)(Br)$PdL_2$

| complex | | $^1$H NMR[a] | | | | | | | $^{31}$P NMR[b] |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta_{H_a}$ | $J_{P-H_a}$ | $\delta_{H_b}$ | $J_{P-H_b}$ | $J_{H_a-H_b}$ | $\delta_{P-Me}$ | $\delta J_{P-Me}$ | |
| (*E*)-1a[c] |  | 5.29 (dt) | 2 | 6.27 (dt)[d] | 10 | 16 | | | 21.1[e] |
| (*E*)-1b |  | 5.51 (dt) | 2 | 6.41 (dt)[d] | 10 | 16 | 2.13 (t) | 3 | 5.7 |
| (*Z*)-1a[f] |  | 5.73 (dt) | 4.6 | 6.31 (dt) | 9 | 9 | | | 20.8[g] |
| (*Z*)-1b |  | 6.28 (dt) | 4.5 | 6.61 (dt) | 9 | 9 | 1.95 (t) | 3 | 3.8 |
| (*E*)-Cl-1[c,h] |  | 5.38 (d) | ≈0 | 6.36 (dt)[d] | 9 | 16 | 2.15 (t) | 3 | 5.3 |

[a] Run in deuteriochloroform relative to $Me_4Si$ at 20 °C; dt = doublet of triplets, t = triplet, d = doublet. [b] Run in THF at −68 °C relative to 10% $Me_3PO_4$ in THF at −68 °C as an external reference. All resonances were singlets. [c] $T$ = −20 °C. [d] Obscured by the ortho protons on the styryl phenyl. [e] Run in deuteriochloroform at −60 °C. [f] $T$ = 7 °C. [g] Run in deuteriochloroform at −50 °C. [h] The styrylphenyl protons gave two doublets at 6.26 and 6.96 ppm, $J_{H-H}$ = 9.

