e.g., Gilbert, B. C.; Trenwith, M. *J. Chem. Soc., Perkin Trans. 2* **1973,** 1834. Lagercrantz, C.; Setaka, M. *Acta Chem. Scand., Ser. B.* **1974,** *28,* 619. Smith, P.; Stevens, R. D.; Gilman, L. G. *J. Phys. Chem.* **1975,** *79,* 2688. Ashworth, B.; Gilbert, B. C.; Smith, P.; Stevens, R. D.; Kaba, R. A. *J. Magn. Reson.* **1975,** *19,* 398. Smith, P.; Gilman, L. G.; Stevens, R. D.; de Hargrave, C. V. *ibid.* **1978,** *29,* 545.
(30) The rate constant for thermal decomposition of *n*-alkanoyl peroxides can be calculated[31] to be ca. 2.2×10^{-7} s^{-1} at 40 °C. Secondary alkanoyl peroxides probably decompose somewhat more rapidly than the primary peroxides.
(31) Guillet, J. E.; Walker, T. R.; Meyer, M. F.; Hawk, J. P.; Towne, E. B. *Ind. Eng. Chem., Prod. Res. Dev.* **1964,** *3,* 257.
(32) Terabe, S.; Konaka, R. *J. Chem. Soc., Perkin Trans. 2* **1973,** 369.
(33) P_{cis} and P_{trans} nitroxides were not distinguishable.
(34) Ratios involving *t*-Bu_3NB refer to the anilino adduct only.
(35) Roginskii, V. A.; Belyakov, V. A. *Dokl. Akad. Nauk SSSR* **1977,** *237,* 1404.
(36) Radical addition to quinones has long been known; see e.g., Waters, W. A. "The Chemistry of Free Radicals", Clarendon Press: Oxford, 1946; p 49.
(37) The trapping of thermally generated *tert*-butyl radicals has been independently confirmed (Chen, K. S.; Foster, T.; Wan, J. K. S. Private communication). This quinone would also appear to have great potential as a spin trap for metal-centered radicals.
(38) Alkyl addition to the 4 position followed by a ring expansion is another possibility suggested by recent work by Nishinaga et al.[39]
(39) Nishinaga, A.; Itahara, T.; Shimizu, T.; Matsuura, T. *J. Am. Chem. Soc.* **1978,** *100,* 1820. Nishinaga, A.; Itahara, T.; Matsuura, T.; Rieker, A.; Koch, D.; Albert, K.; Hitchcock, P. B. *ibid.* **1978,** *100,* 1826. Nishinaga, A.; Nakamura, K.; Matsuura, T. *Tetrahedron Lett.* **1978,** 3557, 3597. Nishinaga, A.; Shimizu, T.; Matsuura, T. *ibid.* **1978,** 3747.
(40) Citterio, A. *Tetrahedron Lett.* **1978,** 2701.
(41) Nelsen, S. F.; Bartlett, P. D. *J. Am. Chem. Soc.* **1966,** *88,* 137.
(42) There were some problems with CH_3· radical trapping. These were overcome by recrystallization of the azocumene. The original material must have contained a source of cumyloxy radicals.
(43) Attempts to measure relative k^T values for Me_3C· generated by thermal decomposition of $Me_3COOC(O)CMe_3$ were frustrated by the simultaneous formation of Me_3CO· and Me· spin adducts with several of the traps. We were unable to prepare pure $Me_3CC(O)OOC(O)CMe_3$.

Mechanism of Reductive Elimination. Reaction of Alkylpalladium(II) Complexes with Tetraorganotin, Organolithium, and Grignard Reagents. Evidence for Palladium(IV) Intermediacy

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Abstract: Coupling products are obtained in good yields from the reaction of tetraorganotin compounds or Grignard reagents and organohalogenopalladium(II) complexes provided that a benzyl bromide is present. Low yields are obtained in the absence of the benzyl bromides, in which case other decomposition pathways (e.g., α elimination) take place, even in the presence of electron acceptors (e.g., oxygen, *m*-dinitrobenzene). The first step in the reaction of benzylhalogenobis(triphenylphosphine)-palladium(II) complexes with MeM (M = $SnMe_3$, MgBr) is metathesis of the benzyl ligand rather than the halogen. This unique carbon-for-carbon transmetalation takes place at 25 °C and is facilitated by electron-donating substituents on the benzyl ligand. The products of this reaction subsequently react at higher temperature in the presence of a benzyl bromide to afford ethylbenzene. Optically active chloro-(α-deuteriobenzyl)bis(triphenylphosphine)palladium yields, upon reaction with tetramethyltin in the presence of *p*-nitrobenzyl bromide, optically active α-deuterioethylbenzene in which overall retention of configuration at carbon has resulted. *cis*-Dimethylbis(triphenylphosphine)palladium(II) reacts with benzyl bromide at 25 °C to afford ethylbenzene and bromomethylbis(triphenylphosphine)palladium(II) rather than ethane. When optically active α-deuteriobenzyl bromide is used in this reaction, optically active α-deuterioethylbenzene is formed, and inversion of configuration at carbon takes place. The reductive elimination process is proposed to take place preferentially from a palladium(IV) intermediate with retention of configuration at carbon.

Introduction

Reductive elimination is a crucial step in low-energy transition-metal mediated transformations of organic compounds to products in which new carbon-carbon bonds have been generated.[1,2] Although there is considerable mechanistic information on oxidative addition reactions of organic compounds to low valent transition-metal complexes,[3-5] there is much less information concerning the reverse, reductive elimination reaction.

Trialkyltriphenylphosphinegold complexes reductively eliminate cis methyl groups by a first-order process.[6] Diaryl-[7] and arylmethylbis(triphenylphosphine)nickel complexes[7,8] decompose to give coupled products. However, the rate of the entire catalytic cycle is faster than the simple reductive elimination step of two organic groups attached to nickel, so that an induction of the reductive elimination by a prior electron-transfer process from nickel has been proposed.[8] Diarylbis(phosphine)platinum complexes decompose by a concerted coupling mechanism, as evidenced by the absence of crossover products or products derived from radical intermediates.[9]

Reductive elimination reactions also take place with six-coordinate di- and trialkylplatinum(IV) complexes.[10] In certain other di- or trimethyl metal complexes, α elimination is observed instead.[11] Dinuclear reductive elimination takes place in osmium clusters.[12] Critical mechanistic studies on the reductive elimination of diorganopalladium complexes are scarce,[7,13] yet palladium has been demonstrated to catalyze a large number of different coupling reactions in which the reductive elimination step probably has a crucial role.[14]

Results and Discussion

Reactions of Benzylpalladium Complexes with Methyllithium and with Tetramethyltin. (a) Reactions. With the purpose of studying the stereochemistry of reductive elimination from palladium(II) complexes, a study of the sequence outlined in Scheme I was undertaken.

The oxidative addition of optically active α-deuteriobenzyl chloride to tetrakis(triphenylphosphine)palladium(0) (**1**) is known[15] to proceed with 74% net inversion of configuration at the benzylic carbon, whereas the oxidative addition of

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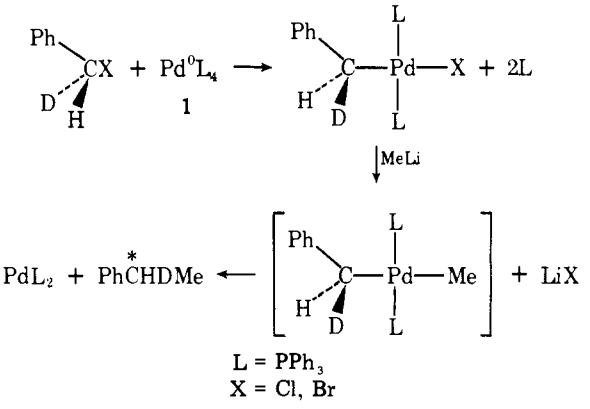
Table I. Reaction of Benzylpalladium(II) Complexes with Methyllithium and Tetramethyltin[a]

entry	complex	MeM	additive	yield of $PhCH_2CH_3$, %	yield of $PhCH_3$, %	other products (%)
1	$PhCH_2Pd(PPh_3)_2Cl$	MeLi		23.3	11.7	biphenyl (45.3) bibenzyl (22.9)
2	$PhCH_2Pd(PPh_3)_2Cl$	MeLi	PPh_3	11.6	29.9	bibenzyl (36.2) $Pd(PPh_3)_4$ (35.3)
3	$PhCH_2Pd(PEt_3)_2Cl$	MeLi		0.6	29.8	bibenzyl (9.6)
4	$PhCH_2Pd(PPh_3)_2Cl$	Me_4Sn		1.8	15.1	
5	$PhCH_2Pd(PPh_3)_2Br$	Me_4Sn		0.0	20.7	benzene (9.2)
6	$PhCH_2Pd(PPh_3)_2Br$	Me_4Sn	O_2	5.3	94.4	benzene (17.4)
7	$3\text{-}CH_3C_6H_4CH_2Pd(PPh_3)_2Br$	Me_4Sn	O_2		63.2	*m*-xylene (32.5) *m*-methylethyl benzene (7.1)
8	$PhCH_2Pd(PPh_3)_2Br$	Me_4Sn	*m*-dinitrobenzene	14.4	74.9	benzene (10.3)
9	$PhCH_2Pd(PPh_3)_2Cl$	Me_4Sn	*m*-dinitrobenzene	8.3	37.4	benzene (14.2)
10	$PhCH_2Pd(PPh_3)_2Cl$	Me_4Sn	*p*-nitrobenzyl bromide	30.7	69.2	
11	$PhCH_2Pd(PPh_3)_2Cl$	Me_4Sn	*p*-nitrobenzyl bromide (inverse addition)	81.3	5.7	
12	$PhCH_2Pd(PPh_3)_2Br$	Me_4Sn	*p*-nitrobenzyl bromide (inverse addition)	87.2	7.5	
13	$PhCH_2Pd(PPh_3)_2Cl$	Me_4Sn	*p*-methoxybenzyl bromide (inverse addition)	22.8	50.4	*p*-methoxyethyl benzene[b] (35.5)
14	$PhCH_2Pd(PPh_3)_2Br$	Me_4Sn	*p*-methylbenzyl bromide	31.0	9.6	*p*-methylethyl benzene (36.5) *p*-xylene (2.1)
15	$4\text{-}NO_2C_6H_4CH_2Pd(PPh_3)_2Cl$	Me_4Sn	benzyl bromide	100.0	0.0	*c*

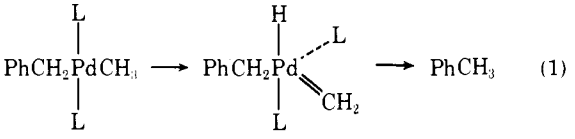
[a] Solvents were ether for reactions involving methyllithium and hexamethylphosphoramide for reaction with tetramethyltin. For reactions involving tetramethyltin, only those performed at 64-66 °C are summarized in this table. [b] *p*-Methoxybenzyl bromide partially decomposes under the reaction conditions as shown by a control experiment in which tetramethyltin was absent. [c] *p*-Nitroethylbenzene was not formed. Yield of ethylbenzene based on benzyl bromide.

