73635-59-3; **38**, 73635-89-9; **39**, 73635-90-2; **40**, 73635-91-3; **41**, 73635-92-4; **42**, 73635-93-5; **43**, 73635-94-6; **54**, 73635-95-7; **55**, 27745-90-0; **56**, 73635-96-8; cyclooctatetraene, 629-20-9; 1-diamantanecarboxylic acid, 30545-18-7; 1-bromodiamantane, 30545-17-6; 1,3-cyclohexadiene, 592-57-4; methylcyclopentadiene, 26519-91-5; bicyclo[3.2.1]octane, 6221-55-2.

Supplementary Material Available: Bond lengths (Table IV); valence angles (Table V); dihedral angles (Table VI) of **13**, **14**, and **8**, including corresponding values calculated by the MM2 method for **6**, **7**, and **8**; standard deviations of the calculated structural parameters of **6**, **7**, and **8** from the observed values (Table VII); listings of final atomic coordinates of **13**, **14**, and **8** (Table VIII); thermal parameters (Tables IX and X) (17 pages). Ordering information is given on any current masterhead page.

Novel Copper Complexes of Chiral Diphosphines: Preparation, Structure, and Use To Form Rhodium Complex Catalysts for Chiral Hydrogenations

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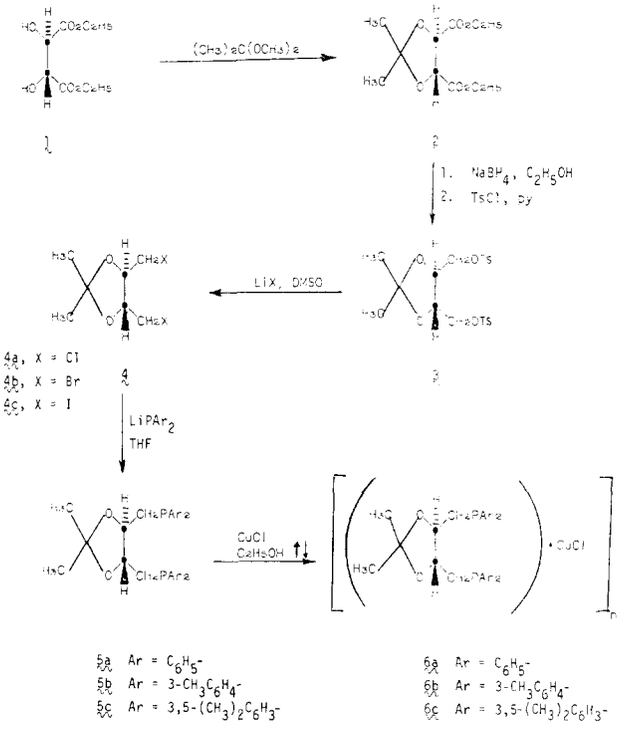
Treatment of chiral diphosphines **5a–c** and **13** ("DIOP", aryl derivatives and related substances) with CuCl in boiling ethanol gave complexes having the composition $[Cu(diphosphine)(Cl)]_n$, **6a–c** and **11**. Crystallizations of **6a–c** from crude 70–80% pure **5a–c** and decomposition of the complexes by ammonia gave the pure diphosphines. Ligand exchange between **6a–c** and $[Rh(diolefin)(Cl)]_2$ in methanol at 23 °C was rapid and complete. Treatment of the resulting solutions with H_2 gave active catalysts for asymmetric hydrogenations.

Homogeneous asymmetric hydrogenations catalyzed by rhodium complexes of chiral chelating diphosphines provide attractive syntheses of many enantiomeric substances.[2] A frequent problem, however, is obtention of the catalyst, especially preparation, isolation, and purification of the chiral phosphine ligand. We describe here a new method of preparing catalysts containing phosphines **5a–c** (DIOP derivatives)[3,4] bound to rhodium, which minimizes the need to isolate and purify the free phosphines. The method is based on the discovery that impure **5a–c**, such as are obtained as crude products of typical synthetic procedures, react with cuprous halides to form complexes which may be purified readily and which will transfer their diphosphine ligand quantitatively to rhodium under mild conditions.

The objective of our work was a practical synthesis of "DIOP" derivatives **5a–c**. The synthesis of **5a–c** outlined in Scheme I is essentially that first described by Kagan et al.[3,5] Synthesis of **3** was improved by replacing $LiAlH_4$[6] with $NaBH_4$ to reduce acetonide diester **2** to the corresponding diol (not shown). The diol was converted directly to **3** in 73% overall yield from **2**. The $NaBH_4$ reduction of the dimethyl ester analogue of **2** was unsatisfactory, probably because the methanol released catalyzes the decomposition of $NaBH_4$.[7] It was possible to condense **3** directly with alkali metal phosphides, but the several byproducts formed in these reactions made isolation of the noncrystalline **5b**[8] and **5c**[4] difficult. Cleaner reaction mixtures were obtained in condensations of lithium diaryl phosphides with dichloride **4a**,[3] which was easily obtained in high yield from **3**. Crude **5b** and **5c** obtained from **4a** could be purified by chromatography. A more attractive procedure, however, was to treat the crude diphosphine