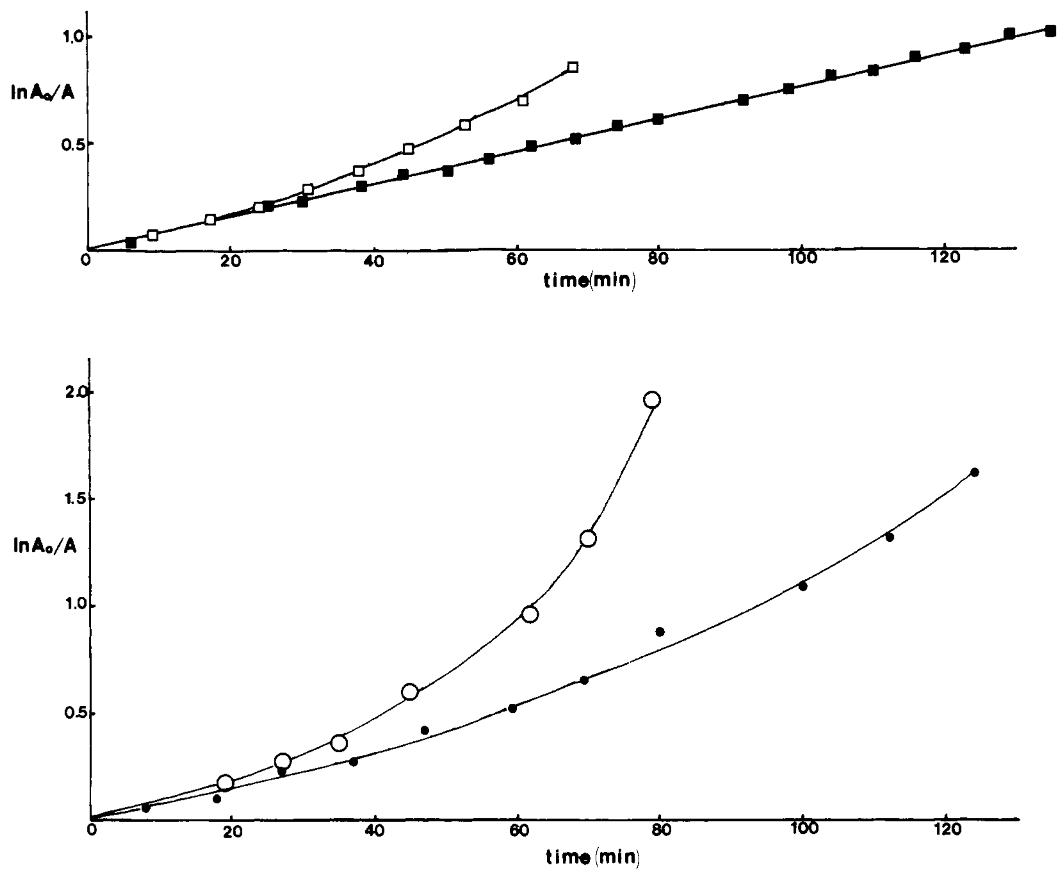


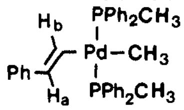
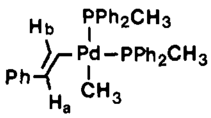
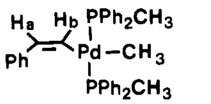
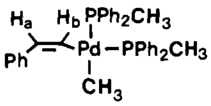

**Figure 4.** Disappearance of *cis*- and *trans*-(*E*)-**2b**: (□) *cis*-(*E*)-**2b** at −30 °C, (■) *cis*-(*E*)-**2b** at −30 °C in the presence of 1.74 equiv of $PPh_2Me$, (○) *trans*-(*E*)-**2b** at −20 °C, (●) *trans*-(*E*)-**2b** at −20 °C in the presence of 1.95 equiv of (*E*)-propenylbenzene. Number of equivalents are based on [$Pd_{total}$].

SE-30 glass capillary column, and a V.G. micromass 16F mass spectrograph equipped with a V.G. data system based on PDP 8/a. IR spectra were recorded on a Beckman IR-12 or a Beckman IR-4240.

**Kinetics.** Quantitative rate data were obtained by $^{31}$P NMR by comparison of the resonance of interest with that of ~0.25 M triphenylphosphine oxide in ethanol, which was contained in the NMR tube by means of an insert. The resonances of interest were normalized to that of triphenylphosphine oxide by integration. First-order plots were made by linear least-squares analysis.

**Transfer of Thermally Sensitive Solids and Solutions.** A disposable pipet was placed above the unstable solid in the low-temperature filter under a high argon flow to purge and cool the pipet. After some solid

Table III. $^1$H NMR of Isolated (*E*)- and (*Z*)-Styrylmethylbis(diphenylmethylphosphine)palladium(II)[a]

| complex | Pd-CH$_3$ | P-CH$_3$ | H$_a$ | H$_b$ | aromatic |
|---|---|---|---|---|---|
| trans E-2b  | −0.74 (t)<br>−0.094 (t)[b]<br>$J_{P-Pd-CH} = 6$ | 2.10 (t)<br>1.97 (t)[b]<br>$J_{P-CH} = 3$ | 5.87 (d)<br>5.80 (d)[b]<br>$J_{H_a-H_b} = 19$ | 6.97 (dt)<br>$J_{P-Pd-C-H_b} = 8$ | 7.0–8.0 |
| cis E-2b  | 0.22 (dd)<br>$J_{P-Pd-CH_{cis}} = 6$<br>$J_{P-Pd-CH_{trans}} = 9$ | 1.47 (d)[c]<br>$J_{P-CH} = 6$ | 6.29 (d)<br>$J_{H_a-H_b} = 20$ | d | |
| trans Z-2b  | −0.93 (t)<br>$J_{P-Pd-CH} = 6$ | e | | | 6.6–8.3[f] |
| cis Z-2b  | −0.13 (dd)<br>$J_{P-Pd-CH_{cis}} = 6$<br>$J_{P-Pd-CH_{trans}} = 9$ | 1.38 (d)[c]<br>$J_{P-CH} = 7$ | | | |

[a] Spectra were run in deuteriochloroform at −30 °C on a JEOL FX-100 with THF as an internal reference set at 3.75 ppm. [b] Assignment made in toluene-$d_8$ at −30 °C with THF as an internal reference set at 3.53 ppm. [c] Disappeared at the same rate as the cis palladium methyl. [d] Obscured by aromatic region. [e] Obscured by THF. [f] Consists of at least four resonances assigned to H$_a$, H$_b$, and aromatic protons.

was scooped up in the tip of the pipet, it was quickly placed in the new vessel which was chilled to -78 °C under a high flow of argon. A blunt needle, chilled several minutes in the pipet, was used to expel the solid.