Scheme I



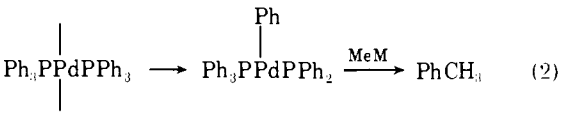
α-deuteriobenzyl bromide to **1** (under CO) proceeds with 68.8% net inversion (vide infra). Reaction of the optically active palladium(II) complexes, α-deuteriobenzylbromobis(triphenylphosphine)palladium(II), with methyllithium was anticipated to yield α-deuterioethylbenzene whose absolute configuration and purity could be determined by measuring its optical rotation. If the reductive elimination is a concerted process, retention of configuration at the benzylic carbon would be expected; however, if methyllithium acts as a nucleophile and attacks the benzyl group directly, inversion of configuration at carbon would be expected. A radical process should be nonstereospecific.

The reaction of various benzylpalladium complexes with methyllithium and the less basic tetramethyltin, however, yielded only small amounts of ethylbenzene (Table I). Other products are formed instead, the major one of which was toluene (see entries 6 and 8). Formation of this product can be rationalized on the basis of an α-elimination process from the intermediate dialkyl complex (eq 1). Such a process has been observed recently with other dialkylpalladium complexes.[13]



(1)

α elimination from the benzyl group could result in methane formation, a product that possibly accounts for the material loss observed in some of the experiments summarized in Table I. However, another source of toluene, when complexes containing the triphenylphosphine ligand are involved, can be oxidative addition of the ligand in an intermediate coordinatively unsaturated Pd(0) complex,[16] for example in $Pd(PPh_3)_2$ (eq 2).



(2)

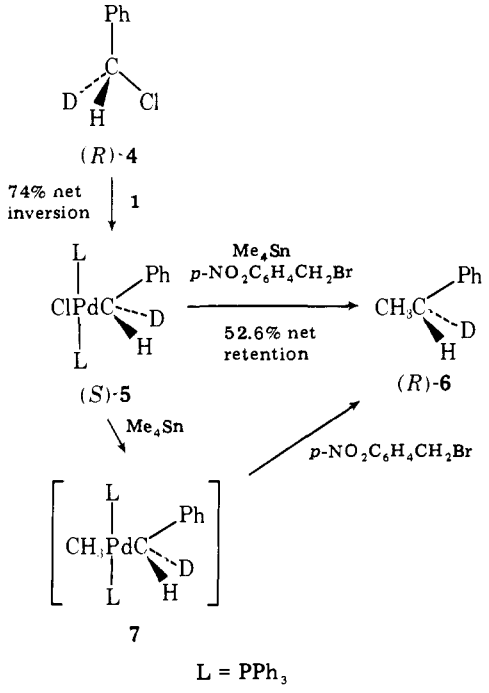
Indeed, both reactions probably are operating. Thus, 3-methylbenzylbromobis(triphenylphosphine)palladium(II) yields, upon reaction with tetramethyltin, both *m*-xylene and toluene (entry 7). However, the source of toluene in the reaction of benzylchlorobis(triethylphosphine)palladium(II) with methyllithium can be attributed only to the benzyl group.

The fact that ethylbenzene is formed only in small amounts when benzylbromobis(triphenylphosphine)palladium(II) (**2**) reacts with tetramethyltin is somewhat surprising, since benzylpalladium complexes are effective catalysts for the coupling of organic halides, including benzyl halides, with tetraorganotins[17] (eq 3).

$$RX + R'_4Sn \xrightarrow{PhCH_2Pd(PPh_3)_2X} RR' + R'_3SnX \qquad (3)$$

In the stoichiometric reaction, as in Scheme I, metathesis of the halogen that is bound to palladium, followed by reductive elimination to release the coupled product, is the most plausible mechanism. However, the major difference between the cat-

Scheme II



alytic and stoichiometric reactions is the presence of a large excess of the organic halide in the first case. Indeed, addition of *p*-nitrobenzyl bromide to the reaction mixture of benzylchlorobis(triphenylphosphine)palladium(II) (**3**) and tetramethyltin increased the yield of ethylbenzene considerably (entry 10). A quantitative amount of ethylbenzene could be obtained when "inverse addition" was performed, i.e., when a solution of complex **2** or **3** was added to a solution of *p*-nitrobenzyl bromide heated at 65 °C, thus assuring an excess of *p*-nitrobenzyl bromide at all times (entries 11 and 12).

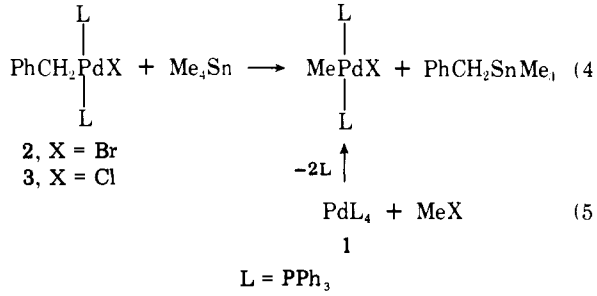
(b) Stereochemistry. The stereochemistry of the process could now be determined under the conditions of reactions 11 and 12 (Table I). Oxidative addition of (*R*)-(−)-benzyl-α-*d* chloride **4** yielded (*S*)-chloro-(α-deuteriobenzyl)bis(triphenylphosphine)palladium(II) (**5**), which upon reaction with tetramethyltin in the presence of *p*-nitrobenzyl bromide (inverse addition) gave a 92.1% yield of (*R*)-(−)-α-deuterioethylbenzene (**6**) (30.3 ± 2.8% ee). Thus, **4** is converted into **6** with overall inversion of configuration and with an overall stereospecificity of 38.9 ± 3.7%. Since oxidative addition of **4** to **1** proceeds with 74% net inversion of configuration,[15] the formation of **6** from **5** takes place with 52.6 ± 5% net *retention* of configuration at carbon (Scheme II). Although **7** could not be isolated, it was reasonable to assume that it is formed by displacement of the palladium-bound chloride with a tin-bound methyl group. Transmetallation reactions between tetraorganotin compounds and platinum complexes, in which an organic group attached to tin replaces a halogen attached to platinum, have been documented recently.[18] Assuming that such a process takes place (Scheme II), the reductive elimination step proceeds with 52.6% net retention of configuration at carbon, since the transmetalation step does not affect the asymmetric center.

(c) Reaction of 5 with Tetramethyltin at 25 °C. The reaction mechanism shown in Scheme II, however, is not strictly correct, and the transformation of **5** to **6** is less straightforward. When the complexes **2** or **3** react with tetramethyltin at 25 °C, *trans*-methylhalobis(triphenylphosphine)palladium(II) and benzyltrimethyltin are formed (eq 4). The same palladium(II) complex is formed upon reaction of **1** with methyl bromide (eq 5). Assignment of the trans configuration is based upon the equivalence of the two phosphorus atoms as shown by ^{31}P

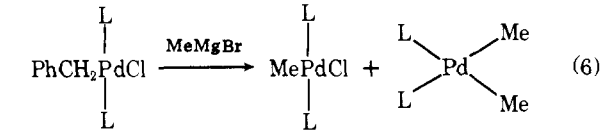
Table II. Substitution of the Benzyl Group in Reactions of $Y\text{-}C_6H_4CH_2\text{-}Pd(PPh_3)_2X$ with MeM[a]

entry	complex Y	complex X	MeM	reaction time, min	yield[b] of $MePd(PPh_3)_2X$, %
1	H	Br	Me_4Sn	35	79.8
2	H	Cl	Me_4Sn	15	83.4
3	H	Cl	MeMgBr	30	55.8[c]
4	4-CH_3	Cl	Me_4Sn	10	89.5
5	4-NO_2	Cl	Me_4Sn	210	70.4

[a] Reactions with tetramethyltin were performed at 25 °C in HMPA. The reaction involving methylmagnesium bromide took place below 25 °C in THF-ether. [b] Isolated, based on starting palladium complex. [c] 36.4% of dimethylbis(triphenylphosphine)palladium(II) was also obtained.



NMR. Thus, substitution of the benzyl group by a methyl group does not alter the trans configuration. The reaction seems to be general with respect to the benzylpalladium group (Table II). To our knowledge, this is the first example of a transformation reaction in which two metal–carbon bonds and no metal–halogen bond is cleaved in a transmetallation reaction. There is 100% preference for cleavage of the $YC_6H_4CH_2$–Pd bond over cleavage of a Pd–X bond (X = Cl, Br) when tetramethyltin is a reactant; traces of halogen substitution products were not detected even when a large excess of tetramethyltin was used. Methylmagnesium bromide (Table II, entry 3) also substitutes the benzyl group first, followed by substitution of the halogen, resulting in a mixture of monomethyl and dimethyl complexes (eq 6). Interestingly, *cis*-



dimethylbis(triphenylphosphine)palladium was obtained; the same cis complex is formed when *trans*-dichlorobis(triphenylphosphine)palladium(II) reacts with methyllithium.[19]

The reactivity of the benzyl group, as judged from the reaction times (Table II), is 4-$CH_3C_6H_4CH_2$ > $C_6H_5CH_2$ > 4-$NO_2C_6H_4CH_2$, in accordance with the expected corresponding Pd–C bond dissociation energies (vide infra).

Reactions of Methylhalobis(triphenylphosphine)palladium with Benzyltrimethyltin and Benzylmagnesium Bromide. Methylhalobis(triphenylphosphine)palladium and benzyltrimethyltin react at 65 °C in HMPA to afford small amounts of ethylbenzene (Table III). However, an almost quantitative yield of ethylbenzene was obtained in the presence of *p*-nitrobenzyl bromide (eq 7).

Reaction of methylbromobis(triphenylphosphine)palladium (**8**) and benzylmagnesium bromides in the presence of benzyl bromide (added after the dialkyl complex was formed in situ) also produces ethylbenzene (Table III).

Taking into account the reactions represented in eq 4 and 7, formation of α-deuterioethylbenzene (**6**) by reaction of **5**

Table III. Ethylbenzene Formed from Reaction of $PhCH_2M$ and $MePd(PPh_3)_2X$[a]

entry	complex	$PhCH_2M$	additive	yield of ethylbenzene,[b] %
1	$MePd(PPh_3)_2Br$	$PhCH_2SnMe_3$		18.5
2	$MePd(PPh_3)_2Br$	$PhCH_2SnMe_3$	*p*-nitrobenzyl bromide	87.2
3	$MePd(PPh_3)_2Cl$	$PhCH_2SnMe_3$	*p*-nitrobenzyl bromide	90.5
4	$MePd(PPh_3)_2Br$	$PhCH_2MgBr$		25.5
5	$MePd(PPh_3)_2Br$	$PhCH_2MgBr$	benzyl bromide	52.3

[a] Hexamethylphosphoramide was the solvent for reactions involving benzyltrimethyltin and ether for reactions with benzylmagnesium bromide. [b] Based on the palladium complexes.

