Synthesis of Partially Hydrogenated 2,2'-Bis(diphenylphosphenyl)-1,1'-binaphthyl (BINAP) Ligands and Their Application to Catalytic Asymmetric Hydrogenation

Xiaoyong Zhang,[a] Kazushi Mashima,[a] Kinko Koyano,[a] Noboru Sayo,[b] Hidenori Kumobayashi,[b] Susumu Akutagawa[b] and Hidemasa Takaya*[,a]

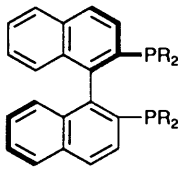
[a] *Division of Material Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan*

[b] *Central Research Laboratory, Takasago International Corporation, Nishiyawata, Hiratsuka, Kanagawa 254, Japan*

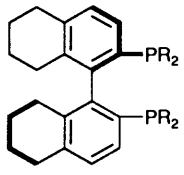
Three pairs of new axially dissymmetric bisphosphane ligands, (*R*)-(−)- and (*S*)-(+)-2,2'-bis(dicyclohexylphosphanyl)-1,1'-binaphthyl [(*R*)-(−)- and (*S*)-(+)-Cy-BINAP, (*R*)-(−)- and (*S*)-(+)-**2**], (*R*)-(+)- and (*S*)-(−)-2,2'-bis(diphenylphosphanyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl [(*R*)-(+)- and (*S*)-(−)-H_8-BINAP, (*R*)-(+)- and (*S*)-(−)-**3**], and (*R*)-(−)- and (*S*)-(+)-2,2'-bis(dicyclohexylphosphanyl)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl [(*R*)-(−)- and (*S*)-(+)-Cy-H_8-BINAP, (*R*)-(−)- and (*S*)-(+)-**4**], have been synthesized. The absolute configurations of the isomers **2** were determined by single-crystal X-ray diffraction of the linear 1:1 polymeric complex of (*S*)-(+)-2,2'-bis(dicyclohexylphosphinoyl)-1,1'-binaphthyl [(*S*)-(+)-Cy-BINAPO, (*S*)-(+)-**6**] and (2*R*,3*R*)-(−)-di-*O*-benzoyltartaric acid [(−)-DBT], and those of the isomers **3** and **4** were established on the basis of CD spectra of the phosphanes and their bisoxides. X-Ray crystallographic studies of two cationic Rh^I complexes, [Rh{(*S*)-Cy-binap}(cod)]ClO_4 [(*S*)-**17**]† and [Rh{(*S*)-H_8-binap}(cod)]ClO_4[(*S*)-**18**], revealed that complex (*S*)-**17** possesses a dissymmetric structure, while complex (*S*)-**18** has a pseudo-C_2-symmetry and shows a significantly large dihedral angle between the two phenyl rings [80.3(4)°]. The potentiality of ligand **3** for asymmetric catalysis was demonstrated in Ru^{II}-catalysed stereoselective hydrogenations of methyl 2-(benzamidomethyl)-3-oxobutanoate (**21**, in up to 92% d.e. and 99% e.e.) and geraniol (**22**, in 98% optical purity).

During the past two decades there have been dramatic advances in homogeneous asymmetric catalysis performed by transition metal complexes using optically active phosphanes as chiral ligands.[1] Among the numerous chiral ligands reported to date, the atropisomeric bis(triarylphosphane) 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl (BINAP, **1**)[2] has been attracting continuous interest due to its intrinsic structural features, remarkable chiral recognition ability, and broad applicability in various transition metal-catalysed asymmetric reactions[3] such as hydrogenation,[1-5] 1,3-hydrogen migration,[6] hydroboration,[7] hydrosilylation,[8] C–C bond formation,[9] and hydroformylation.[10] In general, the C_2-symmetry and molecular pliancy of BINAP have been considered as contributing significantly to the realization of high catalytic efficiencies and enantioselectivities.[3] So far, a wide range of BINAP derivatives with four pendant aryl groups have been prepared, usually by introducing various substituents (*e.g.*, Me, Pr^i, Bu^t, OMe, F, Cl, *etc.*) onto the four phenyl rings in BINAP to tune its electronic and steric properties.[2c,5a] By this approach, optimization of ligand–substrate matches have been accomplished for some asymmetric catalytic reactions. As part of our ongoing investigations in this field, we also designed new types of BINAP variant, Cy-BINAP **2**, H_8-BINAP **3**, and Cy-H_8-BINAP **4**.[11] These bisphosphanes are noteworthy in that they bear either four bulky, electron-donating cyclohexyl groups on the two phosphorus atoms or an atropisomeric 1,1'-bitetralin backbone, or both of them, instead of the four arene groups and/or the binaphthyl moiety characteristic of conventional BINAP ligands. They might be expected to possess unique electronic as well as structural properties, especially in terms of ligand rigidity and axial flexibility about the C(1)–C(1') pivot, and could provide us with a useful probe to identify how such structural features would influence the catalytic properties of their transition metal complexes in asymmetric reactions.

We describe herein details of the synthesis of these new chiral bisphosphanes **2**,[12] **3** and **4**, the structures of cationic Rh^I complexes of ligands **2** and **3**, and the application of compound **3** in ruthenium-catalysed asymmetric hydrogenation of prochiral unsaturated substrates.



(*R*)-(+)-**1** R = Ph
[(*R*)-(+)-BINAP]
(*R*)-(−)-**2** R = C_6H_{11}
[(*R*)-(−)-Cy-BINAP]



(*R*)-(+)-**3** R = Ph
[(*R*)-(+)-H_8-BINAP]
(*R*)-(−)-**4** R = C_6H_{11}
[(*R*)-(−)-Cy-H_8-BINAP]

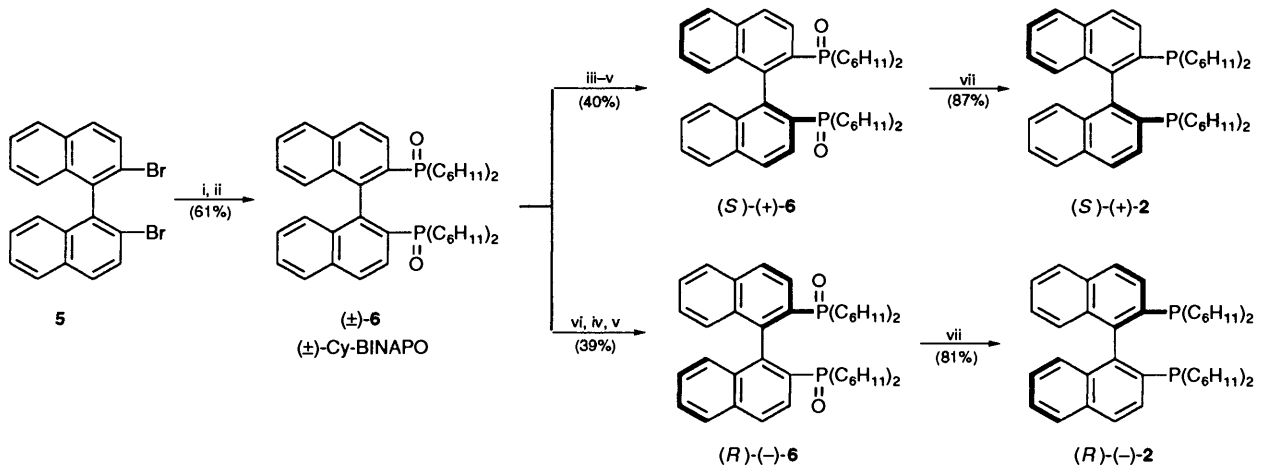
Throughout this paper, Cy = cyclohexyl (C_6H_{11})

Results and Discussion

Bisphosphane Syntheses.—(R)- *and* (S)-*Cy-BINAP* [(R)- *and* (S)-**2**]. Enantiometrically pure ligands (*R*)- and (*S*)-**2** have been prepared through a three-step route starting from (±)-2,2'-dibromo-1,1'-binaphthyl **5**,[2a] as sketched in Scheme 1.

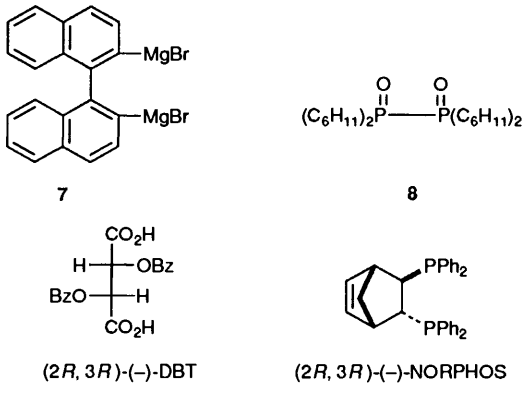
Crystals of the racemic dioxide of ligand **2**, (±)-Cy-BINAPO [(±)-**6**], were obtained in 61% yield by treatment of 2,2'-dibromo-1,1'-binaphthyl **5** with BuLi in tetrahydrofuran (THF) followed by coupling of the resulting dilithio derivative with dicyclohexylphosphinoyl chloride [$(C_6H_{11})_2P(O)Cl$].[13] Synthesis of compound (±)-**6** through the coupling reaction of

† cod = cycloocta-1,5-diene.



Scheme 1 *Reagents, conditions (and yields, in parentheses)*: i, BuLi; ii, $(C_6H_{11})_2P(O)Cl$; iii, (–)-DBT; iv, recrystallization; v, NaOH; vi, (+)-DBT; vii, $HSiCl_3$, NEt_3

$(C_6H_{11})_2P(O)Cl$ with the Grignard reagent **7** in toluene at 0–80 °C was also attempted. However, only a trace amount of compound (±)-**6** was formed, while tetracyclohexyldiphosphane dioxide $[(C_6H_{11})_2P(O)–(O)P(C_6H_{11})_2$, **8**]*,[14] was obtained in 27% yield based on $(C_6H_{11})_2P(O)Cl$ used.



The optical resolution of racemate (±)-**6** was achieved by the use of optically active 2,3-di-*O*-benzoyltartaric acid (DBT).[2c,15] Thus, when a solution of (2*R*,3*R*)-(–)-DBT in ethyl acetate was added to a boiling solution of racemic compound **6** in the same solvent, a 1:1 complex of (+)-**6** and (–)-DBT [hereafter abbreviated (+)-**6**–(–)-DBT] precipitated as a crystalline solid within seconds. X-Ray structure analysis (Fig. 1) revealed that the crystals are built up of infinite close-packed chains in which equimolar (+)-**6** and (–)-DBT are connected in a regularly alternating way through two intermolecular hydrogen bonds between oxygen atoms [O(1) and O(2)] of the P=O groups in compound **6** and hydrogen atoms of the CO_2H groups of DBT. Selected bond distances and angles are listed in Table 1. The O(1)···O(3′) and O(2)···O(5) distances are 2.518(10) and 2.512(10) Å, respectively, and the dihedral angle θ between the least-square planes through the two naphthalene rings is 79.4(2)°. Such a polymeric structure was previously found in the crystal structure of the 1:1 complex between the dioxide of (*R*,*R*)-2-*exo*-3-*endo*-bis(diphenylphosphanyl)bicyclo[2.2.1]heptane [(2*R*,3*R*)-(–)-NORPHOS] and (–)-DBT.[15] The low solubility of complex (+)-**6**–(–)-DBT is attributable to such a linear polymeric structure, and the enantiomeric resolution has thus been achieved by preferential crystallization of this polymeric diastereoisomer. From the internal comparison with (–)-DBT, the absolute configuration of (+)-**6** is defined to be *S*.

Table 1 Selected bond distances and angles for adduct (*S*)-**6**–(–)-DBT

Distances (Å)			
P(1)–C(2)	1.828(10)	P(2)–C(12)	1.818(10)
P(1)–C(21)	1.844(10)	P(2)–C(33)	1.798(10)
P(1)–C(27)	1.833(12)	P(2)–C(39)	1.855(11)
P(1)–O(1)	1.489(7)	P(2)–O(2)	1.496(7)
C(1)–C(11)	1.505(14)	O(3)–C(45)	1.251(13)
O(4)–C(45)	1.210(14)	O(5)–C(48)	1.332(13)
O(6)–C(48)	1.199(13)	O(1)···O(3′)	2.518(10)
O(2)···O(5)	2.512(10)		
Angles (°)			
O(1)–P(1)–C(2)	111.6(4)	O(2)–P(2)–C(12)	110.9(4)
O(1)–P(1)–C(21)	110.7(4)	O(2)–P(2)–C(33)	113.4(4)
O(1)–P(1)–C(27)	111.8(5)	O(2)–P(2)–C(39)	111.4(5)
C(2)–P(1)–C(21)	107.7(5)	C(12)–P(2)–C(33)	108.4(5)
C(2)–P(1)–C(27)	105.4(5)	C(12)–P(2)–C(39)	106.8(5)
C(21)–P(1)–C(27)	109.4(5)	C(33)–P(2)–C(39)	105.6(5)
C(2)–C(1)–C(11)	122.7(8)	C(1)–C(11)–C(12)	122.5(9)
C(10)–C(1)–C(11)	117.8(8)	C(1)–C(11)–C(20)	117.8(8)
P(1)–C(2)–C(1)	126.2(8)	P(2)–C(12)–C(11)	125.3(7)
P(1)–C(2)–C(3)	115.4(7)	P(2)–C(12)–C(13)	115.2(7)
P(1)–C(21)–C(22)	117.0(7)	P(2)–C(33)–C(34)	112.1(7)
P(1)–C(21)–C(26)	110.3(7)	P(2)–C(33)–C(38)	110.5(7)
P(1)–C(27)–C(28)	109.0(8)	P(2)–C(39)–C(40)	117.6(8)
P(1)–C(27)–C(32)	114.9(8)	P(2)–C(39)–C(44)	110.3(7)
O(3)–C(45)–O(4)	129.9(10)	O(5)–C(48)–O(6)	121.6(10)
O(3)–C(45)–C(46)	112.3(9)	O(5)–C(48)–C(47)	113.0(9)
O(4)–C(45)–C(46)	117.8(10)	O(6)–C(48)–C(47)	125.4(10)

Subsequent decomposition of complex (+)-**6**–(–)-DBT with aq. NaOH provided crystals of optically pure (*S*)-(+)-**6** in 40% yield based on (±)-**6** used. On the other hand, treatment of the mother liquor left on removal of (+)-**6**–(–)-DBT with aq. base afforded the crude antipode (*R*)-(–)-**6**. Further purification through similar formation and decomposition of (–)-**6**–(+)-DBT gave pure (*R*)-(–)-**6** in 39% yield starting from (±)-**6**.