Transfers or additions involving thermally unstable speices were carried out by thoroughly purging syringes or cannulas with cold solvent or reagent.

**(*E*)-*p*-Chloro-*β*-bromostyrene.** To 25.0 g (0.137 mol) of *p*-chlorocinnamic acid were added 200 mL of tetrachloroethane and 7.3 mL (0.142 mol) of bromine. Heating and stirring at 95 °C caused a clear solution to form, which soon precipitated a solid. After 2 h, the solid was filtered and rinsed with cold tetrachloroethane and chloroform to produce 39.6 g (0.106 mol, 77% yield) of *p*-chlorocinnamic acid dibromide as a white powder. Recrystallization from acetone–hexane produced white needles, mp 194–195 °C (decomp). Anal. Calcd for $C_9H_7C1O_2Br_2$: C, 31.57; H, 2.06. Found: C, 32.03; H, 2.08. $^1$H NMR (acetone-$d_6$) δ 5.06 (d, -CHBr-, 1 H), 5.49 (d, –CHBr–, 1 H, $J_{HH}$ = 12), 7.34 (d, *o*-H, 2 H), 7.58 (d, *o*-H, 2 H, $J_{H_oH_o}$ = 9), 8.46 (br s, -COOH, 1 H); IR (KBr) 1898 (m), 1710 (s), 1588 (m), 1486 (s), 1420 (s), 1352 (w), 1298 (m), 1281 (s), 1260 (s), 1208 (s), 1183 (w), 1171 (m), 1150 (m), 1136 (s), 1104 (m), 1088 (s), 1010 (s), 952 (w), 925 (w), 885 (m), 834 (w), 822 (s), 770 (w), 715 (s), 699 (s), 648 (w), 632 (m), 570 (m), 502 (m), 477 (w), 407 (s) cm$^{-1}$.

With use of the method of Cristol and Norris,[32] 39.6 g (0.106 mol) of *p*-chlorocinnamic acid dibromide and 29.9 g (0.356 mol) sodium bicarbonate were stirred and heated at reflux for 13 h in 400 mL of acetone predried over potassium carbonate. Upon evaporation of the acetone under reduced pressure at room temperature, the product was extracted into ether and washed several times with water. After the ether layer was dried over sodium sulfate, it was filtered and evaporated to give 20.6 g (0.0947 mol, 89% yield) of (*Z*)-*p*-chloro-*β*-bromostyrene as a yellow liquid. Further purification involved passage through a silica gel column with hexane to remove a dark decomposition product and vacuum distillation (*T* = 50–60 °C, *P* = 0.14–0.20 mm). Anal. Calcd for $C_8H_6ClBr$: C, 44.18; H, 2.78. Found: C, 44.46; H, 2.76. $^1$H NMR ($CDCl_3$) δ 6.32 (d, –CH=CH–, 1 H), 6.87 (d, –CH=CH–, 1 H, $J_{HH}$ = 7.5), 7.19 (d, *o*-H, 2 H), 7.50 (d, *o*-H, 2 H, $J_{H_oH_o}$ = 8); IR (NaCl plates) 3080 (m), 3000 (w), 2920 (w), 1900 (w), 1612 (m), 1588 (m), 1563 (w), 1488 (s), 1460 (w), 1400 (s), 1325 (s), 1310 (s), 1284 (w), 1180 (w), 1110 (m), 1094 (s), 1014 (s), 945 (w), 920 (w), 843 (s), 822 (s), 775 (w), 720 (s), 680 (s), 635 (w).