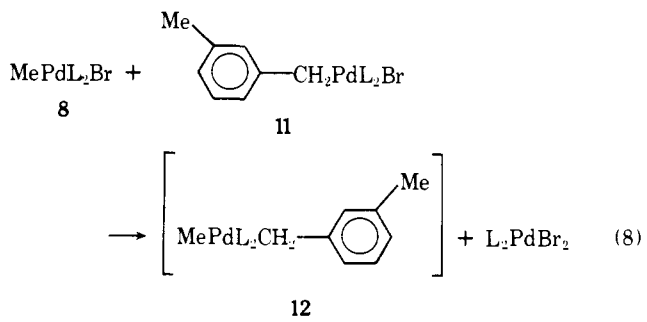
$$MePd(PPh_3)_2X + PhCH_2SnMe_3$$
$$\mathbf{8},\ X = Br$$
$$\mathbf{9},\ X = Cl \qquad (7)$$
$$\longrightarrow [MePd(PPh_3)_2CH_2Ph] + XSnMe_3$$
$$\downarrow\ p\text{-}NO_2C_6H_4CH_2Br$$
$$PhCH_2CH_3 + p\text{-}NO_2C_6H_4CH_2Pd(PPh_3)_2Br$$

and tetramethyltin can best be described as follows (Scheme III).

It is possible, however, that the first step in Scheme III is reversible, although lying far to the right (since it reaches completion at room temperature), and that the dialkylpalladium(II) complex is formed directly from **5** in preference to formation from **9** and **10** (dotted lines in Scheme III). To test this possibility, a reaction between bromomethylbis(triphenylphosphine)palladium(II) (**8**), (3-methylbenzyl)bromobis(triphenylphosphine)palladium(II) (**11**), and an excess of benzyltrimethyltin in the presence of *p*-nitrobenzyl bromide (inverse addition) was carried out (Scheme IV). If the reaction of tetramethyltin and the benzylpalladium ligands affords products without going through **9** and **10**, the amounts of ethylbenzene and 3-methylethylbenzene should correspond to the molar amounts of **8** and **11** (since the methyl substituent in **11**, which is in the meta position, does not exert any appreciable electronic or steric effect).

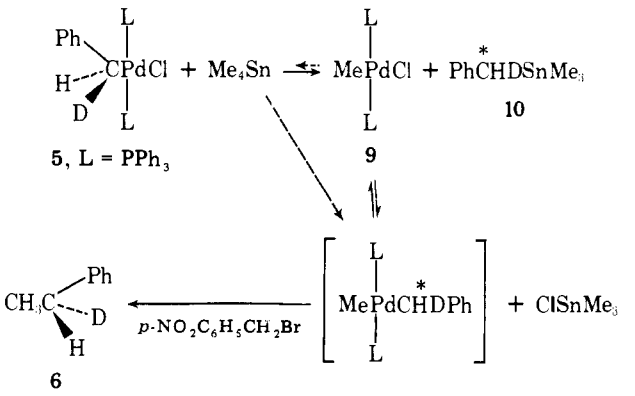
This experiment resulted in a 94.8% yield of ethylbenzene (based on **8**) and a 9.6% yield of 3-methylethylbenzene (based on **11**), establishing that the ethylbenzene formed from the reaction of tetramethyltin and benzylpalladium bromide—without going through **9** (or **8**) and **10**—cannot be more than 10% of the total ethylbenzene. Thus, the reactions according to Scheme III are those responsible for the formation of ethylbenzene.

A symmetrization reaction of **8** and **11** to form the intermediate **12** (eq 8) does not take place, since only traces of

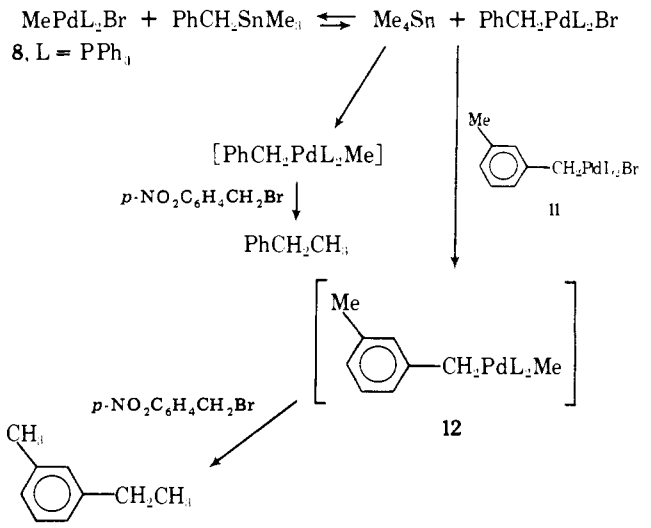


(8)

Scheme III



Scheme IV



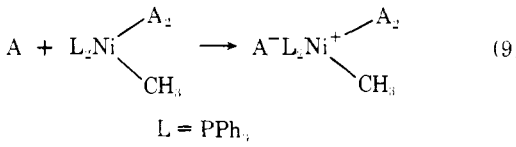
ethylbenzene are formed by the reaction of **8** and benzylbromobis(triphenylphosphine)palladium(II) (**2**) in the presence of *p*-nitrobenzyl bromide.

It is evident, therefore, that in the formation of (*R*)-(−)-α-deuterioethylbenzene from the optically active (*S*)-α-deuteriobenzylchlorobis(triphenylphosphine)palladium(II) (**5**) the benzyl group undergoes transfer twice before the actual reductive elimination takes place. This multiple transfer, and to some extent also the equilibrium that takes place in the first step, is probably responsible for the loss of stereospecificity observed in the process. Nevertheless, it is significant that, in spite of the multiple transfers the benzyl group undergoes, the overall process is considerably stereospecific, thus excluding any radical pathways for the reductive elimination step.

Whichever transfer mechanism is operating, it should be the same for the two tin–palladium(II) transmetalation reactions 4 and 7. Thus, whatever the stereochemistry of these reactions using the α-deuteriobenzyl group is, whether it is two inversions or two retentions at the benzylic carbon, the net result is retention, producing a methylbenzylpalladium complex with the same absolute configuration at carbon as is present in the initial benzylhalopalladium complex **5**. This implies that the reductive elimination reaction proceeds with retention of configuration at carbon.

Role of Added Benzyl Bromide. It is clear that the presence of either a substituted benzyl bromide or excess benzyl bromide is essential to the generation of coupled products from palladium complexes and organotin or Grignard compounds (Tables I and III). Addition of aryl bromides as well as oxygen was found to induce the reductive elimination of arylmethylbis(triphenylphosphine)nickel(II) complexes,[8] and it was sug-

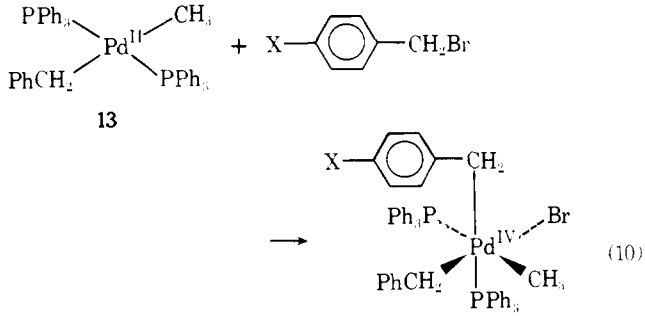
gested that the organic bromide or oxygen acted as electron acceptors (A), with the electron-rich organometal acting as a donor (eq 9). The resulting cation radical should have en-



(9)

L = PPh_3

hanced lability toward reductive elimination.[8] However, oxygen, as well as the excellent electron acceptor *m*-dinitrobenzene, has little effect on the reactions of **2** or **3** with tetramethyltin as far as the reductive elimination product, ethylbenzene, is concerned (compare entries 4 and 9 with entries 5, 6, and 7 in Table I). We suggest that the dialkylpalladium(II) complex (**13**) undergoes further oxidative addition of the benzyl bromide to form an octahedral palladium(IV) complex, **14** (eq 10), which undergoes rapid reductive elimination.

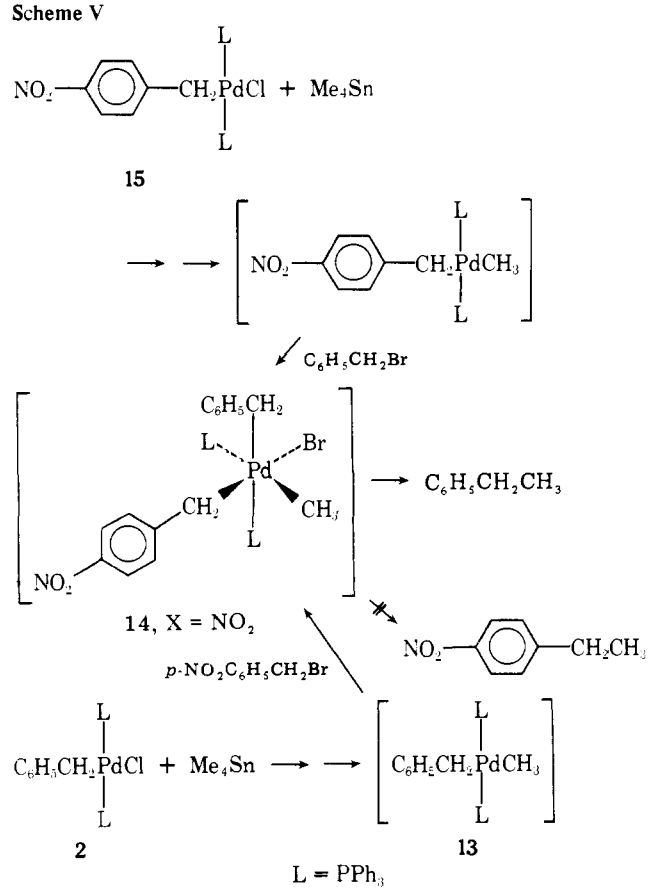


13 **14** (10)

Although platinum(IV) complexes are numerous, palladium(IV) complexes have never been isolated;[20] their existence has been suggested in some cases.[13,21] Nevertheless, even though palladium in complex **13** is formally in the 2+ oxidation state, it can be considered electron rich due to the presence of two alkyl ligands and the absence of π-acceptor ligands such as halogen or carbonyl. Compound **13,** or other dialkylpalladium complexes, presumably can undergo further oxidative addition reactions. Two requirements are met by formation of **14**: (a) The two alkyl groups that have to undergo reductive elimination occupy cis positions in the octahedral **14,** whereas they are trans to each other in the square planar **13**. It is essential that the alkyl groups to be coupled be in the cis position in order for the reductive elimination to take place via nonradical pathways.[6,8] Indeed, the stereospecificity observed in this coupling reaction supports a nonradical pathway. (b) Promotion of the palladium into a higher oxidation state should make its reductive elimination take place more readily.

