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Stereochemistry of Oxidative Addition of Benzyl-α-*d* Chloride and Bromide to Tris(triethylphosphine)palladium(0). Direct Observation of Optical Activity in a Carbon–Palladium σ-Bonded Complex

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Abstract: The absolute configurations of the products of oxidative addition of optically active benzyl-α-*d* chloride (**1a**) and bromide (**1b**) to tris(triethylphosphine)palladium(0) (**6**) were determined using carbonylation and cleavage with Cl_2/MeOH to produce the corresponding methyl esters. In both cases inversion of configuration at carbon was observed; higher optical yields were obtained with benzyl chloride. Neither a nucleophilic exchange mechanism in the neutral benzyl complex nor a σ–π rearrangement in the cationic intermediate (S)-(+)-$PhCHDPd(PEt_3)_2^+$ is responsible for the observed loss of stereochemistry.

Introduction

The catalytic carboalkoxypalladation of various organic halides

$$RX + CO + R'OH \xrightarrow[\text{base}]{\text{LnPd}^0} RCO_2R' \qquad (1)$$

can be carried out under very mild conditions.[1] The key step in the reaction is the oxidative addition of the organic halide to the zerovalent palladium phosphine complex. Since this step also determines the stereospecificity of the reaction, a study of the stereochemistry and the mechanism of the oxidative addition reaction was undertaken.

Optically active benzyl-α-*d* chloride (**1a**) and α-phenethyl bromide (**2**) react with carbonyl tris(triphenylphosphine)palladium(0) **3** with *complete* inversion of configuration at the asymmetric carbon.[2] The reaction of **1** with tetrakis(triphenylphosphine)palladium(0) (**4**) gave an isolable benzyl complex but only 74% net inversion of configuration at carbon was observed. However, when carbon monoxide was present during the oxidative addition, 100% net inversion of configuration on carbon was again realized. In the presence of carbon monoxide, the stereospecificity of the addition of **2** to **4** was found to be essentially the same as in the direct oxidative addition to **3**. When no carbon monoxide was present, facile β-hydride elimination predominated. The predominance of inversion of configuration at carbon is more consistent with a concerted oxidative addition mechanism than with the generation of radical intermediates.

In contrast to these results, CIDNP was observed during the oxidative addition of benzyl bromide to tris(triethylphosphine)platinum(0) (**5**) and isopropyl iodide to tris(triethylphosphine)palladium(0) (**6**). On the other hand, no CIDNP signals were detected in the addition of benzyl chloride to **5**.[3b] Therefore, it was suggested that free-radical processes are involved in the oxidative addition of certain alkyl halides to d^{10} zerovalent metal phosphine complexes, while with others an S_N2-type mechanism operates. In the present study we have tested these ideas using two model compounds, a chiral benzyl chloride and a bromide, as stereochemical probes in the oxidative addition to **6**.

Results and Discussion

Reactions and Product Characterization. Benzyl chloride and bromide react extremely rapidly with **6**[4] under very mild conditions; the stoichiometry of both reactions was found to be consistent with eq 2 and 3.

The products were isolated either by direct crystallization in the benzyl chloride case or by column chromatography in

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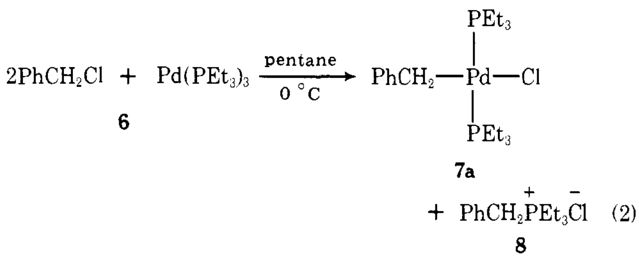
Table I. NMR[a] of $RPd[P(CH_2CH_3)_3]_2X$ Complexes

Compd	^{1}H benzylic[b]	$^{31}P\{^1H\}$[c]	^{13}C benzylic[d]	^{13}C carbonyl	$^{13}C\{^1H\}$ of tertiary phosphines[e] C_α	C_β
7a	2.48, t (7)	14.0, s	15.0, t (137 ± 10)		14.5, t (12.5)	8.44, s
7b	2.84, t (7)	12.6, s	17.6, t (133 ± 1)		15.0, t (12.5)	8.44, s
13a	3.91, s	12.22, s	64.1 dd (12.5; 11.7)	233.8, s	15.3, t (12.1)	8.32, s
13b	3.90, s	11.0, s	63.8 dd (16.9; 16.1)	234.1, s	15.8, t (12.5)	8.35, s

[a] Aromatic resonances are not shown. All the spectra were recorded in C_6D_6. [b] Relative to Me_4Si. J(P-H) in parentheses. [c] Shifts are reported positive downfield with respect to H_3PO_4. [d] Chemical shifts relative to Me_4Si. $J(^{13}C\text{-}H)$ in parentheses for **7a** and **7b** and $|J(\text{P-C})|$ for **13a** and **13b**. [e] $|J(\text{P-C})|$ in parentheses.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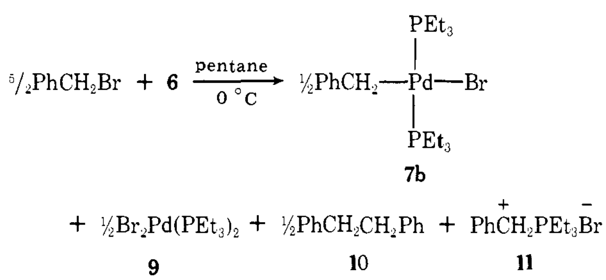
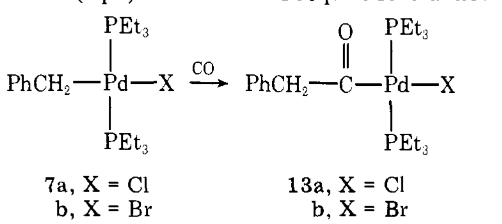

(3)

the benzyl bromide system. The oxidative addition products **7a** and **7b** are very soluble in common organic solvents, and therefore they could be characterized spectroscopically.

