gives a 5:1 preference for the synthesis of L-phenylalanine over the D enantiomer, not the 3:1 reported earlier,[3] but **5** shows *no* detectable enantiomeric preference. However, in the conversion of indolepyruvic acid to tryptophan, **1** shows a 2:1 preference for the L enantiomer while **5** shows an 1.8:1 preference for the D product. This reversal of stereochemical selectivity can be rationalized if the cyclodextrin is thought of formally as a planar (i.e., clockwise or counterclockwise), not helical, chiral element.

Our results show that both the primary- and the secondary-side pyridoxamine cyclodextrins show cooperative catalysis of transaminations, but with differences in rate effects and chiral inductions. Furthermore, the axial opening of the epoxide **3** at C-3 means that other derivatives of cyclodextrin should be available with such axial groups pointing into the cavity or with an altered glucose conformation. Such derivatives could have very different properties from those of functionalized cyclodextrins available heretofore.[14]

Registry No. 2, 84216-71-7; **3**, 84648-78-2; **4**, 84648-79-3; **5**, 84648-80-6; indolepyruvic acid, 392-12-1; tryptophan, 73-22-3; pyruvic acid, 127-17-3; alanine, 56-41-7; phenylpyruvic acid, 156-06-9; phenylalanine, 63-91-2.

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(14) Support of this work by the NIH is gratefully acknowledged, as is the assistance of Dr. Christopher Turner with the NMR studies. The earliest studies on a β-cyclodextrin secondary tosylate and epoxide were performed here a few years ago by Dr. K. Nakasuji and Dr. M. F. Czarniecki, who protected the primary hydroxyls by *tert*-butyldimethylsilylation before tosylation. Their work will be described in the full publication.

Stereochemistry at the Chiral Ruthenium Atom in the Reaction of Diastereomeric $(\eta^5\text{-}C_5H_5)RuCl[(R)\text{-}Ph_2PCH(CH_3)CH_2PPh_2]$ with $SnCl_2$

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For a long time it has been known that the trichlorostannate ligand is able to modify or even to initiate catalytic activity in transition-metal complexes.[1,2] Recently there has been much interest devoted to the role of this ligand in organometallic reactions and in homogeneous catalysis.[3-10] Normally the $SnCl_3$ ligand is formed according to reaction 1, i.e., from transition-metal

$$M\text{-}Cl + SnCl_2 \rightleftharpoons M\text{-}SnCl_3 \quad (1)$$

chloro complexes and $SnCl_2$[2] in a formal insertion reaction in an M-Cl bond and in a formal oxidation addition on Sn.

The stereochemical course of the reaction at the level of the transition metal has not yet been elucidated. It was recently proposed[11] (but not fully demonstrated) that reaction 1 can be highly stereospecific[12] when M-Cl is $(\eta^6\text{-}C_6H_6)RuCl(CH_3)[Ph_2PNHCH(CH_3)Ph]$ and when a molar ratio $SnCl_2$/M-Cl of 1.1 is used. However, it was not possible to determine whether the configuration at the ruthenium atom is retained or inverts during the reaction.[13] This also is of particular interest in view of the possible role of chiral complexes in which the metal is an asymmetry center in homogeneous asymmetric catalysis.[14-16] Indeed chiral diphosphine–platinum chloride–tin chloride catalytic systems have been used in asymmetric hydroformylation and hydrogenation.[17-19]

Recently we reported that in the displacement reaction of PPh_3 from pseudotetrahedral $(\eta^5\text{-}C_5H_5)RuCl(PPh_3)_2$ by (*R*)-1,2-propanediylbis(diphenylphosphine) ((*R*)-prophos)[20] two diastereomers form (**1** and **1′**) in nearly a 1:1 ratio, which differ in the configuration at the ruthenium atom.[21] In the meantime the two diastereomers have been separated;[22] the structure of diastereomer **1**, which has the higher frequency for the cyclopentadienyl protons in the ^1H NMR spectrum (δ 4.43 vs. 4.32 found for **1′**), has been determined by X-ray analysis[23] and has shown *S* configuration at the ruthenium atom, if we assume the priority order $\eta^5\text{-}C_5H_5 > Cl > PCH > PCH_2$[24] (Figure 1). We report here that the reaction of both diastereomers **1** and **1′** with $SnCl_2$ to give **2** and **2′** is highly stereospecific and takes place with retention of the configuration at the ruthenium atom (Scheme I).

