

**Gearing Energy Surface of 1.** Because of the stated inadequacy of the angle bending potential function for large deformations (vide supra), attempts at simulating gear slippage were unsuccessful. Hence, we concentrated in this work on covering the part of the torsional energy surface that pertains to the dynamic gearing process.<sup>36</sup>

The torsional coordinates<sup>36</sup> are used to draw the surface:

$$\phi_1 = (\omega_1 + \omega_2 + \omega_3 + \alpha)/3$$

$$\phi_2 = (\omega_4 + \omega_5 + \omega_6 + \alpha)/3$$

where  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$  are the three torsional angles passing through the ether linkage and terminating at C(9), whereas  $\omega_4$ ,  $\omega_5$ , and  $\omega_6$  are those terminating at C(9'). Angle  $\alpha = 0$  when the smallest  $\omega$  is between 0 and  $\pi/3$ , and  $\alpha = 2\pi$  when the smallest  $\omega$  is between  $\pi/3$  and  $2\pi/3$ . About 70 points near the gearing coordinates were calculated and smoothed<sup>37</sup> to give an energy surface which is reproduced in Figure 6. According to this map, the dynamic gearing of 1 takes place rapidly along an almost flat valley having a finite width. Between the two adjacent energy minima ( $C_s$  and  $C_2$ ) is a very low, unsymmetrical barrier, only 0.93 kcal/mol above  $C_s$ . The calculated low barrier is in accord with the failure to detect it in low-temperature NMR experiments on 1.<sup>2a,d</sup> Our calculations indicate that the C-O-C angle expands further by 1° at the top of the barrier.<sup>38</sup>

(36) In these calculations, the C-O-C angle had to be fixed at the outset of minimization in order to prevent this angle from expanding beyond the artificial maximum in the potential curve, leading to "explosion" of the molecule. Only at the final stage of minimization was the C-O-C angle relaxed.

(37) E. Ōsawa, *J. Comput. Chem.* 1982, 3, 400.

In the hydrocarbon analogues,  $C_s$  conformations (observed in crystals slightly distorted to  $C_1$  point group) are the transition states along the dynamic gearing trajectory with  $C_2$  conformations as the global energy minima.<sup>3b,d</sup> In 1, both of these conformations are energy minima.

The present X-ray analysis and molecular mechanics calculations give the following partial picture of the novel molecule 1: a slightly worn out but still considerably tightly meshed gear with unusually large deformation at the oxygen bridge and with strain in the internal part as strong as in Mislow's hydrocarbon analogues.<sup>3</sup>

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**Supplementary Material Available:** Tables of hydrogen atomic coordinates, anisotropic thermal parameters, and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

(38) The employed potential energy function for the C-O-C valence angle underestimates the increase of the energy and even becomes defective at ca. 140° as the angle increases from the equilibrium value. Therefore, if the valence angle changed drastically along the calculated torsional coordinate, the result should have been regarded invalid. Fortunately, the valence angle change was kept within 1°.

## Preparation and Lithiation of Optically Active 2,2'-Dihalo-1,1'-binaphthyls. A General Strategy for Obtaining Chiral, Bidentate Ligands for Use in Asymmetric Synthesis

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**Abstract:** Chiral, bidentate ligands based on the 1,1'-binaphthyl system have achieved remarkable success in certain asymmetric syntheses that have been reported in the literature. Enantiomeric excesses are often above 90% and may approach 99% or better. In the present paper, it is demonstrated that 2,2'-dibromo-1,1'-binaphthyl and the corresponding diiodide can be obtained in preparative quantities with optical purities in excess of 98%. The compounds can be mono- or dilithiated, and the lithio intermediates are configurationally stable from -131 °C up to at least -44 °C. Yields of the dilithio intermediate are 95% or higher, and the monolithio intermediates can be formed in chemical yields of 80-85%. This discovery provides an efficient, general route for obtaining symmetrical and unsymmetrical chiral, bidentate ligands based on the binaphthyl system. These derivatives are expected to have broad applications in mechanistic studies of asymmetric reactions and in practical synthetic procedures. For example, (*R*)- and (*S*)-BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl), which are reported to give enantiomeric excesses approaching 100% in certain rhodium-catalyzed hydrogenations, have been synthesized from 2-naphthol in overall yields ranging from 16% to 34%.

### I. Introduction

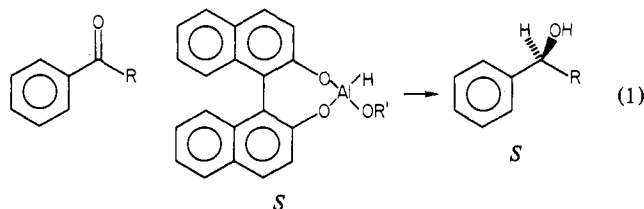
In recent years, optically active 2,2'-disubstituted-1,1'-binaphthyl derivatives have been used in the asymmetric hydride reduction of ketones,<sup>1</sup> in the asymmetric hydrogenation of amino

acrylic acid derivatives,<sup>2a</sup> in the isomerization of allylamines to chiral enamines,<sup>2b</sup> in the asymmetric alkylation and arylation of

(1) R. Noyori, I. Tomino, and Y. Tanimo, *J. Am. Chem. Soc.*, 101, 3129 (1979).