Interestingly, *p*-nitroethylbenzene is not formed in the reaction of **2** or **3** with tetramethyltin in the presence of *p*-nitrobenzyl bromide, whereas according to structure **14** it can be formed. Taking into consideration the relative strength of the 4-$NO_2C_6H_4CH_2$–Pd and $PhCH_2$–Pd bonds, it would be expected that the former would be stronger and less susceptible to reductive elimination. This is supported by the observation that reaction of *p*-nitrobenzylchlorobis(triphenylphosphine)-palladium(II) (**15**) with tetramethyltin in the presence of benzyl bromide gives a quantitative yield of ethylbenzene and no *p*-nitroethylbenzene. Therefore, the geometry of the intermediate **13** is not responsible for the absence of reductive elimination products from the *p*-nitrobenzyl groups (Scheme V), and this phenomenon is due to the strength of the bond of the *p*-nitrobenzyl group to palladium, in agreement with the fact that substituted ethylbenzenes are formed when *p*-methylbenzyl bromide was used (Table I, entry 14). The result of the reaction of **15** and tetramethyltin also supports a pal-

Scheme V

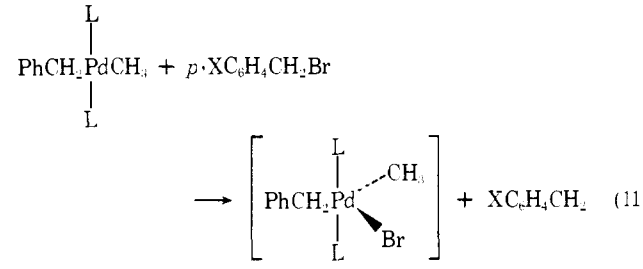


15 **14**, X = NO_2 **2** **13**

L = PPh_3

ladium(IV) intermediate, since benzyl bromide must undergo oxidative addition to palladium in order for ethylbenzene to be formed (Scheme V).

Another mechanism[22] that can account for the requirement of substituted benzyl bromides or excess benzyl bromide in order for the reductive elimination to take place, as well as for the fact that *p*-nitroethylbenzene is not formed when *p*-nitrobenzyl bromide is involved, is the formation of a Pd(III) complex, **20,** and a benzyl radical (eq 11).



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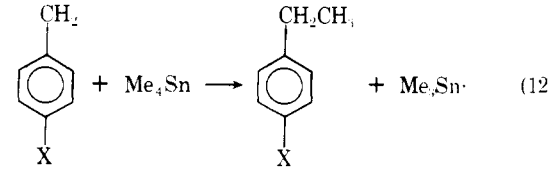
The benzyl radical can react with tetramethyltin and form the substituted ethylbenzene (eq 12). For cases in which very

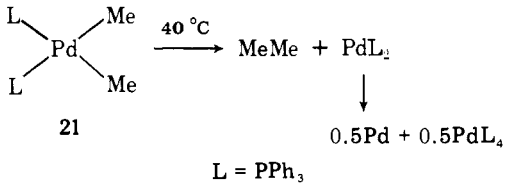


(12)

stable radicals are formed, e.g., the *p*-nitrobenzyl radical, the reaction with tetramethyltin does not take place and the substituted ethylbenzene is not formed. To test this mechanism, a reaction between **2** and tetramethyltin in the presence of *p*-methoxybenzyl bromide was carried out (Table I, entry 13). Since the stability of the *p*-methoxybenzyl radical is about the

same as that of the *p*-nitrobenzyl radical, formation of *p*-methoxyethylbenzene would not be expected if the mechanism involving a Pd(III) intermediate takes place. The formation of *p*-methoxyethylbenzene, however, rules out the Pd(III) mechanism. Moreover, the amount of *p*-methoxyethylbenzene obtained in the reaction is higher than that of ethylbenzene, in accordance with the relative strength of the $PhCH_2$–Pd and 4-$CH_3OC_6H_4CH_2$–Pd bonds. The same phenomenon is observed also in the reaction of **3** with tetramethyltin in the presence of *p*-methylbenzyl bromide; both ethylbenzene and *p*-methylethylbenzene are formed, the latter being slightly predominant (Table I, entry 14).

Reactions of *cis*-Dimethylbis(triphenylphosphine)palladium(II) (17). (a) Mechanism. Solutions of **17** in chloroform or benzene decompose at 40 °C under argon to give ethane.[19] This reaction can be followed clearly by the ^1H NMR (C_6D_6) spectrum. The doublet of doublets at δ 1.095 disappears at ~40 °C, and a singlet due to ethane is formed at δ 0.795. Palladium metal precipitates (eq 13).

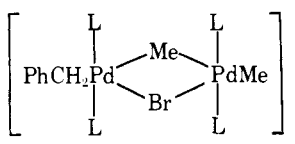


21 (13)

The reductive elimination process seems to be quite straightforward in this case, apparently because the groups undergoing coupling occupy cis positions. However, when benzyl bromide is added to a solution of **17**, reductive elimination takes place even at room temperature, the major products being ethylbenzene and bromomethylbis(triphenylphosphine)palladium(II) (**8**). Only minor amounts of ethane and benzylchlorobis(triphenylphosphine)palladium(II) (**3**) are formed (Scheme VI).

The Pd(IV) intermediate, **18**, decomposes preferentially to ethylbenzene and complex **8**, probably because of the lower $PhCH_2$-Pd bond energy relative to Me-Pd. Ethane and complex **2** can be formed directly by reductive elimination from **18** or by the reductive elimination reaction from the Pd(II) complex, **17**. Bis(triphenylphosphine)palladium(0) (**19**) formed in the reaction of **17** to give ethane can oxidatively add benzyl bromide to form complex **3**, although this pathway is less likely to occur since solutions of **17** are stable at 25 °C.

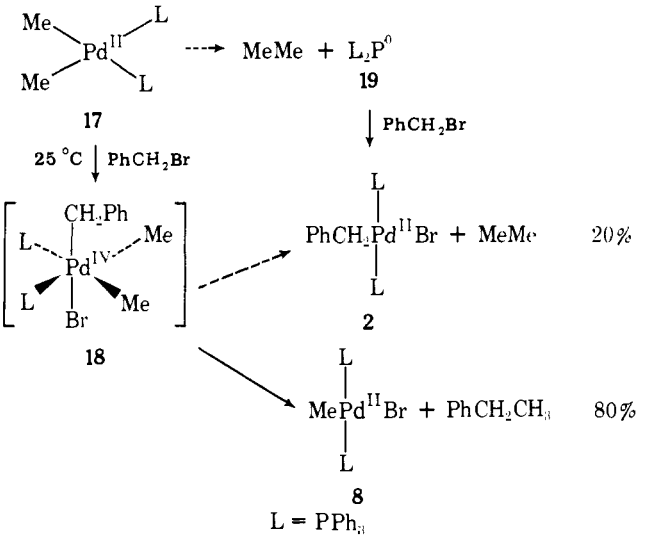
Another pathway that could contribute to formation of ethylbenzene and **8** is the symmetrization reaction between **17** and **2**. Indeed, reaction of these two complexes in the presence of *p*-nitrobenzyl bromide gives ethylbenzene (20%) in addition to complexes **8** and bromo(*p*-nitrobenzyl)bis(triphenylphosphine)palladium(II) (**20**) (Scheme VII). Symmetrization reactions between dimethylplatinum(II) complexes and dibromoplatinum complexes have been observed,[23] and if the mechanism proposed for those reactions is adopted, intermediate **21** could be involved in the reactions between **2** and **17**.



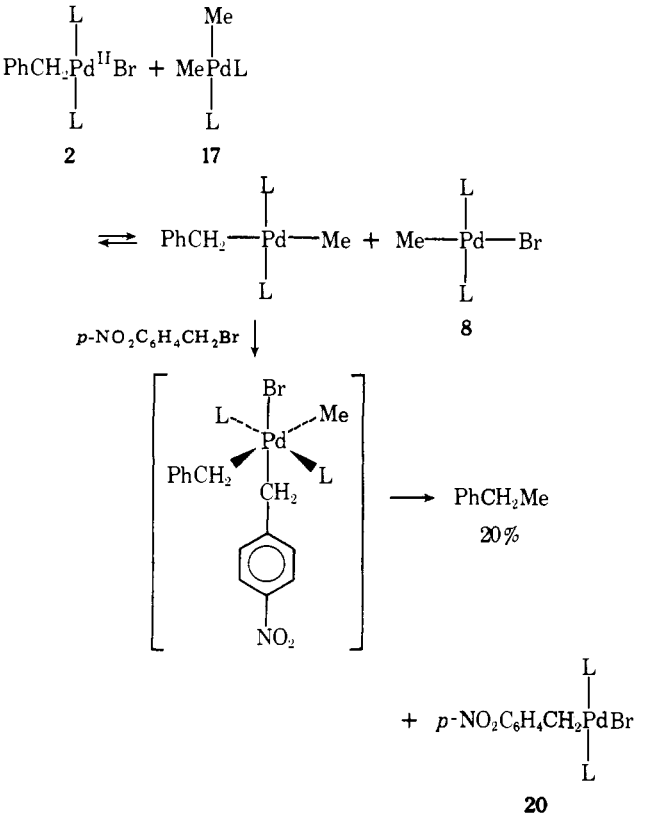
21, L = PPh_3

Some of the ethylbenzene formed in the reaction of **17** with benzyl bromide could be a result of this process. However, the contribution of such a process to the total yield of ethylbenzene obtained in that reaction cannot exceed 10% (based on Pd), since **2** has to be generated from **17**. On the other hand, symmetrization of **2** and **9** to yield ethylbenzene does not take place

Scheme VI



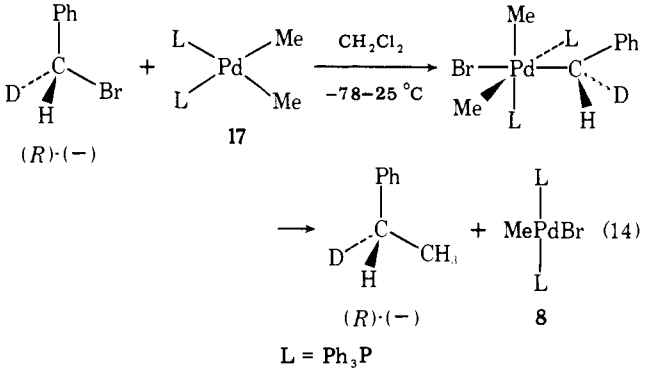
Scheme VII



(vide supra). Thus, the vast majority of ethylbenzene in the reaction of **17** and benzyl bromide is probably formed according to Scheme VI.

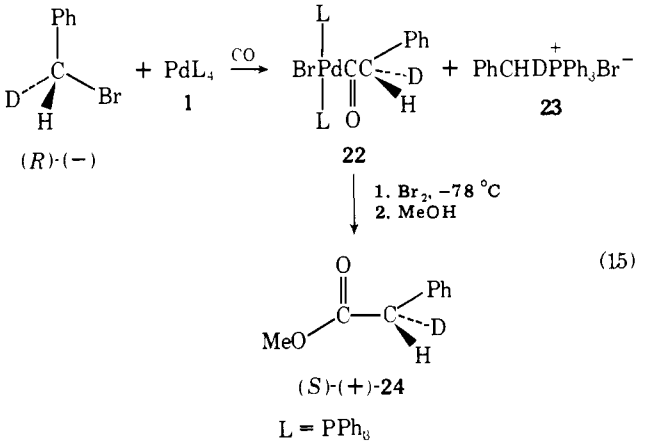
As a result, it is evident that addition of benzyl bromide to a *cis*-dialkylpalladium complex results in a lower energy pathway for reductive elimination, most probably through a palladium(IV) intermediate. Such a process should be even more favorable for *trans*-dialkylpalladium complexes. It has been argued that the reductive elimination of arylalkylnickel complexes is promoted by a prior one electron transfer process.[8] However, it is reasonable to believe that formation of a Ni(IV) intermediate (a two electron transfer) would be much more difficult for nickel than for palladium, due to the much higher ionization potential for the process $Ni^{2+} \rightarrow Ni^{4+}$ (37.85 eV) than for the process $Pd^{2+} \rightarrow Pd^{4+}$ (28.90 eV).

