Unsymmetrical P-Chirogenic Bis(phosphane) Ligands: Their Preparation and Use in Rhodium-Catalyzed Asymmetric Hydrogenation

Atsushi Ohashi,*[a] Shin-ichi Kikuchi,[b] Masaya Yasutake,[b] and Tsuneo Imamoto[b]

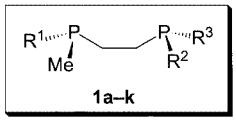
Keywords: Asymmetric catalysis / Hydrogenation / P ligands / Phosphanes / Rhodium

A series of bis(phosphanes) (S_P,$S_{P'}$)-R^1(Me)PCH$_2$CH$_2$P′R^2R^3 (**1a**–**k**; R^1, R^2, and R^3 = 1-adamantyl, *tert*-butyl, cyclohexyl, cyclopentyl, isopropyl, methyl, phenyl; abbreviated as unsymmetrical BisP*) has successfully been synthesized, by coupling of the (R_P)-configured tosylates **5a**–**d** or mesylates **6a**–**g** with lithiated (S_P)-R^1(Me)PH–BH$_3$ adducts. Asymmetric hydrogenations catalyzed by rhodium complexes of the unsymmetrical BisP* moieties as ligands revealed extremely high enantioselectivities – 99% (**9b**) and 98% (**9e**) – when the trisubstituted and tetrasubstituted dehydro-α-amino acid derivatives **8b** and **8e**, respectively, were used as substrates. It was found that unsymmetrical BisP* species tended to exhibit higher enantioselectivity than C_2-symmetrical BisP* species in the Rh-catalyzed hydrogenation of (*Z*)-dehydro-β-amino acid and enamide derivatives. These results implied that the differentiation between the chiral environments at the two phosphorus atoms could effectively achieve higher enantioselectivity. For each substrate, moreover, it was possible to improve the enantioselectivity by changing the combination of substituents on the two phosphorus atoms.

Introduction

Optically active (phosphane)transition metal complexes have played important roles in catalytic asymmetric synthesis.[1−5] Since DIOP was found to display high enantioselectivity in asymmetric hydrogenation catalyzed by rhodium complexes, it has been considered that C_2-symmetrical bis(phosphane) ligands are endowed with superior catalytic properties.[6] A variety of C_2-symmetrical ligands, such as DIPAMP,[7] BINAP,[8] DuPHOS,[9,10] BIPNOR,[11] and PennPHOS,[12] have indeed displayed superior asymmetric induction properties in an array of transition metal catalyzed reactions. On the other hand, it has also been shown that unsymmetrical bis(phosphane) ligands such as Josiphos,[13] Quinaphos,[14] Binaphos,[15] and others,[16,17] with different groups on the two phosphorus atoms, are effective for asymmetric hydrogenation in some cases. However, no unsymmetrical trialkylbis(phosphane) ligand has yet been reported. We have also noted that (S_P,$S_{P'}$)-1,2-bis-[alkyl(methyl)phosphanyl]ethane (alkyl = 1-adamantyl, *tert*-butyl, cyclohexyl, cyclopentyl, 1,1-diethylpropyl; abbreviated as BisP*) provided high enantioselectivities in Rh-catalyzed hydrogenations of dehydro-α-amino acids,[18] and it has also been shown that unsymmetrical versions of BisP* with different substituents on the two phosphorus atoms (i.e., not C_2-symmetric) were effective in some cases of asymmetric hydrogenation.[19,20] Although such unsymmetrical bis(phosphane) ligands seem to be more effective in controlling asymmetric induction, there are few systematic works on catalytic hydrogenation by transition metal complexes with unsymmetrical bis(phosphanes).We have recently prepared a series of new unsymmetrical bis(phosphane) ligands **1a**−**k**, in which a methyl group and R^1 are bound to one phosphorus atom (P) and R^2 and R^3 are bound to the other phosphorus atom (P′). In **1a**−**d**, **1f**−**g**, and **1i**−**k**, both phosphorus atoms are chiral − Bis(P*,P′*) − whereas only one of the two phosphorus atoms is chiral in **1e** and **1h**−**i** − Bis(P*,P).[19] Preliminary work on asymmetric hydrogenations catalyzed by rhodium complexes containing the P-chirogenic unsymmetrical bis(phosphane) ligands revealed high enantioselectivities in the hydrogenation of tetrasubstituted dehydro-α-amino acid derivatives.[20] This paper reports a new synthetic route to unsymmetrical P-chirogenic [Bis(P*,P′*)]Rh and [Bis(P*,P)]Rh catalysts and the highly enantioselective hydrogenation of dehydro-α- and -β-amino acid and enamide derivatives with these catalysts.

[a] Division of Supramolecular Science, Graduate School of Materials Science NARA Institute of Science and Technology (NAIST),
8916-5 Takayama-cho, Ikoma City, Nara 630-0101, Japan
Fax: (internat.) + 81-743/72-6119
E-mail: ohhashi@ms.aist-nara.ac.jp
[b] Department of Chemistry, Faculty of Science, Chiba University, Chiba, Japan
Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.



P-chirogenic unsymmetrical bis(phosphane) ligands

	R^1	R^2	R^3
1a	Ad	*t*Bu	Me
1b	Ad	Cp	Me
1c	Ad	Cy	Me
1d	Ad	*i*Pr	Me
1e	Ad	Me	Me
1f	*t*Bu	Cy	Me
1g	Cy	Cp	Me
1h	Ad	Cy	Cy
1i	Ad	Ph	Ph
1j	Ad	Ph	Me
1k	*t*Bu	*i*Pr	Me

Results

1. Synthesis of P-Chirogenic Unsymmetrical Bis(phosphane) Ligands

The synthetic route to the unsymmetrical BisP*−BH_3 aducts is shown in Scheme 1. [19]

Alkyl- or aryl(dimethyl)phosphane−borane adducts were enantioselectively deprotonated by treatment with *s*BuLi in the presence of (−)-sparteine at −78 °C,[18] and CO_2 was then bubbled through the mixture to afford the (R_P)-configured acids **3a**−**i** (90% *ee*) in 50−70% yields. Reduction of these carboxylic acids by borane−THF afforded quantitative yields of the (R_P)-alcohols **4a**−**i**, which were treated with TsCl or MsCl to give the corresponding (R_P)-cofigured tosylates **5a**−**d** or mesylates **6a**−**g**, respectively. These compounds were then coupled with lithiated (S_P)-alkyl(methyl)phosphane−borane adducts[21] to provide the unsymmetrical (S_P,$S_{P'}$)-BisP*−BH_3 adducts **7a**−**k** (97% *ee*) together with small amounts of the corresponding diastereoisomers. These phosphane−boranes **3**−**7** were also very stable in air. The chemical yields of the coupling reactions are shown in Table 1.

The combinations of 1-adamantyl and *tert*-butyl or 1-adamantyl and cyclohexyl groups provided quantitative yields of coupling products **7a** or **7c** (Entries 1 and 5), while Ad-BisP* (R^1 = R^2 = Ad) was obtained in moderate yield (Entry 3). It is noteworthy that this coupling reaction was not effective for the preparation of compounds **7f** and **7k** (Entries 8 and 13), probably due to inhibition by unknown by-products. An alternative route to **7a**, in which the positions of R^1 and R^2 were exchanged, was also successful (Entry 2). In a similar manner, the unsymmetrical BisP*−BH_3 compounds **7b**, **7d**, **7j**, and **7g** and the monochirogenic unsymmetrical BisP*−BH_3 compounds **7e**, **7h**, and **7i** were obtained in 60−75% yields.

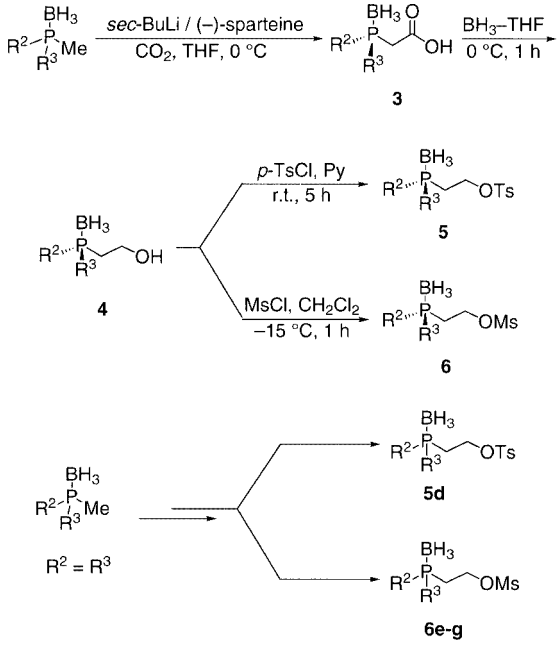
The unsymmetrical (S_P,$S_{P'}$)-BisP*−BH_3 compounds **7a**−**k** were converted into the corresponding cationic rhodium complexes **2a**−**k** by a reported procedure (Scheme 2).[20,22,23]

2. Asymmetric Hydrogenation of Dehydro-α-amino Acid Derivatives

In a preliminary study, hydrogenation of dehydro-*N*-acetylphenylalanine methyl ester (**8b**) in the presence of rhodium complex **2a** provided a quantitative yield of *N*-acetylphenylalanine methyl ester (**9b**) with 99.2% *ee* (*R*) (Scheme 3).

Encouraged by this result, we next examined the asymmetric hydrogenation of seven dehydro-α-amino acid derivatives **8a**−**g** in the presence of 15 different (BisP*)rhodium complexes, with four symmetrical (BisP*)rhodium complexes (Entries 1−4) included for comparison (Table 2).