Reductions of (*S*)-(+)- and (*R*)-(–)-**6** to phosphanes (*S*)-(+)- and (*R*)-(–)-**2**, respectively, were realized in high yields by

* Analytical data of compound **8**: m.p. 219.5–220.5 °C (from toluene) [lit.,[14] 205 °C (from benzene–petroleum spirit)] (Found: C, 67.6; H, 10.5. $C_{24}H_{44}O_2P_2$ requires C, 67.61; H, 10.36%); $\delta_H(CDCl_3)$ 1.18–1.40 (12 H, m), 1.65 (8 H, t, *J* 12.0), 1.68–1.81 (4 H, m), 1.81–2.00 (8 H, m) and 2.00–2.28 (12 H, m); $\delta_C(CDCl_3)$ 26.00, 26.07, 26.20, 26.83, 26.92, 27.04, 27.13, 39.41, 39.82 and 40.25; $\delta_P(CDCl_3)$ 53.19 (s).

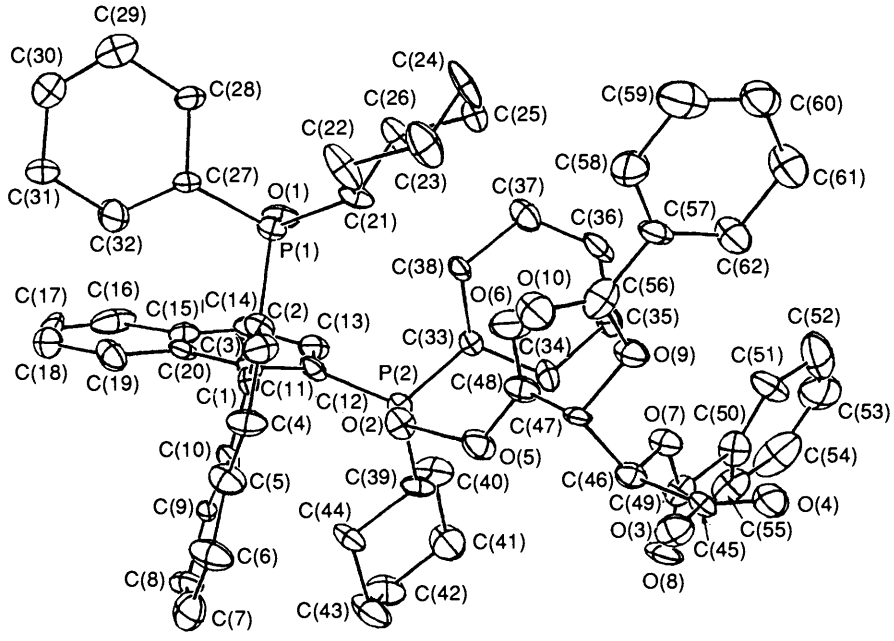


Fig. 1 An ORTEP drawing of the complex (*S*)-(+)-**6**–(2*R*,3*R*)-(−)-DBT showing the atom-numbering scheme. The crystal solvent AcOEt and all hydrogen atoms have been omitted for clarity.

refluxing each phosphane oxide **6** with eighteen-fold excess of a mixture of trichlorosilane and triethylamine in xylene.[2c,16]

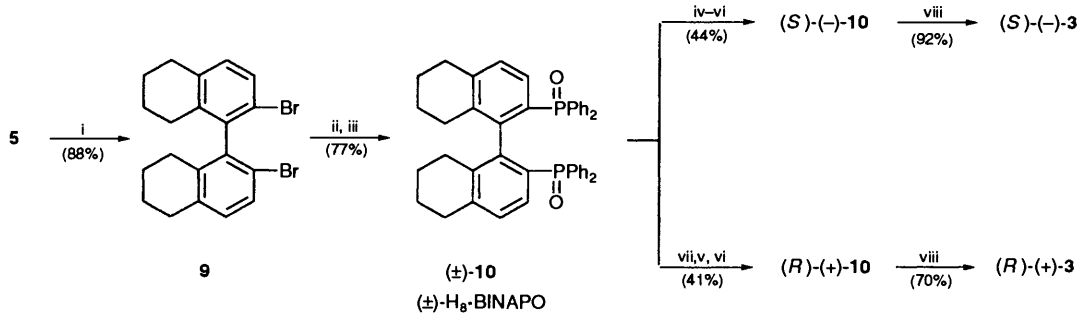
(R)- *and* (S)-*H*$_8$-*BINAP* [(R)- *and* (S)-**3**]. Optically pure ligands (*R*)- and (*S*)-**3** are obtainable in a four-step procedure starting from dibromide **5** as depicted in Scheme 2. Selective hydrogenation of binaphthyl **5** to 2,2′-dibromo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl **9** was accomplished by using 5% ruthenium on carbon as catalyst. Product distribution in the hydrogenation depended remarkably on reaction conditions such as composition of the solvent system, hydrogen pressure, and temperature. When the reaction was run in 95% ethanol, ethyl acetate, benzene, or benzene–95% ethanol (1:1) under various conditions (room temp.–100 °C, 30–60 atm of H_2, 7–70 h), mixtures of compound **9** 2,2′-dibromo-5,6,7,8-tetrahydro-1,1′-binaphthyl **11**, and 2-bromo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl **12** were formed in varying proportions (63:36:1 to 0:100:0) and 9–84% combined yields, while in a 1:1 or 1:2 mixture of ethyl acetate and 95% ethanol hydrogenation of compound **5** went to completion to give compound **9** in 96% selectivity and in 88% isolation yield, along with trace amounts of **11**, **12** and 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl **13** [equation (1)].

Coupling reaction of the Grignard reagent **14** prepared *in situ* from dibromide **9** and diphenylphosphinoyl chloride produced the bisphosphane dioxide, (±)-2,2′-bis(diphenylphosphinoyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl [(±)-**10**, hereafter abbreviated (±)-H$_8$-BINAPO] in 77% yield. Optical resolution of racemate (±)-**10** was carried out in a similar way as described above. In this case needles of (−)-**10**–(−)-DBT formed preferentially upon addition of a solution of (−)-DBT in ethyl acetate to that of racemate (±)-**10** in chloroform. Subsequent reduction of the resolved compound **10** with 15-fold excess of $HSiCl_3$–Et_3N afforded enantiomers (+)- and (−)-**3** in up to 92% yield.

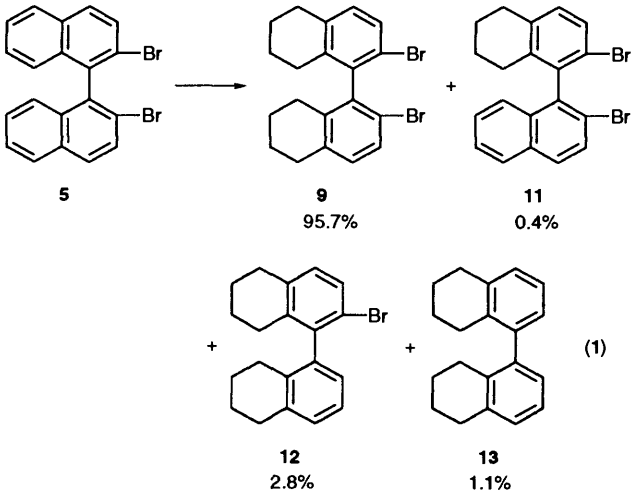
The absolute configuration of compounds (+)-**3** and (+)-**10** has been assigned to be *R* by comparison of their circular dichroism (CD) spectra* with those of (*R*)-(−)- and (*S*)-(+)-2,2′-bis(diphenylphosphanyl)-6,6′-dimethyl-1,1′-biphenyl [(*R*)-(−)- and (*S*)-(+)-BIPHEMP, (*R*)-(−)- and (*S*)-(+)-**15**] and that of the dioxide of (*R*)-(−)-**15**, respectively, since the absolute configurations of enantiomers (−)- and (+)-**15** have been elucidated from the synthetic pathway as well as by X-ray analysis.[17]

(R)- *and* (S)-*Cy*-*H*$_8$-*BINAP* [(R)- *and* (S)-**4**]. As shown in Scheme 3, enantiomers (*R*)- and (*S*)-**4** were synthesized from dibromide **9** through a similar route as described for its analogues (*R*)- and (*S*)-**2**. Dilithiation of dibromide **9** with *tert*-BuLi in a mixture of THF and diethyl ether and subsequent coupling of the resulting dilithio reagent with $(C_6H_{11})_2$-

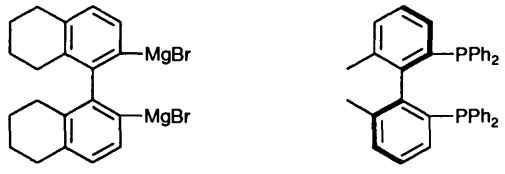
* For CD spectra of (*R*)-(+)-**3**, (*S*)-(−)-**3**, (*R*)-(−)-**4**, (*S*)-(+)-**4**, (*R*)-(+)-**10**, (*S*)-(−)-**10**, (*R*)-(−)-**16**, and (*S*)-(+)-**16**, see Supplementary Material [SUP No. 57019 (4 pp)] (see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, issue 1).



Scheme 2 *Reagents, conditions (and yields, in parentheses)*: i, H_2, 5% Ru–C; ii, Mg; iii, $Ph_2P(O)Cl$; iv, (−)-DBT; v, recrystallization; vi, NaOH; vii, (+)-DBT; viii, $HSiCl_3$, NEt_3



Reagents and conditions: H_2 (125 atm), 5% Ru–C; EtOH–AcOEt (1 : 1), 150 °C, 21 h

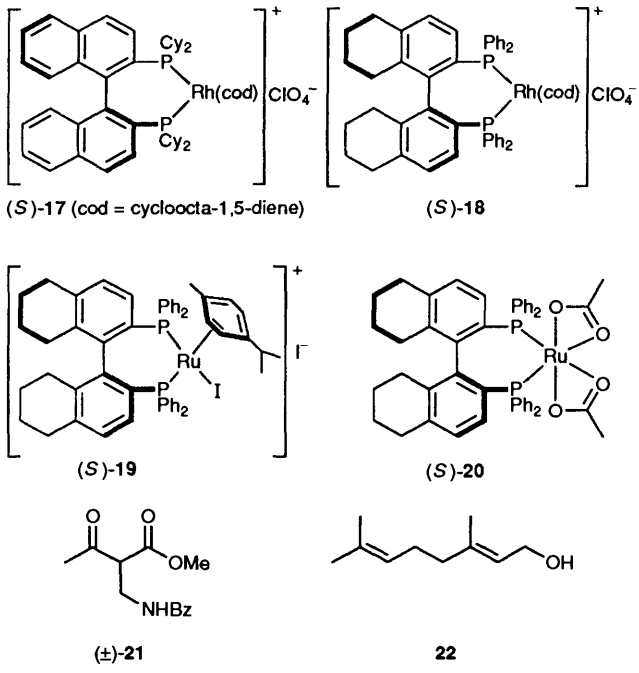


14 (*R*)-(–)-**15** (*R*)-(–)-BIPHEMP

P(O)Cl afforded racemic 2,2′-bis(dicyclohexylphosphinoyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl [(±)-**16**, (±)-Cy-H_8-BINAPO] as crystals in 38% yield. When BuLi was used instead, the dilithiation reaction was much more difficult, as monitored by GLC analysis of the reaction mixture.

Optical resolution of racemate (±)-**16** followed by reduction in a similar manner as described for compound **6** produced enantiomers (+)-**4** and (–)-**4** as needles. The absolute configuration of compounds (–)-**4** and (–)-**16** was determined to be *R* by comparison of their CD spectra with those of (*R*)-(+)-**3** and (*R*)-(+)-**10** as well as those of (*R*)-(–)-**15** and its dioxide.*[17]

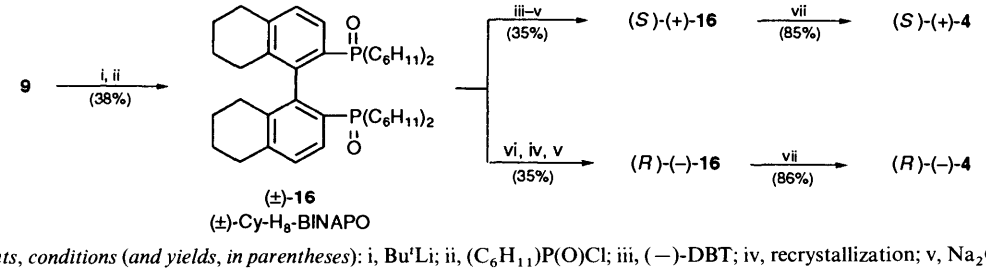
Transition Metal Complexes of Bisphosphanes **2–4**.—To examine the coordinating behaviours of the new chiral bisphosphane ligands **2–4** to transition metals as well as their efficiencies in transition metal-catalysed asymmetric reactions as compared with those of conventional BINAPs, we have synthesized a series of their transition metal complexes such as [Rh(Cy-binap)(cod)]ClO_4 **17**, [Rh(H_8-binap)(cod)]ClO_4 **18**, [RuI(H_8-binap)(*p*-cymene)]I **19**, and Ru$(OAc)_2$(H_8-binap) **20** in good to excellent yields. The fairly air-stable Rh^I complexes (*S*)-**17** and (*S*)-**18** have been subjected to single-crystal X-ray diffraction studies, while the ruthenium(II) complexes (*S*)-**19** and (*S*)-**20** have been used as efficient catalyst precursors in the stereoselective asymmetric hydrogenations of a functionalized ketone, methyl 2-(benzamidomethyl)-3-oxobutanoate **21**, and a functionalized olefin, geraniol **22**, respectively (*vide infra*).