The trans geometry of the oxidative addition products is consistent with singlet signals in the $^{31}P\{^1H\}$ spectra, indicating that the two phosphines are chemically equivalent. Further support for this assignment comes from the AXX′ spin system (A = ^{13}C; X,X′ = ^{31}P) of the triethylphosphine ligands which exhibits a 1:2:1 triplet in the $^{13}C\{^1H\}$ spectrum for the $C\alpha$ atoms. It is well known[5] that when the two phosphines are mutually trans the carbon α to the phosphorus atom always appears as a 1:2:1 triplet. In the cis isomers of these complexes the $^{13}C\alpha\{^1H\}$ resonances should appear as a quintet, a non-1:2:1 triplet, a doublet of doublets, or a doublet.[5a,b]

Carbonylation of the oxidative addition products was carried out in benzene or pentane solutions at room temperature under 2-3 atm of CO (eq 4). The reactions require several hours for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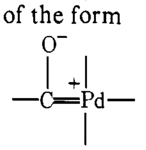
completeness, and in both cases the crystalline trans acyl complexes (**13**) were obtained in high yield. Interestingly, the benzylic carbon in these complexes exhibits in the $^{13}C\{^1H\}$ two slightly different coupling constants to phosphorus suggesting that the phenylacetyl group and the $Pd(PEt_3)_2X$ moiety are approaching coplanarity due to a restricted rotation around the -(CO)-Pd bond (Table I). Restricted rotation in the NMR time scale around the -(C=O)-Pd bond may arise from a resonance contribution of the form



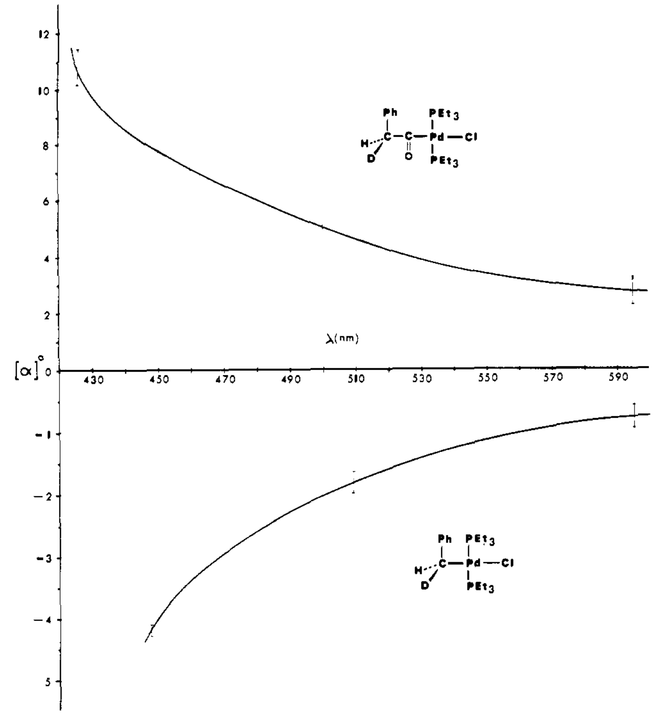
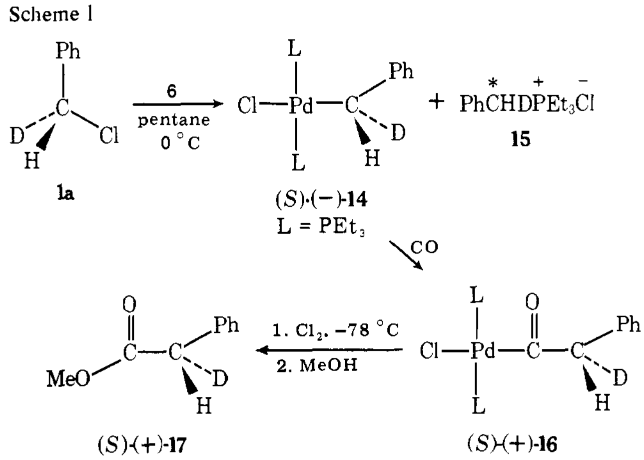


Figure 1. Optical rotatory dispersion curves for **14** and **16**.

which implies increasing the Pd-C double bond character. The lower C=O bond order is reflected in the low carbonyl stretching frequency (1650 cm^{-1}) in the IR spectra of these acyl complexes.

Stereochemistry. Benzyl-α-*d* Chloride. The addition of (*R*)-(−)-benzyl-α-*d* chloride (**1a**) to **6** rapidly gave rise to the levorotatory adduct **14** in quantitative yield (Scheme I). The

Scheme I



only by-product was the chiral phosphonium salt **15**. As expected, the rotation of **14** was found to be wavelength dependent as shown by its plain ORD curve (Figure 1). The con-

Table II. Oxidative Addition of Benzyl-α-*d* Chloride to **6** in Pentane at 0 °C

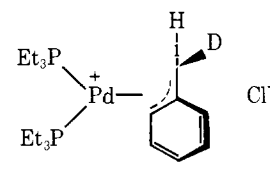
λ, nm	Specific rotations[a] (R)-(−)-**1a**[b]	(S)-(−)-**14**[c]	**15**[d]	(S)-(+)-**16**[e]	(S)-(+)-**17**[f]	Overall stereo-specificity
589	−1.342 (2)	−0.96 (8)	−0.98 (2)	+3.53 (1)	+0.547 (4)	72%
578	−1.402 (2)	−1.04 (8)	−1.06 (2)	+3.69 (1)	+0.567 (4)	
546	−1.785 (2)	−1.33 (8)	−1.20 (2)	+4.38 (2)	+0.642 (4)	
436	−3.365 (2)		−1.97 (2)	+7.2 (2)	+1.104 (4)	

[a] All rotations were measured with a polarometric microcell of path length 10.000 cm at 29 °C. Estimated experimental error in parentheses; last significant figure. [b] ee is 87.7 ± 4%. Calculated from the absolute rotation $[\alpha]^{25}_D$ ±1.53 ± 0.06° (neat, *l* = 0.1).[2] [c] *c* 0.440 g/mL, CH_2Cl_2. [d] *c* 0.100 g/mL, CH_2Cl_2. We assume that **15** has the *S* configuration since it is known that nucleophilic attack of trialkylphosphines on alkyl halides obeys S_N2 kinetics. [e] *c* 0.303 g/mL, CH_2Cl_2. [f] 62.8 ± 10% ee calculated from the absolute rotation $[\alpha]^{28}_D$ ±0.87 ± 0.08° (neat, *l* = 0.1).[2]