For di- or trisubstituted dehydro-α-amino acid derivatives, **8a** and **8b**, very high enantioselectivity was found when **1a** was used as an unsymmetrical BisP* (Entry 5), although **1b**−**k** provided considerably lower enantioselectivities (Ent-



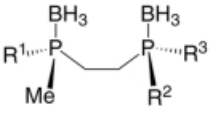
	R^2	R^3
3a	Ad	Me
3b	*t*Bu	Me
3c	Cp	Me
3d	Cy	Me
3e	*i*Pr	Me
3f	Ph	Me
3g	Me	Me
3h	Cy	Cy
3i	Ph	Ph

	R^2	R^3
4a	Ad	Me
4b	*t*Bu	Me
4c	Cp	Me
4d	Cy	Me
4e	*i*Pr	Me
4f	Ph	Me
4g	Me	Me
4h	Cy	Cy
4i	Ph	Ph

	R^2	R^3
5a	Ad	Me
5b	*t*Bu	Me
5c	Cy	Me
5d	Cy	Cy
6a	Ad	Me
6b	Cp	Me
6c	Cy	Me
6d	*i*Pr	Me
6e	Ph	Me
6f	Cy	Cy
6g	Ph	Ph

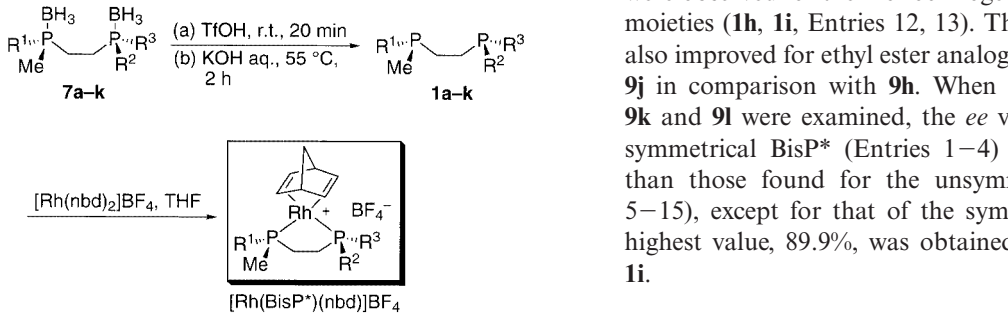
Scheme 1. Synthesis of the unsymmetrical BisP*−BH_3 adducts **7a**−**k**

Table 1. Chemical yields of unsymmetrical BisP*−BH_3 adducts **7a**−**k**

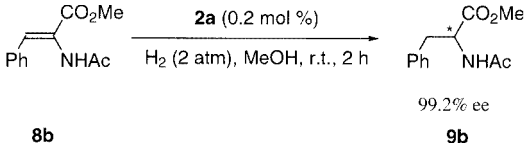


entry[a]		R^1	R^2	R^3	yield (%)
1[b,d]	**7a**	Ad	*t*Bu	Me	quant
2[c]	**7a**	*t*Bu	Ad	Me	quant
3[d,e]	**7l**	Ad	Ad	Me	40
4	**7b**	Ad	Cp	Me	75
5[d]	**7c**	Ad	Cy	Me	quant
6	**7d**	Ad	*i*Pr	Me	62
7	**7e**	Ad	Me	Me	61
8	**7f**	*t*Bu	Cy	Me	10
9	**7g**	Cy	Cp	Me	70
10	**7h**	Ad	Cy	Cy	73
11	**7i**	Ad	Ph	Ph	60
12	**7j**	Ad	Ph	Me	62
13	**7k**	*t*Bu	*i*Pr	Me	19

[a] A mixture of lithiated secondary phosphane−boranes and the mesylates **6** was stirred at 55 °C for 2 h unless otherwise noted. [b] A mixture was stirred at 55 °C for 10 min. [c] A mixture was stirred at room temp. for 1 h. [d] The tosylates **5** were used. [e] Compound **7l** is a symmetrical BisP*.



Scheme 2. Synthesis of the unsymmetrical BisP* compounds **1a**−**k** and the rhodium complexes **2a**−**k**



Scheme 3. Asymmetric hydrogenation of dehydro-*N*-acetylphenylalanine methyl ester **8b** by Rh complex **2a**

ries 6−15).To achieve high enantioselectivities in the hydrogenation of tetrasubstituted dehydro-α-amino acid derivatives has long been regarded as difficult.[24−28] The symmetrical (BisP*)Rh complexes also gave low enantiomeric excesses, as shown for the α-amino acid derivatives **9c**−**g**, except for the case of **9e**, for which somewhat higher values were obtained (Entries 1−4). However, the complexes with **1b**−**d**, **1f**, **1j**, and **1k** displayed very high enantioselectivities for the valine derivative **9d** (Entries 6−8 and 10−12), although the complexes **1g** and **1a**, **1e**, **1h**, and **1i** gave moderate and low values, respectively (Entries 13 and 5, 9, 14, and 15). A similar tendency in the enantioselectivity was observed for **9c**−**g** (Entries 1−13). In order to examine the dependence of enantioselectivity on the different electron densities on the phosphorus atoms, hydrogenations in the presence of the complexes with **1i** and **1h** (Entries 14 and 15) are listed. Opposite enantioselectivies were observed for the two unsymmetrical BisP* compounds.

3. Asymmetric Hydrogenation of (*Z*)-Dehydro-β-amino Acid and Enamide Derivatives

The Rh complexes with several unsymmetrical phosphane ligands were used for the asymmetric hydrogenation of (*Z*)-dehydro-β-amino acid derivatives[28−30] and enamide derivatives.[27] The results are shown in Table 3.

It has been reported that although the hydrogenation of (*E*)-dehydro-β-amino acid derivatives by symmetrical (BisP*)Rh complexes showed extremely high reactivity and enantioselectivity, the (*Z*) isomers of the dehydro-β-amino acid derivatives gave low enantioselectivity when a symmetrical BisP* was used.[28] The enantioselectivity of the formation of the (*Z*)-β-amino acid derivative **9h** was also low (55% *ee*) for the unsymmetrical BisP* species (**1a** and **1d**−**f**). However, considerably higher *ee* values (ca. 70% *ee*) were observed for the monochirogenic unsymmetrical BisP* moieties (**1h**, **1i**, Entries 12, 13). The enantioselectivity was also improved for ethyl ester analogue **9i** and ethyl analogue **9j** in comparison with **9h**. When the enamide derivatives **9k** and **9l** were examined, the *ee* values obtained with the symmetrical BisP* (Entries 1−4) were, in general, lower than those found for the unsymmetrical BisP* (Entries 5−15), except for that of the symmetrical Cp-BisP*. The highest value, 89.9%, was obtained for the unsymmetrical **1i**.

4. Effects of Hydrogen Pressure and Temperature on Enantioselectivity

For the dehydro-α- or -β-amino acid derivatives, the correlation between enantioselectivity and hydrogen pressure or temperature is listed in Table 4. It is plausible to assume that external factors such as hydrogen pressure and temperature should have little influence on the free energy difference at the transition state ($\Delta\Delta G^{\ddagger}$) in asymmetric hydrogenation catalyzed by (BisP*)Rh.

5. Effects of Phosphorus Ligand Electron Density on Enantioselectivity

In order to examine the effects of the electron densities on the phosphorus ligands on the enantioselectivity, cyclohexyl and/or phenyl groups were substituted on the phos-

Table 2. Enantioselectivity of (*Z*)-β-amino acid and enamide derivatives[a]

					%*ee*[b] (config)[c]						
entry		R^1	R^2	R^3	**9a**	**9b**	**9c**	**9d**	**9e**	**9f**	**9g**
1[d]		Ad	Ad	Me	99.6 (*R*)	99.9 (*R*)	9.5 (*R*)	12.4 (*R*)	82.4 (*R*)	18.7 (*R*)	10.0 (*R*)
2[d]		*t*Bu	*t*Bu	Me	98.1 (*R*)	99.9 (*R*)	14.4 (*R*)	35.9 (*R*)	83.6 (*R*)	45.9 (*R*)	33.3 (*R*)
3		Cp	Cp	Me	79.7 (*R*)	43.0 (*R*)	72.9 (*R*)	69.9 (*R*)	93.0 (*R*)	92.6 (*R*)	92.0 (*R*)
4[d]		Cy	Cy	Me	57.0 (*R*)	47.1 (*R*)	55.1 (*R*)	90.9 (*R*)	89.3 (*R*)	75.4 (*R*)	74.9 (*R*)
5	**1a**	Ad	*t*Bu	Me	96.2 (*R*)	99.2 (*R*)	16.3 (*R*)	21.3 (*R*)	79.5 (*R*)	32.4 (*R*)	22.0 (*R*)
6	**1b**	Ad	Cp	Me	66.8 (*R*)	85.7 (*R*)	89.7 (*R*)	96.1 (*R*)	96.0 (*R*)	95.4 (*R*)	95.5 (*R*)
7	**1c**	Ad	Cy	Me	67.9 (*R*)	77.7 (*R*)	87.6 (*R*)	94.0 (*R*)	98.2 (*R*)	96.7 (*R*)	96.1 (*R*)
8	**1d**	Ad	*i*Pr	Me	66.8 (*R*)	77.0 (*R*)	68.2 (*R*)	83.1 (*R*)	94.1 (*R*)	86.7 (*R*)	84.5 (*R*)
9	**1e**	Ad	Me	Me	32.2 (*R*)	52.5 (*R*)	9.0 (*R*)	39.1 (*R*)	48.4 (*R*)	51.5 (*R*)	52.9 (*R*)
10	**1f**	*t*Bu	Cy	Me	60.0 (*R*)	68.7 (*R*)	82.8 (*R*)	93.5 (*R*)	85.8 (*R*)	93.7 (*R*)	93.7 (*R*)
11	**1g**	Cy	Cp	Me	67.8 (*R*)	41.7 (*R*)	63.8 (*R*)	75.1 (*R*)	84.3 (*R*)	60.5 (*R*)	58.3 (*R*)
12	**1h**	Ad	Cy	Cy	70.6 (*R*)	60.8 (*R*)	0	0	42.9 (*R*)	0	6.4 (*S*)
13	**1i**	Ad	Ph	Ph	33.0 (*S*)	48.0 (*S*)	43.6 (*R*)	34.6 (*R*)	0	52.0 (*R*)	45.1 (*R*)
14	**1j**	Ad	Ph	Me	62.9 (*R*)	29.5 (*R*)	91.3 (*R*)	91.6 (*R*)	89.2 (*R*)	95.9 (*R*)	94.2 (*R*)
15	**1k**	*t*Bu	*i*Pr	Me	68.3 (*R*)	75.5 (*R*)	85.9 (*R*)	95.8 (*R*)	96.9 (*R*)	95.3 (*R*)	95.0 (*R*)