Scheme I



with cuprous chloride in hot ethanol solutions. Copper(I) complexes of the formula **6** precipitated from such solutions on cooling. Recrystallizations of **6** and decompositions with NH_3 gave the pure diphosphines **5** without chromatographic separations.[9]

It was also found that combination of **6** with $[Rh(diolefin)(Cl)]_2$[10] in methanol resulted in complete transfer of the diphosphine ligand from copper to rhodium. Thus,

(1) Present address: Catalytica Associates, Santa Clara, CA 95051.
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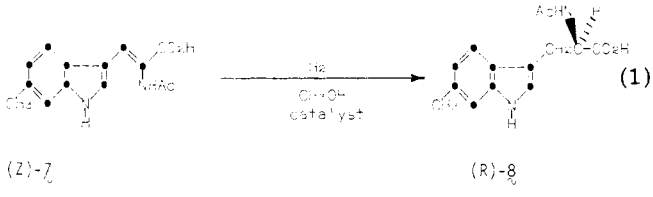
Table I. Chiral Hydrogenations of 7 Using Catalysts Derived from [Rh(1,5-cyclooctadiene)Cl]$_2$ and 5 or 6[a]

catalyst from	substrate/catalyst[b]	rate[c]	product 8, % ee[d]
5a + Rh	1350	1350	73 *R*
6a + Rh	5720	*e*	75 *R*
5b + Rh	5850	5850	82 *R*
6b + Rh	5900	3930	84 *R*
5c + Rh	9470	6050	86 *R*
6c + Rh	6900	10300	87 *R*

[a] All experiments were run in deoxygenated CH_3OH (ca. 5 mL/g of 7) at room temperature and 40 psi initial hydrogen pressure. [b] Mol of substrate/mol of Rh. [c] Turnovers/h, i.e., mol of 7 converted/mol of Rh/h, observed at ca. 50% conversion. [d] Enantiomeric excess determined as described in ref 4. [e] Not observed, but reaction complete after 6-21 h.

the ^{1}H-decoupled ^{31}P NMR spectrum of **6b** in C_6D_6 consisted of a very broad singlet at δ -18.0. However, when equivalent amounts of **6b** and [Rh(norbornadiene)Cl]$_2$ were stirred in CD_3OH containing a few percent CH_2Cl_2 for 30 min at 23 °C and then filtered under argon, the spectrum of the orange red filtrate consisted of a sharp doublet at δ +11.09 ($J_{Rh,P}$ = 143.8 Hz), identical with the spectrum observed for solutions prepared by mixing equal amounts of **5b** and [Rh(norbornadiene)Cl]$_2$.

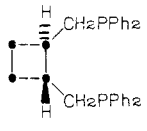
When solutions prepared from **6** and [Rh(diolefin)(Cl)]$_2$ were exposed to hydrogen, active homogeneous hydrogenation catalysts were obtained. The rates and enantioselectivities of the catalysts prepared under these conditions were studied using reaction 1 as a model.[4] The results are given in Table I.



(Z)-7 (R)-8 (1)

Data given in Table I provide a comparison of the performance (rate and enantioselectivity) of catalysts containing **5a–c** produced by combining [Rh(1,5-cyclooctadiene)(Cl)]$_2$ with **5a–c** or with **6a–c**. Catalyst solutions formed from **6a–c** were not filtered so that the Cu product of ligand exchange was present. Rates and enantioselectivity of hydrogenations of **7** effected by the catalysts prepared by the two methods are similar, with no consistent differences. Either catalyst may be used at low catalyst loadings to obtain practically useful excesses of (*R*)-**8**.

The demonstrated utility of **6** led us to prepare several examples with different metals and **5a–c** and **13** as ligands.



13

Properties of the several complexes which we prepared are summarized in Table II. All of these compounds were shown to interact with rhodium(I) precursors to afford active catalysts for chiral hydrogenation which were similar in behavior to catalysts obtained from the free phosphines and rhodium(I). Interestingly, the known complex Ni(**5a**)Cl$_2$[12] forms a less active hydrogenation catalyst with rhodium(I) under similar conditions. Catalysis of (*Z*)-α-(acetylamino)cinnamic acid hydrogenation by the Ni(**5a**)Cl$_2$–Rh(I) derived system was equally enantioselective but approximately five times slower than the same reaction with the Rh(I)–**5a** derived system.[3]

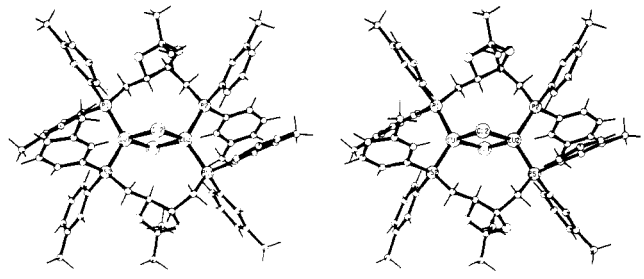


Figure 1. Stereoscopic view of complex **6b**.