(b) Stereochemistry. In order to determine the stereochemistry of the reaction presented in Scheme VI, an excess of (*R*)-(−)-α-deuteriobenzyl bromide ($[\alpha]^{25}_{\Delta}$ −1.076 ± 0.003° (neat, *l* = 1), 89.7 ± 0.3% ee) was allowed to react with **17** in methylene chloride at −78 °C. (*R*)-(−)-α-Deuterioethylbenzene was isolated in 47.5% yield ($[\alpha]^{25}_{\Delta}$ −0.167 ± 0.004° (neat, *l* = 1), corresponding to 22.9 ± 2% ee). The recovered α-deuteriobenzyl bromide was almost completely racemic. The palladium-catalyzed racemization of α-deuteriobenzyl chloride had been observed previously.[15] (*R*)-(−)-α-Deuteriobenzyl bromide, therefore, is converted with overall inversion of configuration at the benzylic carbon to (*R*)-(−)-α-deuterioethylbenzene, the overall stereospecificity being at least 25.5 ± 2.3% and probably much higher, since the bromide racemizes under the reaction conditions. It was shown[15] that oxidative addition of optically active α-phenethyl bromide to carbonyltris(triphenylphosphine)palladium(0) takes place with complete inversion of configuration at the asymmetric carbon, and that optically active α-deuteriobenzyl chloride and bromide (vide infra) oxidatively add to tetrakis(triphenylphosphine)palladium(0) in a similar fashion. Oxidative addition of these compounds to tetrakis(triphenylphosphine)palladium(0) also takes place with high inversion of configuration at carbon.[24] The actual charge on the palladium center in **17** should not be very different from that in Pd(0) complexes, especially those having a carbonyl ligand, since the phosphorus in triphenylphosphine acquires the same charge regardless of the oxidation state of the metal to which it is bonded,[25] and the methyl ligands are nearly neutral.[25] A slight variation of the actual charge on the metal in palladium(0) complexes as a result of changing the ligands does not affect the stereochemistry of oxidative addition (vide supra). Thus, it is reasonable that oxidative addition of α-deuteriobenzyl bromide to **17** also occurs with inversion of configuration at carbon. If this is the case, the reductive elimination process should occur with retention of configuration at carbon (eq 14).



(14)

Since the stereochemistry of oxidative addition of α-deuteriobenzyl bromide to triphenylphosphinepalladium(0) complexes had not been studied, the oxidative addition of (*R*)-(−)-α-deuteriobenzyl bromide to tetrakis(triphenylphosphine)palladium (**1**) was undertaken (eq 15). Oxidative addition of (*R*)-(−)-α-deuteriobenzyl bromide ($[\alpha]^{25}_{D}$ −0.646 ± 0.002° (neat, *l* = 1), 53.8 ± 2% ee) to **1** followed by carbonylation gave acyl complex **22** in a mixture with phosphinium salt **23**. Bromine cleavage followed by methanolysis of the mixture resulted in the known[15] (*S*)-(+)-methyl α-deuteriophenylacetate (**24**) with inverted configuration at carbon ($[\alpha]^{25}_{D}$ +0.322 ± 0.002° (neat, *l* = 1), 37.0 ± 4% ee). Since carbonylation is known to proceed with 100% retention of configuration at carbon[26] and the bromine cleavage has not been performed at the asymmetric center, the oxidative addition step proceeds with 68.8 ± 10% inversion of configuration at carbon. This result can be compared with the 100% inversion obtained with α-deuteriobenzyl chloride[15] and with only 20%



(15)

inversion in the case of oxidative addition of α-deuteriobenzyl bromide to tetrakis(triethylphosphine)palladium.[24]

Experimental Section

The preparation and handling of air-sensitive palladium complexes, as well as other reactions requiring an inert atmosphere, were carried out using Schlenk apparatus in an atmosphere of argon purified by passage through a BASF catalyst. Solvents were distilled and degassed before use. Concentrations of lithium and Grignard reagents were determined before use. ^{1}H NMR spectra were taken on Varian EM360 and on JEOL FX-100 spectrometers. ^{31}P NMR spectra were obtained on a Bruker HX-90E spectrometer. Optical rotations of the deuterated compounds were taken with a Perkin-Elmer 241 polarimeter. IR spectra were obtained on Beckman Acculab 3 and IR 12 spectrophotometers. Molecular weight determinations were taken on a Mechrolab vapor pressure osmometer. Melting points are uncorrected.

Reactions of Benzylchlorobis(triphenylphosphine)palladium(II) (3) and Methyllithium. (a) An ethereal solution of methyllithium (1 mL, 1.84 M) was added via syringe to a yellow suspension of 0.511 g (0.675 mol) of **3**[27] in 12 mL of ether. The suspension, which was heated to the reflux temperature under argon, blackened after 15 min. Refluxing was continued for 1 h; the solution was cooled to room temperature and was hydrolyzed with 5 mL of water. The mixture was filtered, and the organic phase was separated and dried on $MgSO_4$, and the volatile materials were transferred under reduced pressure to a liquid nitrogen cold trap. GLC analysis (130 °C, 10 ft × 0.32 in., 20% Carbowax 20M) of the volatile phase showed the presence of ethylbenzene (23.3% yield) and toluene (11.7% yield) by comparison of retention times. These materials were isolated by preparative GLC and their identity confirmed by NMR ($CDCl_3$): δ (ethylbenzene) 7.20 (s, 5 H, aromatic), 2.67 (q, 2 H, *J* = 5.7 Hz, $PhCH_2$), and 1.25 ppm (t, 3 H, *J* = 7.5 Hz, CH_3); toluene, 7.17 (s, 5 H, phenyl), 2.32 (s, 3 H, CH_3). GLC analysis (175 °C, 10 ft × 0.325 in., 15% DEGS) of the residue showed formation of bibenzyl (22.9% yield) and biphenyl (45.3% yield) by comparison of retention times. Isolation by preparative GLC and ^{1}H NMR ($CDCl_3$) confirmed these identifications: δ (bibenzyl) 7.19 (s, 10 H, aromatic), 2.89 (s, 4 H, CH_2CH_2); biphenyl, 7.7–7.2 (aromatic). Reaction of benzylchlorobis(triethylphosphine)palladium(II)[24] with methyllithium was carried out similarly. Results are shown in Table I.

(b) In the Presence of Triphenylphosphine. A suspension of 0.536 g (0.710 mmol) of **3** in 12 mL of dry ether under argon was cooled with stirring to −78 °C, and 1 mL of a 1.84 M ethereal solution of methyllithium was added dropwise via syringe. Stirring was continued without external cooling, and after 10 min a clear orange solution was obtained. Triphenylphosphine (0.373 g, 1.421 mmol) was immediately added under argon, the stirring was continued, and after a few minutes a yellow solid started to separate. After we stirred the mixture at room temperature for 1 h, the suspension was heated to reflux for another 1 h and was then cooled to room temperature. The yellow solid tetrakis(triphenylphosphine)palladium(0) was isolated by filtration under argon, washed with ether, and vacuum dried to afford 0.273 g (35.3%): mp 114–116 °C (lit.[28] 116 °C); the IR was superimposable with that of an authentic sample of tetrakis(triphenylphosphine)-palladium(0). The filtrate was hydrolyzed with 5 mL of water and the organic phase separated. GLC analysis (same columns as in a) of the

organic phase showed the presence of ethylbenzene (11.6%), toluene (29.9%), and bibenzyl (36.2%). Biphenyl was not formed. Attempts to isolate the intermediate benzylmethylbis(triphenylphosphine)-palladium(II) from the low-temperature reactions did not yield the desired intermediate.

General Procedure for Reaction of Benzylhalogenopalladium(II) Complexes with Tetramethyltin. To a solution of 0.5 mmol of the benzylhalogenopalladium(II) complex (see Table I) in hexamethylphosphoramide (2–8 mL, depending on the solubility of the complex) was added 1.0 mL (7.2 mmol) of tetramethyltin, and the solution was stirred in a closed tube at 62–46 °C for 18–22 h, during which time it blackened. Ether–hexane (1:1) was added, the mixture was filtered, and the solution was analyzed by GLC. In experiments in which *m*-dinitrobenzene was added, 0.7 mmol of this compound was used, together with 0.3 mmol of the complex and 1.4 mmol of tetramethyltin. The reaction was allowed to continue for 48 h, resulting in a dark red solution. Reactions involving benzyl bromides were carried out using 1.3 mmol of these compounds under the same conditions, except in cases where inverse addition was carried out. In these experiments, a solution of 0.7 mmol of the complex and 2.1 mmol of the benzyl bromide in 8 mL of hexamethylphosphoramide was added during 10 h to a solution of 2.1 mmol of the benzyl bromide and 7.2 mmol of tetramethyltin at 65 °C; the reaction was carried out for 32 h. Results of the experiments are summarized in Table I.

Reactions of Benzylchlorobis(triphenylphosphine)palladium(II) with Tetramethyltin in the Presence of Triphenylphosphine. To a solution of 300 mg (0.396 mmol) of benzylchlorobis(triphenylphosphine)-palladium(II) and 208 mg (0.794 mmol) of triphenylphosphine in 1.5 mL of hexamethylphosphoramide under argon was added 0.50 mL (3.6 mmol) of tetramethyltin, and the orange solution was heated at 64 °C with stirring. A yellow precipitate appeared after 30 min, and the solution gradually turned yellow. After 5 h, the mixture was cooled to room temperature and the yellow air-sensitive tetrakis(triphenylphosphine)palladium(0) was isolated by filtration under argon and was washed with ether and dried in vacuo to give 190 mg (41.5% yield) of tetrakis(triphenylphosphine)palladium(0): mp 113–116 °C (lit.[28] 116 °C). The IR and NMR spectra were superimposable upon that of an authentic sample. Addition of pentane to the combined mother liquors and ethereal washings did not cause further precipitation. GLC analysis of this solution showed the presence of ethylbenzene (8.1% yield).

Chloro-(α-deuteriobenzyl)bis(triphenylphosphine)palladium(II). A sample of 3.160 g (2.900 mmol) of (*S*)-(+)-benzyl-α-deuterioalcohol[29] ($[\alpha]^{25}_D$ +1.284 ± 0.002° (neat, *l* = 1), 81.3 ± 0.2% ee) was prepared from benzaldehyde-*1*-*d* containing 1.00 ± 0.05 deuterium per molecule and converted into 2.56 g (69.3%) of (*R*)-(−)-benzyl-α-*d* chloride[27] ($[\alpha]^{25}_D$ −1.194 ± 0.002° (neat, *l* = 1), 77.9 ± 0.2% ee). Oxidative addition of this chloride to 12.1 g (1.05 mmol) of tetrakis-(triphenylphosphine)palladium(0)[15] yielded 7.8 g (98%) of chloro-(α-deuteriobenzyl)bis(triphenylphosphine)palladium(II): mp 142–144 °C dec (lit.[15] 140–144 °C); ^{1}H NMR ($CDCl_3$) δ 7.9–6.3 (m, 38 H, aromatic), 2.70 (br s, 1 H, Ph*CHD*).