[a] Reactions were conducted at room temp. under initial H_2 pressures of 20 atm for **9h**−**j** or 4 atm for **9k** and **9l**, with 0.8 M MeOH solution of substrate and the catalyst precursors $[\{(S_P,S_{P'})\text{-BisP*}\}Rh(nbd)]^+BF_4^-$ (1 mol %). Reaction time was 12−14 h, and complete (100%) conversion was observed in all cases. [b] Enantiomeric excesses were determined by chiral capillary GC with a Chiral Select 1000 column (30 m) (β-amino acid derivatives) or a Chirasil-DEX CB column (30 m) (**9l**), or by HPLC with a Daicel Chiral AD column (**9k**). [c] Absolute configurations were confirmed by comparison of the signs of optical rotation and chiral HPLC or GC elution order with those of configurationally defined examples.

phorus atoms, on the assumption that the two groups would provide similar steric repulsion but would have different electron-donating and -withdrawing characters. Table 5 lists the enantioselectivities observed in the asymmetric hydrogenation of the substrates **8a**−**k** in the presence of the rhodium complexes of **1c**, **1i**, and **1j**, in order to examine the effect of the electron densities on the phosphorus ligands on the enantioselectivity. Although there may be some differences in steric repulsion with the substrate between cyclohexyl and phenyl groups, such variation in the *ee* values should be the result of the different electron-donating and -withdrawing characters of the cyclohexyl and phenyl groups. When the number of phenyl groups bound to the phosphorus atoms was increased, the *ee* values for the formation of **9a**−**f** and **9k** significantly decreased, whereas those for the formation of **9h**−**j** and **9l** increased.

6. Structures of Unsymmetrical (BisP*)Rh Complexes by X-ray Analysis

The molecular structure of **2a** is depicted in Figure 1(a); in Figure 1(b), norbornadiene has been omitted for better clarity.

The bond lengths and angles around the Rh center and the two phosphorus atoms P1 and P2 are approximately the same as their counterparts in the previously reported symmetrical (BisP*)Rh complex.[18,26] However, the conformation of the five-membered chelate ring is strongly distorted in comparison with that in the symmetrical (BisP*)-Rh complex, since the steric repulsion between the 1-adamantyl group bound to the P1 atom and the neighboring atoms is different from that arising from the *tert*-butyl group bound to P2. The degree of distortion is well illustrated by the dihedral angles between the planes defined by P1−Rh−P2 and Rh−P1−C1, and between the planes defined by P1−Rh−P2 and Rh−P2−C2. The dihedral angles of the 1-adamantyl and the *tert*-butyl groups are 46.9 and 26.7°, respectively. The difference in the two dihedral angles, 20.2°, is significant. For the symmetrical (BisP*)Rh complex, the difference is effectively zero.

The molecular structure of **2h** is depicted in Figure 2.

The bond lengths and angles around the Rh center and the two phosphorus atoms are also nearly the same as the corresponding ones in **2a**. The dihedral angle of the 1-ad-

Table 3. Effect of hydrogen pressure and temperature on enantioselectivity

entry		R[1]	R[2]	R[3]	% *ee*[b] (config)[c] **9h**	**9i**	**9j**	**9k**	**9l**
1		Ad	Ad	Me	30.3 (*S*)	27.4 (*S*)	43.5 (*S*)	30.3 (*R*)	29.9 (*R*)
2		*t*Bu	*t*Bu	Me	19.7 (*S*)	3.0 (*S*)	54.8 (*S*)	50.4 (*R*)	8.5 (*R*)
3		Cp	Cp	Me	62.9 (*S*)	68.0 (*S*)	70.3 (*S*)	68.2 (*R*)	89.2 (*R*)
4		Cy	Cy	Me	50.7 (*S*)	37.1 (*S*)	52.0 (*S*)	73.1 (*R*)	57.2 (*R*)
5	**1a**	Ad	*t*Bu	Me	26.4 (*S*)	24.4 (*S*)	71.1 (*S*)	45.4 (*R*)	31.5 (*R*)
6	**1b**	Ad	Cp	Me	54.8 (*S*)	61.7 (*S*)	65.6 (*S*)	45.4 (*R*)	79.7 (*R*)
7	**1c**	Ad	Cy	Me	50.4 (*S*)	53.1 (*S*)	59.8 (*S*)	61.6 (*R*)	68.5 (*R*)
8	**1d**	Ad	*i*Pr	Me	49.4 (*S*)	54.1 (*S*)	57.4 (*S*)	50.8 (*R*)	59.9 (*R*)
9	**1e**	Ad	Me	Me	30.6 (*S*)	36.3 (*S*)	36.6 (*S*)	10.4 (*R*)	25.6 (*R*)
10	**1f**	*t*Bu	Cy	Me	48.5 (*S*)	52.6 (*S*)	57.8 (*S*)	68.4 (*R*)	68.3 (*R*)
11	**1g**	Cy	Cp	Me	54.6 (*S*)	58.9 (*S*)	54.7 (*S*)	83.1 (*R*)	67.0 (*R*)
12	**1h**	Ad	Cy	Cy	66.3 (*S*)	72.2 (*S*)	50.6 (*S*)	8.0 (*R*)	16.9 (*R*)
13	**1i**	Ad	Ph	Ph	68.2 (*S*)	68.7 (*S*)	71.0 (*S*)	46.3 (*S*)	89.9 (*R*)
14	**1j**	Ad	Ph	Me	53.4 (*S*)	60.4 (*S*)	54.9 (*S*)	40.3 (*R*)	73.0 (*R*)
15	**1k**	*t*Bu	*i*Pr	Me	50.8 (*S*)	56.3 (*S*)	63.8 (*S*)	54.6 (*R*)	63.0 (*R*)

Table 4. Effect of phosphorus ligand electron density on enantioselectivity

entry	Cat.	atm	°C	time (h)	% *ee* (config) **9h**	**9c**
1		3		12	57.4 (*S*)	
2		20		12	68.2 (*S*)	
3	**1i**	45		5	70.5 (*S*)	
4			rt	2		87.6 (*R*)
5	**1c**		0	12		88.1 (*R*)

amantyl group is 39.3°, whereas the dihedral angles of the two cyclohexyl groups are 51.1 and 52.0°, respectively. The difference, 11.8° or 12.7°, causes greater asymmetry around the Rh atom. This asymmetry is transferred to the substrate molecule when it comes close to the Rh atom in the transition state.

Discussion

1. Averaged Enantioselectivity of Unsymmetrical BisP* Ligands

A variety of the new Rh complexes with unsymmetrical BisP* ligands **1a**−**k** were synthesized, and the *ee* values for the asymmetric hydrogenation of several types of substrates **8a**−**j** in the presence of the complexes as catalysts were obtained. When the di- and trisubstituted dehydro-α-amino acid derivatives **8a** and **8b** were used as substrates, the enantioselectivities due to catalysis by the Rh complexes with unsymmetrical BisP* ligands were almost the same as those provided by the complexes with symmetrical ligands, as shown in Table 2. In order to explain this result more clearly, the *ee* values observed in the hydrogenation of dehydro-*N*-acetylphenylalanine, one of the best known substrates (when one of the two substituents bound to P1 and

Table 5. Enantioselectivity of α-amino acid derivatives[a]

entry		R1	R2	R3	% *ee* (config) 9a	9b	9c	9d	9e
1	**1c**	Ad	Cy	Me	67.9 (*R*)	77.7 (*R*)	87.6 (*R*)	94.0 (*R*)	98.2 (*R*)
2	**1j**	Ad	Ph	Me	62.9 (*R*)	29.5 (*R*)	91.3 (*R*)	91.6 (*R*)	89.2 (*R*)
3	**1i**	Ad	Ph	Ph	33.0 (*S*)	48.0 (*S*)	43.6 (*R*)	34.6 (*R*)	0
4	**1h**	Ad	Cy	Cy	70.6 (*R*)	60.8 (*R*)	0	0	42.9 (*R*)

% *ee* (config) 9f	9g	9h	9i	9j	9k	9l
96.7 (*R*)	96.1 (*R*)	50.4 (*S*)	53.1 (*S*)	59.8 (*S*)	61.6 (*R*)	68.5 (*R*)
95.9 (*R*)	94.2 (*R*)	53.4 (*S*)	60.4 (*S*)	54.9 (*S*)	40.3 (*R*)	73.0 (*R*)
52.0 (*R*)	45.1 (*R*)	68.2 (*S*)	68.7 (*S*)	71.0 (*S*)	46.3 (*S*)	89.9 (*R*)
0	6.4 (*S*)	66.3 (*S*)	72.2 (*S*)	50.6 (*S*)	8.0 (*R*)	16.9 (*R*)

[a] Reactions were conducted at room temp. and at initial H_2 pressures of 2 atm for **9a** and **9b**, or 6 atm for **9c**−**f**, with 0.8 M MeOH solutions of substrate and the catalyst precursors [{(S_P,$S_{P'}$)-BisP*}Rh(nbd)]$^+BF_4^-$ [0.2 mol % (**9a**, **9b**) or 1 mol % (**9c**−**f**)]. Reaction time was 1−2 h, and complete (100%) conversion was observed in all cases. [b] Enantiomeric excesses were determined by chiral capillary GC with a Chrompack Chiral-L-Val column (25 m) (di- and tetrasubstituted) or by HPLC with a Daicel Chiral OJ column (trisubstituted). [c] Absolute configurations were confirmed by comparison of the signs of optical rotation and chiral HPLC or GC elution orders with those of configurationally defined examples. [d] See ref.[18]

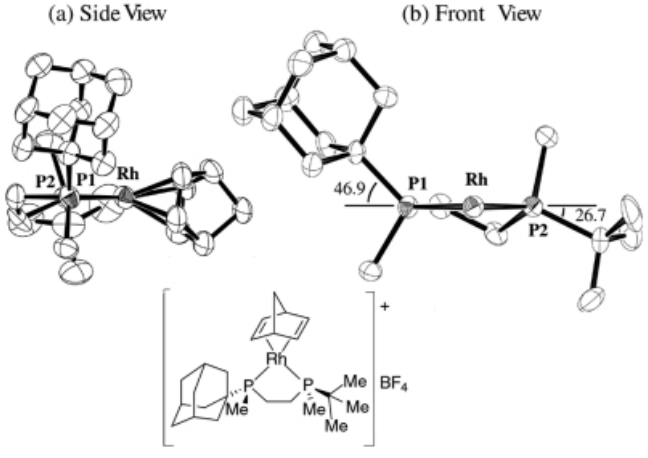


Figure 1. ORTEP drawing of [Rh(Ad*t*Bu-BisP*)(nbd)]BF_4 (**2a**); crystal data: $C_{25}H_{42}BF_4P_2Rh$, monoclinic, space group $P2_1$; a = 11.045(6), b = 13.512(9), c = 17.94(2) Å, β = 91.98(3)°; bond lengths: P1−Rh1 2.315(3), P2−Rh1 2.316(3), nbd−Rh1 ca. 2.2 Å; bond angle: P1−Rh1−P2 82.9°; torsion angle: −48.2(9)°

P2 is fixed as the methyl group) are rearranged in Figure 3. The vertical and horizontal axes indicate the bulkiness of the substituents other than the methyl group on P1 and P2, respectively. Three series of *ee* values are given as follows:

1) The substituent on P1 is fixed as the 1-adamantyl (Ad) group and the substituent on P2 is varied from methyl to Ad.