The structure of **6b** is shown in Figure 1. Two coordinatively saturated copper(I) centers with approximately tetrahedral geometry are bridged by each of the four ligands. There is no metal–metal bond. The structure somewhat resembles those recently reported for so-called "A-frame" complexes of Rh(I),[13] Pd(I),[14] and Pt(I)[15] but provides the only example of which we are aware of a binuclear complex without metal–metal bonds in which all of the ligands bridge the two metal atoms.[16] The structure of **6b** is different from those of [Ni(**5a**)(Cl)$_2$][12] and [Ir(**5a**)(η^4-1,5-cyclooctadiene)(Cl)],[17] both of which are monomeric complexes in which **5a** is a bidentate ligand.

Complex **6a** was shown by X-ray analysis to have a dimeric structure similar to that of **6b**. Structures of the complexes **9–12** are unknown.

The finding that complexes **6a–c** transfer a diphosphine ligand rapidly and quantitatively to rhodium(I) provides a new and convenient method for generation of rhodium(I) catalysts containing the diphosphines **5a–c**. It is of some interest that the several "closed-shell" metal ions tried all form complexes with **5a–c** which rapidly transfer the diphosphine ligand to rhodium(I), a d^8 system. The d^8 complex [Na(**5a**)Cl$_2$] is, however, a less satisfactory source of the **5a** ligand.

It is possible that ligand-transfer chemistry of the type described here may be useful to generate catalysts for other chiral catalytic processes such as isomerization, hydroformylation, and hydrocarboxylation.

Experimental Section

All syntheses of phosphines and metal complexes of phosphines were carried out under argon, using purified deoxygenated reagents and solvents. All catalytic hydrogenations and enantiomeric excess determinations were carried out as previously described.[4]

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(16) However, a number of examples have been reported of all-bridged binuclear species where metal–metal bonding is either suspected or indicated by X-ray analysis. For examples: (a, Cu–Cu) Nardin, G.; Randaccio, L.; Zangrando, E. *J. Organometal. Chem.* **1974**, *74*, C23–C25. (b, Au–Au) Schmidbaur, H.; Scherm, H. P.; Schubert, U. *Chem. Ber.* **1978**, *111*, 764–69 and references therein. (c, Ni–Ni) Karsch, H. H.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 853–54. (d, Rh–Rh) Lewis, N. S.; Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7461–63. (e, Cr–Cr) Cotton, F. A.; Hanson, B. E.; Rice, G. W. *Angew. Chem.* **1978**, *90*, 1015–16 and references therein.

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Table II. Metal Complexes of Chiral Diphosphines[a]

formula	no.	yield, %	mp	$[\alpha]^{25}_D$[b]	m/e	^{31}P NMR (δ)[c] ligand[a]	^{31}P NMR (δ)[c] complex[e]
[Cu(5a)(Cl)]$_2$[f]	6a	63	211-112°	+36.5°	596	-23.5	-17.5
[(CuCl)$_2$(5a)$_3$]$_n$[g,h]	12	45	116-118°		498	-23.5	*i*
[Cu(5b)(Cl)]$_2$	6b	66	108°	+94.3°	652	-23.6	-18.0
[AgClO$_4$(5b)]$_2$[h]	9	65	231-233°	-30.4°	dec.	-23.6	+4.0[j]
[Cu(5c)(Cl)]$_n$[h,k]	6c	62	129-131°	+42.5°	708	-23.9	-26.1
[Cu(13)Cl]$_n$[h]	11	27	197-199.5°	+67.6°	550	-21.7	-19.7
[Zn(5b)(ClO$_4$)$_2$]$_n$[h,l]	10	69					

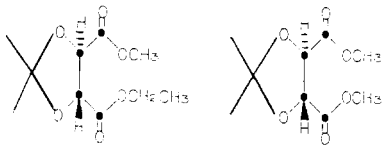
[a] All complexes gave satisfactory elemental analyses for C, H, Cl, P, and Cu unless otherwise noted. Solvent of crystallization was retained in some instances. [b] (*c* 1, $CHCl_3$). [c] Proton noise-decoupled spectra were obtained at 40.5 MHz on a Varian XL-100 spectrometer operating in the Fourier-transform mode. Chemical shifts are relative to 85% H_3PO_4. [d] In $CDCl_3$. Signals are sharp singlets. [e] Spectra of **6a** and **6b** were run in C_6D_6; the others were run in $CDCl_3$. Signals are very broad singlets having widths at half height of 30-80 Hz. [f] Dimeric structure analogous to that of **6b** established by X-ray crystallography. [g] Probably an intermediate in the formation of **6a**. Unstable upon recrystallization. [h] Structure and state of aggregation unknown. [i] At least five signals. [j] d, $J_{P,Ag}$ = 546.7 Hz. [k] Contains 0.67 mol of ethanol. Found: P, 9.44. Calcd: P, 8.36. Analysis for Cu not done. [l] Impure; see Experimental Section.