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(23) The $[(R)_C,(S)_{Ru}]\text{-}(\eta^5\text{-}C_5H_5)RuCl(prophos)$ diastereomer crystallizes in the monoclinic space group $P2_1$ with $a = 9.688$ (3) Å, $b = 15.037$ (4) Å, $c = 10.556$ (2) Å, $\beta = 113.54$ (2)°, $Z = 2$, and $U = 1409.8$ Å^3. The structure was solved by conventional Patterson and Fourier methods on the basis of 2000 significant counter data with $I > 3\sigma(I)$ and refined by full-matrix least squares up to current R and R_w values of 0.042 and 0.045.

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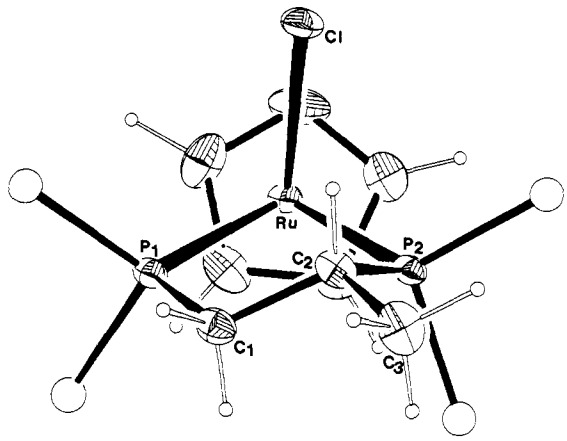
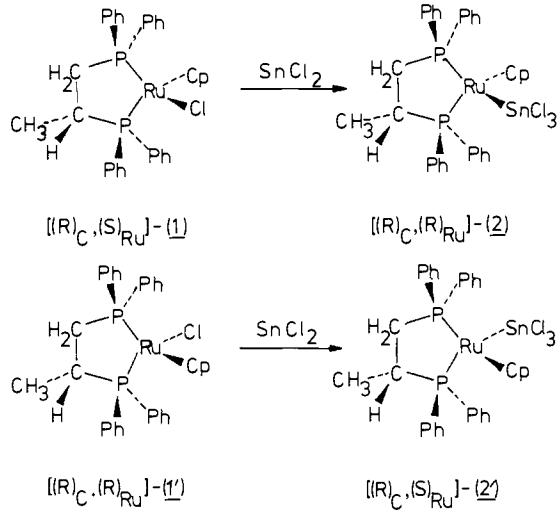


Figure 1. View of the $[(R)_C,(S)_{Ru}]$-$(\eta^5$-$C_5H_5)$RuCl(prophos) diastereomer in its absolute configuration as determined from X-ray analysis. The phenyl rings are omitted for clarity and are represented by their respective first carbon atoms. Relevant bond parameters are as follows: Ru-Cl, 2.444 (2), Ru-P, 2.277 (mean); Ru-Cp, 2.19 (mean) Å.

Scheme I



1 and **1'** have each been reacted at room temperature with a slight excess of $SnCl_2$ in CH_2Cl_2. The reaction takes a few hours for completion; during this time the reaction mixture turns from orange to yellow. After the unreacted $SnCl_2$ was filtered off, **2** and **2'** were precipitated with *n*-hexane for the determination of the diastereomeric composition. Yields of the crude products were about 90%. The pure **2** or **2'** can be recrystallized from CH_2Cl_2/*n*-hexane[25] to give yellow plates or needles, respectively; the diastereomers appear to be configurationally stable both in chlorinated hydrocarbons solution and in the solid state.

The diastereomeric nature of **2** and **2'** is well established by multinuclear NMR spectroscopy (reported in Table I) and by the results of the elemental analysis,[25] which are in accord with the given formulas. Table I also reports the diastereomeric composition of reaction products and starting material, which was determined by integrating the two cyclopentadienyl signals to the ^1H NMR spectrum. Examination of these data shows that reaction 1 is completely stereospecific within the limits of NMR detection for diastereomer **1**, whereas about 10% of **2** is formed by starting with pure **1'**.

Table I. Results of the Reaction between 1 and 1' with $SnCl_2$ To Give 2 and 2', Respectively: NMR Parameters of Reagents and Products[a]

	1 ⟶ 2		1' ⟶ 2'	
diastereomeric composition	>98	>98	>98	≃90
δ η^5-C_5H_5[b]	4.43	4.78	4.32	4.66
δ $^{31}P^1$[c]	86.4	81.7	80.9	81.8
δ $^{31}P^2$[c]	61.3	59.5	74.1	64.7
$J_{P^1-P^2}$, Hz	30.3	30.6	36.7	29.0
δ ^{119}Sn[d]		−30.8		−37.9
$J^{31}P-^{119}Sn$, Hz		409		372

[a] The spectra were measured on a Bruker WM 250. [b] $CDCl_3$ was as the solvent; Me_4Si was the internal standard. [c] CH_2Cl_2/C_6D_6 (4:1) was the solvent; H_3PO_4 85% was the external standard. [d] CH_2Cl_2/C_6D_6 (4:1) was the solvent; $(CH_3)_4Sn$ was the external standard.