figuration of the primary benzylic carbon in **14** has been deduced via carbonylation which produced the dextrorotatory acyl complex **16**. The usual chlorination-methanolysis sequence resulted in the known[2] (*S*)-(+)-methyl α-deuteriophenylacetate (**17**) with inverted configuration at carbon. Since carbonylation is known to proceed with 100% retention of configuration on carbon[7] and chlorine cleavage has not been performed at the chiral center, the observed net inversion must be attributed to the oxidative addition step. Since the optical purities of **1a** and **17** could be determined (Table II) the stereospecificity of the oxidative addition of **1a** to **6** was found to be 72%. The recovered **1a** suffered 29% loss of the original activity. The observed net inversion is very similar to that obtained with the much less reactive palladium complex **4**. Running the oxidative addition in the presence of carbon monoxide did not lead to the expected increase in the overall net inversion. Unlike the triphenylphosphine Pd(0) complex **4**, the highly nucleophilic **6** has very high affinity toward carbon monoxide. On carbonylation of a pentane solution of **6** under 1–3 atm the color of the solution turned from yellow to orange-brown. The IR of the resulting solution exhibited a very strong band at 1945 cm^{-1} assigned to $(Et_3P)_3PdCO$ (**18**)[8] as well as weaker bands at 2010, 1970, and 1810 cm^{-1}, probably arising from a mixture of $(Et_3P)_2Pd(CO)_2$ and bridged carbonyl palladium clusters.[9] This extremely air-sensitive palladium carbonyl mixture reacted sluggishly with benzyl chloride to give a mixture of **7a** and **13a** in low yield together with unreacted palladium carbonyl. The low reactivity of **18** in comparison with **3** is presumably due to a combination of electronic and steric effects. A similar decrease in reactivity toward alkyl halides was found on going from $Ni(PPh_3)_4$ to $(PPh_3)_2Ni(CO)_2$.[1b,10]

Possible Pathways for Racemization. The observed loss of stereochemistry on carbon in the oxidative addition of **1a** to **6** can be accounted for by at least two possible mechanisms which operate *after* formation of a palladium-carbon σ bond has taken place.[11] One is the nucleophilic exchange mechanism previously described.[2,12] Subjecting optically active (*S*)-(−)-**14** to the action of **6** at 25 °C in benzene solution for several hours did not affect its optical activity, since carbonylation[13] of the reaction mixture gave rise to acyl complex **16** which exhibits the usual relatively high rotations (Experimental Section). If the nucleophilic exchange mechanism is responsible for the observed 29% loss of optical activity in the chiral benzyl complex **14** within the first few minutes required for completeness of the oxidative addition, complete loss of optical activity would be expected under prolonged treatment with the reactive Pd(0) complex.

Another possible source of racemization could be a σ-π rearrangement[14] in the postulated cationic intermediate **19** formed during the nucleophilic oxidative addition. A proof that such an intermediate cannot be responsible for the racemization is given in the following paper.[14]



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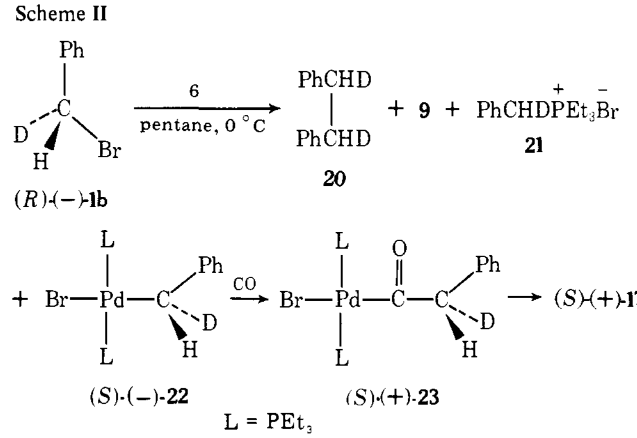
Benzyl-α-*d* Bromide. The reaction of (*R*)-(−)-benzyl-α-*d* bromide (**1b**)[15] with **6** in pentane at 0 °C produces instantaneous separation of crystalline *trans*-dibromobis(triethylphosphine)palladium(II) (**9**), the inactive coupling product, 1,2-dideuterio-1,2-diphenylethane (**20**), the phosphonium salt **21**, and the oxidative addition product **22** (Scheme II). Because

Scheme II



of the low optical activity of the latter compound and in order to facilitate its isolation, it was directly converted to the acyl complex **23**, which in turn was degraded by the usual method to ester **17**. Both **17** and **23** exhibited low optical activity (Table III). Extensive racemization characterized the oxidative addition of **1b** to **6**; nevertheless, ~19% net inversion of configuration at carbon was realized. When the oxidative addition was carried out in the presence of radical scavenger, *m*-dinitrobenzene,[16] no significant change in product distribution or overall net inversion (Table III) was observed. Only an approximate estimation of the degree of net inversion of configuration on carbon could be made, since relatively high uncertainty is associated with the measurement of the small rotations of **17**. It was necessary, however, to determine that the high degree of loss of stereochemistry on carbon was not a result of the lower stability of the carbon-palladium σ bond in the bromobenzyl complex **22** than the chloro analogue **14**.

Taking advantage of the "trans effect" in square planar haloalkyl Pd(II) complexes where halogen trans to the alkyl ligand is easily displaced by an external nucleophile,[17] a correlation between chiral chloro- and bromobenzyl complexes was feasible (Scheme III).

Table III. Oxidative Addition of Benzyl-α-*d* Bromide to **6** in Pentane at 0 °C

	Specific rotations[a] (estd exptl error in parentheses)			
λ, nm	(*R*)-(−)-**1b**[b]	(*S*)-(+)-**23**[c]	(*S*)-(+)-**17**[d]	Overall stereospecificity
	I. Without Inhibitor			
589	−0.594 (1)	+0.44 (1)	+0.08 (2)	~19% (based on (*S*)-(+)-**17**)
578	−0.621 (1)	+0.50 (1)	+0.09 (3)	~26%[h]
546	−0.723 (1)	+0.48 (2)	+0.10 (2)	
436	−1.414 (1)		+0.13 (4)	
	II. With Inhibitor (5 mol % *m*-dinitrobenzene)			
589	−1.067 (1)[e]	+0.99 (1)[f]	0.18 (2)[g]	~23% (based on (*S*)-(+)-**17**)
578	−1.117 (1)	+1.08 (1)	0.20 (2)	~33%[h]
546	−1.308 (1)	+1.00 (3)	0.21 (3)	
436	−2.531 (1)		0.78 (3)	

[a] All rotations measured with 10.000-cm microcell at 29 °C. [b] ee is 49.5 ± 5% based on the absolute rotation of $[\alpha]^{20}_D$ ±1.20 ± 0.1°. This value was determined from the observation that a sample of (*R*)-(−)-PhCHDOH, 41.7 ± 1% ee diluted with $PhCH_2OH$ to $[\alpha]^{20}_D$ −0.103 ± 0.006° (neat, *l* = 1) gave (*S*)-(+)-PhCHDBr ($[\alpha]^{20}_D$ +0.105 ± 0.005, neat, *l* = 1) assuming 100% stereospecific inversion at carbon during the bromination with PBr_3. The alcohol contained 0.87 deuterium per molecule.[15] [c] *c* 0.202 g/mL, CH_2Cl_2. [d] ~10% ee. [e] 89.5 ± 5% ee. [f] *c* 0.216 g/mL, CH_2Cl_2. [g] ~22% ee. [h] Based on the $[\alpha]^{29}_D$ ±5.10 ± 0.5° as the extrapolated absolute rotation of (*S*)-(+)-**23** (see Table IV).