Tetrahydrofuran was purified by distillation from sodium-benzophenone. Dimethyl sulfoxide was distilled from calcium hydride. Methanol and ethanol were purified by hydrogenation over Raney nickel. Pyridine was distilled from barium oxide. *p*-Toluenesulfonyl chloride was recrystallized from hexane. Tris(3-methylphenyl)phosphine was prepared following Willans[18] and cleaved to bis(3-methylphenyl)phosphine following Aguiar[19] or Grim.[20] (4*R*,5*R*)-*trans*-4,5-Bis((diphenylphosphino)-methyl)-2,2-dimethyl-1,3-dioxalane (**5a**) was prepared following Kagan and Dang.[3] Pure (4*R*,5*R*)-*trans*-4,5-bis((bis(3-methylphenyl)phosphino)methyl)-2,2-dimethyl-1,3-dioxalane (**5b**) was prepared by chromatographic purification of the crude condensation product of sodium bis(3-methylphenyl)phosphide and the ditosylate **3** essentially as described by Dang et al.[8] (1*R*,2*R*)-Bis((diphenylphosphino)methyl)cyclobutane was prepared following Aviron-Violet.[11]

Cuprous chloride was obtained following Keller and Wycoff.[21] Anhydrous silver perchlorate and zinc perchlorate hexahydrate were used as received from Research Organic/Inorganic Chemical Corp.

Proton-noise-decoupled ^{31}P NMR spectra were obtained at 40.5 MHz on a Varian XL-100 spectrometer operating in the Fourier-transform mode. Chemical shifts are in parts per million relative to external 85% H_3PO_4, with decreasing field in the positive direction.

(4*S*,5*S*)-*trans*-4,5-Bis(((4-methylphenyl)sulfonyl)oxy)-2,2-dimethyl-1,3-dioxolane (3). Diethyl ester **2** prepared by the procedure of Carmack and Kelly[6] contains considerable ester interchange products i and ii (they report 21% and 2%, respectively). These materials are undesirable for the sodium borohydride reduction as discussed in the text. Therefore, we shortened the distillation time in the Carmack and Kelly procedure from 10 to 2.5 h and obtained **2** contaminated with only 10% i, ~0% ii and ~5% unreacted diethyl tartrate. This material was used in the procedure described below.



i ii

A solution of 100 g (0.406 mol) of diethyl ester **2** in 200 mL of anhydrous ethanol was added dropwise to a vigorously stirred mixture of 46.4 g (1.22 mol) of sodium borohydride with 700 mL of anhydrous ethanol at such a rate that moderate reflux and gas evolution were maintained. Addition required 70–90 min. When the reaction had subsided somewhat, the mixture was brought to reflux until gas evolution ceased (typically 150–210 min at reflux were required). Progress of the reduction of **2** could be followed by GLC (6 ft × $^1/_8$ in. 10% Apiezon L on Gas-Chrom Q column at 100–250 °C (8 °C/min); retention times: **2**, 11.2 min; diol, 8 min). The reaction mixture was allowed to cool, and was then concentrated to a thick slurry under reduced pressure and cooled in an ice bath. Chloroform (500 mL) was added, followed by 150 mL of water added dropwise with vigorous stirring. The resulting mixture was stirred for 1 h at 23 °C and then filtered. The filter cake was rinsed with chloroform (2 × 100 mL). Filtrate and rinses were combined, dried over 10 g of magnesium sulfate, filtered, and concentrated under reduced pressure to give 64.4 g of crude diol. This could be purified by distillation from potassium carbonate but was more conveniently converted directly to the ditosylate **3**.

Crude diol (64.4 g) was dissolved in 400 mL of pyridine, cooled to -20 °C, and treated with 165 g (0.87 mol) of *p*-toluenesulfonyl chloride. The mixture was stirred at 0 °C for 24 h. The mixture was hydrolyzed at ice-bath temperatures by dropwise addition of 625 mL of water. After 30 min, the mixture was filtered and the colorless filter cake was washed with water (2 × 250 mL) and then dried in air. This material, weighing 190 g, was combined with the product obtained from 0.46 mol of diethyl ester. The combined crude ditosylates (**3**) were crystallized from ca. 1.5 L of ethanol to give 313.3 g (77.3%) of pure **3**: mp 89–91 °C; $[\alpha]^{25}_D$ -11.6° (*c* 1.0, $CHCl_3$) [lit.[22] mp 91–92 °C; $[\alpha]^{24}_D$ -12.4° (*c* 5.0, $CHCl_3$); lit.[6] mp 90.5–92 °C; $[\alpha]^{22}_D$ -12.4° (*c* 8.8, $CHCl_3$); lit.[3] mp 92 °C; $[\alpha]^{24}_D$ -12.1° (*c* 4.4, $CHCl_3$)].