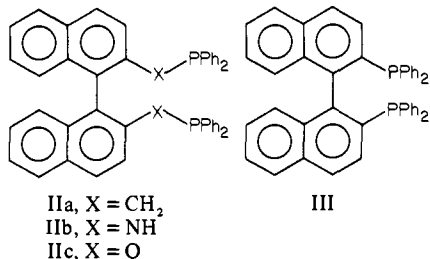
(2) (a) A. Miyashita, A. Yasuda, H. Takaya, K. Toriumi, T. Ito, T. Souchi, and R. Noyori, *J. Am. Chem. Soc.* 102, 7932 (1980); (b) K. Tani, T. Yamagata, S. Otsuka, S. Akutagawa, H. Kumobayashi, T. Taketomi, H. Takaya, A. Miyashita, and R. Noyori, *J. Chem. Soc., Chem. Commun.*, 600 (1982).

aldehydes,<sup>3</sup> and in a stereoselective Michael addition between methyl vinyl ketone and the potassium salt of 2-(methoxycarbonyl)-1-indanone.<sup>4</sup> A common theme of these reactions is coordination of a chiral, bidentate or polydentate ligand to a metal (Al, Rh, Li, K) that formally transfers hydride, alkyl, aryl, or enolate to an electrophile ( $\text{RCOH}$ ,  $\text{RCH}=\text{C}(\text{NHCOR})\text{CO}_2\text{R}$ ,  $\text{CH}_2=\text{CHCOCH}_3$ ), as seen in the following example. The high



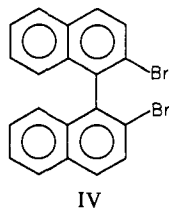
optical yields (95–100% ee) observed<sup>1,2</sup> in these reactions<sup>1–4</sup> with the bidentate binaphthyl derivatives suggest that transferring a nucleophilic group from a metal that is coordinated to ligands at the 2 and 2' positions of a chiral binaphthyl may be a general approach for achieving high optical yields in a variety of chemical transformations.

The effectiveness of the coordinating groups appears to be enhanced when they are attached directly to the 2 and 2' positions rather than to intervening groups such as methylene. For example, the bisphosphine (IIa) gives an optical yield of only 54% (ee) for



the hydrogenation of an aminoacrylic acid derivative,<sup>5</sup> compared to 100% (ee) observed with bisphosphine III.<sup>2</sup> Similar reductions in optical yield are observed for IIb,c.<sup>6,7</sup>

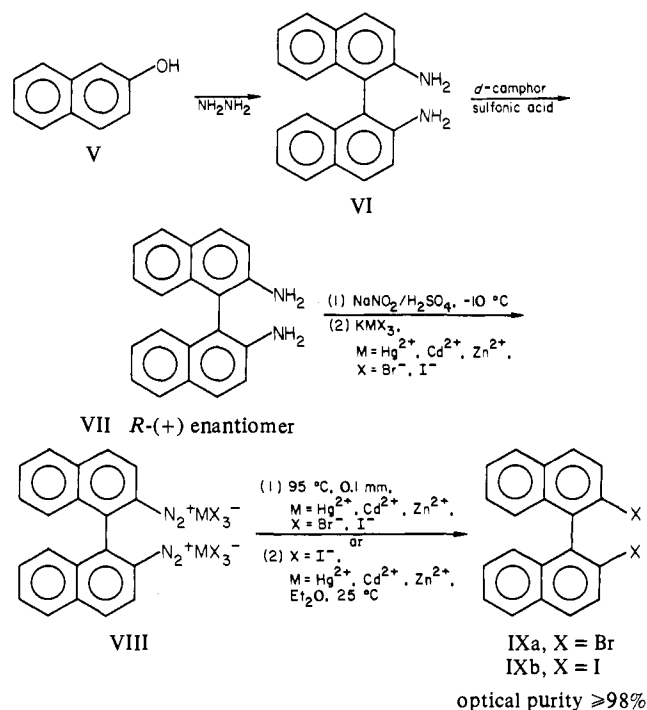
The bis(phosphine) III has been prepared from racemic 2,2'-dibromo-1,1'-binaphthyl (IV) by dilithiation followed by reaction



with diphenylchlorophosphine. The bis(phosphine) III is highly effective in asymmetric hydrogenation reactions. However, it must be resolved after its synthesis, since IV has not previously been available in optically active form, and until now, it has not been established that 2,2'-dilithio-1,1'-biaryls can be prepared and reacted without significant loss of stereochemistry. A serious drawback to the use of *racemic* IV as a starting point for synthesizing chiral bidentate ligands is that individual resolution procedures must be separately worked out for each new binaphthyl derivative.

An alternative to a customized optical resolution for each new product is to use an easily resolvable chiral precursor as the key element of the synthetic strategy. This approach has been taken in the synthesis of chiral ligands such as IIa,b,c or various chiral

Scheme I



amines,<sup>4</sup> which can all be derived from known optically active binaphthyl precursors (e.g., 2,2'-dihydroxy-1,1'-binaphthyl, 2,2'-diamino-1,1'-binaphthyl, 1,1'-binaphthyl-2,2'-dicarboxylic acid), but their effectiveness in asymmetric synthesis is low compared to when the coordinating groups (e.g., Ph<sub>2</sub>P) are attached directly to the binaphthyl nucleus (vide supra). Consequently, synthetic methods of preparing optically pure 2,2'-dihalo-1,1'-binaphthyl and methods of introducing coordinating groups by replacement of halogen without losing optical activity would be novel and of considerable practical importance.<sup>1,2</sup>

Racemic 2,2'-dibromo-1,1'-binaphthyl (DBBN) can be prepared in 45% yield by treating 2,2'-dihydroxy-1,1'-binaphthyl (DHBN) with  $\text{Br}_2/\text{PPh}_3$  at 320 °C. Although optically active DHBN is available,<sup>8,9</sup> the high temperature of the reaction precludes the isolation of DBBN with significant optical activity.

Recently, McKillop, and Taylor<sup>10</sup> have reported syntheses of symmetric biaryls through a regiospecific, oxidative dehydrodimerization resulting from treatment of a variety of aromatic substrates with oxidizing metals in trifluoroacetic acid, in carbon tetrachloride, or in acetonitrile containing boron trifluoride etherate. Although racemic 2,2'-dibromo-1,1'-binaphthyl has been synthesized in 55% yield by treating 2-bromonaphthalene with  $\text{Pb}(\text{O}_2\text{CCH}_3)_4$ , the method is not yet applicable to the direct synthesis of optically active biaryls.