Isomerization was effected by heating 20.6 g (0.0947 mol) of the *Z* isomer to 130 °C for 18 h in the presence of a catalytic amount of iodine. Kugelrohr distillation produced a pink slurry, which was dissolved in ether and shaken with aqueous sodium bisulfate followed by water. The ether layer was dried over sodium sulfate, filtered, and evaporated to produce 16.5 g (80% recovery) of *p*-chloro-*β*-bromostyrene as a white solid, which was 88% *E* and 12% *Z* by $^1$H NMR. Purification to destroy the *Z* isomer, carried out similarly to that described for the unsubstituted species,[32] produced 13.7 g (83% recovery) of crude (*E*)-*p*-chloro-*β*-bromostyrene. Recrystallization from methanol gave 6.8 g (0.0313 mol, 50% recovery, 33% overall yield) of white crystalline (*E*)-*p*-chloro-*β*-bromostyrene in two crops, mp 47–48 °C. Anal. Calcd for $C_8H_6ClBr$: C, 44.18; H, 2.78. Found: C, 44.09; H, 2.75. $^1$H NMR ($CDCl_3$) δ 6.58 (d, –CH=, 1 H), 6.98 (d, –CH=, 1 H, $J_{HH}$ = 14), 7.14 (s, *o*-H, 4 H); IR (KBr) 3064 (m), 3020 (w), 1880 (w), 1605 (m), 1588 (m), 1560 (m), 1484 (s), 1398 (m), 1268 (m), 1220 (m), 1189 (m), 1176 (m), 1098 (s), 1082 (s), 1012 (s), 947 (s), 930 (s), 833 (s), 773 (s), 752 (s).

**(*E*)- and (*Z*)-Styrylbromobis(triphenylphosphine)palladium(II) [(*E*)- and (*Z*)-1a].** To 1.01 g (0.873 mmol) of freshly prepared tetrakis(triphenylphosphine)palladium(0)[34] was added 6.5 mL (50.8 mmol) freshly distilled and deoxygenated (*E*)-*β*-bromostyrene. The yellow slurry lightened to white upon stirring. After 3.5 h, 90 mL of pentane was added. The product was filtered, rinsed thoroughly with ether, and dried in vacuo to produce 0.6608 g (0.812 mmol, 93% yield) of (*E*)-**1a** as a white powder. Anal. Calcd. for $C_{44}H_{37}BrP_2Pd$): C, 64.92; H, 4.58; P, 7.61. Found: C, 64.80; H, 4.61; P, 7.57. $^1$H NMR and $^{31}$P NMR: see Table II. IR (CsI) 1560 (m), 960 (s), 800 (m) cm$^{-1}$.

Similar reaction with (*Z*)-*β*-bromostyrene for 2 h produced a 70% yield of (*Z*)-**1a** as a white powder. (*E*)-**1a** was often a troublesome contaminant. Anal. Calcd for $C_{44}H_{37}BrP_2Pd$: C, 64.92; H, 4.58. Found: C, 65.51; H, 4.64. $^1$H and $^{31}$P NMR: see Table II. IR (CsI) 1572 (w), 778 (w), 650 (vw) cm$^{-1}$.

**(*E*)-Styryl-, (*Z*)-Styryl-, and (*E*)-(*p*-Chlorostyryl)bromobis(diphenylmethylphosphine)palladium(II) [(*E*)-1b, (*Z*)-1b, and (*E*)-Cl-1].** Tetrakis(diphenylmethylphosphine)palladium(0)[35] was freshly prepared from 197.7 mg (1.00 mmol of Pd) of 2-methallylpalladium(II)chloride[36] and dried in vacuo. About 12 mL of toluene and 0.93 mL (7.27 mmol) of deoxygenated (*E*)-*β*-bromostyrene were added. Upon stirring the golden solution, it lightened to pale yellow and produced small amounts of white solid. After 12 h, the sides of the flask were scraped down, and the reaction mixture was transferred into 150 mL of hexane; the reaction flask rinsings with toluene were also added to the hexane mixture. The mixture was chilled to 0 °C, and the sides of the flask were scraped to precipitate a white crystalline solid. The solid was filtered, rinsed with hexane, and dried *in vacuo*, yielding 0.5653 g (0.819 mmol, 82% yield) of (*E*)-**1b**. Anal. Calcd for $C_{34}H_{33}BrP_2Pd$: C, 59.19; H, 4.82; P, 8.98. Found: C, 59.39; H, 4.81; P, 8.98. $^1$H and $^{31}$P NMR: see table II. CsI IR (CsI) 1555 (m), 963 (m), 803 (m) cm$^{-1}$.