Anal. Calcd for $C_{21}H_{26}O_8S_2$: C, 53.60; H, 5.57; S, 13.63. Found: C, 53.54; H, 5.60; S, 13.54.

(4*R*,5*R*)-*trans*-4,5-Bis(chloromethyl)-2,2-dimethyl-1,3-dioxalane (4a).[3,23] A mixture of 6.36 g (0.15 mol) of anhydrous lithium chloride, 80 mL of dimethyl sulfoxide and 23.5 g (0.05 mol) of **3** was stirred at 55–60 °C under argon for 16 h. The clear colorless solution was cooled and poured into ice–water which was extracted with ether (3 × 100 mL). The combined ether extracts were washed with H_2O (2 × 100 mL), dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Distillation of the residue in a Kugelrohr apparatus at ca. 80 °C (1 mm) gave 9.5 g (95%) of **4a** as a colorless oil: NMR ($CDCl_3$) δ 1.42 (s, 6, $(CH_3)_2C$), 3.71 (m, 4, 2 CH_2Cl), 4.16 (m, 2, 2 CH); $[\alpha]^{25}_D$ +5.06° (*c* 2.0, C_6H_6).

Anal. Calcd for $C_7H_{12}O_2Cl_2$: C, 42.23; H, 6.08; Cl, 35.62. Found: C, 42.10; H, 6.13; Cl, 34.94.

The corresponding dibromide **4b**[23] was obtained similarly: colorless oil; yield 95%; NMR ($CDCl_3$) δ 1.43 (s, 6, $(CH_3)_2C$), 3.59 (m, 4, 2 CH_2Br), 4.16 (m, 2, 2 CH); $[\alpha]^{25}_D$ -1.46° (*c* 2.0, C_6H_6).

Anal. Calcd for $C_7H_{12}O_2Br_2$: C, 29.20; H, 4.20; Br, 55.50. Found: C, 29.26; H, 3.95; Br, 55.27.

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The corresponding diiodide **4c**[22,24] was made by using sodium iodide in acetone at 90–95 °C in a sealed system for 4–5 h, following a literature procedure:[22] NMR ($CDCl_3$) δ 1.43 (s, 6, $(CH_3)_2C$), 3.36 (m, 4, 2 CH_2I), 3.84 (m, 2, 2 CH); $[\alpha]^{25}_D$ −16.75° (*c* 5.0, CH_3OH).

Anal. Calcd for $C_7H_{12}O_2I_2$: C, 22.01; H, 3.17; I, 66.45. Found: C, 21.96; H, 3.28; I, 66.36.

((4*R*,5*R*)-*trans*-4,5-Bis(((3-methylphenyl)phosphino)-methyl)-2,2-dimethyl-1,3-dioxalane)copper(I) Chloride Complex (6b). Bis(3-methylphenyl)phosphine (1.7 g, 8 mmol) was dissolved in 20 mL of tetrahydrofuran and the solution was cooled to −75 °C. *n*-Butyllithium in hexane (3.2 mL of 2.5 M solution, 8 mmol) was added dropwise over 2.5 min and stirring was continued for 5 min at −75 °C. A solution of 0.796 g (4 mmol) of the dichloride **4a** in 5 mL of tetrahydrofuran was then added, and the mixture was allowed to warm slowly to room temperature with stirring and to stand at ca. 23 °C overnight. The reaction mixture was then hydrolyzed by addition of 3 mL of water, giving two layers which were separated. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give 1.93 g (87%) of crude phosphine **5b** as a thick colorless oil. This material was dissolved in 30 mL of ethanol containing 0.34 g of cuprous chloride (1 equiv). The mixture was warmed on a steam bath for 5 min, filtered hot through a fine porosity filter, and then allowed to stand at 0 °C for 24 h. The resulting colorless solid was collected by filtration, washed with ethanol, and dried (25 °C, 200 mm, 18 h). The yield of white copper complex **6b** was 1.0 g (45% based on **4a**). Concentration of the mother liquors gave a second crop of 0.156 g. Recrystallization of 0.50 g of the first crop from ethanol gave 0.446 g of pure **6b**·0.5C_2H_5OH, mp 105–106 °C dec. An analytical sample obtained similarly had mp 108 °C dec and the composition **6b**·CH_3CH_2OH: ^1H NMR (C_6D_6) δ 0.95 (t, ~1.5, 0.5 mol of CH_3CH_2OH), 1.0 (br s, 6, $(CH_3)_2C$), 1.40 (br s, ~1, CH_3CH_2OH and HDO), 1.98 and 2.01 (br d, 12, 4 Ar CH_3), 2.75 and 3.15 (m, ~6, CH_2P and CHP), 3.35 (q, ~1, CH_3 CH_2OH), 6.6–7.9 (m, 16, aromatic); ^{31}P NMR (C_6D_6) δ −18.0 (br s, width at half-height = 80 Hz); $[\alpha]^{25}_D$ +94.28 °C (*c* 3.0, benzene).