Table IV. Correlation of Chiral $R(Et_3P)_2PdX$ Complexes

	Specific rotations[a]				
λ, nm	(*S*)-(−)-**22**[b]	(*S*)-(+)-**23**[c]	(*S*)-(+)-**16**[d] from (*S*)-(−)-**14**	(*S*)-(+)-**16**[e] from (*S*)-(+)-**23**	Pure (*S*)-(+)-**23**[f]
589	−0.67 (2)	+3.00 (4)	+2.46 (2)	+2.52 (2)	+5.1 (6)
578	−0.74 (1)	+3.16 (2)	+2.62 (1)	+2.68 (2)	+5.3 (6)
546	−0.98 (2)	+3.72 (2)	+3.12 (1)	+3.17 (1)	+6.3 (6)

[a] For rotations of (*S*)-(−)-**14** see Table II. [b] All rotations measured in CH_2Cl_2, *l* = 1. Estimated experimental error in parentheses; last significant figure. [b] *c* 0.202 g/mL. [c] *c* 0.148 g/mL. [d] *c* 0.166 g/mL. [e] *c* 0.210 g/mL. [f] Calculated on the basis that (*S*)-(−)-**14** was derived from PhCHDCl 80.7 ± 4% ee and that the stereospecificity in the oxidative addition is 72 ± 9%.

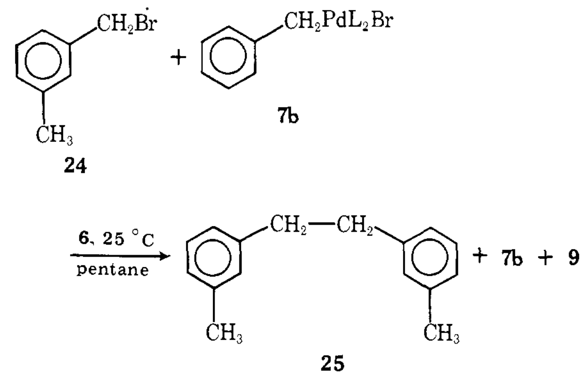
Scheme III

$$\begin{array}{ccc} (S)\text{-}(-)\text{-}\mathbf{14} & \xrightarrow{\text{CO}} & (S)\text{-}(+)\text{-}\mathbf{16} \\ \downarrow{\scriptstyle 25\,^\circ C,\ LiBr,\ MeOH} & & \uparrow{\scriptstyle 25\,^\circ C,\ LiCl,\ Me_2CO-MeOH} \\ (S)\text{-}(-)\text{-}\mathbf{22} & \xrightarrow{\text{CO}} & (S)\text{-}(+)\text{-}\mathbf{23} \end{array}$$

The chloride ligand in (*S*)-(−)-**14** was readily replaced by treatment with LiBr under mild conditions. No racemization occurred at the benzylic carbon during the LiBr exchange since carbonylation of **22** obtained from **14** gave rise to the corresponding chiral acyl complex **23** which was correlated with (*S*)-(+)-**16** via LiCl exchange. The resulting chloroacyl complex exhibited essentially the same rotations as the acyl complex derived directly from (*S*)-(−)-**14** (Table IV).

This substitution pattern clearly demonstrated that the chiral primary carbon was not involved in these transformations, and the bromoalkyl and -acyl complexes **22** and **23**, like their chloro analogues, did not racemize in solution. Furthermore, since the stereospecificity of the oxidative addition and carbonylation steps are known, the absolute rotation of the acyl complex **23** could be extrapolated, thus providing additional estimation for the degree of net inversion in the benzyl-α-*d* bromide system (Table III). Additional support for the stability of achiral **7b** came from the observation that under the reaction conditions the action of benzyl bromide, triethylphosphine, or **6** on **7b** did not lead to bibenzyl (**10**). In contrast, chloro(benzyl)bis(triphenylphosphine)palladium(II) reacts with benzyl chloride at 80 °C to afford **10**,[18] and the analogous Ni(II) complex disproportionates to **10** and $Ni(PPh_3)_3X$ at room temperature in the presence of added PPh_3.[19]

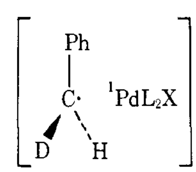
Another possible source of the bibenzyl in our system could involve reaction of the benzyl palladium bromo complex **7b** with a biradical intermediate (vide infra) formed during the course of the oxidative addition of benzyl bromide to **6**. To test this possibility **6** was added to a mixture of **7b** and 3-methylbenzyl bromide (**24**) (eq 5). However, no crossed-coupled bibenzyl was detected in addition to the expected homo-coupling product **25**. Analysis of the products indicated that **7b** did not interfere with the course of the oxidative addition of **24** to **6**. Our observations point out that **7b**, **10**, and **9** are formed during the early stages of the reaction, and **7b** does not serve as a precursor for the other two. Moreover, once the optically active oxidative addition products are formed, they do not racemize under the reaction conditions; thus, the observed loss of stereochemistry on carbon must reflect the nature of the transition state and/or intermediate in the two systems investigated.



$$+\ m\text{-}CH_3C_6H_4CH_2\overset{+}{P}Et_3\overset{-}{Br}\ +\ m\text{-}CH_3C_6H_4CH_2PdL_2Br \quad (5)$$

26 **27**

Inversion of configuration at carbon in both systems suggests an S_N2-like mechanism in which Pd(0) serves as a nucleophile. The loss of stereochemistry in this process may be due to a competitive one-electron transfer[3] leading to a biradical cage intermediate **28**, and this pathway must be more important in the benzyl bromide case. Indeed, the rate of one-electron transfer from the highly nucleophilic pentacyanocobaltate anion to benzyl bromide was found to be four orders of magnitude faster than to benzyl chloride.[20] Either **28** can revert back to the starting halide or collapse to the regular adduct, thus accounting for the partial racemization in reactants and products. Racemization does require, however, that the benzyl radical in **28** rotate 180 °C before formation of the palla-



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dium-carbon σ bond or reversion to benzyl bromide (**1b**). The encounter of **28** by benzyl bromide would lead to the observed coupling products **9** and **10**. The proposed cage biradical intermediate is also in agreement with the observed ineffectiveness of the radical scavenger, and is inconsistent with a free-radical chain mechanism[3a] which requires complete loss of stereochemistry. Attempts to detect CIDNP in the reaction even at low temperatures did not produce emission signals,[21] presumably owing to the very high rate of the reaction, or more likely owing to the presence of paramagnetic Pd(I) species.[22] In the benzyl chloride system, one-electron transfer is very likely unimportant since the reaction is characterized by a relatively high degree of stereospecificity and coupling products are not formed. Scrambling in the trigonal bipyramidal transition state[2] as a result of impure motion of the equatorial groups[23] may be a more plausible explanation for the observed loss of stereochemistry.