Crystal Structures of [*Rh*{(S)-*Cy-binap*}(*cod*)]ClO_4[(S)-**17**] *and* [*Rh*{(S)-H_8-*binap*}(*cod*)]ClO_4[(S)-**18**].—Rh^I complexes (*S*)-**17** and (*S*)-**18** were readily grown to single crystals in methanol and a mixture of dichloromethane and diethyl ether, respectively. ORTEP diagrams of complexes (*S*)-**17** and (*S*)-**18** with labelling schemes are presented in Figs. 2 and 3, respectively. Selected bond distances and angles are compiled in Table 2.

For complex (*S*)-**17**, the dihedral angle θ [74.8(1)°] between the two naphthalene rings lies in the range observed for [Rh{(*R*)-binap}(nbd)]ClO_4[2d] (nbd = norbornadiene) and other Rh–BINAP complexes [71.0(3)–75.5(6)°].[18] However, the structure of complex (*S*)-**17** differs distinctly from those of the latter complexes in that it does not approximate to C_2-symmetry. The four cyclohexyl groups appear to be disposed in an edge–face–face–face arrangement rather than in an edge–face–edge–face orientation, and the seven-membered chelate ring is remarkably distorted from a δ-skew conformation.[2d,18–25] The non-equivalence of the two phosphorus atoms in complex (*S*)-**17** is also reflected in the distinctly

* For CD spectra of (*R*)-(+)-**3**, (*S*)-(–)-**3**, (*R*)-(–)-**4**, (*S*)-(+)-**4**, (*R*)-(+)-**10**, (*S*)-(–)-**10**, (*R*)-(–)-**16**, and (*S*)-(+)-**16**, see Supplementary Material [SUP No. 57019 (4 pp)] (see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, issue 1).



Scheme 3 *Reagents, conditions (and yields, in parentheses)*: i, Bu^{t}Li; ii, $(C_6H_{11})P(O)Cl$; iii, (–)-DBT; iv, recrystallization; v, Na_2CO_3; vi, (+)-DBT; vii, $HSiCl_3$, NEt_3

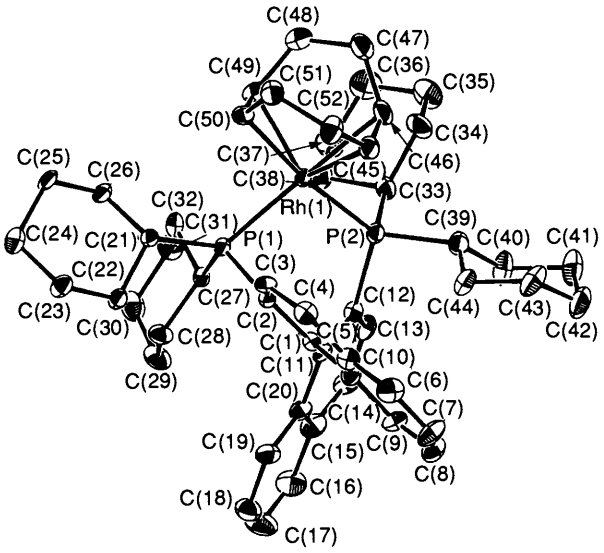


Fig. 2 An ORTEP drawing of [Rh{(*S*)-Cy-binap}(cod)]ClO_4 [(*S*)-**17**] showing the atom-numbering scheme. Two molecules of the crystal solvent MeOH, all hydrogen atoms, and the ClO_4^- anion have been omitted for clarity.

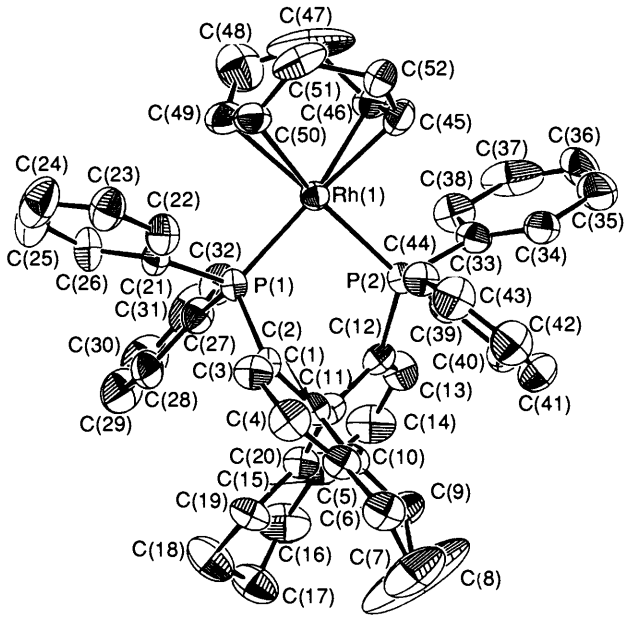


Fig. 3 An ORTEP drawing of [Rh{(*S*)-H_8-binap}(cod)]ClO_4 [(*S*)-**18**] showing the atom-numbering scheme. The crystal solvent CH_2Cl_2, all hydrogen atoms, and the ClO_4^- anion have been omitted for clarity.

variable Rh–P distances [2.331(2) and 2.422(2) Å for P(1) and P(2), respectively] and in the ^{31}P NMR spectrum [δ 12.14 (dd, J_{Rh,P_a} = 145.7 Hz, J_{P_a,P_b} = 19.9 Hz) and 31.12 (dd, J_{Rh,P_b} = 125.2 Hz)]. Varying deviations of flexible 7-membered chelate rings from the pseudo-C_2-conformation have so far been reported for several Rh^I complexes derived from C_2-symmetric bisphosphanes bearing four *P*-phenyl rings,[23] including [Rh(dppb)(nbd)]BF_4 [dppb = 1,4-bis(diphenylphosphanyl)-butane[26]] and [Rh{*trans*-1,2-bis(diphenylphosphanylamino)-cyclohexane}(cod)]ClO_4,[27] as well as the BINAP-related complex [Rh{(*S*)-biphemp}(nbd)]BF_4.[17]

On the other hand, complex (*S*)-**18** possesses a pseudo-C_2-symmetry axis and an alternating edge–face array of the *P*-phenyl rings as observed for conventional BINAP–Rh^I complexes.[2d,18] It is noteworthy that, however, the dihedral angle [80.3(4)°] between the two phenyl rings of the bitetralin moiety is markedly larger than that between the two naphthalene rings in [Rh{(*R*)-binap}(nbd)]ClO_4 [74.4(2)°][2d] and is also larger than that between the two phenyl rings in [Rh{(*S*)-biphemp}(nbd)]ClO_4 (71.8°).[17] This is ascribable to the steric repulsion between the two tetralin moieties of ligand **3**. As is demonstrated in the following section, this new bis(triarylphosphane) is expected to match those prochiral substrates which require a larger dihedral angle than conventional BINAPs.

Ru^{II}-Catalysed Asymmetric Hydrogenations.—By using [RuI{(*S*)-H_8-binap}(*p*-cymene)]I [(*S*)-**19**] as a catalyst, excellent results have been attained in the diastereo- and enantioselective hydrogenation of racemic methyl 2-(benzamidomethyl)-3-oxobutanoate [(±)-**21**] to the *syn*-β-hydroxy ester, (2*R*,3*S*)-**23**, *via* dynamic kinetic resolution (Table 3).[5a,5d,28] As we have previously noted,[5a] there are remarkable solvent effects in this reaction. Higher catalytic activity and stereoselectivity were obtained in CH_2Cl_2 (run 2) than in methanol (run 1), and the highest diastereoselectivity (92%), together with a high conversion, has been realized without alteration of enantioselectivity when the reaction was conducted in a mixture of CH_2Cl_2 and MeOH (7:1) (run 3). Under all these conditions, complex (*S*)-**19** is superior or favourably comparable with the BINAP analogues [RuI{(*S*)- and (*R*)-binap}(*p*-cymene)]I [(*S*)- and (*R*)-**24**] (runs 1–3 *vs.* 6–8).[5a] When the reaction was carried out in CH_2Br_2–MeOH (7:1), the excellent enantioselectivity of substrate (*S*)-**19** remained unchanged, although reaction rate and diastereoselectivity decreased somewhat (run 4). Upon inversion of the ratio of CH_2Br_2 to MeOH to 1:7, the hydrogenation was quite accelerated (run 5). This was, however, completely counteracted by the dramatic decrease in diastereoselectivity.

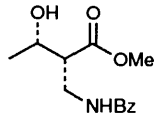
Table 2 Selected bond distances and angles for complexes (*S*)-**17** and (*S*)-**18**

	(*S*)-**17**	(*S*)-**18**
Distances (Å)		
Rh–P(1)	2.331(2)	2.326(3)
Rh–P(2)	2.422(2)	2.337(3)
Rh–C(45)	2.214(8)	2.246(12)
Rh–C(46)	2.268(7)	2.264(12)
Rh–C(49)	2.147(7)	2.268(12)
Rh–C(50)	2.206(7)	2.231(12)
P(1)–C(2)	1.822(6)	1.837(10)
P(1)–C(21)	1.860(6)	1.845(14)
P(1)–C(27)	1.855(6)	1.843(13)
P(2)–C(12)	1.866(7)	1.843(11)
P(2)–C(33)	1.874(7)	1.856(10)
P(2)–C(39)	1.873(7)	1.799(12)
C(1)–C(11)	1.493(9)	1.510(16)
Angles (°)		
P(1)–Rh–P(2)	94.5(1)	90.6(1)
Rh–P(1)–C(2)	84.6(2)	115.2(4)
Rh–P(1)–C(21)	119.9(2)	114.5(4)
Rh–P(1)–C(27)	123.0(2)	112.3(4)
C(2)–P(1)–C(21)	103.0(3)	105.1(5)
C(2)–P(1)–C(27)	115.0(3)	106.4(5)
C(21)–P(1)–C(27)	107.4(3)	102.2(6)
Rh–P(2)–C(12)	118.7(2)	119.6(4)
Rh–P(2)–C(33)	108.4(2)	111.1(4)
Rh–P(2)–C(39)	119.1(2)	109.5(4)
C(12)–P(2)–C(33)	103.2(3)	104.9(5)
C(12)–P(2)–C(39)	103.1(3)	106.5(5)
C(33)–P(2)–C(39)	102.1(3)	104.2(5)
P(1)–C(2)–C(1)	126.0(5)	122.2(9)
P(1)–C(2)–C(3)	114.7(5)	119.4(9)
P(2)–C(12)–C(11)	121.6(5)	120.9(8)
P(2)–C(12)–C(13)	118.7(5)	122.7(9)

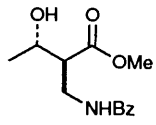
Table 3 Asymmetric hydrogenation of methyl 2-(benzamidomethyl)-3-oxobutanoate (±)-**21**[a]

Run	Catalyst	Conditions S/C[b]	Solvent[c]	Time (*t*/h)	Conv.[d] (%)	*syn*-**23** D.e.[d] (%)	E.e.[e] (%)	Config.
1	(*S*)-**19**	1640	MeOH	20	53	71	93	(2*R*,3*S*)
2	(*S*)-**19**	1640	CH_2Cl_2	20	74	85	99	(2*R*,3*S*)
3	(*S*)-**19**	1640	CH_2Cl_2–MeOH (7:1)[f]	20	80	92	99	(2*R*,3*S*)
4	(*S*)-**19**	1640	CH_2Br_2–MeOH (7:1)[f]	20	73	87	99	(2*R*,3*S*)
5	(*S*)-**19**	1640	CH_2Br_2–MeOH (1:7)	20	100	52	97	(2*R*,3*S*)
6[g]	(*S*)-**24**	100	MeOH	40	100[h]	51	97	(2*R*,3*S*)
7[g]	(*S*)-**24**	100	CH_2Cl_2[i]	40	98	88	97	(2*R*,3*S*)
8[g]	(*R*)-**24**	1000	CH_2Cl_2[j]–MeOH (7:1)	21	91	84	99	(2*S*,3*R*)

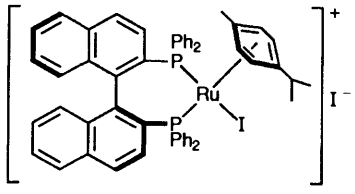
[a] Hydrogenation was carried out in an autoclave under an initial hydrogen pressure of 54 atm at 65 °C (50 atm when at room temp.) unless otherwise stated. [b] Substrate-to-catalyst ratio (mol/mol). [c] Solvents dried and distilled over CaH_2 (for CH_2Cl_2 and CH_2Br_2) or $Mg(OMe)_2$ (for MeOH) were used unless otherwise specified. Ratio of solvent to substrate was 2 cm^3 g^{-1} unless otherwise indicated. [d] As given by HPLC analysis [Cosmosil 5SL, with hexane–$CHCl_3$–MeOH (90:10:2) as the eluent]. [e] Determined by HPLC analysis of the (*R*)-MTPA ester of compound **23** [Cosmosil 5SL, with hexane–THF–MeOH (1000:100:1) as the eluent]. [f] Commercial solvents were used without purification. [g] See ref. 5*a*. Temp. 50–60 °C; ratio of solvent to substrate: 4 cm^3 g^{-1}. [h] Initial hydrogen pressure was 100 atm when at room temp. [i] The solvent was saturated with water at −20 °C by addition of 0.5% v/v water to stirred CH_2Cl_2 (distilled from P_2O_5). [j] CH_2Cl_2 was dried and distilled over P_2O_5.