Anal. Calcd for $C_{35}H_{40}ClCuO_2P_2$·C_2H_5OH: C, 63.51; H, 6.48; Cl, 5.06; P, 8.85; Cu, 9.08. Found: C, 63.50; H, 6.63; Cl, 5.19; P, 9.16; Cu, 9.38.

Use of 6b To Form Rhodium Complex Hydrogenation Catalysts. A slurry of 2.0 g of (*Z*)-α-(acetylamino)-6-methylindole-3-acrylic acid monohydrate **7**[4] and 8.5 mL of deoxygenated methanol was treated under anaerobic conditions with 1.49 mL of a catalyst solution prepared from 14.7×10^{-3} g of complex **6b**, 5.2×10^{-3} g of μ,μ′-dichlorobis[(1,5-cyclooctadiene)rhodium(I)], and 25 mL of methanol. This catalyst solution contains 0.78×10^{-3} g of catalyst per mL of solution; thus use of 1.49 mL corresponds to a substrate/catalyst (S/C) weight ratio of 1720/1. The reaction mixture was placed in a pressure vessel and stirred under an initial hydrogen pressure of 40 psig at 23 °C. After 110 min, approximately 86% of the ultimate pressure drop had occurred and the mixture became homogeneous. After 14 h, no further pressure change was observed. Solvent removal left 2.0 g (100%) of (*R*)-(−)-*N*-acetyl-6-methyltryptophan (**8**), $[\alpha]^{25}_D$ −22.09° (*c* 1.0, CH_3OH). The *R*/*S* enantiomer ratio was determined for the crude amino acid obtained by hydrolysis of the hydrogenation product. The sample contained an 84.4% ee of (*R*)-**8**, according to a quantitative analytical separation of distereomeric dipeptide derivatives of the amino acid.[4]

((4*R*,5*R*)-*trans*-4,5-Bis(bis((3-methylphenyl)phosphino)methyl)-2,2-dimethyl-1,3-dioxalane)silver Perchlorate Complex (9). Phosphine **5b** (0.393 g, 0.71 mmol) and silver perchlorate (0.147 g, 0.71 mmol) were refluxed for 5 min in absolute ethanol (4 mL) and then cooled. Filtration of the cooled mixture gave complex **9**: mp 231–233 °C dec; yield 0.354 g (65%); ^1H NMR ($CDCl_3$) δ 0.87 (s, 6, $(CH_3)_2C$), 2.20 (br s, 12, Ar CH_3), 2.6, 2.9 (2 m, 4, CH_2P), 4.05 (br, 2, 2 CH); ^{31}P NMR ($CDCl_3$) δ +4.0 (br d, $J_{Ag,P}$ = ca. 550 Hz); $[\alpha]^{25}_D$ −30.04° (*c* 1.0, $CHCl_3$).

Anal. Calcd for $C_{35}H_{40}AgClO_6P_2$: C, 55.17; H, 5.28; Cl, 4.65; P, 8.13. Found: C, 55.05; H, 5.24;, Cl, 4.91; P, 8.32.

Use of 9 To Form Rhodium Complex Hydrogenation Catalysts. A hydrogenation was performed as described above with 2.35 mL of turbid solution freshly prepared from 12.4×10^{-3} g of complex **9**, 4.6×10^{-3} g of μ,μ′-dichlorobis[(1,5-cyclooctadiene)rhodium(I)], and 10 mL of methanol (S/C = 500) as catalyst. The product was (*R*)-(−)-*N*-acetyl-6-methyltryptophan (**8**), $[\alpha]^{25}_D$ −22.87°, 81.4% ee of the *R* enantiomer by amino acid analysis.

((4*R*,5*R*)-*trans*-4,5-Bis((bis(3-methylphenyl)phosphino)methyl)-2,2-dimethyl-1,3-dioxalane)zinc(II) Perchlorate Complex (10). Zinc perchlorate hexahydrate (0.324 g) and phosphine **5b** (0.527 g, 10% excess) were refluxed under argon in 5 mL of ethanol for 18 h. After cooling, the solution was evaporated to dryness and the residue (0.714 g) was triturated successively with ether, benzene, water, and ether–petroleum ether. The colorless complex **10** residue (0.58 g, 69%) had apparently undergone slight hydrolysis, according to the microanalysis and to the presence of a moderate OH stretching absorption in its infrared spectrum.

Anal. Calcd for $C_{35}H_{40}Cl_2O_{10}P_2Zn$: C, 51.33; Cl, 4.92; Cl, 8.66. Found: C, 52.18; H, 5.18; C, 8.58.

Use of 10 To Form Rhodium Complex Hydrogenation Catalysts. A hydrogenation was performed as described above with 1.8 mL of a solution prepared from 16.9×10^{-3} g of **10**, 5.1×10^{-3} g of μ,μ′-dichlorobis[(1,5-cyclooctadiene)rhodium(I)], and 10 mL of methanol (S/C = 500) as catalyst. The product was (*R*)-**8**, $[\alpha]^{25}_D$ −22.92°, 81.6% ee of the *R* enantiomer by amino acid analysis.