2) The substituent on P2 is fixed as the cyclohexyl (Cy) group and the substituent on P1 is varied from Cy to Ad.

3) The substituents on P1 and P2 are the same (that is, the symmetrical BisP* species).

As the bulkiness increases, the *ee* value increases in all series, as shown by three arrows. Furthermore, it should be emphasized that the *ee* value obtained in the presence of each unsymmetrical BisP* is close to the averaged one of the two corresponding symmetrical BisP* moieties. For example, the Rh complex with Ad and methyl groups on P1 and cyclopentyl (Cp) and methyl groups on P2 showed an *ee* value of 77.7%, which is close to the averaged *ee* value

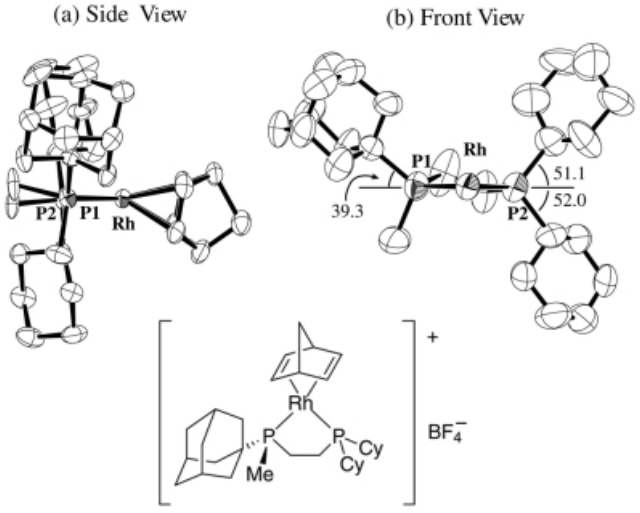


Figure 2. ORTEP drawing of [Rh(AdCy$_2$-BisP*)(nbd)]BF_4 (**2h**); crystal data: $C_{32}H_{52}BF_4P_2Rh$, triclinic, space group *P*1 (no. 1); *a* = 15.207(9), *b* = 21.31(2), *c* = 10.876(3) Å; α = 89.91(2), β = 89.97(3), γ = 88.53(4)°; bond lengths: P1−Rh1 2.303(5), P2−Rh1 2.328(5), nbd−Rh1 ca. 2.2 Å; bond angle: P1−Rh1−P2 83.8°; torsion angle: −44(3)°

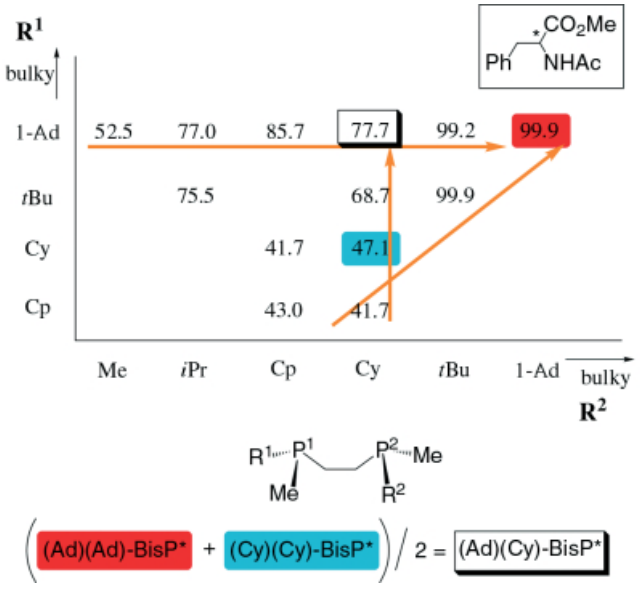


Figure 3. The *ee* values of the product phenylalanine derivative **9b** for the various unsymmetrical BisP* moieties; the arrows indicate increasing *ee* values

of 73.5% between the symmetrical Ad-BisP* and Cp-BisP* [= (99.9 + 47.1)/2].

2. Fine-Tuning of the Enantioselectivity of Unsymmetrical BisP* Species

The *ee* values for one of the tetrasubstituted dehydro-α-amino acid (valine) derivatives were determined in the presence of a series of symmetrical and unsymmetrical BisP* complexes (Table 2). The three series of *ee* values given are the same as for the di- or trisubstituted dehydro-α-amino acid in Figure 3. For symmetrical BisP* complexes, the highest *ee* value, 90.9%, was observed for the Cy-BisP* complex. As the bulkiness of the substituent decreases, the *ee* value increases, as shown by an arrow. On the other hand, the highest *ee* value, 96.1%, was observed for substituents of medium size, AdCp-BisP*, but the *ee* values obtained for the complexes with the smallest (Me) and the largest (*t*Bu) substituents were 39.1 and 21.3%, respectively. For the second series, in which the substituent on P2 was fixed as the cyclohexyl (Cy) group and the substituent on P1 was varied from Cy to Ad, the *ee* values showed a complicated change. The "medium-sized complex", CpCy-BisP*, gave the smallest *ee* value, 75.1%, close to the averaged value of the two symmetrical Cp-BisP* and Cy-BisP* complexes [(69.9% + 90.9%)/2]. The averaged *ee* value was also observed in the first series for the unsymmetrical Ad*t*Bu-BisP* [that is, 23.1% is close to the average of the values obtained with the symmetrical Ad-BisP* and *t*Bu-BisP*: (12.4% + 35.9%)/2]. These results may be taken to indicate that the *ee* value of an unsymmetrical BisP* complexes tends to the average of the those of the two corresponding symmetrical BisP* complexes if the *ee* value is not so high (80%). If, however, the *ee* values obtained in the presence of the unsymmetrical BisP* complexes were greater than 80%, they were independent of the bulkiness of the substituents on the phosphorus atoms. It must be emphasized that the *ee* values obtained for the unsymmetrical BisP* complexes were notably better than those obtained with the symmetrical ones.

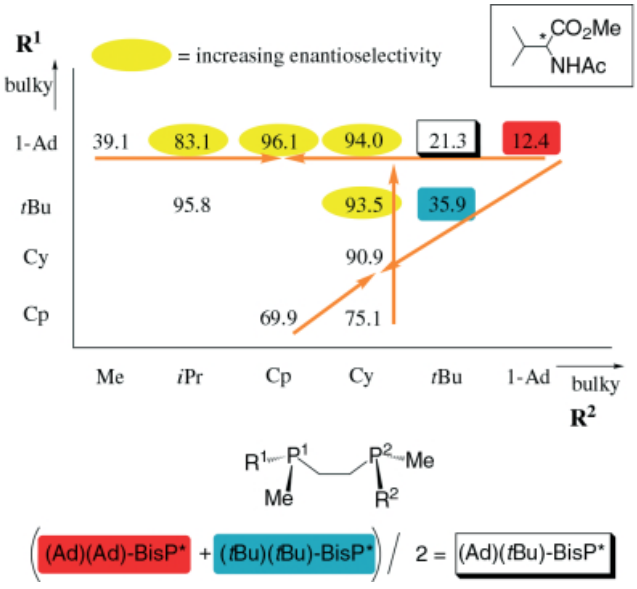


Figure 4. The *ee* values of the valine derivative product **9d** obtained with the various unsymmetrical BisP* complexes; the arrows indicate increasing *ee* values

For the (*Z*)-dehydro-β-amino acid derivatives, the very low enantioselectivity has been interpreted as being due to the intramolecular hydrogen bond between the C=O group and the N−H group.[31] Although the unsymmetrical BisP* complexes gave higher *ee* values than obtained with the symmetrical BisP* compounds, the *ee* values were still less

than 73%. This indicates that the best combination of unsymmetrical substituents on the two phosphorus atoms has not yet been obtained. For the enamide derivatives, *ee* values obtained with the unsymmetrical BisP* complexes were, in general, higher than those for the symmetrical BisP* counterparts. However, very high *ee* values were observed both for the symmetrical Cp-BisP* and for the unsymmetrical $AdPh_2$-BisP* complexes. This indicates that the combination of the substituents on the two phosphorus atoms is suitable for asymmetrical induction.Analysis of the molecular structures of the norbornadiene complexes should enable the best-fit combination of the substituents to be estimated.

Conclusion

In summary, a variety of rhodium complexes with unsymmetrical BisP* ligands have been synthesized in high chemical yields, and high enantioselectivity (98.2%) was obtained when the asymmetrical hydrogenation of the tetrasubstituted dehydro-α-amino acid cyclohexylglycine derivative **8e** was catalyzed by a rhodium complex with the unsymmetrical AdCy-BisP* ligand. With all the tetrasubstituted dehydro-α-amino acid derivatives as substrates, the unsymmetrical BisP* complexes produced very high *ee* values, significantly higher than those obtained with symmetrical BisP* complexes. With (*Z*)-dehydro-β-amino acid and enamide derivatives as substrates, the *ee* values obtained from the unsymmetrical BisP* complexes were, in general, greater than those from the symmetrical BisP* complexes. The unsymmetrical BisP* complexes have two independent chiral phosphorus atoms in the vicinity of the active site, whereas the symmetrical BisP* complexes have two chiral phosphorus atoms with the same chirality. This suggests that the degree of the chirality of the two phosphorus atoms can be modified significantly by changing the combination of the substituents on the phosphorus atoms, and that fine-tuning to obtain higher *ee* values is feasible. At present, however, it is not possible to estimate the structure of the ligand that would best suit the substrate. X-ray analyses of many catalyst analogues and theoretical calculations should afford effective guidelines with which to design the best ligand for a substrate in the near future.