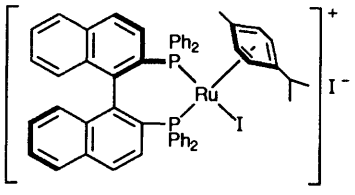
syn-(2*R*,3*S*)-**23**



anti-(2*S*,3*S*)-**23**

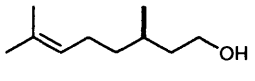


(*S*)-**24**

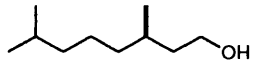


(*R*)-**24**

High levels of regio- and enantio-selectivity have also been realized in the hydrogenation of geraniol **22**, an allylic alcohol, catalysed by $Ru(OAc)_2$\{(*S*)-H_8-binap\}(*S*)-**20**. The hydrogenation was completed (100% conversion) in methanol (S/C 5400 mol/mol, 25 °C, 100 atm of H_2, 5 h), and gave (*R*)-citronellol (*R*)-**25** almost quantitatively in 98% optical purity. Dihydrocitronellol **26** was produced in this case in only 1.5% yield. This result is comparable to that obtained with $Ru(OAc)_2$\{(*S*)-binap\} under similar conditions (S/C 530 mol/mol, 20 °C, 100 atm of H_2, 98% o.p. and 96% e.e.)[29]



(*R*)-**25**



(*R*)-**26**

Conclusions

From a common starting material, 2,2′-dibromo-1,1′-binaphthyl **5**, the partially hydrogenated BINAP variants (*R*)- and (*S*)-Cy-BINAP **2**, H_8-BINAP **3**, and Cy-H_8-BINAP **4** have been synthesized in three or four steps. As expected, these new bisphosphanes possess interesting structural features in their transition metal complexes. Unlike the situation found for crystal structures of Rh^I–BINAP complexes, the Cy-BINAP-bearing complex (*S*)-**17** adopts a dissymmetric crystal structure and a pseudo-edge–face–face–face array of *P*-cyclohexyl rings. On the other hand, the pseudo-C_2-symmetric complex (*S*)-**18** exhibits a significantly larger dihedral angle between the two phenyl rings of the tetralin moieties of H_8-BINAP than those between the naphthalene or phenyl rings in the BINAP and BIPHEMP (**15**) analogues. These structures suggest that the present new ligands possess quite different axial flexibilities from conventional BINAPs and BIPHEMPs. Such intrinsic structural features, and also their electronic properties, should be reflected in the catalytic properties of their transition metal complexes as compared with those of the BINAP analogues. Indeed, complex **17** proves to be much more stereoselective than its BINAP analogue for the asymmetric catalytic hydrosilylation of certain aliphatic ketones with a prochiral naphthylphenylsilene (in as high as 98% e.e.).[30] Similarly, the cationic Ir^I complexes [Ir\{(*R*)- and (*S*)-H_8-binap\}(cod)]BF_4 serve as more effective catalyst precursors for the asymmetric hydrogenation of two β-thiacycloalkanones, tetrahydrothiophen-3-one and tetrahydrothiapyran-3-one (82 and 70% e.e., respectively), than does the analogous [Ir\{(*S*)-binap\}(cod)]BF_4 (60 and 40% e.e., respectively).[5c] These results, together with those obtained on the above asymmetric hydrogenations of substrates **21** and **22** catalysed by the Ru^{II} complexes (*S*)-**19** and (*S*)-**20**, demonstrate the potentiality of the present new bisphosphanes for asymmetric catalysis. Further studies on their applications could thus be expected to contribute towards a systematic understanding of the relation between ligand structures and efficiencies of asymmetric induction in various catalytic processes, as well as aiding exploration of new effective ligand–substrate matches.

Experimental

General.—Nuclear magnetic resonance [^1H (270 or 400 MHz), ^{13}C (68 or 100 MHz) and ^{31}P (109 or 161 MHz) NMR] spectra were recorded on a JEOL JNM-EX270 or a Bruker AM-400 spectrometer with $SiMe_4$ (internal) or 85% phosphoric acid (external) as reference; *J*-values are in Hz. Other spectra were measured on the following instruments: IR, on a Hitachi 295 or a JASCO IR-810; optical rotation, on a JASCO DIP-360 ($[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}); CD, on a JASCO J-600 (*c* 1.0 × 10^{-3}–6.0 × 10^{-3}, EtOH); low-resolution

mass spectra, on a JEOL D300 (70 eV) or a Hitachi M-80B. Gas chromatographic (GLC) analyses were conducted on a Hitachi 263-30 (capillary columns: OV-1701 or PEG-HT, 0.25 mm I.D. × 25 m) or on an HP 5890A (capillary column: HP-1, 0.20 mm I.D. × 25 m) equipped with a flame ionization detector; HPLC analyses were performed with a Shimadzu LC-4A or a Hitachi L-6000 using a L-4000 UV detector (columns: Waters, Cosmosil 5SL, and Daicel Chiralcel OG, 4.6 I. D. × 250 mm; detection: 254 nm light). Elemental analyses were performed by the Elemental Analysis Center, Kyoto University. All m.p.s were determined with a Yanagimoto or a Yanako MP-500D melting point apparatus and were not corrected.

Materials.—All manipulations involving air- and moisture-sensitive organometallic compounds were carried out with the standard Schlenk technique under argon purified by passage through a BASF-Catalyst R3-11 column. (±)-2,2′-Dibromo-1,1′-binaphthyl **5** [2a,b] was prepared according to the previously reported method. $(C_6H_{11})_2P(O)Cl$,[13] $[Rh(cod)_2]ClO_4$,[31] $[RhCl(cod)]_2$,[32] $[RuI_2(p\text{-cymene})]_2$,[19b] $[RuCl_2(cod)]_n$,[33] and methyl 2-(benzamidomethyl)-3-oxobutanoate (±)-**21** [34] were synthesized according to literature methods. Diphenylphosphinoyl chloride, (2*R*,3*R*)-(−)- and (2*S*,3*S*)-(+)-DBT monohydrates (Tokyo Kasei Kogyo Co.), α-methoxy-α-(trifluoromethyl)phenylacetic acid [(*R*)-MTPA] (Aldrich Co.), trichlorosilane (Shin-Etsu Co.), 5% Ru–C catalyst (N. E. Chemcat. Co.), BuLi (Aldrich Co.), and *tert*-BuLi (Aldrich Co.) were of commercial origin and were used as supplied. Geraniol (Aldrich Co.) was purchased and distilled before used. Oxygen-free dry solvents were prepared as follows: dichloromethane, dibromomethane, benzene, toluene, xylene (a commercial mixture), hexane, and diethyl ether were distilled under argon from calcium hydride; dichloromethane was alternatively dried over P_2O_5; methanol and ethanol were dried over the corresponding magnesium alkoxides; THF was dried over sodium benzophenone ketyl, Na–K alloy, or 70% sodium bis-(2-methoxyethoxy)aluminium hydride in toluene; triethylamine was distilled from BaO.

Preparation of (±)-2,2′-*Bis*(*dicyclohexylphosphinoyl*)-1,1′-*binaphthyl* [(±)-*Cy-BINAPO*, (±)-**6**].—To a solution of 2,2′-dibromo-1,1′-binaphthyl **5** (93.7% purity; 10.37 g, 23.6 mmol) in THF (370 cm^3) cooled at −60 °C was added dropwise a solution of BuLi (63.8 mmol) in hexane (44 cm^3). The resultant yellow-green slurry was stirred below −60 °C for 2.5 h and at −40 °C for 0.5 h. A white emulsion, which had been a colourless solution at room temperature, of dicyclohexylphosphinoyl chloride (15.35 g, 61.7 mmol) in THF (300 cm^3) was added dropwise, while cooled to −78 °C, during 10 min. After the reaction mixture had been stirred at −65 °C for 0.5 h, the cooling bath was removed and the mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure. Water (200 cm^3) was added to the yellow residue, and the mixture was extracted with dichloromethane (3 × 100 cm^3). The combined organic layers were washed with water (2 × 100 cm^3), dried over sodium sulfate, and concentrated under reduced pressure. The solid residue was heated at reflux in ethyl acetate (50 cm^3) for 30 min. After the mixture had been stored at room temperature for 2 days, the solid was separated *via* filtration and dried *in vacuo* at 85 °C for 3 h to afford *title racemate* (±)-**6** (9.81 g, 61% yield) as a powder, m.p. 334–337 °C (decomp.) (Found: C, 77.75; H, 8.4. $C_{44}H_{56}O_2P_2$ requires C, 77.85; H, 8.31%); $\delta_H(CDCl_3)$ 0.80–1.94 (38 H, m, C_6H_{11}), 1.98–2.15 (4 H, m, C_6H_{11}), 2.46 (2 H, q, *J* 11.4, C_6H_{11}), 7.05–7.21 (4 H, m, ArH), 7.38–7.52 (4 H, m, ArH) and 7.82–7.96 (4 H, m, ArH); $\delta_P(CDCl_3)$ 43.94 (s).

Optical Resolution of (±)-*Cy-BINAPO* [(±)-**6**].—To a solution of racemate (±)-**6** (15.44 g, 22.74 mmol) in ethyl acetate (3.45 dm^3) stirred at reflux temperature was added a hot solution of (−)-DBT (8.56 g, 22.7 mmol) in ethyl acetate (63 cm^3). Precipitation occurred within seconds. The mixture was stirred at reflux temperature for an additional 20 min and was then kept at room temperature for 6 days. The precipitate was separated by filtration, washed with ethyl acetate (2 × 50 cm^3), and dried *in vacuo* (0.04 mm Hg) at room temperature for 15 h to give the 1:1 complex (+)-**6**–(−)-DBT [11.81 g, 46% based on (±)-**6** used] as needles, m.p. 230–232 °C (decomp.); $[\alpha]_D^{22}$ −27.8 (*c* 0.99, $CHCl_3$). Recrystallization from a mixture of chloroform (100 cm^3) and ethyl acetate (1.3 dm^3) and subsequent drying of the crystals *in vacuo* at room temperature for 8 h afforded pure *complex* (+)-**6**–(−)-DBT [11.62 g, 45% based on (±)-**6** used], m.p. 227.0–227.5 °C (decomp.); $[\alpha]_D^{26}$ −31.4 (*c* 0.96, $CHCl_3$) (Found: C, 69.9; H, 6.9. $C_{62}H_{70}O_{10}P_2 \cdot MeCO_2Et$ requires C, 70.45; H, 6.99%); $\delta_H(CDCl_3)$ 0.70–1.87 (38 H, m, C_6H_{11}), 1.26 (3 H, t, *J* 7.3, $MeCO_2CH_2\mathit{Me}$), 1.87–2.03 (4 H, m, C_6H_{11}), 2.04 (3 H, s, $\mathit{Me}CO_2Et$), 2.40 (2 H, q, *J* 9.9, C_6H_{11}), 3.70 (2 H, br s, CO_2H) 4.12 (2 H, q, $MeCO_2C\mathit{H}_2Me$), 5.68 (2 H, s, CHOCO), 6.98 (2 H, d, *J* 8.4, ArH), 7.12 (2 H, td, *J* 7.6 and 1.2, ArH), 7.36 (4 H, t, *J* 8.4, ArH), 7.45 (4 H, t, *J* 7.4, ArH), 7.58 (2 H, tt, *J* 7.4 and 1.2, ArH), 7.75 (2 H, d, *J* 8.4, ArH), 7.85 (2 H, dd, *J* 8.4 and 2.3, ArH), 8.09 (2 H, d, *J* 1.6, ArH) and 8.12 (2 H, s, ArH); $\delta_P(CDCl_3)$ 47.85 (s). The crystal structure of this complex was determined by single-crystal X-ray analysis (*vide infra*), and the absolute configuration of enantiomer (+)-**6** follows as *S* from internal comparison with (2*R*,3*R*)-(−)-DBT.

The recrystallized complex (+)-**6**–(−)-DBT (11.28 g, 10.02 mmol) was dissolved in chloroform (150 cm^3). To this was added 1 mol dm^{-3} aq. NaOH (300 cm^3), and the mixture was stirred at room temperature for 2 h. The aqueous layer was extracted with chloroform (2 × 50 cm^3). The combined organic layers were washed with water (400 cm^3 × 3), dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The resultant solid was dried *in vacuo* (0.04 mmHg) at 70 °C for 9 h to give crude enantiomer (+)-**6** [6.63 g, 98% based on complex (+)-**6**–(−)-DBT used and 44% based on (±)-**6** used], m.p. > 305 °C; $[\alpha]_D^{30}$ +39.2 (*c* 1.00, $CHCl_3$). This product was stirred in diethyl ether (25 cm^3) at reflux for 30 min and the mixture was then stored at room temperature for 2 days. Filtration and subsequent drying of the solid at 70 °C (0.04 mmHg) for 7 h gave compound (*S*)-(+)-**6** [5.95 g, 88% based on (+)-**6**–(−)-DBT used and 40% from starting (±)-**6**] as crystals, m.p. 338.0–339.5 °C (decomp.); $[\alpha]_D^{27}$ +42.3 (*c* 1.08, $CHCl_3$).

The mother liquor left after separation of complex (+)-**6**–(−)-DBT was evaporated under reduced pressure to give a solid (13.5 g), m.p. 175–177 °C. This was treated with 1 mol dm^{-3} aq. NaOH (300 cm^3) in chloroform (150 cm^3). The aqueous layer was separated, and extracted with chloroform (100 cm^3). The combined extracts were washed successively with 1 mol dm^{-3} NaOH (100 cm^3) and water (400 cm^3 × 3), dried over sodium sulfate, and evaporated under reduced pressure to afford crude enantiomer (−)-**6** (9.63 g) as a solid, m.p. > 305 °C; $[\alpha]_D^{25}$ −27.3 (*c* 1.91, $CHCl_3$). To a boiling solution of this product in ethyl acetate (500 cm^3) was added a hot solution of (+)-DBT (5.34 g, 14.2 mmol) in ethyl acetate (40 cm^3). The mixture was heated at reflux for 20 min, kept at room temperature for 5 days, and filtered to give adduct (−)-**6**–(+)-DBT [11.32 g, 44% yield based on (±)-**6**], m.p. 226.5–228.0 °C (decomp.); $[\alpha]_D^{26}$ +33.5 (*c* 0.99, $CHCl_3$). Recrystallization (9.76 g, 9.22 mmol) from a mixture of $CHCl_3$ (50 cm^3) and ethyl acetate (500 cm^3) followed by drying of the isolated solid at room temp. (0.06 mmHg) for 8 h afforded pure adduct (−)-**6**–(+)-DBT [9.63 g, 43% yield based on (±)-**6**], m.p. 225.0–226.5 °C (decomp.); $[\alpha]_D^{27}$ +31.9 (*c* 1.00, $CHCl_3$).