Reaction of Chloro-(α-deuteriobenzyl)bis(triphenylphosphine)palladium(II) with Tetramethyltin in the Presence of *p*-Nitrobenzyl Bromide. Formation of (*R*)-(−)-α-Deuterioethylbenzene. A solution of 7.80 g (1.03 mmol) of chloro-(α-deuteriobenzyl)bis(triphenylphosphine)palladium(II) and 4.00 g (1.85 mmol) of *p*-nitrobenzyl bromide in 200 mL of hexamethylphosphoramide under argon in a pressure equalizing regulated addition dropping funnel was added during 40 h to a stirred solution of 7.00 mL (50.6 mmol) of tetramethyltin and 4.00 g (1.85 mmol) of *p*-nitrobenzyl bromide in 30 mL of hexamethylphosphoramide heated at 65 °C. After the addition was complete, the solution was cooled to room temperature and analyzed by GLC. α-Deuterioethylbenzene (92.1%), together with traces of toluene and benzene, was formed. Water, 100 mL, was added to the solution, and the mixture was transferred to a liquid–liquid extractor and extracted with 100 mL of pentane over a 6-day period. The pentane and excess tetramethyltin were transferred under reduced pressure (0.05 mmHg) at 25 °C to a liquid nitrogen cold trap. GLC analysis of the residual solution and the transferred solution showed that only a small amount of α-deuterioethylbenzene underwent transfer, most of it remaining in the residual solution. The α-deuterioethylbenzene was vacuum transferred (0.05 mmHg, 35 °C) to a liquid nitrogen cold trap over a period of 5 h. GLC analysis of the transferred product indicated that it consisted of 99.5% α-deuterioethylbenzene and 0.5% toluene. The 357 mg of (*R*)-(−)-α-deuterioethylbenzene obtained was diluted to 1 mL with ethylbenzene, showing $[\alpha]^{25}_D$ −0.221 ± 0.004° (neat, *l* = 1); 30.3 ± 2.8% ee.[31] Overall, (*R*)-(−)-benzyl-α-*d* chloride (77.9 ± 0.2% ee) was converted into (*R*)-(−)-α-deuterioethylbenzene (inversion of configuration at the benzylic carbon) in 38.9 ± 3.7% optical yield.

Benzylbromobis(triphenylphosphine)palladium(II) (2). A suspension of 1.324 g (1.147 mmol) of tetrakis(triphenylphosphine)palladium(0) and 0.392 g (2.292 mmol) of benzyl bromide in 20 mL of benzene was stirred at room temperature under argon for 1 h, after which all of the complex dissolved, forming an orange solution. The solution was allowed to stand undisturbed for 20 h and the crystalline benzyltriphenylphosphonium bromide that precipitated was collected by filtration, washed with ether, and dried in vacuo to afford 419 mg (42.2% yield based on the bromide), mp 273–274 °C (lit.[31] 274–275 °C).

The solution was concentrated by evaporation and 200 mL of ether–hexane (1:1) was added. The yellow precipitate was filtered and washed with ether and hexane and dried in vacuo to yield 0.870 g (94.7%): mp 136–139 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.76–7.14 (m, 30 H, aromatic), 7.00–6.35 (m, 5 H, benzyl aromatic), 2.77 (s, 2 H, CH_2). Anal. Calcd for $C_{43}H_{37}BrP_2Pd$: C, 64.40; H, 4.52; Br, 9.97. Found: C, 64.94; H, 4.96; Br, 9.35.

Reaction of Benzylbromobis(triphenylphosphine)palladium(II) with Benzyl Bromide and Tetramethyltin. Formation of *trans*-Bromomethylbis(triphenylphosphine)palladium(II). To a suspension of 265 mg (0.331 mmol) of benzylbromobis(triphenylphosphine)palladium(II) and 56.8 mg (0.332 mmol) of benzyl bromide in 4 mL of hexamethylphosphoramide under argon was added 0.4 mL (3 mmol) of tetramethyltin, and the suspension was stirred at 64 °C. All of the complex dissolved after 5 min, forming a dark orange solution; 5 min later the color changed to yellow and a white precipitate formed. As the amount of the precipitate increased, the yellow color of the solution faded. After 3.5 h, the mixture was cooled to 0 °C overnight, and the precipitate was filtered, washed well with ether and hexane, and dried in vacuo to give 174 mg of product: mp 188–190 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.8–7.2 (m, 30 H, aromatic), 0.085 (t, *J* = 6 Hz, 3 H, CH_3); ^{31}P NMR ($CDCl_3$) δ 30.689 (relative to phosphoric acid); ^{13}C NMR ($CDCl_3$) δ 136.417–127.970 (m, aromatic), 8.610 (s, CH_3); mol wt (benzene) 688 ± 40. Crystallation from chloroform yielded yellow transparent leaflets: mp 190–191 °C dec; ^{1}H NMR shows the presence of 1 mol of $CHCl_3$. Anal. Calcd for $C_{37}H_{33}BrP_2Pd{\cdot}CHCl_3$: C, 53.98; H, 4.02; Br, 9.46; Cl, 12.61; P, 7.33. Found: C, 53.70; H, 3.93; Br, 10.17; Cl, 11.19; P, 7.02.

The melting point, ^{1}H NMR, and IR of this complex were identical with those of the oxidative addition product of methyl bromide to tetrakis(triphenylphosphine)palladium(0). Upon addition of hexane to the mother liquor obtained after filtration of the complex, another 43 mg of the same complex was collected for a total 90.5% yield.

Oxidative Addition of Methyl Bromide to Tetrakis(triphenylphosphine)palladium(0). To a suspension of 547 mg (0.474 mmol) of tetrakis(triphenylphosphine)palladium(0) in 11 mL of benzene under argon was added 1.5 mL of methyl bromide. The tube was sealed and the suspension was stirred at room temperature for 22 h. The heavy white precipitate that formed was filtered, washed well with ether and hexane, and vacuum dried to give 437 mg of product. ^{1}H NMR ($CDCl_3$) revealed that this solid is a mixture of 326.8 mg of methyltriphenylphosphonium bromide [δ 3.30 (d, *J* = 13 Hz)] and 137 mg of bromomethylbis(triphenylphosphine)palladium(II) [δ 0.085 (t, *J* = 6 Hz)].

Hexane was added to the combined mother liquor and washings, and the precipitate formed was washed with ether and hexane to give 178 mg of *trans*-bromomethylbis(triphenylphosphine)palladium(II), mp 188–190 °C. The ^{1}H NMR and IR spectra were identical with that described above. The overall yield of the complex was 91.5%. When the oxidative addition was carried out in hexamethylphosphoramide, mainly the phosphonium salt and only a small amount of the oxidative addition product were formed.

Reaction of Benzylchlorobis(triphenylphosphine)palladium(II) with Methyl Metals at Room Temperature. Formation of Chloromethylbis(triphenylphosphine)palladium(II). (a) Tetramethyltin. A solution of 340 mg (0.449 mmol) of benzylchlorobis(triphenylphosphine)-palladium(II) and 0.400 mL (2.89 mmol) of tetramethyltin in 4 mL of hexamethylphosphoramide was stirred under argon at room temperature for 15 min and then kept at 0 °C overnight, during which time a white precipitate was formed. Hexane (10 mL) was added, and the precipitate was isolated by filtration under argon. The filtrate was washed with hexane and dried in vacuo to give 255 mg (83.4%) of

chloromethylbis(triphenylphosphine)palladium(II): mp 205–210 °C. The ^1H NMR was identical with those described above for the material before crystallization except for the presence of 1 mol of $CHCl_3$. Anal. Calcd for $C_{37}H_{33}P_2ClPd \cdot CHCl_3$: C, 56.90; H, 4.25; Cl, 17.74; P, 7.75. Found: C, 56.30; H, 4.02; Cl, 16.95; P, 8.01.

(b) Methylmagnesium Bromide. Formation of Chloromethylbis(triphenylphosphine)palladium(II) and Dimethylbis(triphenylphosphine)palladium(II). A solution of 299 mg (0.395 mmol) of benzylchlorobis(triphenylphosphine)palladium(II) in 3 mL of tetrahydrofuran under argon was cooled to −78 °C and 0.4 mL of a 3.0 M ethereal solution of methylmagnesium bromide was added. The solution was stirred for 15 min at −78 °C and for 15 min without external cooling. A white precipitate appeared, was isolated by filtration under argon, and was washed well with ether. This material did not contain hydrogen (^1H NMR). The combined mother liquor and washings were hydrolyzed by addition of 1 mL of water and the mixture was filtered under argon. The small amount of precipitate that formed was washed with methylene chloride, and the washings were added to the filtrate. Yellow crystals started to separate from this solution, which was kept at −15 °C for 4 h. The yellow transparent cubic crystals were isolated by filtration under argon, washed with pentane, and dried in vacuo to give 150 mg (55.8% yield) of chloromethylbis(triphenylphosphine)palladium(II): mp 221–223 °C dec. ^1H NMR $(CDCl)_3$ showed the presence of 1 mol of CH_2Cl_2, and other than that was identical with the one described above. Evaporation of the mother liquor under argon yielded 95 mg (36.4%) of a white solid whose melting point, ^1H NMR, and IR were identical with those of dimethylbis(triphenylphosphine)palladium(II) prepared from dichlorobis(triphenylphosphine)palladium(II) and methyllithium.

Reaction of Benzylbromobis(triphenylphosphine)palladium(II) and Tetramethyltin at Room Temperature. Formation of Bromomethylbis(triphenylphosphine)palladium(II) and Benzyltrimethyltin. A suspension of 169 mg (0.211 mmol) of benzylbromobis(triphenylphosphine)palladium(II) and 200 mL (1.445 mmol) of tetramethyltin in 3 mL of hexamethylphosphoramide was stirred under argon at room temperature for 25 min and kept at 0 °C overnight. A very small amount of yellow precipitate was present. The mixture was stirred at room temperature for 10 min, and the precipitate was removed by filtration. Upon addition of 100 mL of ether–hexane (1:3) to the filtrate, a white precipitate appeared. The mixture was concentrated to a volume of 50 mL, and the precipitate was isolated by filtration, washed with hexane, and dried in vacuo to give 122 mg (79.8%) of bromomethylbis(triphenylphosphine)palladium(II); melting point and ^1H NMR were identical with those described before.