In the present work, optically pure DBBN and 2,2'-diiodo-1,1'-binaphthyl (DIBN) have both been obtained through a route starting with 2-naphthol.

The transformation of the diamine VII to the dibromide IXa is similar to one previously reported by Pichat<sup>11</sup> and others.<sup>12,13</sup> Pichat decomposed the bis(diazonium) salt (VIII,  $\text{MX}_3^- = \text{HgBr}_2^-$ ) at atmospheric pressure ( $\sim 140$  °C), and under these conditions the decomposition leads to rapid evolution of nitrogen, bubbling of the tarry, molten reaction products, and recovery of largely<sup>14</sup> racemic dibromide. However, we have found<sup>14</sup> that at

(8) J. Jacques and C. Fouquet, *Tetrahedron Lett.*, 4617 (1971).

(9) S. Murata, R. Noyori, and H. Takaya, *J. Am. Chem. Soc.*, **103**, 6971 (1981).

(10) A. McKillop, A. G. Turrell, D. W. Young, and E. C. Taylor, *J. Am. Chem. Soc.*, **102**, 6504 (1980).

(11) L. Pichat and J. Clement, *Bull. Soc. Chim. Fr.*, 525 (1961).

(12) A. I. Vogel, "A Textbook of Practical Organic Chemistry", Wiley, New York, 1966.

(13) C. R. Noller, "Chemistry of Organic Compounds", W. B. Saunders Co., Philadelphia, 1951.

(3) J. P. Mazaleyrat and D. J. Cram, *J. Am. Chem. Soc.*, **103**, 4585 (1981).

(4) D. J. Cram and G. D. Y. Sogah, *J. Chem. Soc., Chem. Comm.*, 625 (1981).

(5) K. Tamao, H. Yamamoto, H. Matsumoto, N. Miyoko, T. Hayashi, and M. Kumada *Tetrahedron Lett.*, 1389 (1977).

(6) S. Miyano, M. Nawa, and H. Hashimoto, *Chem. Lett.*, 729 (1980).

(7) R. H. Grubbs and R. A. Devries, *Tetrahedron Lett.*, 1879 (1977).

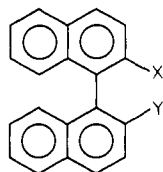
~0.1 torr pressure, the decomposition can be carried out smoothly at 95 °C without the formation of molten material and with little or no loss of optical activity in the recovered dibromide. Pichat reports yields of racemic dibromide IX from the diamine VII in the neighborhood of 80%, and we<sup>14</sup> have found that the yields of optically pure dibromide IX are comparable if the starting diamine is carefully purified and if the diazotization conditions are closely monitored.

It was also discovered that bis(diazonium) metal iodide complexes (VIII) can be decomposed by washing with dry ether at room temperature to yield DIBN after chromatographing the filtrate.<sup>14</sup> Again, little or no loss of optical activity occurs. One synthesis of racemic diiodide has been reported in the literature,<sup>28</sup> and yields are on the order of 18% (on the basis of 2,2'-diamino-1,1'-binaphthyl). We have produced optically pure DIBN in yields up to 50% (Scheme I), and part of the reason for the increased yield over the normal Sandmeyer reaction probably lies in the fact that the bis(diazonium) complexes can be decomposed in the absence of water thereby minimizing phenol formation and diazo coupling reactions.

It should also be noted that while this is the first reported synthesis of optically pure 2,2'-dihalo-1,1'-binaphthyls, there has been a report of the partial resolution of small quantities of 2,2'-dibromo-1,1'-binaphthyl by HPLC.<sup>9</sup>

The value of having optically pure 2,2'-dihalo-1,1'-binaphthyls depends on whether the halogens can be replaced with appropriate groups without significant loss of optical activity. In the Experimental Section, the mono- and dilithiation of DBBN and DIBN are described, and it is shown that metalation and subsequent reaction with a variety of electrophiles takes place at -50 to -131 °C without appreciable loss of optical activity. This result is interesting when compared with the work of Schleyer and co-workers,<sup>15</sup> who have demonstrated that 2,2'-dilithiobiphenyl has a structure in which the two lithium atoms are arranged symmetrically above and below a planar  $\pi$ -system. Our experimental results indicate configurational stability for the 2,2'-dilithio-1,1'-binaphthyl intermediate, and consequently, symmetrical bridging by the lithiums is not always a structural feature in the ground states of all dilithiobiaryls.

The monolithiation of 2,2'-dihalo-1,1'-binaphthyls with preservation of optical activity is particularly significant, since this transformation provides a simple route to chiral, *unsymmetrical* bidentate ligands of the type



X, X = Br; Y = PPh<sub>2</sub>

The optical activity of this class of compounds derives from a common precursor (DABN), and no separate resolutions of new members in the series are necessary.

## II. Results

The aim of the present work is to establish the extent to which optical activity can be preserved when (*R*)- or (*S*)-2,2'-diamino-1,1'-binaphthyl undergoes successive transformations to 2,2'-dibromo- or 2,2'-diiodo-1,1'-binaphthyl, to the 2,2'-dilithio- or 2-halo-2'-lithio-1,1'-binaphthyl, and ultimately to products derived from reactions of the lithio intermediates with electrophiles such as chlorophosphines, aldehydes, and others. The discussion of this determination is organized around three general and independent lines of experiment: (1) recrystallization and purification of the 2,2'-dihalo-1,1'-binaphthyls to constant specific rotation; (2) preparation of 2,2'-bis(diphenylphosphino)-1,1'-bi-

naphthyl from DIBN via 2,2'-dilithio-1,1'-binaphthyl and determination of the optical purity of the bis(phosphine) by a <sup>31</sup>P NMR technique; (3) preparation of 2-(hydroxyphenylmethyl)-1,1'-binaphthyl from DIBN and DBBN via the dilithio or monolithio intermediate and determination of the optical purity of the monoalcohol using proton NMR and the chiral shift reagent Eu(dcm)<sub>3</sub> (tris(*d,d*-dicampholylmethanato)europium(III)).<sup>16</sup> The employment of both <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy, two different optically active derivatives prepared from DBBN and DIBN, and the classical technique of crystallizing to constant rotation minimizes the uncertainty associated with any one technique for determining optical purity.