((4*R*,5*R*)-*trans*-4,5-Bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxalane)copper(I) Chloride Complex (6a). The phosphine **5a** (1.0 g, 2.0 mmol) and cuprous chloride (0.198 g, 2.0 mmol) were refluxed together in ethanol (20 mL) for 15 min, whereupon product had begun to precipitate from solution. The cooled reaction mixture was filtered and the filter cake was dissolved in chloroform, and the resulting solution was filtered, to remove traces of cuprous chloride, and then concentrated under reduced pressure. The residual powder (0.763 g, 63%, mp 211–12.5 °C) was twice crystallized from 1:1 methanol–benzene to give the pure 1:1 **5a**·CuCl complex **6a**: mp 211–212 °C; yield 0.15 g (13%); $[\alpha]^{25}_D$ −36.5° (*c* 1.0, $CHCl_3$); ^1H NMR (C_6D_6) δ 1.05 (s, 6, $(CH_3)_2C$), 2.60 (br m, 4, 2 CH_2P), 3.10 (br m, 2, 2 CH); ^{31}P NMR (C_6D_6) δ −17.5 (br s).

Anal. Calcd for $C_{31}H_{32}ClCuO_2P_2$: C, 62.31; H, 5.40; Cl, 5.93; P, 10.37. Found: C, 62.30; H, 5.38; Cl, 5.69; P, 10.69.

Use of 6a To Form Rhodium Complex Hydrogenation Catalysts. A hydrogenation was performed as described above, using as catalyst 1.0 mL of a solution prepared from 7.6×10^{-3} g of complex **6a**, 3.1×10^{-3} g of μ,μ′-dichlorobis[(1,5-cyclooctadiene)rhodium(I)], and 10 mL of methanol (S/C = 2000). The product (*R*)-**8** obtained had $[\alpha]^{25}_D$ −19.8°, 75.4% ee by amino acid analysis.

((+)-(4*R*,5*R*)-*trans*-4,5-Bis((bis(3,5-dimethylphenyl)-phosphino)methyl)-2,2-dimethyl-1,3-dioxalane)copper(I) Chloride Complex (6c). The phosphine **5c** (0.328 g, 0.537 mmol) and 0.053 g (0.535 mmol) of cuprous chloride were combined with absolute ethanol (4 mL) and refluxed for 5 min. The solution was filtered hot to remove traces of unreacted cuprous chloride and cooled to give 0.324 g (85%) of crude **6c**. Recrystallization from ethanol gave pure **6c**·CuCl complex which contained approximately 0.67 mol of ethanol: yield 0.238 g (62%); mp 129–131 °C; $[\alpha]^{25}_D$ +42.5° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.20 (t, ca. 2, CH_3CH_2OH), 1.35 (br s, 6, $(CH_3)_2C$), 2.20 (br d over m, 26, 8 Ar CH_3 plus 2 CH of CH_2P), 2.95 (br m, 2, 2 CH of CH_2P), 3.65 (q, ca. 1, CH_3CH_2OH), 4.0 (m, 2, CH–O), 6.98 (m, 4, aromatic), 7.32 (m, 8, aromatic); ^{31}P NMR ($CDCl_3$) δ −26.1 (br s, width at half-height = 30 Hz).

Anal. Calcd for $C_{39}H_{48}ClCuO_2P_2$·0.67CH_3CH_2OH: C, 65.42; H, 7.08; Cl, 4.79; P, 8.36. Found: C, 65.31; H, 7.32; Cl, 4.76; P, 9.44.

Use of 6c To Form Rhodium Complex Hydrogenation Catalysts. A hydrogenation was performed as described above, using as catalyst 2.3 mL of a solution prepared from 8.1×10^{-3} g of **6c**, 2.8×10^{-3} g of μ,μ′-dichlorobis[(1,5-cyclooctadiene)rhodium(I)], and 25 mL of methanol (S/C = 2000). The product (*R*)-**8** had $[\alpha]^{25}_D$ −22.88°, 87% ee of the *R* enantiomer by amino acid analysis.

(24) Ogura, K.; Yamashita, M.; Tsuchihashi, G. *Tetrahedron Lett.* **1976**, 759–62.

Dichlorotris((4*R*,5*R*)-*trans*-4,5-bis((diphenylphosphino)methyl)-2,2-dimethyl-1,3-dioxalane)dicopper(I) Complex (12). Phosphine **5a** (0.5 g, 1 mmol) and cuprous chloride (0.099 g, 1 mmol) were refluxed in absolute ethanol (8 mL) for 5 min, filtered, and cooled to room temperature. When no complex percipitated, the ethanol was removed at reduced pressure, and the residue (0.34 g) was crystallized from cyclohexane. There was obtained 0.273 g (45%) of colorless solid, mp 116–118 °C, complex **12**. The microanalysis of this material suggested the formulation $(CuCl)_2(DIOP)_3 \cdot 1.5$cyclohexane: ^1H NMR ($CDCl_3$) δ 1.10 (v br s, 6, $(CH_3)_2C$), 1.42 (s, 6, cyclohexane), 2.30 (v br m, 4, 2 CH_2P), 3.80 (v br m, 2, CH–O), 6.95–7.55 (m, 20, aromatic); ^{31}P NMR ($CDCl_3$) δ –21.2 (br), –15.1 (br), –8.6 (br), +16.7 (s), +29.7 (s).