This complex (9.53 g) was treated with aq. NaOH in a similar manner as described above to give crude enantiomer (−)-**6** (5.77 g), m.p. > 305 °C; $[\alpha]_D^{26}$ −37.6 (*c* 1.05, $CHCl_3$). This

product was stirred in diethyl ether (25 cm^3) at reflux for 30 min, and the mixture was stored at room temperature for two days. The precipitate was isolated by filtration and dried *in vacuo* at 70 °C for 7 h to afford (*R*)-(−)-**6** [5.19 g, 90% based on adduct (−)-**6**–(+)-DBT used and 39% starting from (±)-**6**] as crystals, m.p. 337.0–338.5 °C (decomp.); $[\alpha]_D^{28}$ −41.7 (*c* 1.04, $CHCl_3$).

Reduction of (S)-(+)-*Cy-BINAPO* [(S)-(+)-**6**] *to* (S)-(+)-*Cy-BINAP* [(S)-(+)-**2**].—This experiment is representative for the reduction of enantiomers (+)-**6** and (−)-**6** to phosphanes (+)-**2** and (−)-**2**, respectively. To a solution of compound (+)-**6** (4.06 g, 5.98 mmol) in xylene (200 cm^3) were added triethylamine (15.0 cm^3, 10.9 g, 108 mmol) and trichlorosilane (10.8 cm^3, 14.6 g, 108 mmol). The mixture was heated at 80 °C for 39 h and at 120 °C for 6 h. To this was added 35% aq. NaOH (40 cm^3) carefully at room temperature and the mixture was stirred for 2 h. The aqueous phase was separated, and extracted with toluene (100 cm^3). The combined organic layers were washed with brine (2 × 150 cm^3), dried over sodium sulfate, and concentrated under reduced pressure. Column chromatography [SiO_2; hexane–AcOEt (5:1 to 4:1)] of the residue thus obtained afforded compound (+)-**2** as a solid (3.52 g, 91%), m.p. 297–299 °C; $[\alpha]_D^{29}$ +92.6 (*c* 1.20, benzene). Recrystallization of this product (3.49 g, 5.40 mmol) from a mixture of toluene (15 cm^3) and methanol (60 cm^3) gave *compound* (S)-(+)-**2** (3.35 g, 87%) as needles, m.p. 295–297 °C; $[\alpha]_D^{28}$ +92.9 (*c* 1.19, benzene); $[\alpha]_D^{28}$ +95.0 (*c* 0.54, toluene). An analytically pure sample was obtained by further recrystallization from toluene, m.p. 297.0–297.7 °C; $[\alpha]_D^{22}$ +96.1 (*c* 0.51, toluene) (Found: C, 81.5; H, 8.8. $C_{44}H_{56}P_2$ requires C, 81.70; H, 8.72%); $\delta_H(CDCl_3)$ 0.64–1.07 (10 H, m, C_6H_{11}), 1.08–1.59 (22 H, m, C_6H_{11}), 1.60–1.96 (10 H, m, C_6H_{11}), 2.03–2.26 (2 H, m, C_6H_{11}), 6.98 (2 H, d, *J* 8.6, ArH), 7.14 (2 H, t, *J* 7.5, ArH), 7.39 (2 H, t, *J* 7.5, ArH), 7.72 (2 H, d, *J* 8.3, ArH), 7.87 (2 H, d, *J* 8.3, ArH) and 7.91 (2 H, d, *J* 8.6, ArH); $\delta_P(CDCl_3)$ −9.20 (s).

Reduction of compound (−)-**6** in a similar manner as described above gave the phosphane (*R*)-(−)-**2** in 81% yield, m.p. 295–297 °C; $[\alpha]_D^{28}$ +95.5 (*c* 0.54, toluene).

Synthesis of 2,2′-*Dibromo*-5,5′,6,6′,7,7′,8,8′-*octahydro*-1,1′-*binaphthyl* **9**.—A mixture of compound **5** (93.7% purity; 35.0 g, 79.6 mmol) and 5% Ru–C catalyst (5.25 g) was vigorously stirred in 1:1 ethyl acetate–95% ethanol (300 cm^3) in a 500 cm^3 autoclave under 120–135 atm of hydrogen at 150 °C for 21 h. Conversion of compound **5** (100%) and product distribution (**9**, 95.7%; **11**, 0.4%; **12**, 2.8%; **13**, 1.1%) were determined by GLC analysis of the reaction mixture with an OV1701 capillary column at 250 °C, and products **11**, **12** and **13** were identified by GLC–MS analysis. The reaction mixture was passed through a pad of Celite at 70 °C. The filtrate was concentrated under reduced pressure to ~30 cm^3 and was then kept at ambient temperature overnight. The precipitate was collected and recrystallized twice from a mixture of ethyl acetate and ethanol (1:4) to afford title product **9** (95.8% purity; 30.6 g, 88%) as crystals, m.p. 146.0–147.0 °C. Column chromatography [SiO_2; hexane–AcOEt (10:1 to 4:1)] of this product afforded, after recrystallization from benzene, analytically pure crystals of *compound* **9**, m.p. 148.4–149.4 °C [Found: C, 57.3; H, 4.7%; M^+ (^{179}Br, ^{181}Br), 420. $C_{20}H_{20}Br_2$ requires C, 57.17; H. 4.80%; M (^{179}Br, ^{181}Br), 420]; $\delta_H(CDCl_3)$ 1.62–1.78 (8 H, m, 6-, 6′-, 7- and 7′-H_2), 2.09 (2 H, dt, $J_{8a,8b}$ 17.7 and $J_{7,8a}$ 6.0, 8- and 8′-H^a), 2.33 (2 H, dt, $J_{8a,8b}$ 17.7 and $J_{7,8b}$ 6.3, 8- and 8′-H^b), 2.70–2.83 (4 H, m, 5- and 5′-H_2), 6.98 (2 H, d, $J_{3,4}$ 8.2, 4- and 4′-H) and 7.42 (2 H, d, 3- and 3′-H); *m/z* 422 [M^+ (^{181}Br, ^{181}Br), 20%], 420 [M^+ (^{179}Br, ^{181}Br), 40], 418 [M^+ (^{179}Br, ^{179}Br), 21] and 260 (M^+ − 2Br, 100).

Preparation of (±)-2,2′-*Bis*(*diphenylphosphinoyl*)-5,5′,6,6′,7,7′,8,8′-*octahydro*-1,1′-*binaphthyl* [(±)-H_8-*BINAPO*, (±)-**10**].—In a 1 dm^3, four-necked flask equipped with a mechanical stirrer, a reflux condenser, a thermometer, and an addition funnel were placed magnesium powder (6.64 g, 0.273 g-atom) and iodine (50 mg). THF (30 cm^3) and 1,2-dibromoethane (1.0 cm^3) were added. The mixture was stirred at room temperature until the colour of iodine faded. To this was added dropwise a solution of dibromide **9** (94.6% purity; 50.00 g, 0.113 mol) in a mixture of THF (120 cm^3) and toluene (450 cm^3) over a period of 5 h during which the temperature was raised from 50 to 90 °C. The mixture was stirred at reflux temperature for an additional hour and then was cooled to −5 °C. To this was added dropwise a solution of diphenylphosphinoyl chloride (62.07 g, 0.262 mol) in toluene (75 cm^3) during 1 h at 0–5 °C. After the addition was complete, the mixture was heated at 80 °C for 16 h and then was cooled to ambient temperature. Aq. hydrochloric acid (0.8 mol dm^{-3}; 150 cm^3) was added. The mixture was stirred at 80 °C for 30 min and was then filtered at room temperature. The precipitate was washed successively with water (100 cm^3 × 3), ethanol (100 cm^3), and toluene–hexane (1:4; 100 cm^3), and dried *in vacuo* to give a solid (57.23 g). Further, the aqueous layer in the above filtrate was separated, and extracted with chloroform (100 cm^3). The combined organic layers were washed successively with 0.4 mol dm^{-3} NaOH (150 cm^3) and water (150 cm^3 × 3), dried over sodium sulfate, and concentrated to a volume of 100 cm^3. The precipitate was collected by filtration to provide an additional crop (5.82 g) of solid. The combined crude products (63.05 g) were treated with H_2O_2 (6% aq., 350 cm^3) in $CHCl_3$ (400 cm^3) at 0 °C for 1 h and at room temperature overnight. The aqueous phase was separated, and extracted with $CHCl_3$ (200 cm^3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated to a solid residue, which was then stirred at reflux in a mixture of ethyl acetate (60 cm^3) and methanol (60 cm^3) for 1 h. The solid was collected *via* filtration at room temperature and was dried at 80 °C (0.06 mmHg) for 20 h to afford *racemate* (±)-**10** as crystals (57.57 g, 77%), m.p. 345.3–346.5 °C (decomp.) (Found: C, 79.6; H, 6.1%; M^+, 662. $C_{44}H_{40}O_2P_2$ requires C, 79.74; H, 6.08%; M, 662); ν_{max}(KBr)/cm^{-1} 3050m, 2935s, 2860m, 2835w, 1585m, 1485m, 1440s, 1390m, 1315m, 1205s and 1110s; $\delta_H(CD_2Cl_2)$ 0.82–0.92 (2 H, m, 7- and 7′-H^a), 1.14–1.24 (2 H, m, 7- and 7′-H^b), 1.40 (2 H, dt, $J_{8a,8b}$ 17.5 and $J_{7,8a}$ 6.0, 8- and 8′-H^a), 1.41–1.51 (4 H, m, 6- and 6′-H_2), 1.65 (2 H, ddd, $J_{8a,8b}$ 17.5, $J_{7,8b}$ 7.5 and *J* 5.4, 8- and 8′-H^b), 2.64–2.77 (4 H, m, 5- and 5′-H_2), 6.933 and 7.007 (2 H, AB, $J_{3,4}$ 7.9, 3- and 4-H), 6.967 and 7.014 (2 H, AB, $J_{3',4'}$ 7.9, 3′- and 4′-H), 7.33–7.38 (4 H, m, Ph), 7.41–7.47 (6 H, m, Ph), 7.48–7.54 (2 H, m, Ph), 7.62–7.69 (4 H, m, Ph) and 7.74–7.82 (4 H, m, Ph); $\delta_C(CDCl_3)$ 22.36, 22.70, 27.16, 30.15, 127.49, 127.63, 127.90, 127.94, 128.02, 128.06, 130.35, 130.49, 130.80, 130.82, 130.93, 130.95, 132.30, 132.39, 132.53 and 132.63; $\delta_P(CDCl_3)$ 28.80 (s); *m/z* 662 (M^+, 28%) and 461 (M^+ − $POPh_2$, 100).

Optical Resolution of (±)-H_8-*BINAPO* [(±)-**10**].—To a solution of racemate (±)-**10** (56.75 g, 85.6 mmol) in chloroform (1.1 dm^3) stirred at reflux was poured a warm solution of (−)-DBT (32.21 g, 85.6 mmol) in ethyl acetate (730 cm^3). Precipitation occurred within seconds. The mixture was stirred at reflux temperature for 30 min and then was stored at room temperature for two days. The precipitate was isolated by filtration and was dried at room temperature (0.06 mmHg) for 7 h to give adduct (−)-**10**–(−)-DBT [42.52 g, 49% based on (±)-**10** used] as crystals, m.p. 236.5–237.5 °C (decomp.); $[\alpha]_D^{25}$ −73.3 (*c* 0.50, EtOH). Recrystallization from a boiling mixture of chloroform (300 cm^3), ethanol (60 cm^3) and ethyl acetate (600 cm^3) afforded pure *adduct* (−)-**10**–(−)-DBT [39.81 g, 46% based on (±)-**10** used], m.p. 238.5–239.5 °C (decomp.); $[\alpha]_D^{25}$ −73.7 (*c* 0.50, EtOH) (Found: C, 72.5; H, 5.05. $C_{62}H_{54}O_{10}P_2$ requires C, 72.93; H, 5.33%); ν_{max}(KBr)/cm^{-1} 3440m, 3055m,

2940m, 2860w, 1735s, 1605w, 1487w, 1465m, 1440m, 1332w, 1317m, 1265s, 1245m, 1176s, 1103s, 1075m, 1028w, 880w, 840w, 755m, 723s, 710w, 698s, 658m, 563m, 535m and 503m; δ_H[$CDCl_3$–CD_3OD (2:1)] 0.94–1.06 (2 H, m, 7- and 7'-H^a), 1.23–1.33 (2 H, m, 7- and 7'-H^b), 1.45–1.55 (4 H, m, 6- and 6'-H_2), 1.60 (2 H, dt, $J_{8a,8b}$ 18.2 and $J_{7,8a}$ 6.0, 8- and 8'-H^a), 1.76 (2 H, dt, $J_{8a,8b}$ 18.2 and $J_{7,8b}$ 6.0, 8- and 8'-H^b), 2.64–2.80 (4 H, m, 5- and 5'-H_2), 6.02 (2 H, s, CHOCO), 7.01 (2 H, d, J 8.5, ArH), 7.02 (2 H, d, J 8.5, ArH), 7.31–7.37 (4 H, m, Ph), 7.42–7.57 (12 H, m, Ph), 7.57–7.72 (10 H, m, Ph) and 8.12 (4 H, dd, J 8.4 and 1.3, Ph); δ_P[$CDCl_3$–CD_3OD (2:1)] 31.21 (s).

The recrystallized adduct (−)-**10**–(−)-DBT (52.33 g, 51.2 mmol) was treated with 1.5 mol dm^{-3} aq. NaOH (1 dm^3) and the mixture was extracted with chloroform (2 × 1 dm^3). The combined extracts were washed successively with 1.5 mol dm^{-3} NaOH (400 cm^3) and water (1.0 dm^3 × 2), dried over sodium sulfate, and evaporated under reduced pressure. The solid obtained was washed with ethyl acetate (130 cm^3) and dried at 70 °C (0.06 mmHg) for 10 h to give enantiomer (*S*)-(−)-**10** [32.48 g, 96% yield based on (−)-**10**–(−)-DBT used and 44% yield starting from (±)-**10**] as crystals, m.p. 253.5–254.5 °C; $[\alpha]_D^{24}$ −33.9 (*c* 0.50, $CHCl_3$). Enantiomeric excess (100%) of (*S*)-(−)-**10** was determined by HPLC analysis with a Chiralcel OG column with (±)-**10** as a reference [hexane–propan-2-ol (9:1); flow rate 1.0 cm^3 min^{-1}; t_R = 8.3 (*S*) and 11.6 min (*R*)].