(A) **Maximum Observed Rotation of DBBN and DIBN. (1) 2,2'-Dibromo-1,1'-binaphthyl.** Recrystallization of optically active DBBN from 95% ethanol leads to two distinct crystal forms (see Experimental Section). The high-rotating crystals (mp = 155–157 °C, corrected) consistently gave specific rotations between 32° and 34°, and no change is noted after repeated cycles of crystallization and sublimation. Consequently, the specific rotation of optically pure DBBN can be estimated to be 33 ± 1° (pyridine, *c* 1.0–2.0).

(2) **2,2'-Diiodo-1,1'-binaphthyl.** The crude DIBN was generally recrystallized once from 80% hexane/20% xylene and then sublimed. Repeated cycles of crystallization/sublimation did not change the specific rotations within experimental error. The average  $[\alpha]_D^{25}$  of twelve samples was found to be 16.2 ± 0.2° (pyridine, *c* 1.0–2.0). The range covers 15.8–16.6°. All twelve samples melted sharply over a range of 1 to 2 °C (mp = 215–217 °C, corrected; see Experimental Section).

(B) **Optical Purity of 2-(hydroxyphenylmethyl)-1,1'-binaphthyl Derived from DBBN and DIBN.** 2-(Hydroxyphenylmethyl)-1,1'-binaphthyl (HPMBN) contains two elements of chirality: one associated with the binaphthyl unit and one associated with the carbon substituent at the 2-position. Thus, the compound consists of four stereoisomers that can be grouped into two sets of diastereomers, each of which contains two enantiomers. The configuration of the benzylic carbon at the 2-position has not yet been established for certain,<sup>17</sup> but it is clear that the pair of enantiomers comprising each set of diastereomers will correspond to opposite configurations for the binaphthyl rings. Consequently, if HPMBN is synthesized from racemic DBBN and the two diastereomers HPMBN-1 and HMPBN-2 (Experimental Section) are separated, it will be found that each diastereomer will consist of two enantiomers (present in equal amounts) that differ by the configuration of the binaphthyl unit. If 100% optically pure DBBN (e.g., *R* configuration) is used as starting material and if there is no loss of stereochemistry during metalation and subsequent reaction, then the two diastereomers will be formed in the same ratio as in the first experiment, but each will contain only a single enantiomer where the binaphthyl unit has the *R* configuration. If the DBBN is not 100% optically pure or if racemization occurs during metalation, then each diastereomer of HPMBN will consist of a mixture of its two corresponding enantiomers. Consequently, measuring the optical purity of HPMBN-1 provides information on the original optical purity of DBBN, the loss of optical activity on conversion to the 2,2'-dilithio-1,1'-binaphthyl or to 2-bromo-2'-lithio-1,1'-binaphthyl, and any loss of optical activity in the formation or in the workup of HPMBN-1.

The results of these determinations are listed in Table I. In the first set of experiments, it was found that a sample of HPMBN-1 (prepared from (*R*)-DBBN,  $[\alpha]_D^{21}$  25.75 ± 1.0°, by monolithiation) consists of its two enantiomers in a ratio of 6.2 (±0.3):1, corresponding to an enantiomeric excess of 72.22 ± 3%. On the basis of a maximum specific rotation of 33° ± 1° for

(16) M. D. McCreary, D. W. Lewis, D. L. Wernick, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 1038 (1974).

(17) K. J. Brown and J. R. Murdoch, manuscript in preparation. The diastereomeric selectivity for addition of an aldehyde to a 2'-substituted 2-lithio-1,1'-binaphthyl is highly dependent upon the substituent. 2'-Substituents that have been examined include H, Br, I, Li, CHOLiPh (*R* and *S*), and CHOLi-2'-naphthyl (*R* and *S*), and the selectivities range from 86% in favor of one diastereomer to 90% in favor of the opposite diastereomer.

(14) J. R. Murdoch, K. J. Brown, and M. S. Berry, manuscript in preparation.

(15) U. Schubert, W. Nengebauer, and P. v. R. Schleyer, *J. Chem. Soc., Chem. Commun.* 1184 (1982).

Table I. Preservation of Enantiomeric Purity for Binaphthyl Derivatives Prepared from 2,2'-Dihalo-1,1'-binaphthyl