Experimental Section

General Remarks: The instruments used for NMR, HPLC, and optical rotation were JEOL LA 400, Hitachi D 2500, and JASCO DIP 370 machines, respectively. Diethyl ether, tetrahydrofuran (THF), and toluene were distilled from sodium benzophenone ketyl under argon prior to use. (Adamantyl)dimethylphosphane−borane, (*tert*-butyl)dimethylphosphane−borane, (cyclohexyl)dimethylphosphane−borane, (cyclopentyl)dimethylphosphane−borane, (isopropyl)dimethylphosphane−borane, and dimethyl(phenyl)phosphane−borane were prepared by a procedure described in the literature.[17]

(R_P)-Acid (3b): *s*BuLi (36 mL of a 1.0 M cyclohexane/*n*-hexane solution, 37 mmol) was added at −78 °C, under Ar, to a stirred solution of (−)-sparteine (9.0 g, 37 mmol) in ether (100 mL). After 15 min, a solution of (*tert*-butyl)dimethylphosphane−borane (4.4 g, 33 mmol) in ether (40 mL) was added dropwise, and the mixture was stirred at the same temperature; 3 h later, dry CO_2 gas was bubbled through the mixture, and the flask was allowed to warm gradually to ambient temperature. After stirring for an additional 2 h, the reaction mixture was made acidic with 1 N HCl and extracted three times with EtOAc (60 mL). Next, in order to remove substrate, the mixture was made basic with aqueous Na_2CO_3 and the precipitate was filtered off. The sodium salt of the acetic acid derivative was acidified with 1 N HCl and extracted into EtOAc (120 mL). The combined extracts were washed with brine and dried with $MgSO_4$, and the solvents were removed under reduced pressure. The residue was recrystallized from ether/hexane to give pure **3b** as colorless needles (4.2 g, 70% yield). M.p. 120−122 °C. $[\alpha]_D$ = 11 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.0−0.9 (brq, 3 H), 1.2 (d, J_{HP} = 14.6 Hz, 9 H), 1.5 (d, J_{HP} = 9.8 Hz, 3 H), 2.7−2.8 (dq, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.7 (d, $J_{C,P}$ = 34 Hz), 24.9, 28.1 (d, $J_{C,P}$ = 33 Hz), 29.2 (d, $J_{C,P}$ = 22 Hz), 173.8 (d, $J_{C,P}$ = 5 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2970, 2910, 2370, 1705, 1295, 925 cm^{-1}. FAB MS: m/z = 175 [M^+ − H]. $C_7H_{18}BO_2P$ (176.0): calcd. C 47.77, H 10.31; found C 47.52, H 10.23.

(R_P)-Alcohol (4b): BH_3−THF (72 mL of a 1.0 M THF solution, 71 mmol) was added at 0 °C, under Ar, to a stirred solution of **3b** (3.3 g, 18 mmol) in THF (80 mL). The mixture was stirred at ambient temperature for 2 h. The reaction was quenched by addition of ice/water. The organic layers were separated, and the aqueous layer was extracted three times with EtOAc (40 mL). The combined extracts were washed with brine and dried with Na_2SO_4, and the solvents were removed under reduced pressure. The crude product was recrystallized from EtOAc/hexane to give pure **4b** as colorless needles (2.9 g, quant). M.p. 50.5−52.5 °C. $[\alpha]_D$ = −1.7 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.0−0.9 (brq, 3 H), 1.2 (d, J_{HP} = 13.8 Hz, 9 H), 1.3 (d, J_{HP} = 9.9 Hz, 3 H), 1.8−2.0 (m, 2 H), 2.4 (s, 1 H), 3.9−4.0 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.3 (d, $J_{C,P}$ = 35 Hz), 24.6 (d, $J_{C,P}$ = 32 Hz), 24.8 (d, $J_{C,P}$ = 2 Hz), 27.2 (d, $J_{C,P}$ = 35 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3290, 2970, 2370, 1040 cm^{-1}. FAB MS: m/z = 161 [M^+ − H]. $C_7H_{20}BOP$ (162.0): calcd. C 51.89, H 12.44; found C 51.84, H 12.52.

(R_P)-Tosylate (5b): *p*-Toluenesulfonyl chloride (2.0 g, 10 mmol) was added at 0 °C, under Ar, to a stirred solution of **4b** (0.5 g, 3 mmol) in pyridine (15 mL). The mixture was stirred for 6 h at ambient temperature. The reaction was quenched by addition of water. The organic layers were separated, and the aqueous layer was extracted three times with EtOAc (40 mL). The combined extracts were washed with aq. $NaHCO_3$ and brine, and dried with $MgSO_4$, and the solvents were removed under reduced pressure. The crude product was recrystallized from ether/hexane to give pure **5b** as colorless needles (0.9 g, 94%). M.p. 72.0−72.4 °C. $[\alpha]_D$ = 5 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.2−0.7 (brq, 3 H), 1.1 (d, J_{HP} = 14 Hz, 9 H), 1.3 (d, J_{HP} = 9.9 Hz, 3 H), 1.95−2.10 (m, 2 H), 2.5 (s, 1 H), 4.2−4.4 (m, 2 H), 7.4 (d, J_{HP} = 8.2 Hz, 2 H), 7.8 (d, J_{HP} = 8.2 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6 (d, $J_{C,P}$ = 34 Hz), 21.6, 21.8 (d, $J_{C,P}$ = 20 Hz), 24.7 (d, $J_{C,P}$ = 2 Hz), 27.3 (d, $J_{C,P}$ = 34 Hz), 65.8 (d, $J_{C,P}$ = 5 Hz), 129 (d, $J_{C,P}$ = 208 Hz), 132, 145 ppm. IR (KBr): $\tilde{\nu}$ = 2970, 2380, 1360, 1185, 940, 725, 555 cm^{-1}. FAB MS : m/z = 315 [M^+ − H]. $C_{14}H_{26}BO_3PS$ (316.2): calcd. C 53.18, H 8.29; found C 53.35, H 8.07.

(R_P)-Mesylate (6a): Methanesulfonyl chloride (0.8 mL, 10 mmol) was added at −15 °C, under Ar, to a stirred solution of **4a** (2.0 g, 9 mmol) in dichloromethane (20 mL). The mixture was stirred for 1 h at the same temperature. The reaction was quenched by addition of 1 N HCl. The organic layers were separated, and the aqueous layer was extracted three times with ether (40 mL). The combined extracts were washed with aq. $NaHCO_3$ and brine and dried with $MgSO_4$, and the solvents were removed under reduced pressure. The crude product was recrystallized from ether to give pure **6a** as a colorless solid (2.4 g, 85%). M.p. 79−80 °C. $[\alpha]_D$ = 2.6 (c = 1.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.0−0.9 (brq, 3 H), 1.3 (d, J_{HP} = 9.6 Hz, 3 H), 1.7−2.0 (m, 17 H), 3 (s, 3 H), 4.4−4.5 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 4.8 (d, $J_{C,P}$ = 35 Hz), 20.5 (d, $J_{C,P}$ = 31 Hz), 30 (d, $J_{C,P}$ = 34 Hz), 35.4, 36.3, 37.5, 66 (d, $J_{C,P}$ = 4 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2900, 2380, 1350, 1170, 970 cm^{-1}. FAB MS: m/z = 317 [M^+ − H]. $C_{14}H_{28}BO_3PS$ (318.2).

(S_P,$S_{P'}$)-Ad*t*Bu-BisP*−BH_3 (7a). Method A: *n*BuLi (1.5 mL of a 1.6 M hexane solution, 2.4 mmol) was added under Ar to a stirred, cooled (0 °C) solution of (S_P)-1-adamantyl(methyl)-phosphane−borane (430 mg, 2.2 mmol) in THF (4 mL). After 20 min, **5b** was added, and the solution was heated at 55 °C for 1 h. The mixture was gradually cooled to room temperature, and was quenched with 1 N HCl. The organic layer was separated, and the aqueous layer was extracted three times with EtOAc (40 mL). The combined extracts were washed with aq. $NaHCO_3$ and brine and dried with $MgSO_4$, and the solvents were removed under reduced pressure. The crude product was recrystallized from toluene to give pure **7a** as colorless needles (748 mg, quant). **Method B:** The compound was prepared from (S_P)-*tert*-butyl(methyl)-phosphane−borane (126 mg, 1.1 mmol) and **6a** (332 mg, 1 mmol) by the same procedure. The crude product was recrystallized from toluene to give pure **7a** as colorless needles (340 mg, quant). M.p. 198−200 °C. $[\alpha]_D$ = 5.7 (c = 0.93, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.0−0.9 (brq, 6 H), 1.1−1.2 (m, 15 H), 1.5−1.6 (m, 3 H), 1.7−2.0 (m, 16 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 4.1 (d, $J_{C,P}$ = 35 Hz), 5.6 (d, $J_{C,P}$ = 34 Hz), 14.4 (d, $J_{C,P}$ = 31 Hz), 15.9 (d, $J_{C,P}$ = 31 Hz), 25.2, 27.5 (d, $J_{C,P}$ = 9 Hz), 27.8, 30.6 (d, $J_{C,P}$ = 35 Hz), 35.9, 36.4 ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 24.2 (J_{PB} = 33 Hz), 28.6−28.9 (J_{PB} = 105 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2900, 2380, 1060, 890 cm^{-1}. FAB MS: m/z = 339 [M^+ − H]. $C_{18}H_{40}B_2P_2$ (340.1): calcd. C 63.57, H 11.86; found C 63.38, H 11.84.