Experimental Section

Preparation and handling of palladium complexes was carried out using a Schlenk technique in an inert atmosphere of argon purified by a passage through a BASF catalyst. Solvents were carefully degassed before use. Optical rotations of the deuterated compounds were taken with a Perkin-Elmer Model 141 polarimeter. ORD spectra were taken using a Cary 60 with a polarimetric cell of path length 1.00 cm. ^1H NMR spectra were run on a Varian EM360 spectrometer; ^{31}P and ^{13}C spectra were obtained on a Bruker HX-90E spectrometer. IR spectra were taken on a Beckman IR-20A instrument. Melting points are uncorrected.

Oxidative Addition of Benzyl Chloride to Tris(triethylphosphine)palladium(0) (6). A solution of tris(triethylphosphine)palladium(0)[4] (787 mg, 1.707 mmol) in 10 mL of pentane was cooled to 0 °C and treated with benzyl chloride (540 mg, 4.27 mmol). The solution was stirred for 1 h, during which a white precipitate was formed. After dilution with 10 mL of pentane the mixture was filtered and the white solid was washed well with pentane to yield 237 mg (57%) of product: mp 186-187 °C; ^1H NMR ($CDCl_3$) δ 7.8-7.32 (m, 5 H, Ph), 4.24 (d, 2 H, J = 15 Hz, $-CH_2-$) 2.75-2.1 (m, 6 H, PCH_2-) 1.50-0.82 (m, 9 H, CH_3). The melting point and NMR spectrum were identical with those of authentic $PhCH_2P^+Et_3Cl^-$ prepared from triethylphosphine and benzyl chloride in benzene.

The pentane-soluble portion of the reaction product was concentrated under reduced pressure until crystallization commenced. After 2 h at −15 °C the crystals were collected, washed quickly with cold pentane, and dried for 4 h at 25 °C (4 μm) to give 790 mg (98%) of *trans*-chloro(benzyl)bis(triethylphosphine)palladium(II) (**7a**), mp 77-79 °C. Anal. Calcd for $C_{19}H_{37}ClP_2Pd$: C, 48.62; H, 7.89; Cl, 7.56; P, 13.22. Found: C, 48.05; H, 8.08; Cl, 7.82; P, 13.10.

Oxidative Addition of Benzyl Bromide to Tris(triethylphosphine)palladium(0) (6). A solution of tris(triethylphosphine)palladium(0) (3.183 g, 18.2 mmol) in 20 mL of pentane was cooled to 0 °C and with vigorous stirring a solution of benzyl bromide (3.12 g, 18.2 mmol) in 10 mL of pentane was added. Copious white and yellow crystals separated immediately. After stirring for 1 h the reaction mixture was warmed up to room temperature and 25 mL of benzene was added. After most of the yellow crystals were dissolved, the remaining white precipitate was filtered and washed well with pentane to give 440 mg of white crystals: mp 178-180 °C; ^1H NMR ($CDCl_3$) δ 7.38 (m, 5 H, Ph), 4.18 (d, 2 H, J = 15 Hz, $-CH_2-$), 2.8-2.2 (m, 6 H, PCH_2-), 1.5-0.9 (m, 9 H, CH_3-). The melting point and NMR spectrum were identical with those of authentic $PhCH_2P^+Et_3Br^-$ prepared from triethylphosphine and benzyl bromide in benzene.

To the soluble portion of the reaction product was added 15 g of alumina (Woelm, activity III) and the solvent was concentrated in vacuo, giving a yellow powder which was packed on top of 2 × 40 cm neutral alumina column of the same activity grade. Elution with petroleum ether (bp 40-60 °C) yielded a colorless oil which was distilled in a Kugelrohr apparatus at 0.5 mmHg to give 733 mg (97%) of colorless crystals of 1,2-diphenylethane (**10**): mp 50-52 °C (reported 52 °C); ^1H NMR ($CDCl_3$) δ 7.15 (m, 10, Ph), 2.85 (s, 4 H, $-CH_2CH_2-$).

Elution with methylene chloride-petroleum ether (1:3) caused migration of the yellow band of dibromobis(triethylphosphine)palladium(II) (**9**) obtained as yellow needles, 2.21 g (106%). Recrystallization from hexane gave an analytical sample, mp 126-127 °C. Anal. Calcd for $C_{12}H_{30}Br_2P_2Pd$: C, 28.66; H, 6.01. Found: C, 28.75; H, 6.11.

On elution with methylene chloride another yellow band, *trans*-bromo(benzyl)bis(triethylphosphine)palladium(II) (**7b**), 1.51 g (71%), was obtained as an orange oil. Crystallization from pentane gave long, yellow prisms, mp 89-90 °C. Anal. Calcd for $C_{19}H_{37}BrP_2Pd$: C, 44.42; H, 7.26; Br, 15.55; P, 12.06. Found: C, 44.63; H, 7.19; Br, 15.80; P, 11.77.

Some decomposition occurred on the column, as indicated by a residual very polar yellow band, eluted with 5% methanol-methylene chloride. This band consisted of a mixture of unidentified palladium complexes, having no benzyl group as a ligand.

Carbonylation of the benzyl complexes. *trans*-Chloro(phenylacetyl)bis(triethylphosphine)palladium(II) (13a). A stirred solution of *trans*-chloro(benzyl)bis(triethylphosphine)palladium(II) (**7a**, 200 mg, 0.27 mmol) in 7 mL of anhydrous benzene was carbonylated at room temperature under 3 atm in a 50-mL glass medium pressure gas reactor.[24] After 5 h, the solvent was removed in vacuo. The residual oil was dissolved in 10 mL of pentane, treated with carbon black, filtered, and then concentrated to about half its volume. On cooling to −15 °C for 2 h, 170 mg (80%) of pale-yellow needles of the acyl complex **13a** was obtained: mp 65-66 °C; IR ($CHCl_3$) 1650 cm^{-1} (RCOPd). Anal. Calcd for $C_{20}H_{37}ClOP_2Pd$: C, 48.30; H, 7.44. Found: C, 48.77; H, 7.55.