expt	starting material	ee <sup>h</sup> (DBBN or DIBN), %	intermediate <sup>a</sup>			product	enantiomeric ratio	ee <sup>i</sup> (HPMBN or BDPBN), %	derived maximum rotation for dihalo-binaphthyl
			X	Y	T, °C				
1	(R)-DBBN, $[\alpha]_D^{23}$ 25.75 ± 1.0°	78.0 ± 4	Br	Li	-44	HPMBN	6.2 ± 0.3 <sup>b</sup>	72.2 ± 3	35.65 ± 1.7°
2	(R)-DBBN, $[\alpha]_D^{21,4}$ 31.8 ± 1.2°	96.4 ± 4	Br	Li	-44	HPMBN	>99 <sup>c</sup>	>98	32.5 ± 1.2°
3	(R)-DBBN, $[\alpha]_D^{25}$ 29.2 ± 1.5°	88.5 ± 5	Li	Li	-44	BDPBN	13.808 ± 0.2 <sup>g</sup>	86.5 ± 1	33.8 ± 1.7°
4	(R)-DIBN, $[\alpha]_D^{21}$ 7.8 ± 0.34°	48.1 ± 2	I	Li	-131	HPMBN	2.79 ± 0.29 <sup>d</sup>	47.2 ± 3	16.5 ± 1.6°
5	(R)-DIBN, $[\alpha]_D^{25}$ 7.08 ± 0.20°	43.7 ± 1	I	Li	-131	HPMBN	2.49 ± 0.26 <sup>e</sup>	42.7 ± 3	16.6 ± 1.7°
6	(R)-DIBN, $[\alpha]_D^{23}$ 16.2 ± 0.2°	>98	Li	Li	-131	HPMBN	>99 <sup>f</sup>	>98	16.5 ± 0.2°
7	(S)-DIBN, $[\alpha]_D^{23}$ -9.34 ± 0.5°	57.7 ± 3	Li	Li	-131	BDPBN	3.669 ± 0.027 <sup>g</sup>	57.2 ± 1	16.3 ± 0.9°

<sup>a</sup> See structure X for key to X and Y. <sup>b</sup> Average of two experiments at 15 °C and one at 25 °C. <sup>c</sup> One experiment at 25 °C. <sup>d</sup> One experiment at 0 °C. <sup>e</sup> Average of four experiments at 25 °C and one at 10 °C. <sup>f</sup> One experiment at 5 °C. <sup>g</sup> Two experiments at 25 °C. <sup>h</sup> Derived from maximum observed specific rotation of DBBN (33 ± 1°) or DIBN (16.2 ± 0.2°) and measured specific rotation of starting material. <sup>i</sup> Derived from enantiomeric ratio measured for products (HPMBN or BDPBN) obtained from either DBBN or DIBN.

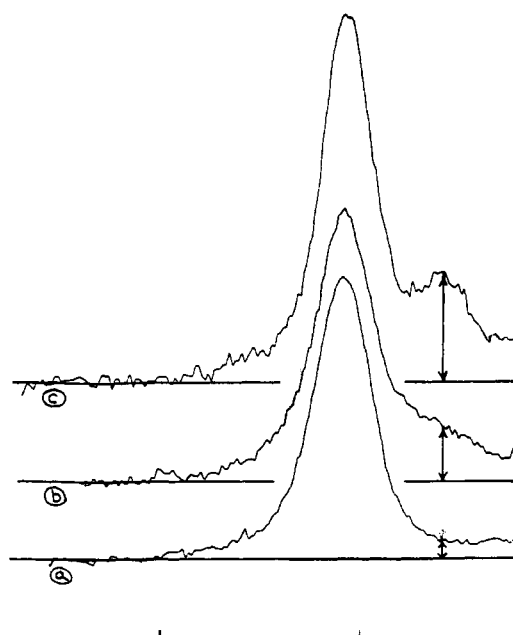
DBBN, the enantiomeric excess of the starting DBBN is 78.0 ± 4%, which, within experimental error, is equal to the enantiomeric excess observed in the final product, HPMBN-1. We can also use the measured enantiomeric excess for HPMBN-1 (72.22 ± 3%) and the measured specific rotation of the starting DBBN (25.75 ± 1.0°) to derive a value for the specific rotation of optically pure DBBN (35.65 ± 1.7°) that agrees, to within experimental error, with the value of 33 ± 1° obtained by crystallization.

Since the enantiomeric signals in the NMR spectra are not quite base-line separated, a systematic error exists in the integrated peak areas due to the partial overlap of the peaks. Because the two peaks are of different areas, this overlap leads to a value for the ratio of integrated areas that is too small. Moreover, the relative magnitude of this error increases as the difference between the two areas becomes larger. Consequently, the integrated ratios are lower limits and the corresponding calculated maximum rotation,  $[\alpha]_D^{23}$  35.65°, is an upper limit (vide infra).

In experiment 2, the specific rotation of DBBN is 31.8 ± 1.2°, and the minor enantiomer was not detected (Figure 1). Small increments of a sample of racemic HPMBN-1 were then added to the NMR tube and the presence of the minor enantiomer became apparent. From the increase in the area of the signal originating from the minor enantiomer and the amount of racemic HPMBN-1 added to the NMR tube, it can be estimated that the original sample is no less than 98% optically pure. This would correspond to a maximum specific rotation for DBBN of 32.5 ± 1.2° and is in excellent agreement with the value determined by crystallization. This number for the specific rotation of DBBN closely coincides with the specific rotation achieved for most samples of DBBN after one or two recrystallization/sublimation cycles and suggests that heroic measures are unnecessary in order to obtain preparative samples of DBBN with optical purities in excess of 98%. This experiment also sets an upper limit (<2%) on the amount of racemization encountered along the series of transformations (DBBN → 2-bromo-2'-lithio-1,1'-binaphthyl → HPMBN). The first step in this series was carried out over the course of 5–15 min at -44 °C.

Experiments 4 and 5 (Table I) provide an upper limit to the maximum specific rotation for DIBN just as experiment 1 did for DBBN.<sup>18</sup> The maximum specific rotation derived from experiments 3 and 4 is 16.55 ± 1.7° and is in agreement with that found by recrystallizing to constant rotation ( $[\alpha]_D^{23}$  16.2 ± 0.2°). Note that the enantiomeric excess is smaller for these experiments with DIBN than with DBBN (experiment 1) and that there is closer agreement between the two experimental values of the maximum specific rotation (16.55° vs. 16.2°). The results also demonstrate the degree to which the intermediate, 2-iodo-2'-lithio-1,1'-binaphthyl, is configurationally stable (<2.5% racemization at -131 °C over ~30 min).