Ether (20 mL) was added to the filtrate, followed by 20 mL of water, and the organic phase was separated, washed with water, and dried over magnesium sulfate. Evaporation of the filtrate yielded 45 mg (83.3%) of benzyltrimethyltin: ^1H NMR $(CDCl)_3$ δ 6.9–7.5 (m, 5 H, phenyl), 2.30 (s, 2 H, PhCH_2), 0.03 (s, 9 H, CH_3Sn); $J_{^{117}SnCH_3}$ = 25 Hz; $J_{^{119}SnCH_3}$ = 26 Hz; $J_{^{117}SnCH_2Ph}$ = 30 Hz. The ^1H NMR spectrum was identical with that of an authentic sample of benzyltrimethyltin prepared from triphenyltin bromide and benzylmagnesium bromide.

***p*-Nitrobenzylbromobis(triphenylphosphine)palladium(II) (20).** A suspension of 1.25 g (1.08 mmol) of tetrakis(triphenylphosphine)palladium(0) and 466 mg (2.16 mmol) of *p*-nitrobenzyl bromide in 20 mL of benzene was allowed to react under the same conditions as in the preparation of benzylbromobis(triphenylphosphine)palladium (**2**) (vide supra), to give 863 mg (94.4% yield) of *p*-nitrobenzylbromobis(triphenylphosphine)palladium(II): mp 148–150 °C dec; ^1H NMR $(CDCl_3)$ δ 7.90–7.15 (m, 34 H, aromatic), 2.88 (br s, 2 H, CH_2); IR $(CHCl_3)$ ν_{NO_2} = 1510 cm^{-1} (s). Anal. Calcd for $C_{43}H_{36}BrNO_2P_2Pd$: C, 60.95; H, 4.28; N, 1.65. Found: C, 60.23; H, 4.32; N, 1.80.

***p*-Nitrobenzylchlorobis(triphenylphosphine)palladium(II) (14).** A suspension of 1.75 g (1.51 mmol) of tetrakis(triphenylphosphine)palladium and 0.97 g (5.6 mmol) of *p*-nitrobenzyl chloride in 50 mL of benzene was stirred at 25 °C under argon for 25 h, after which the mixture was concentrated and 100 mL of ether followed by 200 mL of pentane were added. The yellow *p*-nitrobenzylchlorobis(triphenylphosphine)palladium(II) was isolated by filtration and was washed with ether and pentane and dried in vacuo to give 1.13 g (93.2%) of **18**: mp 143–145 °C dec; ^1H NMR $(CDCl_3)$ δ 8.0–6.8 (m, 30 H, aromatic), 6.70–6.15 (m, 4 H, benzyl aromatic), 2.65 (br s, 2 H, CH_2); IR $(CHCl_3)$ ν_{NO_2} 1510 cm^{-1}(s) Anal. Calcd for $C_{43}H_{36}ClNO_2P_2Pd$: C, 64.33; H, 4.52; N, 1.74. Found: C, 64.81; H, 4.56; N, 1.73.

***p*-Methylbenzylchlorobis(triphenylphosphine)palladium(II)** was prepared from *p*-methylbenzyl chloride and tetrakis(triphenylphosphine)palladium(0) as above in a 91.6% yield: mp 158–160 °C dec; ^1H NMR $(CDCl_3)$ δ 7.85–7.10 (m, 30 H, aromatic), 6.53 (q, A_2B_2, J = 15 Hz, 4 H, benzyl aromatic), 2.67 (s, 2 H, CH_2), 2.15 (s, 3 H, CH_3). Anal. Calcd for $C_{44}H_{39}ClP_2Pd$: C, 68.47; H, 5.09. Found: C, 68.25; H, 4.90.

***m*-Methylbenzylbromobis(triphenylphosphine)palladium(II).** A suspension of 1.10 g (0.95 mmol) of tetrakis(triphenylphosphine)palladium(0) and 352 mg (1.902 mmol) of *m*-methylbenzyl bromide in 17 mL of benzene was stirred under argon at 25 °C for 20 min, after which the complex dissolved completely. The solution was allowed to stand undisturbed at 25 °C for 15 h and then cooled at 0 °C for 1 h. The precipitate that formed was isolated by filtration, washed with a little ether, and dried in vacuo to give 150 mg of *m*-methylbenzyltriphenylphosphonium bromide: mp 260 °C; ^1H NMR $(CDCl_3)$ δ 7.7–7.0 (m, 19 H, aromatic), 5.45 (d, J = 14 Hz, 2 H, CH_2), 2.05 (s, 3 H, CH_3).

The filtrate was concentrated by evaporation, and 20 mL of ether was added to the residue followed by 200 mL of hexane. The yellow precipitate, isolated by filtration, was washed with hexane and a little ether and dried in vacuo to give 0.72 g (93%) of *m*-methylbenzylbromobis(triphenylphosphine)palladium(II): mp 134–136 °C: ^1H NMR $(CDCl_3)$ δ 7.45 (m, 30 H, phenyls), 6.90 (m, 4 H, benzyl aromatics), 2.75 (s, 2 H, CH_2), 2.05 (s, 3 H, CH_3). Anal. Calcd for $C_{44}H_{39}BrP_2Pd$: C, 64.77; H, 4.78; P, 7.60. Found: C, 64.79; H, 4.57; P, 7.47.

Reaction of *p*-Methylbenzylchlorobis(triphenylphosphine)palladium(II) with Tetramethyltin at Room Temperature. This reaction was performed under the same condition as the equivalent reaction using benzylbromobis(triphenylphosphine)palladium(II) (vide supra), taking 10 min to reach completion as indicated by TLC, forming bromomethylbis(triphenylphosphine)palladium(II) in 89.5% yield.

Reaction of *p*-Nitrobenzylbromobis(triphenylphosphine)palladium(II) with Tetramethyltin at Room Temperature. Formation of Methylbromobis(triphenylphosphine)palladium(II). An orange suspension of 344 mg (0.405 mmol) of *p*-nitrobenzylbromobis(triphenylphosphine)palladium(II) and 200 mL (1.445 mmol) of tetramethyltin in 4 mL of hexamethylphosphoramide was stirred at room temperature under argon. The suspension turned brown after approximately 1 min, and a few minutes later it turned to a red that faded as the reaction proceeded. After 3.5 h the suspension was filtered and the white complex was washed with ether and hexane and dried in vacuo, to give 208 mg (70.4% yield) of methylbromobis(triphenylphosphine)palladium(II), the melting point and ^1H NMR of which were identical with those described above. Upon addition of water and hexane to the filtrate, a yellow solid precipitated and was isolated by filtration. The solid was washed with hexane and dried in vacuo to give 44 mg of a mixture of the starting complex and methylbromobis(triphenylphosphine)palladium(II), as shown by ^1H NMR.

Reactions of Bromomethylbis(triphenylphosphine)palladium(II) (8) with Benzyltrimethyltin. (a) A suspension of 204 mg (0.281 mmol) of bromomethylbis(triphenylphosphine)palladium(II) and 141 mg (0.554 mmol) of benzyltrimethyltin[32] in 8 mL of hexamethylphosphoramide was stirred at 65 °C under argon. The complex dissolved completely after 10 min, forming a clear yellow solution that blackened after 70 min. Heating was continued for 3 h, after which time the solution was cooled to room temperature, and a solution of ether–hexane (1:1) was added. The mixture was filtered and GLC analysis of the filtrate showed the presence of toluene (46.4%), ethylbenzene (18.5%), and benzene (3.0%). In a similar experiment conducted at 25 °C for 96 h, all of the starting complex was recovered unchanged.

(b) In the Presence of *p*-Nitrobenzyl Bromide (Inverse Addition). A solution of 270 mg (0.372 mmol) of bromomethylbis(triphenylphosphine)palladium(II) and 130 mg (0.603 mmol) of *p*-nitrobenzyl bromide in 10 mL of hexamethylphosphoramide (HMPA) was added dropwise from a pressure equalizing addition funnel under argon during 11 h to a stirred solution of 409 mg (1.607 mmol) of benzyltrimethyltin and 130 mg (0.603 mmol) of *p*-nitrobenzyl bromide in 1 mL of HMPA at 66 °C. After 52 h, the solution was cooled to 0 °C, a solution of ether–hexane (1:1) was added, and the mixture was filtered. GLC analysis of the filtrate showed the presence of ethylbenzene (87.2%), toluene (41.1%), and a trace of benzene. In a similar experiment chloromethylbis(triphenylphosphine)palladium(II) was

used instead of the bromo complex, to give ethylbenzene (90.5%) and toluene (23.6%).

(c) In the Presence of *m*-Methylbenzylbromobis(triphenylphosphine)palladium(II) (11) and *p*-Nitrobenzyl Bromide. A solution of 297 mg (0.410 mmol) of **8**, 332 mg (0.410 mmol) of **11**, and 132 mg (0.610 mmol) of *p*-nitrobenzyl bromide in 10 mL of hexamethylphosphoramide in a pressure equalizing dropping funnel under argon was added dropwise during 24 h to a stirred solution of 574 mg (2.253 mmol) of benzyltrimethyltin and 130 mg (0.603 mmol) of *p*-nitrobenzyl bromide in 1 mL of hexamethylphosphoramide at 65 °C under argon. After 45 h, the solution was cooled to 0 °C, a solution of ether–hexane (1:3) was added, and the mixture was filtered. GLC analysis of the filtrate showed the presence of ethylbenzene (94.8%, based on **8**) and *m*-methylethylbenzene (10.6%, based on **11**).

Reaction of Bromomethylbis(triphenylphosphine)palladium(II) with Benzylmagnesium Bromide. (a) After addition of benzyl bromide to a suspension of 212 mg (0.292 mmol) of bromomethylbis(triphenylphosphine)palladium(II) in 2 mL of tetrahydrofuran under argon, the mixture was cooled to −78 °C and 3 mL of a 0.57 M solution of benzylmagnesium bromide in ether was added. The stirred suspension was allowed to warm up to 0 °C and was kept at this temperature for 2.5 h during which time it turned orange. Benzyl bromide, 1.8 mL (15.1 mmol), was added and the stirring was continued at 0 °C for 3 h during which all of the solids dissolved. After stirring the solution at 25 °C for 14 h, a yellow solid precipitated, the mixture was hydrolyzed with 1 mL of water, and 10 mL of hexane was added. The mixture was filtered, and the filtrate was analyzed by GLC to show the presence of ethylbenzene (52.3%). The precipitate was washed with methylene chloride and the solvent was removed by evaporation. Upon addition of hexane to the residue, a yellow solid separated, which was isolated by filtration, washed well with pentane, and dried in vacuo to give 65 mg of bromomethylbis(triphenylphosphine)palladium(II) containing 1 mol equiv of CH_2Cl_2. The melting point and ^1H NMR were identical with those described above. Benzylbromobis(triphenylphosphine)palladium(II) could not be detected.

(b) A similar experiment in the absence of benzyl bromide yielded only 25.5% of ethylbenzene.

Dimethylbis(triphenylphosphine)palladium(II). This compound was prepared from dichlorobis(triphenylphosphine)palladium(II) and methyllithium[19] in 65.5% yield. This product was thermally unstable in solution: mp 118–121 °C; ^1H NMR (C_6D_6, 8 °C, argon) δ 7.511 (m, 12 H, phenyl *o*-hydrogen), 6.885 (m, 18 H, phenyl *m,p*-hydrogens), 1.095 (d of d, J = 6.34, 3.17 Hz, 6 H, *cis*-CH_3); ^1H NMR ($CDCl_3$, 8 °C, argon) δ 7.183 (m, 30 H, phenyl), 0.201 (d of d, J = 5.86, 2.93 Hz, 6 H, *cis*-CH_3); IR (KBr) ν Pd–Me (cm^{-1}) 1130, 530, 485 (lit.[19] 1129, 529, 482).