(S_P,$S_{P'}$)-AdCp-BisP*−BH_3 (7b): This compound was prepared from (S_P)-1-adamantyl(methyl)phosphane−borane (459 mg, 2.3 mmol) and mesylate **6b** (590 mg, 2.3 mmol) by the procedure described for the preparation of **7a**. The crude product was recrystallized from toluene to give pure **7b** as colorless needles (607 mg, 75% yield). M.p. 164−165 °C. $[\alpha]_D$ = −3.1 (c = 0.6, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.0−0.9 (brq, 6 H), 1.1 (d, J_{HP} = 9 Hz, 3 H), 1.2 (d, J_{HP} = 10 Hz, 3 H), 1.5−2.0 (m, 28 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.7 (d, $J_{C,P}$ = 35 Hz), 7.6 (d, $J_{C,P}$ = 36 Hz), 13.7 (d, $J_{C,P}$ = 31 Hz), 19.0 (d, $J_{C,P}$ = 32 Hz), 26.2 (d, $J_{C,P}$ = 8 Hz), 26.5 (d, $J_{C,P}$ = 8 Hz), 27.4 (d, $J_{C,P}$ = 15 Hz), 27.5 (d, $J_{C,P}$ = 6 Hz), 30.4 (d, $J_{C,P}$ = 34 Hz), 33.4 (d, $J_{C,P}$ = 37 Hz), 35.8, 36.4 (d, $J_{C,P}$ = 2 Hz) ppm. ^{31}P NMR (161 MHz, $CDCl_3$): δ = 20.3 (J_{PB} = 49 Hz), 25.2 (J_{PB} = 52 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2900, 2360, 1060 cm^{-1}. FAB MS: m/z = 347 [M^+ − 5 H]. $C_{19}H_{40}B_2P_2$ (352.1): calcd. C 64.81, H 11.45; found C 64.80, H 11.29.

(S_P,$S_{P'}$)-AdCy-BisP*−BH_3 (7c). Method A: This compound was prepared from (S_P)-1-adamantyl(methyl)phosphane−borane (300 mg, 1.5 mmol) and tosylate **5c** (500 mg, 1.5 mmol) by the procedure described for the preparation of **7a**. The crude product was recrystallized from toluene to give pure **7c** as colorless needles (549 mg, quant). **Method B:** The compound was prepared from (S_P)-1-adamantyl(methyl)phosphane−borane (437 mg, 2.2 mmol) and mesylate **6c** (652 mg, 2.5 mmol) by the same procedure. The crude product was recrystallized from toluene to give pure **7c** as colorless needles (805 mg, quant.). M.p. 197−199 °C. $[\alpha]_D$ = 2.9 (c = 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.0−0.9 (brq, 6 H), 1.1−1.2 (m, 15 H), 1.5−1.6 (m, 3 H), 1.7−2.0 (m, 16 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 4.1 (d, $J_{C,P}$ = 35 Hz), 5.6 (d, $J_{C,P}$ = 34 Hz), 14.4 (d, $J_{C,P}$ = 31 Hz), 15.9 (d, $J_{C,P}$ = 31 Hz), 25.2, 27.5 (d, $J_{C,P}$ = 9 Hz), 27.8, 30.6 (d, $J_{C,P}$ = 35 Hz), 35.9, 36.4 ppm. ^{31}P NMR (161 MHz, $CDCl_3$): δ = 19.2 (J_{PB} = 49 Hz), 25.2 (J_{PB} = 52 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2930, 2360, 1450, 1060, 900 cm^{-1}. FAB MS: m/z = 365 [M^+ − H]. $C_{20}H_{42}B_2P_2$ (366.1): calcd. C 65.61, H 11.56; found C 65.57, H 11.75.

(S_P,$S_{P'}$)-Ad*i*Pr-BisP*−BH_3 (7d): This compound was prepared from (S_P)-1-adamantyl(methyl)phosphane−borane (535 mg, 2.7 mmol) and mesylate **6d** (617 mg, 2.7 mmol) by the procedure described for the preparation of **7a**. The crude product was recrystallized from toluene/hexane to give pure **7d** as colorless needles (545 mg, 62% yield). M.p. 156−157 °C. $[\alpha]_D$ = −4.3 (c = 0.65, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.0−0.9 (brq, 6 H), 1.1−1.2 (m, 12 H), 1.5−2.0 (m, 20 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.7 (d, $J_{C,P}$ = 35 Hz), 5.9 (d, $J_{C,P}$ = 36 Hz), 13.5 (d, $J_{C,P}$ = 31 Hz), 16.2 (d, $J_{C,P}$ = 2 Hz), 16.4, 17.3 (d, $J_{C,P}$ = 32 Hz), 23.1 (d, $J_{C,P}$ = 35 Hz), 27.5 (d, $J_{C,P}$ = 9 Hz), 30.4 (d, $J_{C,P}$ = 33 Hz), 36.1 (d, $J_{C,P}$ = 57 Hz), 52.7 (d, $J_{C,P}$ = 11 Hz), ppm. ^{31}P NMR (161 MHz, $CDCl_3$): δ = 23.0 (J_{PB} = 83 Hz), 25.1 (J_{PB} = 62 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2910, 2360, 1070, 890 cm^{-1}. FAB MS: m/z = 323 [M^+ − 3 H]. $C_{17}H_{38}B_2P_2$ (326.0): calcd. C 62.62, H 11.75; found C 62.81, H 11.86.

(S_P,$S_{P'}$)-AdMe$_2$-BisP*−BH_3 (7e): This compound was prepared from (S_P)-1-adamantyl(methyl)phosphane−borane (494 mg, 2.5 mmol) and mesylate **6h** (500 mg, 2.5 mmol) by the procedure described for the preparation of **7a**. The crude product was recrystallized from toluene to give pure **7e** as colorless needles (454 mg, 61% yield). M.p. 186−187 °C. $[\alpha]_D$ = −8.4 (c = 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.0−0.9 (brq, 6 H), 1.1 (d, J_{HP} = 10 Hz, 3 H), 1.3 (dd, J_{HP} = 13 Hz, 6 H), 1.5−2.0 (m, 25 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.6 (d, $J_{C,P}$ = 34 Hz), 10.5 (d, $J_{C,P}$ = 36 Hz), 11.3 (d, $J_{C,P}$ = 37 Hz), 13.6 (d, $J_{C,P}$ = 31 Hz), 20.8 (d, $J_{C,P}$ = 35 Hz), 27.5 (d, $J_{C,P}$ = 9 Hz), 30.5 (d, $J_{C,P}$ = 35 Hz), 36.1 (d, $J_{C,P}$ = 57 Hz), 52.0 ppm. ^{31}P NMR (161 MHz, $CDCl_3$): δ = 8.8 (J_{PB} = 195 Hz), 25.2 (J_{PB} = 118 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2910, 2365, 1420, 1060, 920 cm^{-1}. FAB MS: m/z = 283 [M^+ − 15 H]. $C_{15}H_{34}B_2P_2$ (298.0): calcd. C 60.46, H 11.50; found C 60.26, H 11.42.

(S_P,$S_{P'}$)-AdPh-BisP*−BH_3 (7j): This compound was prepared from (S_P)-1-adamantyl(methyl)phosphane−borane (196 mg, 1 mmol) and mesylate **6e** (261 mg, 1 mmol) by the procedure described for the preparation of **7a**. The crude product was recrystallized from toluene to give pure **7j** as colorless needles (223 mg, 62% yield). M.p. 186−187 °C. $[\alpha]_D$ = 22.8 (c = 0.24, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.0−0.9 (brq, 6 H), 1.1 (dd, J_{HP} = 10 Hz, 3 H), 1.4−2.2 (m, 28 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.8 (d, $J_{C,P}$ = 38 Hz), 11.9 (d, $J_{C,P}$ = 39 Hz), 13.4 (d, $J_{C,P}$ = 34 Hz), 21 (d, $J_{C,P}$ = 37 Hz), 27 (d, $J_{C,P}$ = 8 Hz), 30 (d, $J_{C,P}$ = 34 Hz), 36 (d, $J_{C,P}$ = 65 Hz), 128 (d, $J_{C,P}$ = 54 Hz), 129 (d, $J_{C,P}$ = 10 Hz), 131.8, 131.9 ppm. ^{31}P NMR (161 MHz, $CDCl_3$): δ = 12.0 (J_{PB} = 105 Hz), 24.1 (J_{PB} = 105 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2900, 2370, 1420, 1060, 910, 740 cm^{-1}. FAB MS: m/z = 355 [M^+ − 3 H].

$C_{20}H_{36}B_2P_2$ (360.0): calcd. C 66.71, H 10.08; found C 66.53, H 10.02.

(S_P,$S_{P'}$)-*t*BuCy-BisP*−BH_3 (7f): This compound was prepared from (S_P)-*tert*-butyl(methyl)phosphane−borane (0.7 g, 5.9 mmol) and tosylate **5c** (1.6 g, 1.5 mmol) by the procedure described for the preparation of **7a**. The crude product was recrystallized from toluene to give pure **7f** as colorless needles (116 mg, 10% yield). M.p. 136−138 °C. $[\alpha]_D$ = −12 (*c* = 0.29, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.0−0.9 (brq, 6 H), 1.1−1.2 (m, 20 H), 1.4−2.0 (m, 10 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.2 (d, $J_{C,P}$ = 34 Hz), 6.3 (d, $J_{C,P}$ = 36 Hz), 15.0 (d, $J_{C,P}$ = 30 Hz), 17.1 (d, $J_{C,P}$ = 34 Hz), 25.1 (d, $J_{C,P}$ = 2 Hz), 25.7 (d, $J_{C,P}$ = 2 Hz), 26.0 (d, $J_{C,P}$ = 2 Hz), 26.2, 26.4 (d, $J_{C,P}$ = 2 Hz), 26.5 (d, $J_{C,P}$ = 4 Hz), 27.6 (d, $J_{C,P}$ = 34 Hz), 32.9 (d, $J_{C,P}$ = 34 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.2 (J_{PB} = 100 Hz), 28.9 (J_{PB} = 104 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2930, 2370, 1065, 910, 760 cm^{-1}. FAB MS: *m*/*z* = 287 [M^+ − H]. $C_{14}H_{36}B_2P_2$ (288.0): calcd. C 58.38, H 12.60; found C 58.42, H 12.70.