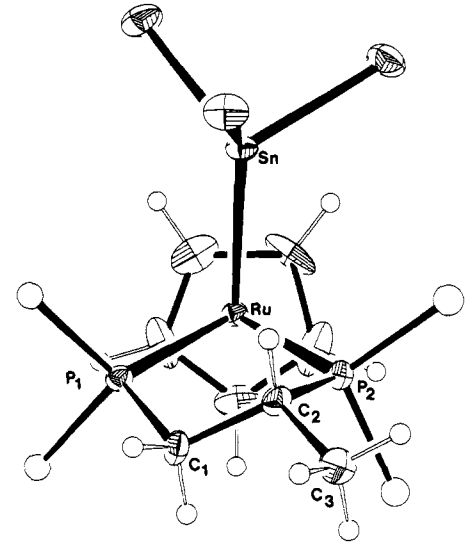


Figure 2. View of the $[(R)_C,(R)_{Ru}]$-$(\eta^5$-$C_5H_5)$Ru$(SnCl_3)$(prophos) diastereomer in its absolute configuration as determined from X-ray analysis. Phenyl rings are omitted. Relevant bond parameters are as follows: Ru-Sn, 2.551 (1); Ru-P, 2.888 (mean); Ru-Cp, 2.21 (mean); Sn-Cl 2.385 (mean) Å.

The stereochemistry of the reaction was completely identified through the crystal structure determination[26] of **2** (Figure 2). Comparison of the crystal structure of **2** with that of the parent chloro compound (**1**, Figure 1) shows that the chloro ligand has been substituted by the trichlorostannato one with retention of the geometry at the ruthenium atom. According to the proposed nomenclature the configuration at the ruthenium atom in **2** is *R*, whereas in the parent compound **1** it is *S*. The observed stereospecific transformation where the configuration is retained (Scheme I) could result from different intermediates and/or transition states. In principle, $SnCl_2$ could attack at the ruthenium atom or at the chlorine atom or at both to give a tricentered transition state. At the present, however, we cannot distinguish among these possibilities, although dissociation of a phosphorus atom for the formation of the trichlorostannato complex can be excluded.

Registry No. 1, 79732-92-6; **1'**, 79681-92-8; **2**·CH_2Cl_2, 84537-81-5; **2'**, 84621-20-5; $SnCl_2$, 7772-99-8.

Supplementary Material Available: Tables of positional and thermal parameters for compounds **1** and **2** (2 pages). Ordering information is given on any current masthead page.

(25) Diastereomer **2**: Anal. Calcd for CpRu$(SnCl_3)$(prophos)·CH_2Cl_2 ($C_{33}H_{33}P_2RuSnCl_5$): C, 44.57; H, 3.74. Found: C, 45.04; H, 3.76. ^1H NMR ($CDCl_3$) δ 7.84–7.34 (20 H, m, C_6H_5), 4.78 (5 H, s, C_5H_5), 3.74–2.82 (2 H, m, CH_2), 2.02–1.86 (1 H, m, CH), 1.19 (3 H, dd, CH_3, J_{P-H} = 11.9 Hz, J_{H-H} = 6.4 Hz). Diastereomer **2'**: Anal. Calcd for CpRu$(SnCl_3)$(prophos)·CH_2Cl_2: C, 44.57; H, 3.74; Cl, 19.93. Found: C, 44.86; H, 3.76; Cl, 19.92. ^1H NMR ($CDCl_3$) δ 7.72–7.16 (20 H, m, C_6H_5), 4.66 (5 H, s, C_5H_5), 2.94–2.65 (3 H, m, $CHCH_2$), 1.15 (3 H, dd, CH_3, J_{P-H} = 11.9 Hz, J_{H-H} = 6.4 Hz).

(26) The $[(R)_C,(R)_{Ru}]$-$(\eta^5$-$C_5H_5)$Ru$(SnCl_3)$(prophos)·CH_2Cl_2 diastereomer crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 19) with a = 9.436 (2) Å, b = 17.263 (4) Å, c = 21.692 (4) Å, Z = 4, and U = 3553.5 Å^3. The structure was solved by Patterson and Fourier methods based on 1952 significant reflections with $I > 3\sigma(I)$. The absolute configuration was determined by taking into account the anomalous scattering effects. The results were in agreement with the previously known absolute configuration of the prophos ligand.[20] The current R and R_w values are 0.033 and 0.034, respectively.