In experiment 6, a sample of DIBN ( $[\alpha]_D^{23}$  16.2 ± 0.2°) was converted to 2,2'-dilithio-1,1'-binaphthyl and reacted with 1 equiv



**Figure 1.** (a) Proton NMR spectrum of HPMBN-1 in the presence of Eu(dcm)<sub>3</sub>. The observed signal is due to the benzylic hydrogen. HPMBN-1 was prepared from DBBN with specific rotation of 31.8° (see Table I). (b) Same spectrum as in (a), but with a small amount of added racemic HPMBN-1. The added minor enantiomer is about 3% of the original amount of major enantiomer. (c) Same as in (a), but with 10% added minor enantiomer. For (b) and (c), an ~equivalent amount of Eu(dcm)<sub>3</sub> is added with the racemic sample. All spectra were run on a Bruker WP-200 FT NMR spectrometer in 33% CDCl<sub>3</sub>/CCl<sub>4</sub> (v/v) that for spectrum (a) contains ca. 1 mg HPMBN-1 + 6.6 mg Eu(dcm)<sub>3</sub> per 0.6 mL solvent. The spectra are run at a sweep width of 2500 Hz with ca. 16 000 points and a pulse width of 2.5 μs. The number of scans is 7672 (a); 2264 (b); 1200 (c).

of benzaldehyde (see Experimental Section). No signals due to the presence of the second enantiomer of HPMBN-1 could be detected, and additions of racemic HPMBN-1 established that the original sample of HPMBN and DIBN is at least 98% optically pure. This sets an upper limit of 16.5 ± 0.2° on the specific rotation of DIBN and is in excellent agreement with the value estimated by crystallization. This last experiment is particularly significant, since it demonstrates that 2,2'-dilithio-1,1'-binaphthyl is configurationally stable under the reaction conditions (-131 °C, 30 min).

**(C) Optical Purity of 2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl Derived from DBBN and DIBN. (1) General Considerations.** As a first step in the optical purity determination,<sup>19</sup> a sample of the bisphosphine prepared from either partially racemic

(18) This assumes no racemization during the formation of HPMBN (see next paragraph).

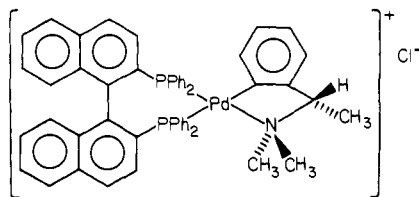
(19) E. P. Kyba and S. P. Rines, *Abstr. Pap.-Am. Chem. Soc.*, **183rd** (1982).

Table II.  $^{31}\text{P}$  NMR Spectra of Bis(phosphine)/Pd Complex

peak	chemical shift <sup>a,b,e</sup>	$J$ , Hz <sup>d</sup>	assignment of peaks <sup>c</sup>
1	38.8043	44.2	$S,S$ -a
2	38.2582		
3	38.0481	43.2	$R,S$ -a'
4	37.5150		
5	11.8963	43.6	$R,S$ -b'
6	11.3578		
7	11.2764	44.3	$S,S$ -b
8	10.7293		

<sup>a</sup> Chemical shift is in ppm from internal phosphoric acid. Solvent is  $\text{CDCl}_3$ . <sup>b</sup> Accuracy is estimated at  $\pm 0.002$  ppm. <sup>c</sup> The first configuration refers to the binaphthyl ring and the second refers to the asymmetric carbon in XII. The letters (a,b) and (a',b') distinguish the two diastereotopic phosphorous atoms within the  $S,S$  and  $R,S$  complexes, respectively. <sup>d</sup> Accuracy is estimated at  $\pm 0.4$  Hz. <sup>e</sup> Spectra are run at 81.02 MHz on a Bruker WP-200 FT-NMR spectrometer. Sweep width is 3000 Hz. Number of points is ca. 16 000. The number of scans is 7000.

DIBN or DBBN was reacted with  $\mu$ -(dichloro)bis[( $S$ )- $N,N$ -dimethyl-(1-phenylethyl)amine-2 $C,N$ ]dipalladium(II)<sup>19</sup> to form the palladium complex,



XI

The complex has two elements contributing to its optical activity (the asymmetric carbon and the twisted binaphthyl unit), and consequently, two diastereomers are possible. In addition, the two phosphorous atoms are not equivalent, as they are in the original bis(phosphine), so that observable magnetic coupling between the two phosphorous atoms is possible in the complex. Therefore, the  $^{31}\text{P}$  NMR spectrum of the complex will theoretically show a pair of doublets for each diastereomer. If the complex is made from racemic or partially racemic bis(phosphine), then we can expect that the  $^{31}\text{P}$  NMR spectrum will contain a maximum of eight lines: a pair of doublets (four lines) from each of the two diastereomeric complexes.

The  $^{31}\text{P}$  NMR spectra ( $\text{CDCl}_3$ ) of the complex (made with racemic bis(phosphine)) generally exhibited all eight lines, which appear as a downfield group of four lines near 38 ppm and an upfield group of four lines near 11 ppm (Table II). All lines in the spectrum of the complex made with racemic bis(phosphine) are of equal area to within 2%, which is within the error limits for the integration. The assignment of the  $^{31}\text{P}$  signals to the respective diastereomeric palladium/bis(phosphine) complexes was made by examining the spectrum of a palladium complex made from bisphosphine enriched in the  $R$  enantiomer (( $R$ )-DBBN was in the starting material). It was observed that the two lowest field peaks and the two highest field peaks were reduced in intensity. The assignment of the two low-field signals and the two high-field signals to one diastereomer is also confirmed by the observed coupling constants (Table II). In  $\text{CDCl}_3$ , the outermost peaks of the group at  $\sim 38$  ppm and at  $\sim 11$  ppm are base-line separated.