The mother liquor left after the separation of adduct (−)-**10**–(−)-DBT was evaporated under reduced pressure to give a solid (49.22 g), m.p. 224–226 °C, which was in turn dissolved in $CHCl_3$ (500 cm^3) and treated with 1.5 mol dm^{-3} NaOH (670 cm^3). The aqueous layer was separated, and washed with $CHCl_3$ (2 × 200 cm^3). The combined organic layers were washed successively with 1.5 mol dm^{-3} NaOH (200 cm^3) and brine (300 cm^3 × 2), dried over sodium sulfalte, and evaporated under reduced pressure to afford crude enantiomer (+)-**10** as a solid (33.33 g), m.p. 246–249 °C; $[\alpha]_D^{23}$ +29.6 (*c* 0.47, $CHCl_3$).

To a solution of this product in boiling chloroform (300 cm^3) was added a hot solution of (+)-DBT (16.11 g, 42.8 mmol) in ethyl acetate (350 cm^3). After being stirred at reflux for 30 min, the mixture was kept at room temperature for two days. The precipitate (42.86 g, 49%) was collected, and recrystallized from a mixture of chloroform (300 cm^3), ethanol (60 cm^3) and ethyl acetate (600 cm^3) to afford pure adduct (+)-**10**–(+)-DBT [37.97 g, 43% yield based on (±)-**10** used] as crystals, m.p. 238.5–239.5 °C (decomp.); $[\alpha]_D^{26}$ +73.0 (*c* 0.50, EtOH).

Decomposition of this complex (48.22 g, 47.2 mmol) in a similar manner to that described above provided enantiomer (*R*)-(+)-**10** [29.81 g, 95% yield based on adduct (+)-**10**–(+)-DBT used and 41% yield starting from (±)-**10**] as crystals, m.p. 253.5–254.5 °C; $[\alpha]_D^{24}$ +34.7 (*c* 0.50, $CHCl_3$). The enantiomeric excess was 100% according to HPLC analysis.

Reduction of (S)-(−)-*H_8-BINAPO* [(S)-(−)-**10**] *to* (S)-(−)-*H_8-BINAP* [(S)-(−)-**3**].—In a 2 dm^3, 3-necked flask fitted with a thermometer, a reflux condenser, an argon inlet, and a mechanical stirrer were charged the dioxide (−)-**10** (32.00 g, 48.3 mmol), xylene (1.4 dm^3), triethylamine (83.99 g, 0.830 mol), and trichlorosilane (103.43 g, 0.763 mol). The mixture was stirred for 2.5 h at 100 °C and then for 20 h at reflux. After the reaction mixture had been cooled to room temperature, 35% aq. NaOH (300 cm^3) was added carefully. The resultant mixture was heated at 60 °C until both phases became clear. The aqueous layer was separated at room temperature and extracted with xylene (600 cm^3). The combined organic layers were washed with water (500 cm^3) and concentrated to give an oily residue. Purification by silica gel chromatography [hexane–EtOAc (4:1)] and recrystallization from a mixture of hexane (40 cm^3) and methanol (200 cm^3) afforded the *bisphosphane* (*S*)-(−)-**3** (27.93 g, 92%) as crystals, m.p. 207–208 °C; $[\alpha]_D^{24}$ −72.4 (*c* 0.50, toluene) (Found: C, 83.5; H, 6.4%; M^+ 630. $C_{44}H_{40}P_2$ requires C, 83.79; H, 6.39%; M, 630); ν_{max}(KBr)/cm^{-1} 3055m, 3005w, 2930m, 2860w, 2830w, 1590m, 1480s, 1453m, 1438s, 1390w, 1315m, 1190w, 1095m, 1030m, 814s, 746s, 700s, 552s, 516s, 503s, 490m and 440m; δ_H(CD_2Cl_2) 0.83–0.93 (2 H, m, 7- and 7'-H^a), 1.22–1.33 (2 H, m, 7- and 7'-H^b), 1.39–1.52 (4 H, m, 6- and 6'-H_2), 1.54 (2 H, dt, $J_{8a,8b}$ 17.6 and $J_{7,8a}$ 5.9, 8- and 8'-H^a), 1.83 (2 H, ddd, $J_{8a,8b}$ 17.6, $J_{7,8b}$ 8.7 and J 5.6, 8- and 8'-H^b), 2.64 (2 H, dt, $J_{5a,5b}$ 20.9 and $J_{5a,6}$ 6.6, 5- and 5'-H^a), 2.71 (2 H, dt, $J_{5a,5b}$ 20.9 and $J_{5b,6}$ 6.4, 5- and 5'-H^b), 6.98 (2 H, dt, $J_{3,4}$ 7.9 and $J_{3,8}$ 1.5, 3-and 3'-H), 7.03 (2 H, d, $J_{3,4}$ 7.9, 4- and 4'-H), 7.10–7.22 (10 H, m, Ph) and 7.28–7.34 (10 H, m, Ph); δ_C($CDCl_3$) 22.60, 22.69, 27.44, 29.98, 127.33, 128.00, 128.03, 128.05, 128.19, 128.23, 128.27, 128.57, 128.78, 131.65, 132.62, 132.72, 132.82, 135.10, 135.21 and 135.32; δ_P($CDCl_3$) −15.34 (s); *m/z* 630 (M^+, 4%), 446 ($M^+ - PPh_2 + 1$, 42) and 445 ($M^+ - PPh_2$, 100).

Reduction of (R)-(+)-*H_8-BINAPO* [(R)-(+)-**10**] *to* (R)-(+)-*H_8-BINAP* [(R)-(+)-**3**].—In a similar manner as described above, dioxide (*R*)-(+)-**10** (33.89 g, 51.1 mmol) was reduced with a mixture of trichlorosilane (78.0 g, 0.576 mol) and triethylamine (63.0 g, 0.620 mol) in xylene (1.4 dm^3) to bisphosphane (*R*)-(+)-**3** (22.62 g, 70%) as crystals, m.p. 207–208 °C; $[\alpha]_D^{24}$ +72.4 (*c* 0.52, toluene).

For all the enantiomers (+)-**3**, (−)-**3**, (+)-**10**, and (−)-**10**, CD spectra were measured in ethanol (*c* 1.0 × 10^{-3}–6.0 × 10^{-3}).* Furthermore, the absolute configuration of compounds (+)-**3** and (+)-**10** have been assigned to be *R* by comparison of their CD spectra with those of (*R*)-(−)- and (*S*)-(+)-BIPHEMP [(*R*)-(−)- and (*S*)-(+)-**15**], and that of the dioxide of compound (*R*)-(−)-**15**, respectively, since the absolute configurations of compounds (−)- and (+)-**15** have been confirmed by synthesis as well as by X-ray analysis.[17]

Preparation of 2,2'-*Bis*(*dicyclohexylphosphinoyl*)-(±)-5,5',6,6',7,7',8,8'-*octahydro*-1,1'-*binaphthyl* [(±)-*Cy-H_8-BINAPO*, (±)-**16**].—To a solution of dibromide **9** (94.6% purity, 27.70 g; 62.4 mmol) in a mixture of THF (540 cm^3) and diethyl ether (360 cm^3) was added *tert*-BuLi (92.6 cm^3 of a 1.77 mol dm^{-3} pentane solution, 0.164 mol) *via* a syringe at −78 °C. The light yellow solution was stirred at −78 °C for 7 h. Additional *tert*-BuLi (92.6 cm^3, 0.164 mol) was added in two portions and the mixture was stirred for another 7 h. GLC monitoring showed that the dilithiation was almost complete. An emulsion of dicyclohexylphosphinoyl chloride (43.62 g, 0.175 mol) in THF (500 cm^3) was added at −78 °C during 30 min. After the resultant dark brown solution had been stirred at −78 °C for 30 min, the cooling bath was removed and the mixture was further stirred at room temperature for 34 h. The solvents were removed under reduced pressure and the residue was taken up with $CHCl_3$ (800 cm^3). The extract was washed successively with brine (500 cm^3 × 2) and water (500 cm^3), dried over Na_2SO_4, and concentrated under reduced pressure. Column chromatography [SiO_2; hexane–acetone (9:1 to 2:1)] of the residue afforded, after washing with hot hexane (35 cm^3 × 2), *racemate* (±)-**16** (16.88 g, 38%) as crystals, m.p. 271–273 °C (decomp.) (Found: C, 74.5; H, 9.5%; M^+, 686. $C_{44}H_{64}O_2P_2 \cdot H_2O$ requires C, 74.97; H, 9.43%. $C_{44}H_{64}O_2P_2$ requires M, 686); δ_H($CDCl_3$) 1.01–1.53 (20 H, m), 1.55–2.13 (32 H, m), 2.34 (2 H, dt, J 16.7 and 5.0), 2.48 (2 H, qt, J 12.2 and 2.5), 2.75–2.92 (4 H, m, 5- and 5'-H_2) and 6.97–7.16 (4 H, m, 3-, 3'-, 4- and 4'-H); δ_P($CDCl_3$) 44.02 (s); *m/z* 687 (M^+ + 1, 21%), 686 (M^+, 43), 604 (M^+

* For CD spectra of (*R*)-(+)-**3**, (*S*)-(−)-**3**, (*R*)-(−)-**4**, (*S*)-(+)-**4**, (*R*)-(+)-**10**, (*S*)-(−)-**10**, (*R*)-(−)-**16**, and (*S*)-(+)-**16**, see Supplementary Material [SUP No. 57019 (4 pp)] (see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, issue 1).

$-C_6H_{11}+1$, 52), 603 ($M^+ - C_6H_{11}$, 100), 521 ($M^+ - 2C_6H_{11}+1$, 60), 474 [$M^+ - PO(C_6H_{11})_2+1$, 100], 391 [$M^+ - PO(C_6H_{11})_2 - C_6H_{11}+1$, 100] and 262 [$M^+ - 2PO(C_6H_{11})_2+2$, 31].

In addition to racemate (±)-**16**, crops (6.63 g, ~22%) of 2-(dicyclohexylphosphinoyl)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl [m.p. 202.5–204.5 °C (Found: M^+, 474. $C_{32}H_{43}OP$ requires M, 474); $\delta_P(CDCl_3)$ 47.39 (s); *m/z* 475 ($M^+ + 1$, 40%), 474 (M^+, 100), 392 ($M^+ - C_6H_{11}+1$, 48) and 391 ($M^+ - C_6H_{11}$, 30)] and (1.62 g, 10%) of 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl [**13**, m.p. 94.5–95.5 °C (lit.,[35] 93.5–94 °C)] were obtained. The former was contaminated with small amounts of unidentified impurities.

Optical Resolution of (±)-*Cy-H*$_8$-*BINAPO* [(±)-**16**].—To a boiling solution of racemate (±)-**16** (15.35 g, 21.77 mmol) in ethyl acetate (600 cm^3) was added a hot solution of acid (−)-DBT (8.41 g, 22.4 mmol) in ethyl acetate (70 cm^3). After the mixture had been stirred at reflux for 10 min, a precipitate began to deposit. The mixture was stirred at reflux for an additional hour and was then kept at ambient temperature for 5 days. The precipitate was separated through filtration, washed with ethyl acetate (2 × 25 cm^3), and dried *in vacuo* (0.06 mmHg) at room temperature for 7 h to give the 1:1 complex (+)-**16**–(−)-DBT [8.81 g, 38% based on (±)-**16** used] as needles, m.p. 233–235 °C (decomp.); $[\alpha]_D^{26}$ −4.4 (*c* 1.19, $CHCl_3$). Recrystallization from a mixture of chloroform (30 cm^3) and ethyl acetate (250 cm^3) afforded, after drying *in vacuo* at room temperature for 7 h, pure *adduct* (+)-**16**–(−)-DBT [8.48 g, 37% based on (±)-**16** used], m.p. 237–238 °C (decomp.); $[\alpha]_D^{30}$ −3.0 (*c* 1.17, $CHCl_3$) [Found: C, 70.7; H, 7.5. $C_{62}H_{78}O_{10}P_2$·(AcOEt)$_{0.2}$ requires C, 70.97; H, 7.54%]; $\delta_H(CDCl_3)$ 0.85–1.40 (20 H, m), 1.40–1.98 (32 H, m), 2.04 (0.6 H, s, 0.2 equiv. of $MeCO_2Et$), 2.20 (2 H, dt, *J* 16.5 and 5.0), 2.36 (2 H, q, *J* 10.9), 2.53–2.80 (4 H, m), 4.13 (0.4 H, q, 0.2 equiv. of $AcOCH_2Me$), 4.45 (2 H, br s, CO_2H), 5.81 (2 H, s, CHOCO), 6.92 (2 H, s, ArH), 6.95 (2 H, s, ArH), 7.44 (4 H, t, *J* 7.5, ArH), 7.57 (2 H, dt, *J* 7.5 and 1.3, ArH), 8.12 (2 H, d, *J* 1.3, ArH) and 8.15 (2 H, s, ArH); $\delta_P(CDCl_3)$ 48.80 (s).

The recrystallized adduct (+)-**16**–(−)-DBT (8.35 g, 7.86 mmol) was treated with 1.5 mol dm^{-3} aq. Na_2CO_3 (250 cm^3) and chloroform (150 cm^3), and the aqueous layer was extracted with chloroform (100 cm^3). The combined organic layers were washed successively with 1.5 mol dm^{-3} Na_2CO_3 (70 cm^3) and brine (200 cm^3 × 3), dried over anhydrous sodium sulfate, and evaporated under reduced pressure. The resultant residue (5.79 g) was dissolved in a mixture of ethyl acetate (10 cm^3) and diethyl ether (5 cm^3). Removal of the solvent and drying at 70 °C (0.06 mmHg) for 13 h gave compound (*S*)-(+)-**16** [5.23 g, 94% yield based on (+)-**16**–(−)-DBT used and 35% yield starting from (±)-**16**], m.p. 273.5–275.0 °C; $[\alpha]_D^{26}$ +41.8 (*c* 1.24, $CHCl_3$).