Similar treatment with (*Z*)-*β*-bromostyrene gave a 56% yield of *Z*-**1b**. *E*-**1b** was often a troublesome contaminant. Anal. Calcd for $C_{34}H_{33}BrP_2Pd$: C, 59.19; H, 4.82. Found: C, 58.36; H, 4.78. $^1$H and $^{31}$P NMR: see Table II. IR (CsI) 1542 (vw), 770 (w), 638 (vw) cm$^{-1}$.

Similar treatment with (*E*)-*p*-chloro-*β*-bromostyrene gave a 74% yield of (*E*)-Cl-**1** as a white powder. Anal. Calcd for $C_{34}H_{32}ClBrP_2Pd$: C, 56.38; H, 4.45; P, 8.55; Cl, 4.89. Found: C, 55.58; H, 4.38; P, 8.38; Cl, 4.90. $^1$H and $^{31}$P NMR: see Table II. IR (CsI) 1542 (m), 1083 (m), 952 (m), 809 (w), 764 (w) cm$^{-1}$.

**(*E*)-Propenylbenzene from the Reaction of (*E*)-Styrylbromobis(triphenylphosphine)palladium(II) [(*E*)-1a] and Methyllithium.** To a mixture

(34) Coulson, D. R. *Inorg. Syn.* **1972**, *13*, 121.
(35) Kuran, W.; Musco, A. *Inorg. Chim. Acta* **1974**, *12*, 187.
(36) Dent, W. T.; Long. R.; Wilkinson, A. J. *J. Chem. Soc.* **1964**, 1585.
(37) Mann, B. E.; Musco, A. *J. Chem. Soc., Dalton Trans.* **1975**, 1673.

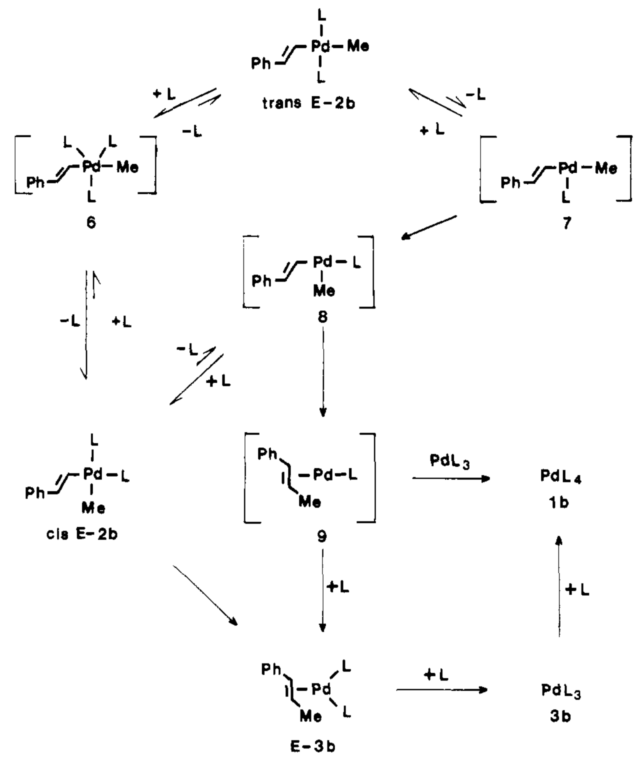



**Figure 5.** Reductive elimination of *cis*-(*E*)-**2b** and isomerization of *trans*-(*E*)-**2b**.

of 0.900 g (1.106 mmol) (*E*)-**1a** and 0.20 mL (1.468 mmol, GC standard) of tetralin in 15.0 mL of benzene was added 0.90 mL (1.32 mmol) of 1.47 M methyllithium in ether at room temperature. The slurry darkened during the methyllithium injection and was stirred for 17 h. GC injection on 20% Carbowax at 148 °C confirmed the formation of (*E*)-propenylbenzene in 98% yield, uncontaminated with the *Z* isomer, when compared to a GC standard of molar ratio 2.41:1 tetralin/(*E*)-propenylbenzene.