(2) **Bis(phosphine) Derived from DBBN.** Experiment 3 (Table I) involves bis(phosphine) prepared from ( $R$ )-DBBN ( $[\alpha]_D^{25} = 29.2 \pm 1.5^\circ$ , pyridine), which gives the relative areas of peak 4 and peak 1 as  $13.808 \pm 0.2$ . The relative areas correspond to an enantiomeric excess of  $86.49 \pm 0.4\%$ , which in turn yields a value for the maximum rotation of  $R$ -DBBN equal to  $33.8 \pm 1.7^\circ$ , which is in excellent agreement with the value determined by crystallization and by conversion of ( $R$ )-DBBN to 2'-(hydroxyphenylmethyl)-1,1'-binaphthyl. In this case, the bisphosphine was prepared by lithiation of DBBN at  $-44^\circ\text{C}$ , and the result es-

tablishes the configurational stability of 2,2'-dilithio-1,1'-binaphthyl at  $-44^\circ\text{C}$ , over the course of 30 min.

(3) **Bis(phosphine) Derived from DIBN.** Experiment 7 employed ( $S$ )-DIBN ( $[\alpha]_D^{23} = -9.34 \pm 0.5^\circ$ , pyridine) that was converted to 2,2'-dilithio-1,1'-binaphthyl at  $-131^\circ\text{C}$  and reacted with diphenylchlorophosphine to give the desired bis(phosphine). The ratio of peak 1 to peak 4 ( $3.669 \pm 0.027$ ) corresponds to an enantiomeric excess of  $57.16 \pm 0.25\%$  and a maximum specific rotation for ( $S$ )-DIBN of  $-16.34 \pm 0.9^\circ$ . The results are again in excellent agreement with the determinations of the maximum specific rotation obtained by crystallization and from the monoalcohol derivative with the  $R$  configuration.

### III. Conclusions

In the present paper, it is shown that 2,2'-dibromo-1,1'-binaphthyl and 2,2'-diiodo-1,1'-binaphthyl can be obtained in preparative quantities with optical purities in excess of 98%. Both compounds can be converted to 2,2'-dilithio-1,1'-binaphthyl in high chemical yields (>95%) with essentially complete retention (>98%) of optical activity at temperatures ranging from  $-131$  to  $-44^\circ\text{C}$ . Likewise, each dihalobinaphthyl derivative can be monolithiated (at temperatures ranging from  $-131$  to  $-44^\circ\text{C}$ ) to give 2-lithio-2'-halo-1,1'-binaphthyl in chemical yields of at least 80–85% and with complete retention of optical activity (>98%). This discovery provides an efficient, general route for obtaining symmetrical and unsymmetrical chiral, bidentate ligands which are derived from the binaphthyl system. These derivatives are expected to have broad applications in mechanistic studies of asymmetric reactions and in practical synthetic operations.

### IV. Experimental Section

Full experimental details are available as supplementary information. The preparation of 2,2'-diamino-1'-binaphthyl (DABN), the resolution of DABN, and the conversion of ( $R$ )-DABN (or ( $S$ )-DABN) to ( $R$ )-2,2'-dibromo-1,1'-binaphthyl (( $R$ )-DBBN) and to ( $R$ )-2,2'-diiodo-1,1'-binaphthyl (( $R$ )-DIBN) have been described.<sup>14</sup>

**2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (BDPBN) from DIBN.** (a) **Dilithiation of DIBN with  $t$ -BuLi at  $-131^\circ\text{C}$ .** Approximately 350 mL of dimethyl ether was thoroughly dried and then placed on the vacuum line where it was degassed by successive freeze-pump-thaw cycles. From this point onward, all glassware that came in contact with dimethyl ether had been flame dried prior to use. Once degassed, the  $\text{Me}_2\text{O}$  (200–300 mL) was vacuum transferred into a Schlenk flask containing DIBN (0.5 g, 0.9881 mmol) and a stir bar. The  $\text{Me}_2\text{O}$  was then brought to  $-78^\circ\text{C}$ , and the DIBN was completely dissolved. Next, the flask was cooled to  $-131^\circ\text{C}$  (pentane slush) and to the stirring solution 1.34 mL (2.948 mmol) of 2.2 M  $t$ -BuLi (in hexane, Alfa) was added under a positive argon pressure over 30 s. The solution turned bright yellow immediately and was stirred for 8 min, producing the dilithio intermediate, to which was added 1.8 mL (10.3 mmol) of diphenylchlorophosphine. The solution (now colorless or nearly colorless) was stirred at  $-131^\circ\text{C}$  for 45 min and then at  $-78^\circ\text{C}$  overnight under argon.

The reaction was quenched with 0.5 mL of  $\text{CH}_3\text{OD}$ , and the  $\text{Me}_2\text{O}$  was vacuum transferred back into the original flask. To the remaining precipitate was added 1 M sodium bicarbonate (50 mL) and  $\text{CH}_2\text{Cl}_2$  (50 mL). This mixture was vigorously stirred for 1–2 h and then extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 300$  mL). The crude product was chromatographed on silica gel by using 50/50  $\text{CCl}_4/\text{CH}_2\text{Cl}_2$  (v/v). Yields of bis(phosphine) range from 62% to 72% and are not optimized. The melting point of racemic BDPBN is  $274$ – $277^\circ\text{C}$ , uncorrected;  $287.4$ – $290.6^\circ\text{C}$ , corrected. The melting point of ( $R$ )-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl is  $224$ – $226^\circ\text{C}$ , uncorrected;  $234.1$ – $236.3^\circ\text{C}$ , corrected. Low-resolution mass spectra (16 eV) showed an extremely small parent peak at  $m/e = 622$ , but this was not reproducible even with the same sample. Elemental analysis (Schwarzkopf) found: C (84.75%), H (4.91%), P (10.01%). Calcd for  $\text{C}_{44}\text{H}_{32}\text{P}_2$ : C (84.87%), H (5.18%), P (9.95%). Under high-resolution conditions, no parent ion was observed in the mass spectrometer, but ions corresponding to  $m/e = 437.1464$  ( $\text{C}_{32}\text{H}_{22}\text{P}^+$  requires 437.1459) and  $m/e = 183.0362$  ( $\text{C}_{12}\text{H}_8\text{P}^+$  requires 183.0364) were observed. Direct evidence of the presence of two phosphorous atoms comes from the  $^{31}\text{P}$  NMR spectra (vide infra) of a palladium complex in which the two phosphorous atoms become diastereotopic. A sample of BDPBN, prepared from DIBN ( $[\alpha]_D^{23} = -9.34^\circ$ ; pyridine, 20 mg/2 mL), gave  $[\alpha]_D^{26} = -105.74^\circ$  (pyridine, 20 mg/2 mL).