***trans*-Bromo(phenylacetyl)bis(triethylphosphine)palladium(II) (13b).** *trans*-Bromo(benzyl)bis(triethylphosphine)palladium(II) (**7b**, 571 mg, 1.11 mmol) in 20 mL of pentane was carbonylated under the same conditions to give, after crystallization from pentane, 350 mg (58%) of yellow needles of product: mp 73-74 °C; IR ($CHCl_3$) 1665 cm^{-1} (RCOPd). Anal. Calcd for $C_{20}H_{37}BrOP_2Pd$: C, 44.34; H, 6.88; Br, 14.75. Found: C, 44.47; H, 6.64; Br, 15.32.

(*R*)-(−)-Benzyl-α-*d* Chloride (1a). A mixture of 2.71 g (27.8 mmol) of (*S*)-(+)-benzyl-α-*d* alcohol (from enzymatic reduction[25] of benzaldehyde-1-*d*[30] containing 1.00 ± 0.05 deuterium per molecule, $[\alpha]^{25}{}_D$ +1.32 ± 0.02° (neat, l = 0.1)), 83.5 ± 1.9% ee, and 4.13 mL of dry pyridine in 5 mL of dry methylene chloride was added dropwise to a stirred solution of 2.40 mL (4.024 g, 26.2 mmol) of $POCl_3$ in 5 mL of methylene chloride with the temperature being kept at −10 to −15 °C. A white precipitate appeared during the addition. After 1 h at this temperature the mixture was kept for 2 h at 0 °C, and then poured on ice-water. The organic layer was extracted with methylene chloride, washed with 10% aqueous H_2SO_4, saturated aqueous $NaHCO_3$, and water, and dried over $MgSO_4$. Concentration of the solvent through a short-path distillation column followed by distillation at 3.0 mmHg gave 2.19 g (69%) of a colorless oil: bp 43.5-45 °C; $[\alpha]^{25}{}_D$ −1.28 ± 0.02° (neat, l = 0.1); 83.5 ± 1.9% ee.

Oxidative Addition of Optically Active Benzyl-α-*d* Chloride (1a) to Tris(triethylphosphine)palladium(0) (6). To a solution of 2.55 g (5.53 mmol) of tris(triethylphosphine)palladium(0) in 20 mL of pentane cooled to 0 °C was added 1.635 g (12.8 mmol) of (*R*)-(−)-benzyl-α-*d* chloride, $[\alpha]^{28}{}_D$ −1.342 ± 0.002° (neat, l = 1) in 10 mL of pentane. The reaction mixture was stirred for 1 h. The chiral benzyl-α-*d*-triethylphosphonium chloride (**15**, 110 mg) was filtered, washed with pentane, and dried in vacuo. For rotations, see Table II. The filtrate was concentrated and cooled to crystallize the pale yellow complex which was isolated by filtration and then washed quickly with cold pentane to afford 2.43 g (94%) of the optically active chloro(α-deuteriobenzyl)bis(triethylphosphine)palladium(II) (**14**): mp 77-78 °C; ^1H NMR ($CDCl_3$) δ 7.5-6.9 (m, 5 H, Ph), 2.88 (t, 1 H, J = 7 Hz, $-CHD-$), 2.1-1.5 (m, 12 H, PCH_2-), 1.5-0.75 (m, 18 H, CH_3-). Rotations are given in Table II. The ORD spectrum (Figure 1) was measured at 26 °C, c 0.125 g/mL (CH_2Cl_2, l = 0.1).

The combined filtrates were concentrated to give a pale yellow oil (837 mg) consisting (NMR) of a 10:3 ratio of PhCHDCl to $PhCHDPd\text{-}(PEt_3)_2Cl$. The mixture was passed through a neutral alumina column. Elution with petroleum ether (bp 40-60 °C) gave 424 mg of colorless oil which was further purified by flash distillation at 40 °C (2 mmHg) to give 278 mg of (*R*)-(−)-benzyl-α-*d* chloride, $[\alpha]^{29}{}_D$ −0.965 ± 0.007°, $[\alpha]_{578}$ −0.997 ± 0.007°, $[\alpha]_{546}$ −1.161 ± 0.007° (neat, l = 1), 63 ± 4.6% ee.

Carbonylation of Chloro(α-deuteriobenzyl)bis(triethylphosphine)palladium(II) (14). A solution of 2.43 g (5.18 mmol) of chloro(α-deuteriobenzyl)bis(triethylphosphine)palladium(II) in 10 mL of anhydrous benzene was carbonylated as described before. The usual workup afforded 2.38 g (94%) of chloro(α-deuteriophenylacetyl)-

bis(triethylphosphine)palladium(II) (**16**): mp 65–66 °C; ^{1}H NMR ($CDCl_3$) δ 7.14 (s, 5 H, Ph), 3.89 (bs, 1 H, -CHD-), 2.0–1.4 (m, 12 H, PCH_2-), 1.4–0.75 (m, 18 H, CH_3-). Rotations are given in Table II. The ORD spectrum (Figure 1) was measured at 26 °C, c 0.057 g/mL (CH_2Cl_2, l = 0.1).

Chlorine Cleavage of Optically Active Chloro(α-deuteriophenylacetyl)bis(triethylphosphine)palladium(II) (16). Formation of (*S*)-(+)-Methyl α-Deuteriophenylacetate (17). The acyl complex **16** (2.38 g, 4.8 mmol) was dissolved in 18 mL of methylene chloride and the solution was cooled to −78 °C. A 9.7-mL solution of 0.501 M chlorine (4.86 mmol) in carbon tetrachloride was added slowly and the mixture was stirred at −78 °C for 15 min. A dark green solution was obtained which turned to yellow upon warming to 25 °C. The solution was kept at room temperature for an additional 45 min and then 8 mL of methanol was added. After 15 min small amounts of moist $NaHCO_3$ were added with vigorous stirring until the solution was weakly basic. The water layer was separated and the organic phase was dried over $MgSO_4$. Concentration in vacuo gave a mixture of yellow crystals and an oil which was extracted thoroughly with pentane. The pentane extracts were concentrated and the residue was distilled in a Kugelrohr to give 484.6 mg (67.2%) of (*S*)-(+)-methyl α-deuteriophenylacetate (**17**): ^{1}H NMR ($CDCl_3$) δ 7.25 (s, 5 H, Ph), 3.65 (s, 3 H, OCH_3), and 3.58 (t, 1 H, -CHD-, J = 2.2 Hz). Rotations taken of a solution of **17** diluted to 1 mL with methyl phenylacetate are given in Table II.