The mother liquor left after removal of adduct (+)-**16**–(−)-DBT was evaporated under reduced pressure to give a solid, m.p. 210–215 °C (decomp.); $[\alpha]_D^{28}$ −65.5 (*c* 3.25, $CHCl_3$). This was treated with 1 mol dm^{-3} aq. NaOH (300 cm^3) and chloroform (150 cm^3). The aqueous layer was extracted with chloroform (100 cm^3). The combined organic layers were washed successively with 1 mol dm^{-3} NaOH (100 cm^3) and brine (200 cm^3 × 3), dried over sodium sulfate, and evaporated under reduced pressure to afford crude compound (−)-**16** (9.75 g) as a solid, $[\alpha]_D^{28}$ −22.5 (*c* 1.02, $CHCl_3$).

To a boiling solution of this solid in ethyl acetate (300 cm^3) was added a hot solution of acid (+)-DBT (4.21 g, 11.2 mmol) in ethyl acetate (35 cm^3). The mixture was refluxed for 40 min, kept at room temperature for 2 days, and filtered. The collected solid was washed with ethyl acetate (2 × 25 cm^3) and dried at room temperature (0.06 mmHg) for 12 h to give adduct (−)-**16**–(+)-DBT [8.75 g, 38% yield based on (±)-**16**], m.p. 232.5–234.0 °C (decomp.); $[\alpha]_D^{27}$ +4.4 (*c* 1.16, $CHCl_3$). Recrystallization (1.82 g) from a mixture of $CHCl_3$ (6 cm^3) and ethyl acetate (50 cm^3) following by drying at room temp. (0.06 mmHg) for 7 h gave pure adduct (−)-**16**–(+)-DBT [1.78 g, 37% based on (±)-**16**], m.p. 235.5–237.5 °C (decomp.); $[\alpha]_D^{30}$ +3.5 (*c* 1.20, $CHCl_3$). This complex (1.73 g, 1.63 mmol) was treated with aqueous 1.5 mol dm^{-3} Na_2CO_3 (50 cm^3) in a similar manner as described above to give compound (*R*)-(−)-**16** [1.08 g, 97% based on the complex and 35% based on (±)-**16** used] as crystals, m.p. 274.5–276.0 °C; $[\alpha]_D^{30}$ −41.7 (*c* 1.17, $CHCl_3$).

As described for the corresponding enantiomers of compounds **3** and **10**, CD spectra have been determined for (+)-**4**, (−)-**4**, (+)-**16** and (−)-**16**, respectively, in ethanol, and the absolute configuration of (−)-**4** and (−)-**16** are assigned to be *R* by comparison of their CD spectra with those of (*R*)-(+)-**3** and (*R*)-(+)-**10** as well as those of (*R*)-(−)-**15** and its dioxide.*[,17]

Reduction of (R)-(−)-*Cy-H*$_8$-*BINAPO* [(R)-(−)-**16**] *to* (R)-(−)-*Cy-H*$_8$-*BINAP* [(R)-(−)-**4**].—This operation illustrates the reduction of enantiomers (+)- and (−)-**16** to (+)- and (−)-**4**, respectively. To a solution of dioxide (−)-**16** (0.938 g, 1.33 mmol) in xylene (40 cm^3) were added triethylamine (2.21 g, 21.8 mmol) and trichlorosilane (2.96 g, 21.8 mmol) *via* syringes. The mixture was stirred at 80 °C for 53 h and 120 °C for 17 h, and then was cooled to room temperature. Aq. NaOH (20%; 20 cm^3) was added, and the mixture was stirred at room temperature for 2 h. The aqueous layer was separated, and extracted with toluene (40 cm^3). The combined organic layers were washed with brine (100 cm^3), dried over Na_2SO_4, and evaporated under reduced pressure. Purification of the residue by column chromatography [SiO_2; hexane–ethyl acetate (5:1 to 4:1)] gave crude bisphosphane (−)-**4** (0.980 g) as a solid. This solid was recrystallized from hexane (22 cm^3) to give, after drying at 80 °C (0.06 mmHg) for 13 h, compound (*R*)-(−)-**4** (0.350 g, 40%) as needles, m.p. 237.0–238.0 °C; $[\alpha]_D^{29}$ −72.9 (*c* 0.66, toluene). Concentration of the mother liquor of recrystallization to ~3 cm^3 and filtration of the residue afforded an additional crop (0.401 g; total 86%) of enantiomer (R)-(−)-**4**, m.p. 237.5–238.5 °C; $[\alpha]_D^{28}$ −71.6 (*c* 0.66, toluene) (Found: C, 80.45; H, 9.9. $C_{44}H_{64}P_2$ requires C, 80.69; H, 9.84%); $\delta_H(CDCl_3)$ 0.95–1.35 (20 H, m), 1.35–1.87 (28 H, m), 1.87–2.24 (8 H, m), 2.73–2.93 (4 H, m), 7.05 (2 H, d, $J_{3,4}$ 7.9, 3- and 3′-H) and 7.27 (2 H, d, 4- and 4′-H); $\delta_P(CDCl_3)$ −10.43 (s).

Reduction of compound (*S*)-(+)-**16** in a similar manner as described above afforded compound (*S*)-(+)-**4** in 85% yield, m.p. 235.5–236.0 °C; $[\alpha]_D^{22}$ +73.8 (*c* 0.63, toluene).

Preparation of [*Rh*{(S)-(+)-*Cy-binap*}(*cod*)]*ClO*$_4$[(S)-**17**].—To a solution of $[RhCl(cod)]_2$ (81.6 mg, 0.190 mmol) in acetone (20 cm^3) was added $AgClO_4$ (78.7 mg, 0.380 mmol), and the mixture was stirred at room temperature for 1 h. The precipitate deposited was removed by filtration and washed with acetone (2 × 1 cm^3). To the combined light yellow filtrate and washings was added bisphosphane (*S*)-**2** (261.2 mg, 0.404 mmol). The resulting mixture was stirred at ambient temperature for 2 h and was then filtered through a Celite pad. The orange filtrate was concentrated to ~2 cm^3. To this was slowly added diethyl ether (20 cm^3) and the mixture was kept at room temperature for 24 h. The crystals were separated, washed with diethyl ether (2 cm^3 × 2) and hexane (2 cm^3 × 2), and dried *in vacuo* at room temperature for 24 h to give *complex* (S)-**17** (335.1 mg, 87%) as orange crystals, m.p. 200–203 °C (decomp.) [Found: C, 62.9;

* For CD spectra of (*R*)-(+)-**3**, (*S*)-(−)-**3**, (*R*)-(−)-**4**, (*S*)-(+)-**4**, (*R*)-(+)-**10**, (*S*)-(−)-**10**, (*R*)-(−)-**16**, and (*S*)-(+)-**16**, see Supplementary Material [SUP No. 57019 (4 pp)] (see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, issue 1).

H, 7.25. $C_{52}H_{68}ClO_4P_2Rh\cdot(C_4H_{10}O)_{0.25}\cdot(C_3H_6O)_{0.1}\cdot(H_2O)_2$ requires C, 62.90; H, 7.43%]; $\delta_H(CDCl_3)$ −1.30 to −1.01 (1 H, m), −0.23–0.05 (2 H, m), 0.39–0.74 (4 H, m), 0.74–2.18 (41 H, m), 1.23 [1.5 H, t, *J* 6.9, 0.25 equiv. of $(MeCH_2)_2O$], 2.18–2.37 (2 H, m), 2.20 (0.6 H, s, 0.1 equiv. of Me_2CO), 2.37–2.54 (2 H, m), 2.54–2.93 (3 H, m), 3.01–3.25 (1 H, m), 3.43 [1 H, q, 0.25 equiv. of $(MeCH_2)_2O$], 4.32–4.55 (2 H, m, =CH of COD), 5.18–5.42 (2 H, m, =CH of COD), 6.64 (1 H, d, *J* 8.6, ArH), 7.07–7.37 (3 H, m, ArH), 7.49 (1 H, t, *J* 7.3, ArH), 7.60 (1 H, t, *J* 6.8, ArH), 7.87–8.12 (3 H, m, ArH) and 8.18–8.37 (3 H, m, ArH); $\delta_P(CDCl_3)$ 12.14 (dd, $J_{Rh,Pa}$ 145.7 and $J_{Pa,Pb}$ 19.9) and 31.12 (dd, $J_{Rh,Pb}$ 125.2).

Single crystals of complex (*S*)-**17**·$(MeOH)_2$ suitable for *X*-ray studies were grown from a saturated solution of this product in methanol at low temperature.

Preparation of [*Rh*{(S)-H_8-*binap*}(*cod*)]ClO_4 [(S)-**18**].—*Method 1.* A mixture of bisphosphane (*S*)-**3** (0.411 g, 0.652 mmol) and $[Rh(cod)_2]ClO_4$ (0.225 g, 0.537 mmol) was dissolved in CH_2Cl_2 (3.0 cm^3). The resulting orange-yellow solution was stirred at room temperature for 1 h and was then concentrated to ~ 1.5 cm^3. Diethyl ether (6 cm^3) was added, and the mixture was stored at room temperature for two days. The precipitate was collected, and dried *in vacuo* at room temperature to give complex (*S*)-**18** (0.480 g, 95%) as an orange-yellow solid. This solid (0.450 g) was dissolved in methanol (50 cm^3). The insoluble materials were removed by filtration through a Celite pad, and the filtrate was evaporated under reduced pressure to afford complex (*S*)-**18** (0.410 g, 87%) as bright orange microcrystals, m.p. 213 °C (decomp.); $\delta_H(CDCl_3)$ 1.10–1.25 (2 H, m), 1.33 (2 H, dt, *J* 18.4 and 5.7), 1.34–1.47 (4 H, m), 1.48–1.58 (2 H, m), 1.75–1.85 (2 H, m), 2.03–2.14 (2 H, m), 2.20–2.38 (6 H, m), 2.52 (2 H, quin, *J* 7.7), 2.58 (2 H, dt, *J* 17.3 and 5.7), 4.25–4.34 (2 H, m, =CH of COD), 4.64–4.72 (2 H, m, =CH of COD), 6.91 (2 H, d, $J_{3,4}$ 8.1, 4- and 4′-H), 7.31 (4 H, t, *J* 7.1, Ph), 7.39 (2 H, t, *J* 7.0, Ph) and 7.45–7.66 (16 H, m, 3- and 3′-H and Ph); $\delta_P(CDCl_3)$ 25.01 (d, $J_{Rh,P}$ 146.3).

Orange prisms of *compound* (S)-**18**·CH_2Cl_2 suitable for a single-crystal X-ray structure determination were obtained by diffusion of diethyl ether (15.0 cm^3) into a solution of this product (75.0 mg) in a mixture of CH_2Cl_2 (1.0 cm^3) and MeOH (0.5 cm^3) (Found: C, 62.4; H, 5.3. $C_{52}H_{52}ClO_4P_2Rh\cdot CH_2Cl_2$ requires C, 62.03; H, 5.30%).

Method 2. From $[RhCl(cod)]_2$ (0.364 g, 0.738 mmol) $AgClO_4$ (0.306 g, 1.48 mmol), and bisphosphane (*S*)-**3** (0.934 g, 1.48 mmol), orange microcrystals of complex (*S*)-**18** (1.31 g, 94%) were prepared in a similar manner as described for complex (*S*)-**17**. The analytical data were consistent with those of complex (*S*)-**18** prepared by Method 1.

Preparation of [*RuI*{(S)-H_8-*binap*}(p-*cymene*)]*I* [(S)-**19**].—To a mixture of bisphosphene (*S*)-**3** (0.304 g, 0.481 mmol) and $[RuI_2(p\text{-cymene})]_2$ (0.236 g, 0.241 mmol) were added CH_2Cl_2 (16 cm^3) and MeOH (32 cm^3). The resulting brown solution was stirred at reflux temperature for 2.5 h and was then passed through a Celite pad at room temperature. The filtrate was concentrated under reduced pressure and dried *in vacuo* at room temperature for 15 h to give *complex* (S)-**19** (0.530 g, 96%) as a brown-violet solid which contains 0.3 mol equiv. of CH_2Cl_2 as the crystal solvent, m.p. 141–144 °C (decomp.) (Found: C, 56.7; H, 4.8. $C_{54}H_{54}I_2P_2Ru\cdot(CH_2Cl_2)_{0.3}$ requires C, 56.94; H, 4.80%); $\delta_H(CDCl_3)$ 0.82–0.97 (2 H, m), 0.99 (3 H, d, *J* 6.8, CH*Me*), 1.05–1.17 (1 H, m), 1.32 (3 H, d, *J* 7.0, CH*Me*), 1.36–1.58 (6 H, m), 1.59–1.72 (2 H, m), 1.96 (3 H, s, Me), 2.20–2.32 (2 H, m), 2.50–2.65 (3 H, m), 3.27–3.39 (1 H, m, CH), 6.45 (1 H, d, *J* 6.6, ArH of *p*-cymene), 6.64 (1 H, d, *J* 7.9, ArH of *p*-cymene), 6.74 (1 H, d, *J* 6.6, ArH of *p*-cymene), 6.89 (1 H, d, *J* 7.9, ArH of *p*-cymene) and 6.99–8.00 (24 H, m, ArH); $\delta_P(CDCl_3)$ 23.24 (d, $J_{Pa,Pb}$ 60.1) and 39.77 (d).