**(*E*)-Propenylbenzene from the Reaction of (*E*)-Styrylbromobis(diphenylmethylphosphine)palladium(II) [(*E*)-1b] and Methyllithium.** To a solution of 0.1730 g (0.251 mmol) of *E*-**1b** in 3.4 mL of THF, cooled to −78 °C, was slowly added 0.60 mL (0.252 mmol) of 0.42 M methyllithium in ether within 3 min. As the low-temperature bath warmed, the color changed from light yellow to dark red between −27 and −21 °C. At 10 °C, 0.017 mL of tetralin (0.125 mmol, GC standard) was injected. Workup involved concentration of the mixture at 0 °C, followed by Kugelrohr distillation be allowing the temperature to quickly rise to 250 °C and holding the temperature at 250 °C for about 45 min. GLC analysis of the concentrated distillate on 20% Carbowax at 160 °C showed a trace of styrene and a 82% yield of (*E*)-propenylbenzene, uncontaminated with the *Z* isomer, by using a GC standard of molar ratio 0.479:1 tetralin/(*E*)-propenylbenzene.

**(*Z*)-Propenylbenzene from the Reaction of (*Z*)-Styrylbromobis(triphenylphosphine)palladium(II) [(*Z*)-1a] and Methyllithium.** To a mixture of 0.2276 g (0.280 mmol) of *E*-**1a**, 0.1177 g (0.449 mmol) of triphenylphosphine, and 0.029 mL (0.213 mmol, GC standard) of tetralin in 2.0 mL of benzene was added 0.25 mL (0.400 mmol) of 1.60 M methyllithium at room temperature. Immediately, the white slurry partially dissolved to form a yellow slurry and then quickly precipitated a yellow solid. The solid was further precipitated with hexane, filtered, and rinsed with hexane. The filtrate, concentrated at 0 °C, was analyzed by GLC on a 20% Carbowax column at 150 °C. A small amount of styrene, plus (*Z*)-propenylbenzene, uncontaminated with (*E*)-propenylbenzene, was detected in 99% yield, based on comparison to a GC standard of molar ratio 0.954:1 tetralin/(*Z*)-propenylbenzene.

**Isolation of (*E*)- and (*Z*)-Styrylmethylbis(diphenylmethylphosphine)palladium(II) [(*E*)-2b and (*Z*)-2b].** To a solution of 0.2148 (0.311 mmol) of (*E*)-**1b** in 5.0 mL of THF, cooled to −78 °C, was slowly added 0.21 mL (0.315 mmol) of 1.50 M methyllithium. The turbid sample immediately dissolved to form a yellow solution. The reaction mixture was transferred through a chilled cannula into a low-temperature gravity filter containing 100 mL of pentane at −78 °C. A white solid precipitated, which was washed 5 times with 75-mL portions of pentane at −78 °C. Occluded THF was removed by solution in deuteriochloroform on the frit at −60 °C, followed by precipitation and rinsing with several portions of pentane at −78 °C. The solid was then rinsed with several portions of butane (Matheson) at −78 °C and dried in vacuo for 24 h. Similarly, (*Z*)-**2b** was isolated. $^1$H NMR and $^{31}$P NMR: see Tables I and III.

**In Situ Generation of (*E*)- and (*Z*)-Styrylmethylbis(diphenylmethylphosphine)palladium(II) [(*E*)- and (*Z*)-2b].** The following is typical for in situ $^{31}$P NMR studies: A solute of 33.4 mg (0.0484 mmol) of (*E*)-**1b** and 0.50 mL of THF were placed in a 5-mm NMR tube. Mixing for addition of any species at low temperature in an NMR tube was achieved by a needle immersed in the sample, providing a gentle flow of argon. After the sample cooled to −78 °C, 0.10 mL (0.043 mmol) of 0.43 M methyllithium in ether was injected, and the solution was allowed to mix for several minutes. The needle was then raised above the level of the solution and a higher flow rate of argon was applied to further purge the tube. The sample was kept at −78 °C until it was quickly placed in the $^{31}$P NMR probe equilibrated at −68 °C. No darkening of the yellow solution occurred during this manipulation.