Oxidative Addition of Optically Active Benzyl-α-*d* Bromide (1b) to Tris(triethylphosphine)palladium(0) (6). Formation of (*S*)-(+)-Methyl α-Deuteriophenylacetate (17). To a solution of 2.77 g (6.02 mmol) of tris(triethylphosphine)palladium(0) in 20 mL of pentane cooled to 0 °C under argon in a 50-mL glass medium-pressure gas reactor[28] was added 2.064 g of (*R*)-(−)-benzyl-α-*d* bromide,[18] $[\alpha]^{28}{}_D$ −0.621 ± 0.002° (neat, l = 1) in 10 mL of pentane. Yellow crystals separated immediately. After 10 min the reactor was pressurized to 3 atm of CO, and stirring was continued for 7 h. The crude dibromobis(triethylphosphine)palladium(II) (1.263 g, 83%) was collected and washed thoroughly with pentane. The filtrate was concentrated and refiltered to afford 320 mg of white crystals of benzyl-α-*d*-triethylphosphonium bromide (**21**). The compound exhibited negligible rotation. Concentration of the filtrate gave an orange oil which was chromatographed on neutral alumina, activity grade III. Elution with petroleum ether (bp 40–60 °C)gave 662 mg of colorless oil which was further purified by distillation in a Kugelrohr at 80 °C (0.5 mmHg). There was obtained 530 mg (95.6%) of 1,2-dideuterio-1,2-diphenylethane (**20**) optically inactive, mp 50–52 °C. Elution with petroleum ether (bp 40–60 °C)–methylene chloride (1:3) gave 639 mg of (*S*)-(−)-bromo(α-deuteriophenylacetyl)bis(triethylphosphine)palladium(II) (**23**) as a yellow oil, homogeneous by TLC: $[\alpha]^{28}{}_D$ +0.39 ± 0.01° (CH_2Cl_2, l = 1); ^{1}H NMR ($CDCl_3$) δ 7.24 (s, 5 H, Ph), 3.91 (bs, 1 H, CHD-), 2.25–1.45 (m, 12 H, PCH_2), 1.45–0.8 (m, 18 H, CH_3-). Further elution with methylene chloride gave 354 mg of bromo(α-deuteriobenzyl)bis(triethylphosphine)palladium(II) (**22**) as an oil which solidified on standing: ^{1}H NMR ($CDCl_3$) δ 7.7–6.8 (m, 5 H, Ph), 2.70 (t, 1 H, J = 7 Hz, -CHD-), 2.3–1.5 (m, 12 H, PCH_2-), 1.5–0.7 (m, 18 H, CH_3-). The complex was carbonylated directly under the usual conditions to afford 398 mg of the corresponding chiral α-deuteriophenylacetyl complex, $[\alpha]^{28}{}_D$ +0.44 ± 0.01° (CH_2Cl_2, l = 1). The combined acyl complexes, 993 mg (1.83 mmol, 60.7%), were dissolved in 20 mL of methylene chloride and the solution was cooled to −78 °C before the addition of 3.8 mL of a 0.501 M solution of chlorine (1.9 mmol) in carbon tetrachloride. Usual workup followed by distillation in a Kugelrohr at 120 °C (4 mmHg) gave 182 mg (66%) of colorless (*S*)-(+)-methyl α-deuteriophenylacetate (**17**). Rotations taken on a solution of **17** in 1 mL of methyl phenylacetate are given in Table III-1.

Oxidative Addition of Optically Active Benzyl-α-*d* Bromide (1b) to Tris(triethylphosphine)palladium(0) (6) in the Presence of *m*-Dinitrobenzene. Formation of (*S*)-(+)-Methyl α-Deuteriophenylacetate (17). To a solution of 1.6 g (3.48 mmol) of tris(triethylphosphine)palladium(0) in 5 mL of pentane under argon in a 50-mL glass medium-pressure gas reactor[28] was added a solution of 84 mg (0.5 mmol) of *m*-dinitrobenzene (recrystallized from cyclohexane, mp 89–91 °C) in 20 mL of pentane–benzene (19:1). A dark blue color developed immediately. The mixture was cooled to 0 °C and with vigorous stirring, 1.534 g (8.92 mmol) of (*R*)-(−)-benzyl-α-*d* bromide, $[\alpha]^{28}{}_D$ −1.067 ± 0.001°, in 5 mL of pentane was added. The dark blue color was discharged immediately and a yellow solution was obtained. After 5 min the reaction mixture was pressurized to 3 atm of CO and stirring was continued overnight. The precipitated dibromobis(triethylphosphine)palladium(II) was filtered and washed thoroughly with pentane to give 707 mg (82%) of the crude product. The filtrate was concentrated to give a yellow oil which contained (TLC and NMR analysis) approximately 30% of bromo(α-deuteriobenzyl)bis(triethylphosphine)palladium(II). This oil was carbonylated further in 10 mL of benzene for 3 h and TLC analysis indicated complete conversion to the acyl complex. The solvent was concentrated in vacuo and the residue was chromatographed on neutral alumina by the usual method to give 534 mg of a colorless oil. The oil was dissolved in 10 mL of anhydrous ether and 3 mL of triethylamine was added. After standing for 1 h the precipitated α-deuteriobenzyltriethylammonium bromide was filtered and washed quickly with ether. The combined filtrates were concentrated and the residue was distilled in a Kugelrohr apparatus to give 266 mg (83%) of 1,2-dideuterio-1,2-diphenylethane (**20**), mp 50–52 °C. Further elution with methylene chloride gave 432 mg (0.797 mmol, 46%) of (*S*)-(+)-bromo(α-deuteriophenylacetyl)-bis(triethylphosphine)palladium(II) (**23**) as an orange, viscous oil, homogeneous by TLC. The complex was dissolved in 10 mL of methylene chloride and the solution was cooled to −78 °C before the addition of 2.44 mL of a 0.327 M solution of chlorine (0.798 mmol) in carbon tetrachloride. Usual workup followed by distillation in a Kugelrohr apparatus at 80 °C (1.5 mmHg) gave 93.3 mg (77.5%) of (*S*)-(+)-methyl α-deuteriophenylacetate (**17**). Rotations taken of a solution of **17** diluted to 1 mL with methylphenylacetate are given in Table III-II.