Anal. Calcd for $C_{93}H_{98}Cu_2Cl_2O_6P_6 \cdot C_9H_{18}$: C, 67.31; H, 6.31; Cl, 3.90; P, 10.21. Found: C, 67.28; H, 6.46; Cl, 3.75; P, 10.08.

An attempt to repeat this preparation and to obtain crystals from ethanol or ethanol–hexane gave lower melting (mp 110–115 °C, 90–110 °C, 105–108 °C) or gummy solids, depending on crystallization solvent and conditions. A sample of colorless powder which precipitated from hot cyclohexane had mp 105–108 °C and the following microanalysis: C, 67.09; H, 6.12; Cl, 3.25; P, 10.79.

We suspect this material is an intermediate, or a mixture containing an intermediate, in the formation of **6a**.

Use of 12 To Form Rhodium Complex Hydrogenation Catalysts. A hydrogenation was performed as described above, using as catalyst 1.14 mL of a solution prepared from 17.2×10^{-3} g of **12**, 6.4×10^{-3} g of μ,μ'-dichlorobis[(1,5-cyclooctadiene)rhodium(I)], and 25 mL of methanol (S/C = 2000). The product was (*R*)-(–)-*N*-acetyl-6-methyltryptophan (**8**), $[\alpha]^{25}_D$ –20.86°, 73% ee of the *R* enantiomer by amino acid analysis.

((1*R*,2*R*)-*trans*-1,2-Bis((diphenylphosphino)methyl)-cyclobutane)copper(I) Chloride Complex (11). Phosphine **13**[11] (0.452 g, 1 mmol) and 0.1 g (1 mmol) of cuprous chloride were combined with absolute ethanol and heated over a steam bath for 5–10 min. Crude crystalline **13**·CuCl complex (0.3 g, 54%) was obtained upon cooling. Recrystallization from ethanol gave 0.15 g (27%) of pure complex: mp 197–199.5 °C; $[\alpha]^{25}_D$ +67.6° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.32 (m, 2), 1.6–2.5 (m, 8), 7.33 (m, 12, aromatic), 7.67 (m, 8, aromatic); ^{31}P NMR ($CDCl_3$) δ –19.7 (br s, width at half-height = 50 Hz).

Anal. Calcd for $C_{30}H_{30}ClCuP_2$: C, 65.34; H, 5.48; Cu, 11.52; Cl, 6.43; P, 11.23. Found: C, 65.48; H, 5.27; Cu, 11.53; Cl, 6.34; P, 11.52.

Use of 11 To Form Rhodium Complex Hydrogenation Catalysts. A hydrogenation reaction was performed as described above, using as catalyst 3.1 mL of a solution prepared from 2.5×10^{-3} g of complex **11**, 1.1×10^{-3} g of μ,μ'-dichlorobis[(1,5-cyclooctadiene)rhodium(I)] and 10 mL of methanol (S/C = 1790). The product was (*R*)-(–)-*N*-acetyl-6-methyltryptophan (**8**), $[\alpha]^{25}_D$ –17.57°, 60.4% ee of *R* enantiomer by amino acid analysis.

Crystallographic Experimental Data. Crystals of **6b**, obtained from methanol, are triclinic, space group $P\bar{1}$, with a = 9.677(1), b = 12.961(2), c = 14.891(3) Å, α = 106.07(1), β = 94.49(1), γ = 92.23(1)°, and d_{calcd} = 1.275 g cm^{-3} for Z = 1 [$(C_{35}H_{40}ClCuO_2P_2)_2 \cdot 2CH_3OH$, M = 1371.37]. The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse height discrimination). The size of the crystal used for data collection was approximately 0.10 × 0.20 × 0.30 mm; the data were corrected for absorption (μ = 26.5 cm^{-1}). Of the 4803 independent reflections for $\theta < 57°$, 4271 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by the heavy-atom method and was refined by block diagonal least squares in which the matrix was partitioned into five blocks. In the final refinement, anisotropic thermal parameters were used for the heavier atoms and isotropic temperature factors were used for the hydrogen atoms. The solvent of crystallization, which was assumed to be methanol, was represented by two oxygen atoms which were refined isotropically. The hydrogen atoms were included in the structure-factor calculations, but their parameters were not refined. The final discrepancy indices are R = 0.059 and R_w = 0.074 for the 4271 observed reflections. The final difference map has no peaks greater than ±0.6 e A^{-3}.

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Supplementary Material Available: Final atomic parameters, final anisotropic thermal parameters, bond lengths, and bond angles for **6b** (10 pages). Ordering information is given on any current masthead page.