**Decomposition of the Mixture *cis*-(*E*)-*p*-Chlorostyrylmethylbis(diphenylmethylphosphine)palladium(II) (*cis*-(*E*)-Cl-2) and *cis*-(*E*)-Styrylperdeuteriomethylbis(diphenylmethylphosphine)palladium(II) (*cis*-(*E*)-D-2b).** To a solution of 208.1 mg (0.287 mmol) of (*E*)-Cl-**1** in 3.0 mL of THF at −78 °C was added 0.56 mL (0.286 mmol) of 0.51 M methyllithium in ether to form a pale-yellow solution. After the solution was stirred for 26 min, 0.22 mL (1.16 mmol) of diphenylmethylphosphine at room temperature was slowly added dropwise to give the reaction mixture at −78 °C. The free phosphine was added to prevent or lessen any reaction between the *p*-chloro group and reduced palladium once reaction occurred. Meanwhile, 199.9 mg (0.290 mmol) of (*E*)-**1b** was dissolved in 3.0 mL of THF at room temperature and the mixture chilled at −78 °C. Freshly prepared deuteriomethyllithium in ether, (0.44 mL, 0.290 mmol, 0.66 M) was slowly injected with stirring. This caused the yellowish slurry to form a white slurry (reaction mixture b).

Reaction mixture a was transferred through a cannula, chilled by passage of THF held at −78 °C, into mixture b. A clear yellow mixture c was formed. Approximately 0.60 mL of this was carefully transferred to an NMR tube by a chilled syringe. A $^{31}$P NMR spectrum of mixture c showed that some tetrakis(diphenylmethylphosphine)palladium(0) was present, but not enough to account for the complete coupling of a.

Mixture c was slowly warmed to room temperature over a 5-h period and stirred at room temperature for an additional 12 h. Workup involved a Kugelrohr distillation followed by drying the distillate in THF over molecular sieves for 3 h, filtering the liquid, and concentrating it at 0 °C to give a pale-yellow liquid. GC/MS analysis using variable-temperature programming indicated two GC peaks of interest. The mass spectrum at each maximum was taken. The first eluted species gave a parent peak at $m/e$ 121 and base peak at $m/e$ 120; the second eluted species gave a parent peak at $m/e$ 152 (and p + 2 peak at $m/e$ 154 at one-third the intensity of $m/e$ 152) and base peak at $m/e$ 117. A small peak at $m/e$ 155 was also present, but no P + 2 peak at $m/e$ 157, which was within the detection limit. Mass $m/e$ 155 is probably a $^{13}$C contribution of $m/e$ 154, at least in part.

**Decomposition of (*E*)-Styrylmethylbis(diphenylmethylphosphine)palladium(II) [(*E*)-2b] in the Presence of Deuteriomethyl Iodide.** To 125.0 mg (0.181 mmol) of *E*-**1b** in 3.0 mL of THF at −78 °C was added 0.36 mL (0.184 mmol) of 0.51 M methyllithium in ether. After deoxygenating deuteriomethyl iodide as received (Aldrich) by the freeze–pump–thaw method at −78 °C, 67 μL (~1.05 mmol) was added to the reaction mixture slowly over 2 min. The low-temperature bath was allowed to warm to room temperature over about 3.5 h. The color of the solution changed from pale yellow to red by the time −17 °C was reached. Around 0 °C the intensity of the red color was diminished and by 17 °C the color was yellow. Workup involved Kugelrohr distillation and concentration of the distillate at 0 °C. GC/MS analysis at 110 °C showed two overlapping maxima of interest: the first maximum giving a parent peak at $m/e$ 121 and base peak at $m/e$ and 120 the second giving peaks at $m/e$ 117 and 118 of equal intensity. A computer-drawn diagram of the overlapping GC peaks indicates an approximate area ratio of the second peak to the first peak of 4.

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