Preparation of Ru(OAc)$_2${(S)-H_8-*binap*} [(S)-**20**].—To a mixture of $[RuCl_2(cod)]_n$ [0.985 g, 3.38 mmol per $RuCl_2(cod)$] and bisphosphane (*S*)-**3** (2.40 g, 3.81 mmol) were added toluene (100 cm^3) and triethylamine (2.0 cm^3, 14 mmol). The brown suspension was stirred at reflux temperature for 15 h, and the resulting clear red-brown solution was cooled to room temperature. The solvent was removed under reduced pressure to give a red-brown solid (3.25 g). To this solid (1.94 g) were added anhydrous sodium acetate (0.98 g, 12 mmol) and *tert*-butyl alcohol (50 cm^3). The mixture was stirred and heated at reflux for 10 h and was then concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (40 cm^3) and insoluble material was removed *via* filtration through a pad of Celite. The filtrate was concentrated under reduced pressure, and the green solid residue was extracted with absolute ethanol repeatedly (total 60 cm^3). The combined extracts were evaporated to dryness under reduced pressure to give a green solid. This was recrystallized from a mixture of toluene (8 cm^3) and hexane (16 cm^3) to afford, after drying *in vacuo* at room temperature for 20 h, *complex* (S)-**20** (1.48 g, 79%). An analytically pure sample was obtained on a second recrystallization from toluene–hexane (1:7), m.p. 165–170 °C (decomp.) [Found: C, 69.4; H, 6.4. $C_{48}H_{46}O_4P_2Ru\cdot(C_7H_8)_{0.3}\cdot(C_6H_{14})_{0.6}$ requires C, 69.41; H, 6.16%]; $\delta_H(CDCl_3)$ 0.88 (3.6 H, t, *J* 6.8, 0.6 equiv. of *Me*$[CH_2]_4$*Me*), 0.99–1.17 (4 H, m), 1.22–1.50 (10.8 H, m, aliphatic protons including 0.6 equiv. of Me$[CH_2]_4$Me), 1.61 (6 H, s, OAc), 1.65–1.79 (2 H, m), 2.23–2.37 (2 H, m), 2.36 (0.9 H, s, 0.3 equiv. of Ph*Me*), 2.52 (2 H, dt, *J* 16.5 and 5.6), 6.75 (2 H, d, *J* 8.4, ArH), 7.08 (4 H, t, *J* 7.3, ArH), 7.15–7.32 (7.5 H, m, ArH including 0.3 equiv. of PhMe), 7.33–7.46 (8 H, m, ArH) and 7.65–7.75 (4 H, m, ArH); $\delta_P(CDCl_3)$ 64.81 (s).

Asymmetric Hydrogenation of Methyl 2-*Benzamidomethyl*-3-*oxobutanoate* [(±)-**21**].[5a]—This manipulation is illustrative for the asymmetric hydrogenation of racemate (±)-**21**. To a mixture of racemate (±)-**21** (3.56 g, 14.3 mmol) and [RuI{(*S*)-H_8-binap}(*p*-cymene)]I [(*S*)-**19**] (10.0 mg, 8.73 × 10^{-3} mmol) was added dry dibromomethane (0.89 cm^3) and methanol (6.20 cm^3) under nitrogen. The resulting mixture was transferred into a 100 cm^3 autoclave and was stirred under an initial hydrogen pressure of 54 atm at 65 °C (50 atm when at room temp.) for 20 h. Conversion (100%) of keto ester **21** and the ratio of products *syn*-**23** to *anti*-**23** (77.7:25.3, 52% d.e.) were determined by HPLC analysis of the orange-yellow reaction mixture on a Cosmosil 5SL column [eluent: hexane–chloroform–methanol (90:10:2); flow rate 2.5 cm^3 min^{-1}; t_R: 7.38 (**21**), 14.23 (*syn*-**23**) and 18.24 min (*anti*-**23**)]. The reaction mixture was evaporated to obtain an orange-yellow, oily residue (3.68 g), which was then chromatographed on silica gel eluted with hexane–propan-2-ol (85:15) to give a mixture of the two diastereoisomers *syn*-**23** and *anti*-**23** (3.35 g, 93%) as an oil. Enantiomeric excesses of *syn*-**23** [97% (2*R*,3*S*)] and *anti*-**23** [95% (2*S*,3*S*)] were measured by HPLC analysis of the sample obtained on esterification of the above mixture of *syn*-**23** and *anti*-**23** with 1.5 mol equiv. of (*R*)-MTPA[36] using a Cosmosil 5SL column [eluent: hexane–THF–methanol (1000:100:1); flow rate 1.0 cm^3 min^{-1}; t_R = 50.17, 52.74, 63.93 and 76.91 min for the (*R*)-MTPA esters of *syn*-(2*S*,3*R*)-**23**, *syn*-(2*R*,3S)-**23**, *anti*-(2*R*,3*R*)-**23**, and *anti*-(2*S*,3*S*)-**23**, respectively]. The ratio of [*syn*-(2*S*,3*R*)-**23** + *syn*-(2*R*,3*S*)-**23**] to [*anti*-(2*R*,3*R*)-**23** + *anti*-(2*S*,3*S*)-**23**] was 76.7:23.3 (53% d.e.) under these conditions.

Asymmetric Hydrogenation of Geraniol **22**.[29]—A solution of geraniol **22** (8.41 g, 9.5 cm^3, 54.5 mmol) and $Ru(OAc)_2$\{(*S*)-H_8-binap\}[(*S*)-**20**] (9.3 mg, 10 × 10^{-3} mmol) in methanol (9.5

Table 4 Experimental crystallographic details for complexes (*S*)-**6**-(−)-DBT, (*S*)-**17** and (*S*)-**18**

	(*S*)-**6**-(−)-DBT	(*S*)-**17**	(*S*)-**18**
Recrystallized from	$CHCl_3$–AcOEt	MeOH	CH_2Cl_2–MeOH–Et_2O
Formula	$C_{62}H_{70}O_{10}P_2{\cdot}C_4H_8O_2$	$C_{52}H_{68}ClO_4P_2Rh{\cdot}(MeOH)_2$	$C_{52}H_{52}ClO_4P_2Rh{\cdot}CH_2Cl_2$
Relative formula mass	1125.29	1021.50	1026.22
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a(Å)	22.625(2)	24.813(6)	14.444(2)
b(Å)	20.949(3)	17.263(3)	15.335(2)
c(Å)	12.873(1)	11.836(2)	11.208(3)
β(°)			94.68(1)
Z	4	4	2
V(Å^3)	6101(1)	5070(2)	2474(1)
D_{calc} (g cm^{-3})	1.225	1.338	1.377
Diffractometer	Rigaku AFC 5R	Rigaku AFC 5	Rigaku AFC 5R
Radiation	Cu-Kα	Mo-Kα	Mo-Kα
Reflections measured	$+h, +k, +l$	$+h, +k, +l$	$\pm h, +k, +l$
Crystal size (mm)	0.22 × 0.35 × 0.48	0.20 × 0.28 × 0.34	0.35 × 0.37 × 0.40
μ (cm^{-1})	1.38	4.95	5.19
Scan mode	2θ–ω	$\omega(2\theta \leq 15°)$ 2θ–$\omega(15 < 2\theta \leq 60°)$	2θ–ω
Temp. (T/°C)	25	−120	25
Scan speed (deg min^{-1})	4	3	4
Scan width (deg)	1.2 + 0.15 tan θ	1.0 + 0.5 tan θ	1.2 + 0.5 tan θ
Bkgd count (s)	3	8	5
$2\theta_{max}$ (deg)	120	60	60
Data collected	5233	9121	6844
Unique data [$\|F_o\| > 3\sigma(F_o)$]	3235	5700	5168
No. of variables	994	802	756
R	0.067	0.053	0.070
R_w [a]	0.079	0.063	0.096
a [a]	0.03	0.015	0.03
GOF [b]	2.56	1.51	4.66
Δ (e Å^{-3})	0.48	0.71	1.66

[a] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. The weighting scheme $1/w = \sigma_c^2 + (a|F_o|)^2$ was employed. [b] Goodness-of-fit.

cm^3) was charged on a 100 cm^3 autoclave. Hydrogen (100 atm) was introduced and the mixture was stirred at 25 °C for 5 h. Conversion (100%) of geraniol **22** and chemical selectivities of citronellol (**25**, 98.5%) and dihydrocitronellol (**26**, 1.5%) were determined by GLC analysis of the reaction mixture [PEG-HT capillary column, starting from 100 °C to 200 °C at a rate of 5 °C min^{-1}; t_R: 6.87 (**26**), 8.65 (**25**), and 10.02 min (**22**)]. The solvent was removed from the reaction mixture under reduced pressure and the resulting residue was distilled *in vacuo* (72 °C, 0.2 mmHg) to give citronellol (*R*)-**25** as an oil (7.99 g, 94%), which was contaminated with 1.5% of dihydrocitronellol **26**, $[\alpha]_D^{27}$ +5.11 (*c* 20.0, $CHCl_3$) (98% optical purity) {lit.,[29] $[\alpha]_D^{25}$ +5.12 (*c* 21.0, $CHCl_3$) for (*R*)-**25** in 98% e.e.; lit.,[37] $[\alpha]_D^{20}$ +2.5 (neat), and lit.,[38] $[\alpha]_D$ +4.0 (*c* 1.6, $CHCl_3$) for (*R*)-**26**}.

X-Ray Structure Determinations.—(S)-(+)-*Cy-BINAPO*-(−)-*DBT* [(+)-**6**-(−)-*DBT*]. Needles of adduct (+)-**6**-(−)-DBT· AcOEt, which were obtained on recrystallization from hot ethyl acetate, were sealed in a thin-walled glass capillary under a mixture of argon and ethyl acetate vapour and were mounted on a Rigaku AFC-5 difractometer.

Preliminary measurements of several crystals yielded rough cell dimensions and peak profiles. A suitable crystal with dimensions of 0.22 × 0.35 × 0.58 mm was finally mounted on the diffractometer and centred in the beam. An automatic peak search and indexing procedure yielded the primitive cell. The pertinent details of data collection and the final cell dimensions, which were obtained from a least-squares refinement of 2θ-values of 50 independent reflections in the range of $30° < 2\theta < 40°$, are given in Table 4.

The 3235 unique raw intensity data with $|F_o| > 3\sigma(F_o)$ were converted into values of the structure factor by correction for Lorentz and polarization effects. An azimuthal scan of a reflection having χ near 90° indicated that no correction for absorption was necessary. Inspection of the standard three reflections measured after every 100 reflections showed no systematic variation in intensity. Correction for extinction effect was not made.

The systematic absences indicated the space group being $P2_12_12_1$. The structure was solved by direct methods (MULTAN-78). A series of standard block-diagonal least-squares refinements and Fourier synthesis revealed all non-hydrogen atoms of the complex and solvated ethyl acetate. The absolute structure of dioxide (+)-**6** was determined as *S* based on the absolute configuration of (2*R*,3*R*)-(−)-DBT. Hydrogen atoms were located by the difference Fourier synthesis or by calculated methods. All non-hydrogen atoms (anisotropic) and hydrogen atoms (as isotropic temperature factors) were refined to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.067$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}} = 0.079$. A weighting scheme, $1/w = \sigma_c^2 + (0.03|F_o|)^2$, was employed, where σ_c, defined as $\sigma_c = (N)^{\frac{1}{2}}$, is a counting statistics error with Gaussian distribution function $P(N) = (1/2N)^{\frac{1}{2}} \exp[-(N - \bar{N})^2/2N]$. Final difference Fourier maps indicated no significant peak remained which were greater than 0.48 e Å^{-3}. Crystallographic calculations were performed at the IMS Computer Center by using the UNICS-III program system. Tables of fractional atomic coordinates, bond distances, and bond angles, together with other crystallographic data, have been deposited at the Cambridge Crystallographic Data Centre.*

[*Rh*{(S)-(+)-*Cy-binap*}(*cod*)]ClO_4 [(S)-**17**]. Orange crystals of (*S*)-**17**·$(MeOH)_2$ were sealed in thin-walled glass capillaries under argon. Upon exposure to X-rays at room temperature, the crystal became cloudy and its diffraction profiles were noted

* For full details of the CCDC deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, issue 1.

to be significantly broadened with decreasing intensities. Therefore, diffraction data were collected at −120 °C. Intensities were measured by ω-scan in the range 2–15° and 2θ–ω-scan in the range 15–60°. Cell parameters and details of data collection are given in Table 4.

The systematic absences of reflections indicated that the space group was $P2_12_12_1$. The position of the rhodium atom was determined by the Patterson map. The absolute structure of the complex was defined on the basis of the absolute configuration of the free ligand (*S*)-**2** as estalished by X-ray structure analysis of adduct (*S*)-(+)-**6**–(2*R*,3*R*)-(−)-DBT (*vide supra*). Most of the atoms appeared on the resulting Fourier map, and the remaining atoms were located by a series of standard block-diagonal least-squares refinements and Fourier synthesis. After the anisotropic stage of refinement had been reached, atoms of ClO_4^-, two solvated methanols, and some hydrogen atoms were located on a difference Fourier synthesis and the remaining hydrogen atoms were placed at calculated positions. The final refinement cycle refined to $R = 0.053$ and $R_w = 0.063$. Tables of fractional atomic coordinates, bond distances, and bond angles, together with other crystallographic data, have been deposited at the Cambridge Crystallographic Data Centre.*

[*Rh*{(S)-H_8-*binap*}(*cod*)] ClO_4 [(S)-**18**]. One piece of a large orange crystal of adduct (*S*)-**18**·CH_2Cl_2 was cut off with a razor to almost a cubic form, which was then sealed in a thin-walled glass capillary under argon and mounted on a Rigaku AFC-5R diffractometer. The space group was determined to be $P2_1$ based on the systematic absences, (0 *k* 0) with k = odd, and the dissymmetry of the complex. A summary of data collection and cell parameters is given in Table 4.

The position of the rhodium atom was determined by the Patterson map and was fixed in its y parameter. The absolute structure of the complex was assumed on the basis of the absolute configuration of the free ligand (*S*)-**3** as defined by CD spectroscopic analysis (*vide supra*). Most of the atoms were located by a series of standard block-diagonal least-squares refinements and Fourier synthesis. Atoms of ClO_4^-, solvated dichloromethane and some hydrogen atoms were located in a difference Fourier synthesis and the remaining hydrogen atoms were placed at calculated positions. The final refinement cycle was reached to $R = 0.070$ and $R_w = 0.096$. The somewhat high values for R and R_w might be a result of disorder (0.5 occupancy) in one molecule of solvated dichloromethane and large temperature factors of the ClO_4^- counterion. Tables of fractional atomic coordinates, bond distances, and bond angles, together with other crystallographic data, have been deposited at the Cambridge Crystallographic Data Centre.*

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* For full details of the CCDC deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, issue 1.

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