Symmetrization Reactions. (a) Reaction of Dimethylbis(triphenylphosphine)palladium(II) and Benzylbromobis(triphenylphosphine)palladium(II). Formation of Ethylbenzene. A solution of 128 mg (0.194 mmol) of dimethylbis(triphenylphosphine)palladium(II) and 167 mg (0.208 mmol) of benzylbromobis(triphenylphosphine)palladium(II) in 2 mL of benzene was stirred under argon at 0 °C for 1 h and then at 25 °C for 12 h, during which time the solution blackened. Chloroform was added followed by hexane, and the solution was filtered. GLC analysis of the filtrate showed the presence of ethylbenzene (19.5%) and toluene (8.3%). Some unidentified complexes could be isolated from the precipitate. However, bromomethylbis(triphenylphosphine)palladium could not be detected.

(b) Addition of *p*-Nitrobenzyl Bromide. Formation of Ethylbenzene and $MePd(PPh_3)_2Br$. In a similar experiment, a solution of 110 mg (0.167 mmol) of dimethylbis(triphenylphosphine)palladium(II), 154 mg (0.192 mmol) of benzylbromobis(triphenylphosphine)palladium(II), and 701 mg (3.247 mmol) of *p*-nitrobenzyl bromide in 2 mL of benzene was stirred under argon at 0 °C for 30 min and then at 25 °C for 20 h. Hexane was added and the mixture was filtered. GLC analysis of the filtrate showed the presence of ethylbenzene (20.5%). The solid was washed well with hexane and ether and dried in vacuo to give 109 mg of a mixture that consisted (NMR) of 61 mg (50.4%) of bromomethylbis(triphenylphosphine)palladium(II) and 48 mg of *p*-nitrobenzylbromobis(triphenylphosphine)palladium(II).

(c) Reaction of Bromomethylbis(triphenylphosphine)palladium(II) with Benzylbromobis(triphenylphosphine)palladium(II). A suspension of 115 mg (0.159 mmol) of bromomethylbis(triphenylphosphine)-palladium(II) and 128 mg (0.160 mmol) of benzylbromobis(triphenylphosphine)palladium(II) in 4 mL of hexamethylphosphoramide was heated at 65 °C with stirring for 20 h. Ether and hexane were added, the mixture was filtered, and the solution was analyzed by GLC to show the presence of ethylbenzene (3% yield). The solid was washed well with ether and hexane to give 212 mg of the original mixture of the starting complexes.

Thermal Decomposition of Dimethylbis(triphenylphosphine)palladium(II) (17). A solution of **17** in C_6D_6 was heated at 40 °C for 15 min in an NMR tube, during which decomposition occurred and the solution turned black: ^1H NMR (C_6D_6, argon) δ 7.443 (m), 7.419 (m), 0.795 (**s**), the last absorption coinciding with that of an authentic sample of ethane.

Reaction of *cis*-Dimethylbis(triphenylphosphine)palladium(II) (17) with Benzyl Bromide. Formation of Bromomethylbis(triphenylphosphine)palladium(II) (9) and Ethylbenzene. (a) Followed by ^1H NMR. A 20-mg sample of **17** was dissolved in 0.5 mL of $CDCl_3$ containing 50 μL of benzyl bromide in a 5-mm NMR tube. The tube was heated at ~40 °C and the solution was analyzed by ^1H NMR: δ 2.90 (s, $PhCH_2Pd(PPh_3)_2Br$, 1), 2.64 (q, J = 8 Hz, $PhCH_2CH_3$, 10), 1.22 (t, J = 8 Hz, $PhCH_2CH_3$, 15), 0.85 (s, CH_3CH_3, 4), 0.08 (t, J = 6 Hz, $CH_3Pd(PPh_3)_2Br$, 15), corresponding to 79% ethylbenzene, 21% ethane, 91% of $MePd(PPh_3)_2Br$, and 9% of $PhCH_2Pd(PPh_3)_2Br$.

(b) Formed in Situ. To a suspension of 505.3 mg (0.720 mmol) of dichlorobis(triphenylphosphine)palladium(II) in 8 mL of ether at −78 °C under argon was added 1.8 mL of a 1.8 M solution of methyllithium in ether. The yellow suspension was allowed to stir without external cooling until the reached temperature 0 °C; the mixture was kept at this temperature for 1.5 h, during which time it turned white. The suspension was filtered under argon while being kept at 0 °C at all times. The white precipitate, a mixture of dimethylbis(triphenylphosphine)palladium(II) (**17**) and lithium chloride, was washed twice with 5 mL of cold degassed benzene to dissolve the complex, leaving only the lithium chloride. The combined ether and benzene solutions were kept at 0 °C, and the residual methyllithium was hydrolyzed by the dropwise addition of 1.5 mL of ice-cold water and stirring for 15 min after the addition was complete. A cold solution of 3 mL of benzyl bromide in 3 mL of benzene was added, and the mixture was stirred at 0 °C for 3 h, followed by stirring at 25 °C overnight. The mixture was filtered and the precipitate was washed well with benzene. The organic solution was analyzed by GLC to show the presence of ethylbenzene (59.3%, based on the starting complex). The solvent was removed by evaporation and hexane was added to the residue. The light yellow precipitate was isolated by filtration, washed well with hexane, and dried in vacuo to give 280 mg (53.6%) of bromomethylbis(triphenylphosphine)palladium(II) (**9**) contaminated by traces of benzylbromobis(triphenylphosphine)palladium(II) (**3**) as shown by ^1H NMR and TLC. Crystallization from chloroform yielded pure **9** containing 1 mol equiv of chloroform; melting point, ^1H NMR, and IR were identical with those described above.

Reaction of *cis*-Dimethylbis(triphenylphosphine)palladium(II) (17) with (*R*)-(−)-α-Deuteriobenzyl Bromide. Formation of (*R*)-(−)-α-Deuterioethylbenzene. To a solution of 2.740 g (15.93 mmol) of (*R*)-(−)-α-deuteriobenzyl bromide,[33] $[\alpha]^{25}_D$ −1.076 ± 0.003° (neat, l = 1), containing 1.00 ± 0.05 deuterium per molecule, 89.7 ± 0.3% ee, in methylene chloride at −78 °C under argon was added 2.54 g (3.85 mmol) of *cis*-dimethylbis(triphenylphosphine)palladium(II), and the resulting suspension was stirred at that temperature for 1 h followed by stirring at 0 °C for 16 h and at 25 °C for 24 h. The solvent was transferred in vacuo to a liquid nitrogen trap and pentane (2.10 mL) added to the residue, which was filtered under argon pressure. Since GLC analysis showed that the dichloromethane contained some α-deuterioethylbenzene, it was combined with the pentane solution and the solution was concentrated to a volume of ~5 mL by distillation of the solvent through a 20-cm Vigreux column. The volume was measured exactly and it was found to contain 195.6 mg (47.5%) of α-deuterioethylbenzene by GLC analysis using standard solutions of ethylbenzene. Ethylbenzene, 693.6 mg, was added, and the solvent was removed by distillation through a short column. The residue was fractionally distilled under reduced pressure to give 1.01 mL of pure ethylbenzene and (*R*)-(−)-α-deuterioethylbenzene (bp 65–66 °C (20 mmHg); $[\alpha]^{25}_D$ −0.167 ± 0.004° (neat, l = 1), corrected for dilution by ethylbenzene; 22.9 ± 2% ee)[33] and 2.37 g of (*S*)-(+)-α-deuteriobenzyl bromide (bp 76–78 °C (7 mm); $[\alpha]^{25}_D$ +0.011 ± 0.001 (neat, l = 1); 0.9 ± 0.1% ee).

Oxidative Addition of (*R*)-(−)-α-Deuteriobenzyl Bromide to Tetrakis(triphenylphosphine)palladium(0) (1) under Carbon Monoxide. Formation of Optically Active Bromo(α-deuteriophenylacetyl)bis(triphenylphosphine)palladium(II). Upon solubilization of 6.30 g (5.45

mmol) of tetrakis(triphenylphosphine)palladium(0) in 65 mL of carbon monoxide saturated benzene, 1.87 g (10.9 mmol) of (*R*)-(−)-α-deuteriobenzyl bromide,[33] $[\alpha]^{25}_D$ −0.646 ± 0.002° (neat, *l* = 1), 53.8 ± 0.3% ee, was added. The solution was stirred under carbon monoxide at 25 °C for 69 h, during which a precipitate appeared that was isolated by filtration, was washed with 10 mL of benzene, and was dried in vacuo to give 5.3 g of a creamy-white solid, consisting of a mixture of bromo(α-deuteriophenylacetyl)bis(triphenylphosphine)palladium(II) (4.5 g, 100%) and triphenyl(α-deuteriobenzyl)-phosphonium bromide (0.8 g) by ^{1}H NMR ($CDCl_3$): δ 6.3-8.3 (m, phenyl, 71), 5.33 (d, Ph*CH*DP, 1), 3.30 (s, Ph*CH*DCOPd, 1.9); IR ($CHCl_3$) 1670 cm^{-1} (RCOPd).

Bromine Cleavage of Optically Active Bromo(α-deuteriophenylacetyl)bis(triphenylphosphine)palladium(II) and Subsequent Methanolysis of the Acid Bromide. Formation of (*S*)-(+)-Methyl α-Deuteriophenylacetate. To a vigorously stirred suspension of 5.3 g of a mixture of bromo(α-deuteriophenylacetyl)bis(triphenylphosphine)palladium(II) and triphenyl(α-deuteriobenzyl)phosphonium bromide (containing 4.5 g, 5.42 mmol of the palladium complex) in 130 mL of methylene chloride under argon was added 0.62 g (3.87 mmol) of bromine at −78 °C. A heavy yellow precipitate appeared immediately. The reaction mixture was stirred for 15 min at −78 °C and was allowed to warm to 25 °C. Dry methanol, 21 mL, was added, and the mixture was stirred at 25 °C for 20 min. The yellow dibromobis(triphenylphosphine)palladium was removed by filtration and was washed with 20 mL of dichloromethane and 10 mL of methanol. The solvent of the combined filtrate and washing was removed by evaporation and the residue was extracted with 6 × 50 mL of pentane, the pentane solution was filtered, and the solvent was removed by evaporation. The residue was distilled in a Kugelrohr apparatus to give 426 mg (54%) of (*S*)-(+)-methyl α-deuteriophenylacetate: ^{1}H NMR ($CDCl_3$) δ 7.25 (s, 5 H, Ph), 3.65 (s, 3 H, OCH_3), 3.58 (t, *J* = 2.2 Hz, 1 H, CHD). This material was diluted to 1 mL with methyl phenylacetate, $[\alpha]^{25}_D$ +0.322 ± 0.002° (neat, *l* = 0.1), 37 ± 4% ee.

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