(S_P,$S_{P'}$)-*t*Bu*i*Pr-BisP*−BH_3 (7k): This compound was prepared from (S_P)-*tert*-butyl(methyl)phosphane−borane (0.6 g, 5 mmol) and mesylate **6d** (1.1 g, 5 mmol) by the procedure described for the preparation of **7a**. The crude product was recrystallized from toluene to give pure **7k** as colorless needles (190 mg, 19% yield). M.p. 124−125 °C. $[\alpha]_D$ = −4.9 (*c* = 0.22, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.0−0.9 (brq, 6 H), 1.1−1.2 (m, 21 H), 1.4−2.0 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.1 (d, $J_{C,P}$ = 35 Hz), 5.9 (d, $J_{C,P}$ = 35 Hz), 15.0 (d, $J_{C,P}$ = 31 Hz), 16.2 (d, $J_{C,P}$ = 23 Hz), 17.3 (d, $J_{C,P}$ = 33 Hz), 22.9 (d, $J_{C,P}$ = 28 Hz), 25.0 (d, $J_{C,P}$ = 3 Hz), 27.5 (d, $J_{C,P}$ = 34 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 21.9 (J_{PB} = 101 Hz), 28.9 (J_{PB} = 104 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2980, 2370, 1065, 890 cm^{-1}. FAB MS: *m*/*z* = 245 [M^+ − 3 H]. $C_{11}H_{32}B_2P_2$ (247.9): calcd. C 53.29, H 13.01; found C 53.05, H 13.28.

(S_P,$S_{P'}$)-CyCp-BisP*−BH_3 (7g): This compound was prepared from (S_P)-cyclohexyl(methyl)phosphane−borane (310 mg, 2.1 mmol) and mesylate **6c** (540 mg, 2.1 mmol) by the procedure described for the preparation of **7a**. The crude product was recrystallized from toluene to give pure **7g** as colorless needles (210 mg, 70% yield). M.p. 105−106 °C. $[\alpha]_D$ = −9.6 (*c* = 0.3, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.0−0.9 (brq, 6 H), 1.2−1.3 (m, 11 H), 1.6−2.1 (m, 19 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.1 (d, $J_{C,P}$ = 35 Hz), 7.4 (d, $J_{C,P}$ = 36 Hz), 16.6 (d, $J_{C,P}$ = 32 Hz), 18.4 (d, $J_{C,P}$ = 32 Hz), 25.9 (d, $J_{C,P}$ = 38 Hz), 26.1 (d, $J_{C,P}$ = 17 Hz), 26.2 (d, $J_{C,P}$ = 9 Hz), 27.3 (d, $J_{C,P}$ = 17 Hz), 27.4, 33.1 (d, $J_{C,P}$ = 34 Hz), 33.5 (d, $J_{C,P}$ = 36 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.1 (J_{PB} = 75 Hz), 19.3 (J_{PB} = 100 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2930, 2380, 1420, 1060, 910 cm^{-1}. FAB MS: *m*/*z* = 297 [M^+ − 3 H]. $C_{15}H_{36}B_2P_2$ (300.0): calcd. C 60.05, H 12.09; found C 59.88, H 12.29.

(S_P,$S_{P'}$)-AdCy$_2$-BisP*−BH_3 (7h). Method A: This compound was prepared from dicyclohexylphosphane (0.37 mL, 1.9 mmol) and mesylate **6a** (0.5 g, 1.6 mmol) by the procedure described for the preparation of **7a**. The crude product was recrystallized from toluene to give **7h** (trace). **Method B:** This compound was prepared from (S_P)-1-adamantyl(methyl)phosphane−borane (136 mg, 0.7 mmol) and tosylate (**5d**) (312 mg, 0.76 mmol) by the procedure described for the preparation of **7a**. The crude product was recrystallized from toluene to give pure **7h** as colorless needles (221 mg, 73% yield). M.p. 141−143 °C. $[\alpha]_D$ = −4.0 (*c* = 0.71, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.0−0.9 (brq, 6 H), 1.2 (d, J_P = 33 Hz, 3 H), 1.2−1.3 (m, 10 H), 1.4−1.5 (m, 2 H), 1.6−2.0 (m, 29 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.6 (d, $J_{C,P}$ = 34 Hz), 12.7 (d, $J_{C,P}$ = 30 Hz), 14.3 (d, $J_{C,P}$ = 31 Hz), 26.0 (d, $J_{C,P}$ = 2 Hz), 26.6 (d, $J_{C,P}$ = 2 Hz), 26.7 (d, $J_{C,P}$ = 2 Hz), 26.8 (d, $J_{C,P}$ = 8 Hz), 26.9 (d, $J_{C,P}$ = 8 Hz, 27.0 (d, $J_{C,P}$ = 34 Hz), 27.6 (d, $J_{C,P}$ = 9 Hz), 30.4 (d, $J_{C,P}$ = 35 Hz), 31.9 (d, $J_{C,P}$ = 34 Hz), 36.1 (d, $J_{C,P}$ = 61 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 24.2 (J_{PB} = 70 Hz), 27.8 (J_{PB} = 56 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2930, 2370, 1450, 1060 cm^{-1}. FAB MS: *m*/*z* = 433 [M^+ − H]. $C_{25}H_{50}B_2P_2$ (434.2): calcd. C 69.15, H 11.61; found C 69.15, H 11.84.

(S_P,$S_{P'}$)-AdPh$_2$-BisP*−BH_3 (7i). Method A: This compound was prepared from diphenylphosphane (0.26 mL, 1.4 mmol) and mesylate **6a** (450 mg, 1.4 mmol) by the procedure described for the preparation of **7a**. The crude product was recrystallized from toluene to give pure **7i** as colorless needles (200 mg, 35% yield). **Method B:** The compound was prepared from (S_P)-1-adamantylmethylphosphane−borane (454 mg, 2.3 mmol) and mesylate **6e** (785 mg, 2.4 mmol) by the procedure described for the preparation of **7a**. The crude product was recrystallized from toluene to give pure **7i** as colorless needles (582 mg, 60% yield). M.p. 167−169 °C. $[\alpha]_D$ = 6.4 (*c* = 0.67, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.0−0.9 (brq, 6 H), 1.1−1.2 (m, 20 H), 1.4−2.0 (m, 10 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.2 (d, $J_{C,P}$ = 34 Hz), 6.3 (d, $J_{C,P}$ = 36 Hz), 15.0 (d, $J_{C,P}$ = 30 Hz), 17.1 (d, $J_{C,P}$ = 34 Hz), 25.1 (d, $J_{C,P}$ = 2 Hz), 25.7 (d, $J_{C,P}$ = 2 Hz), 26.0 (d, $J_{C,P}$ = 2 Hz), 26.2, 26.4 (d, $J_{C,P}$ = 2 Hz), 26.5 (d, $J_{C,P}$ = 4 Hz), 27.6 (d, $J_{C,P}$ = 34 Hz), 32.9 (d, $J_{C,P}$ = 34 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.2 (J_{PB} = 100 Hz), 28.9 (J_{PB} = 104 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 2910, 2380, 1440, 1065, 740 cm^{-1}. FAB MS: *m*/*z* = 287 [M^+ − H]. $C_{14}H_{36}B_2P_2$ (288.0): calcd. C 58.38, H 12.60; found C 58.42, H 12.70.

General Procedure for the Preparation of Unsymmetrical BisP* Ligands 1a−k: Trifluoromethanesulfonic acid (444 μL, 5 mmol) was slowly added under Ar to a stirred, cooled (0 °C) solution of unsymmetrical BisP*−BH_3 (**7a**−**k**) (1 mmol) in toluene (2 mL). The mixture was allowed to warm to room temperature and stirred until the unsymmetrical BisP*−BH_3 had disappeared by TLC. The solvent was removed in vacuo to leave a pasty oil, to which a solution of 3 N KOH/degassed EtOH (531 mg/3 mL) was slowly added with vigorous stirring. The mixture was stirred at 55 °C until BisP*−borane triflate had disappeared according to TLC (ca. 2 h), and allowed to cool to room temperature. The mixture was extracted with degassed ether (70 mL) and dried (Na_2SO_4). The solution was passed through a column (1 cm diameter) of basic alumina (20 g) with degassed ether. The eluent was evaporated under reduced pressure to give pure unsymmetrical BisP* (**1a**−**k**) as a solid or an oil.

General Procedure for the Preparation of Rhodium Complexes 2a−k: A solution of unsymmetrical BisP* (1 mmol) in THF (4 mL) was added under Ar to a stirred suspension of $[Rh(nbd)_2]BF_4$ (374 mg, 1 mmol) in THF (9 mL). The suspension gradually turned within 30 min into an almost clear solution, which was filtered under Ar to remove a small amount of precipitates. The filtrate was concentrated in vacuo, and the residue was washed with hexane to give an orange powder, which was dried under reduced pressure. Complexes **2a** and **2h** were recrystallized from THF/hexane to give dark red prisms and plates, respectively.

X-ray Crystallographic Analysis of [Rh(1a)(nbd)]BF_4 (2a):[20] $C_{25}H_{42}BF_4P_2Rh$; monoclinic, space group $P2_1$ (no. 4); *Z* = 2; *D* = 1.475 g cm^{-1}; cell constants *a* = 11.045(6) Å, *b* = 13.512(9) Å, *c* = 17.94(2) Å; β = 91.98(3)°; *V* = 2675(3) $Å^3$; temperature data collection 193 K; 4361 reflections measured, 4259 unique reflections [$I \geq 2.00\sigma(I)$]; 596 variables; *R* = 0.055; *Rw* = 0.075; GOF = 1.75;

bond lengths Rh−P1 2.315(3), Rh−P2 2.316(3), Rh−nbd ca. 2.2 Å, bond angles P1−Rh−P2 82.9(1), 1-Ad−P1−Me 106.3(6), *t*Bu−P2−Me 104.8°, torsion angle P1−C−C−P2 −48.2(9)°.