Reaction of 3-Methylbenzyl Bromide(24) with Tris(triethylphosphine)palladium(0) (6) in the Presence of Bromo(benzyl)bis(triethylphosphine)palladium(II) (7b). To a solution of 363 mg (0.787 mmol) of tris(triethylphosphine)palladium(0) in 10 mL of pentane was added a solution of 380 mg (0.741 mmol) of bromo(benzyl)bis(triethylphosphine)palladium(II) (**7b**) in 10 mL of pentane–benzene (9:1). The stirred mixture was treated with 0.212 mL (1.574 mmol) of 3-methylbenzyl bromide for 15 h. The resulting yellow solution was filtered to remove the white crystals of 3-methylbenzyl(triethylphosphonium) bromide, the filtrate was concentrated in vacuo, and the residue was chromatographed on neutral alumina (activity grade III). Elution with petroleum ether gave a colorless oil which was dissolved in ~5 mL of ether and treated with triethylamine. After standing for 15 h at room temperature a few colorless crystals of 3-methylbenzyltriethylammonium bromide separated. The ether was decanted and concentrated in vacuo, and the residue was distilled in a Kugelrohr apparatus at 100 °C (1 mmHg) to afford 78 mg (94%) of 1,2-di(*m*-tolyl)ethane as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 6.9 (m, 4 H, aromatic), 3.8 (s, 4 H, $-CH_2CH_2-$), 2.29 (s, 6 H, CH_3-); mass spectrum (70 eV) m/e 210 (M^+) (no peak at m/e 196). Anal. Calcd for $C_{16}H_{18}$: C, 91.43; H, 8.57. Found: C, 91.90; H, 8.41.

Gradual increase of methylene chloride concentration eluted a mixture of $Br_2Pd(PEt_3)_2$ and benzyl palladium complexes (641 mg). The mixture was dissolved in 10 mL of benzene–petroleum-ether (1:1) and carbonylated at 2 atm for 5 h. The solvent was evaporated in vacuo and the residue was dissolved in a suspension of 200 mg of CaO of 20 mL of methanol. After stirring under 1 atm of CO for 24 h, the solution was filtered and the yellow filtrate was exposed to air. Rapid precipitation of palladium black was noticed. Carbon black was added and the mixture was filtered. The filtrate was concentrated in vacuo and the residue was distilled in a Kugelrohr apparatus at 100 °C (8 mmHg). The product, 30 mg of a colorless oil, was shown to be a mixture of 80% methyl phenylacetate and 17% *m*-tolyl acetate by GLC analysis (160 °C, 10 ft × 0.375 in., 20% Carbowax 20M on Chromosorb W 60/80) confirmed by comparison of retention times with authentic samples.

Attempted Racemization of (*S*)-(−)-Chloro(α-deuteriobenzyl)bis(triethylphosphine)palladium(II) (14) by Tris(triethylphosphine)palladium(0) (6). To a solution of 400 mg (0.853 mmol) of *S*-(−)-chloro(α-deuteriobenzyl)bis(triethylphosphine)palladium(II) in 3 mL of benzene ($[\alpha]^{28}_{578}$ −0.618 ± 0.005°) was added 60 mg (0.13 mmol) of tris(triethylphosphine)palladium(0). The orange solution was kept at room temperature for 3 h and then carbonylated at 3 atm overnight. The orange-brown solution was passed through a neutral alumina column. Elution with petroleum ether gave a small amount of orange-brown oil which decomposed immediately on exposure to air. Gradual increase of the methylene chloride concentration eluted a very pale yellow oil (183 mg, 43%) of (*S*)-(+)-chloro(α-deuteriophenylacetyl)bis(triethylphosphine)palladium(II), which readily solidified on standing, and was homogeneous by TLC and NMR analysis. Specific rotations measured at 29 °C in a 10-cm cell of (*S*)-(−)-**14** at a concentration of 0.4 g/mL (C_6H_6) were −0.55 (589 nm), −0.62 (578 nm), and −0.80 (546 nm), ±0.04°, and of (*S*)-(+)-**16** at concentrations of 0.183 g/mL ($CHCl_3$) were +3.84 (589 nm), +4.02 (578 nm), and +4.70 (546 nm), ±0.01°.

Metathetical Replacements. 1. (*S*)-(−)-Bromo(α-deuteriobenzyl)bis(triethylphosphine)palladium(II) (22). Conversion to (*S*)-(+)-Bromo(α-deuteriophenylacetyl)bis(triethylphosphine)palladium(II) (23). To a solution of LiBr (430 mg, 4.95 mmol) in 10 mL of degassed anhydrous methanol was added with stirring 468 mg (0.988 mmol) of (*S*)-(−)-chloro(α-deuteriobenzyl)bis(triethylphosphine)palladium(II). After a few minutes yellow crystals separated. Stirring was continued at room temperature for 3 h, and then about half of the solvent was evaporated under reduced pressure. The residue was diluted with 20 mL of 10% aqueous LiBr followed by extraction with pentane (3 × 25 mL) until the aqueous layer became colorless. The argon-degassed extract was dried over $MgSO_4$ and evaporated to give 494 mg (96%) of the optically active bromo derivative **22**, recrystallized from pentane, mp 89–90 °C. Rotations are given in Table IV. The product of this reaction was carbonylated under 3 atm in 20 mL of pentane for 5 h to give 533 mg (98%) of (*S*)-(+)-bromo-(α-deuteriophenylacetyl)bis(triethylphosphine)palladium(II), mp 73–74 °C (from pentane). Rotations are given in Table IV.

2. (*S*)-(+)-Chloro(α-deuteriophenylacetyl)bis(triethylphosphine)palladium(II) (16) from (*S*)-(+)-Bromo(α-deuteriophenylacetyl)bis(triethylphosphine)palladium(II) (23). To a carefully degassed solution of LiCl (629 mg, 14.8 mmol) in 5 mL of methanol was added a solution of (*S*)-(+)-bromo(α-deuteriophenylacetyl)bis(triethylphosphine)palladium(II) (538 mg, 0.991 mmol, $[\alpha]^{28}{}_D$ +3.00 ± 0.04°, CH_2Cl_2, $l = 1$) and the reaction mixture was stirred under 3 atm of carbon monoxide for 2.5 h. The solvent was concentrated to about half the original volume and the residue was taken up with pentane (3 × 25 mL), washed with 10% aqueous LiCl, and dried over $MgSO_4$. Concentration of the pentane extract under reduced pressure gave a dark oil which solidified on standing. It consisted (TLC) of a mixture of the desired chlorophenylacetyl complex **16** and a smaller proportion of the starting bromophenylacetyl complex **23.** The crude reaction product was dissolved in pentane, carbon black was added, and the light yellow filtrate was cooled to −10 °C. The resulting yellow crystals (210 mg) were recrystallized from pentane to afford 152 mg (30.9%) of **16** contaminated (TLC analysis) by traces of the bromo complex **23**, mp 66–67 °C. Rotations are given in Table IV.

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