X-ray Crystallographic Analysis of [Rh(1h)(nbd)]BF_4 (2h): $C_{32}H_{52}BF_4P_2Rh$; triclinic, space group P_1 (no. 1); $Z = 4$; $D = 1.569$ g cm^{-1}; cell constants $a = 15.207(9)$, $b = 21.31(2)$, $c = 10.876(3)$ Å; $\alpha = 89.91(2)$, $\beta = 89.97(3)$, $\gamma = 88.53(4)°$; $V = 3523(3)$ Å^3; temperature data collection 293 K; 10134 reflections measured, 9712 unique reflections [$I \geq 2.00\sigma(I)$]; 1531 variables; $R = 0.088$; $Rw = 0.114$; GOF = 2.80; bond lengths Rh−P1 2.310(6), Rh−P2 2.327(6), Rh−nbd ca. 2.2 Å, bond angles P1−Rh−P2 84.0(2), 1-Ad−P1−Me 106(1), Cy−P2−Cy 103(1)°, torsion angle P1−C−C−P2 −45(3)°.

CCDC-172256 (**2h**) and -172257 (**2a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

General Procedure for Rh-Catalyzed Asymmetric Hydrogenation: A 50-mL Fisher−Porter tube was charged with 1 mmol of substrate and 2 μmol of the Rh catalyst. The tube was connected to a hydrogen tank through stainless steel tubing. The vessel was evacuated and filled with hydrogen gas (Nippon Sanso, 99.9999%) to a pressure of about 2 atm. This operation was repeated and the bottle was immersed in a dry ice/ethanol bath. The upper cock of the bottle was opened, and anhydrous methanol (2 mL) was added quickly by syringe. After four vacuum/H_2 cycles, the tube was pressurized to an initial pressure of 2−20 atm. The tube was closed and the cooling bath was removed. The solution was stirred at room temperature until no further hydrogen uptake was observed. The resulting solution was submitted to direct analysis of the enantiomeric excess values by HPLC or GC.

***N*-Acetylalanine Methyl Ester (9a):** Capillary GC, Chrompack Chiral-L-Val column (25 m), 120 °C, isothermal, carrier gas: N_2 (flow rate 10 cm/s); (*R*): $t_1 = 8.5$ min; (*S*): $t_2 = 9.1$ min.

***N*-Acetylphenylalanine Methyl Ester (9b):** HPLC, Daicel Chiralcel OJ, 1.0 mL/min, 10% *i*PrOH/hexane; (*R*): $t_1 = 11$ min; (*S*): $t_2 = 17$ min.

***N*-Acetyl-α-cyclopentylglycine Methyl Ester (9c):** Capillary GC, Chrompack Chiral-L-Val column (25 m), 135 °C, isothermal, carrier gas: N_2 (flow rate 53 cm/s); (*R*): $t_1 = 8$ min; (*S*): $t_2 = 9$ min.

***N*-Acetylvaline Methyl Ester (9d):** Capillary GC, Chrompack Chiral-L-Val column (25 m), 135 °C, isothermal, carrier gas: N_2 (flow rate 8 cm/s); (*R*): $t_1 = 10$ min; (*S*): $t_2 = 11$ min.

***N*-Acetyl-α-cyclohexylglycine Methyl Ester (9e):** Capillary GC, Chrompack Chiral-L-Val column (25 m), 135 °C, isothermal, carrier gas: N_2 (flow rate 53 cm/s); (*R*): $t_1 = 10$ min; (*S*): $t_2 = 11$ min.

(2*R*,3*S*)-*N*-Acetyl-*allo*-isoleucine Methyl Ester (9f): Capillary GC, Chrompack Chiral-L-Val column (25 m), 135 °C, isothermal, carrier gas: N_2 (flow rate 12 cm/s); (*R*): $t_1 = 9$ min; (*S*): $t_2 = 10$ min.

(2*R*,3*S*)-*N*-Acetylisoleucine Methyl Ester (9g): Capillary GC, Chrompack Chiral-L-Val column (25 m), 135 °C, isothermal, carrier gas: N_2 (flow rate 12 cm/s); (*R*): $t_1 = 8$ min; (*S*): $t_2 = 9$ min.

Methyl 3-Acetoamidebutanoate (9h): Capillary GC, Chiral Select 1000 column (30 m), 130 °C, carrier gas: N_2 (flow rate 20 cm/s); (*S*): $t_1 = 26$ min; (*R*): $t_2 = 27$ min.

Ethyl 3-Acetoamidobutanoate (9i): Capillary GC, Chiral Select 1000 column (30 m), 135 °C, carrier gas: N_2 (flow rate 10 cm/s); (*S*): $t_1 = 56$ min; (*R*): $t_2 = 58$ min.

Methyl 3-Acetoamidopentanoate (9j): Capillary GC, Chirasil DEX-CB column (30 m), 130 °C, carrier gas: N_2 (flow rate 20 cm/s); (*S*): $t_1 = 16$ min; (*R*): $t_2 = 17$ min.

***N*-Acetyl-1-(2′-methylphenyl)etheneamide (9k):** HPLC, Daicel Chiralcel AD, 1.0 mL/min, 10% *i*PrOH/hexane; (*R*): $t_1 = 7$ min; (*S*): $t_2 = 9$ min.

***N*-(1,2,3,4-Tetrahydronaphthalen-1-yl)acetamide (9l):** Capillary GC, Chiral Select 1000 column (30 m), 180 °C, carrier gas: N_2 (flow rate 10 cm/s); (*R*): $t_1 = 12$ min; (*S*): $t_2 = 13$ min.

Acknowledgments

The authors thank Dr. Hiroshi Danjo for helpful discussions and Kosuke Katagiri for X-ray analyses. This work was supported by a Grant-in-Aid from the Japanese Ministry of Education, Science, Culture, Sport and Technology.

[1] Review: I. Ojima (Ed.), *Catalytic Asymmetric Synthesis*, 2nd ed., Wiley-VCH, Weinheim, **2000**.
[2] Review: R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley & Sons, New York, **1994**.
[3] Review: T. Hayashi, K. Tomioka, O. Yonemitsu, *Asymmetric Synthesis*, Kodansha, Tokyo, **1998**.
[4] Review: E. N. Jacobsen, A. Pfaltz, H. Yamamoto, *Comprehensive Asymmetric Catalysis*, Springer, Berlin, **1999**.
[5] Review: H. B. Kagan, *Asymmetric Synthesis*, (Ed.: J. D. Morrison), Academic Press, Orlando, **1985**, vol. 5, chapter 1.
[6] H. B. Kagan, T. -P. Dang, *J. Am. Chem. Soc.* **1972**, *94*, 6429−6433.
[7] B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, D. J. Weinkauff, *J. Am. Chem. Soc.* **1977**, *99*, 5946−5952.
[8] A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souchi, R. Noyori, *J. Am. Chem. Soc.* **1980**, *102*, 7932−7934.
[9] M. J. Burk, *J. Am. Chem. Soc.* **1991**, *113*, 8518−8519.
[10] M. J. Burk, F. Bienewald, M. Harris, A. Z. Gerosa, *Angew. Chem. Int. Ed.* **1998**, *37*, 1931−1933.
[11] F. Robin, F. Mercier, L. Richard, F. Mathey, M. Spagnol, *Chem. Eur. J.* **1997**, *3*, 1365−1370.
[12] Q. Jiang, Y. Jiang, D. Xiao, P. Cao, X. Zhang, *Angew. Chem. Int. Ed.* **1998**, *37*, 1100−1107.
[13] A. Togni, C. Breutel, A. Schnyder, F. Spindler, H. Landert, A. Tijani, *J. Am. Chem. Soc.* **1994**, *116*, 4062−4066.
[14] G. Franciò, F. Faraone, W. Leitner, *Angew. Chem. Int. Ed.* **2001**, *39*, 1428−1430.
[15] G. Franciò, K. Wittmann, W. Leitner, *J. Organomet. Chem.* **2001**, *621*, 130−142.
[16] K. Yoshikawa, N. Yamamoto, M. Murata, K. Awano, T. Morimoto, K. Achiwa, *Tetrahedron; Asymmetry* **1992**, *3*, 13−16.
[17] D. Carmichael, H. Doucet, J. M. Brown, *Chem. Commun.* **1999**, 261−262.
[18] T. Imamoto, J. Watanabe, Y. Wada, H. Masuda, H. Yamada, H. Tsuruta, S. Matsukawa, K. Yamaguchi, *J. Am. Chem. Soc.* **1998**, *120*, 1635−1636.
[19] A. Ohashi, T. Imamoto, *Tetrahedron Lett.* **2001**, *42*, 1099−1101.
[20] A. Ohashi, T. Imamoto, *Org. Lett.* **2001**, *3*, 373−375.
[21] K. Nagata, S. Matsukawa, T. Imamoto, *J. Org. Chem.* **2000**, *65*, 4185−4188.
[22] L. McKinstry, T. Livinghouse, *Tetrahedron Lett.* **1994**, *35*, 9319−9322.

[23] L. McKinstry, T. Livinghouse, *Tetrahedron* **1994**, *50*, 6145−6154.
[24] I. D. Gridnev, N. Higashi, K. Asakura, T. Imamoto, *J. Am. Chem. Soc.* **2000**, *122*, 7183−7194.
[25] I. D. Gridnev, N. Higashi, T. Imamoto, *J. Am. Chem. Soc.* **2000**, *122*, 10486−10487.
[26] I. D. Gridnev, Y. Yamanoi, N. Higashi, H. Tsuruta, M. Yasutake, T. Imamoto, *Adv. Synth. Catal.* **2001**, *343*, 118−136.
[27] I. D. Gridnev, N. Higashi, T. Imamoto, *J. Am. Chem. Soc.* **2001**, *123*, 5268−5276.
[28] M. Yasutake, I. D. Gridnev, N. Higashi, T. Imamoto, *Org. Lett.* **2001**, *3*, 1701−1704.
[29] M. J. Burk, M. F. Gross, J. P. Martinez, *J. Am. Chem. Soc.* **1995**, *117*, 9375−9376.
[30] M. Sawamura, R. Kuwano, Y. Ito, *J. Am. Chem. Soc.* **1995**, *117*, 9602−9603.
[31] W. D. Lubell, M. Kitamura, R. Noyori, *Tetrahedron: Asymmetry* **1991**, *2*, 543−554.

Received May 24, 2001
[O01252]