(b) **Dilithiation of DIBN with  $n$ -BuLi ( $-44$  and  $-131^\circ\text{C}$ ).** The conversion of DIBN to 2,2'-dilithio-1,1'-binaphthyl (DLBN) can also be

accomplished following the same general procedures outlined above with *n*-BuLi (ca. 2 M, Alfa) replacing *t*-BuLi. At -44 °C, a reaction time of 90 s and 2.2 equiv of *n*-BuLi will quantitatively convert DIBN to DLBN, as judged by analysis for 1,1'-binaphthyl, 2-iodo-1,1'-binaphthyl, and DIBN (TLC, silica gel, Merck 5775, hexane eluant) in aliquots that had been removed from the reaction and quenched. At -131 °C, a reaction time of 30 min and 2.2 equiv of *n*-BuLi was sufficient for quantitative conversion. Yields and physical characteristics of BDPBN prepared in this fashion were identical with those found when the dilithiation was carried out with *t*-BuLi at -131 °C.

**2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (BDPBN) from DBBN.** The general procedure was analogous to the preparation from DIBN.

(a) **Dilithiation of DBBN with *n*-BuLi at -44 °C.** The metalation was carried out at -44 °C (acetonitrile slush) using 2.2 equiv of *n*-BuLi and a reaction time of 30 min. After the solution was cooled to -131 °C, a 5- to 10-fold excess of diphenylchlorophosphine was added, and stirring was continued for 15 to 30 min. The solution was then left to stir at -78 °C overnight. Workup of the crude product proceeded as in the previous case. TLC of the crude products generally showed the absence of dibromobinaphthyl and bromobinaphthyl, and occasionally traces of binaphthyl were present. If metalation was incomplete, varying amounts of 2-bromo-2'-diphenylphosphino-1,1'-binaphthyl were observed as a bright, yellowish green fluorescent spot that moved slightly ahead of the bis(phosphine) (appearing as a bright blue spot), on silica gel TLC plates (Merck 5775) eluted with CCl<sub>4</sub>. Optimized yields of bisphosphine range from 92% to 98%. Physical characteristics and mass spectra are identical with the material prepared from DIBN. A sample of BDPBN, prepared from DBBN ([α]<sub>D</sub><sup>25</sup> 29.2°; pyridine, 27.4 mg/2 mL), gave [α]<sub>D</sub><sup>20</sup> 156.4° (pyridine, 23 mg/2 mL).

(b) **Attempted Dilithiation of DBBN with *t*-BuLi at -131 °C.** Reaction of 4.2 equiv of *t*-BuLi with DBBN for 2.5 h at -131 °C followed by quenching with methanol yielded a mixture of binaphthyl and monobromobinaphthyl.

**2-Bromo-2'-(diphenylphosphino)-1,1'-binaphthyl (DPBBN). Monolithiation of DBBN with *n*-BuLi at -44 °C.** The metalation was carried out in exactly the same fashion as in the preparation of BDPBN from DBBN except that 1.1 equiv of *n*-BuLi and a reaction time of 5 min were employed. Since 2,2'-dibromo-1,1'-binaphthyl, 2-bromo-1,1'-binaphthyl, and 1,1'-binaphthyl are readily separated by TLC (Merck No. 5775, silica gel, hexane eluant), it may be advantageous to monitor the degree of metalation by quenching aliquots and analyzing them by TLC. From metalation of optically active 2,2'-dibromo-1,1'-binaphthyl ([α]<sub>D</sub><sup>25</sup> 31.8°; pyridine, 42 mg/2 mL) and workup of the crude product, white crystals were isolated and recrystallized from 1/2 toluene/ethanol (v/v) (mp 177-180 °C, uncorrected; 183.6-186.8 °C, corrected). The crystals gave a rotation of [α]<sub>D</sub><sup>25</sup> 68.4° (pyridine, 11.8 mg/mL). TLC analysis (Merck 5775, silica gel, CCl<sub>4</sub> eluant) of the crystallized material showed a single bright-green fluorescent spot under short-wave UV light and the absence of the bisphosphine, which is characterized by a bright blue fluorescence and a smaller *R<sub>f</sub>* value. No material was left at the origin, indicating the absence of phosphine oxides. 2-(Diphenylphosphino)-1,1'-binaphthyl, present in crude reaction mixtures when 2,2'-dilithio-1,1'-binaphthyl is reacted with insufficient diphenylchlorophosphine, was also absent. No trace of butyldiphenylphosphine, 1,1'-binaphthyl, 2,2'-dibromo-1,1'-binaphthyl, or 2-bromo-1,1'-binaphthyl was evident. Duplicate elemental analyses (Schwarzkopf) of a single sample gave: C (73.06%), H (4.38%), P (5.41%), C (73.32%), H (4.40%), P (5.86%), Br (14.04%). Calcd for C<sub>32</sub>H<sub>22</sub>PBr: C (74.28%), H (4.29%), P (5.99%), Br (15.44%). Both analyses give a C/H molar ratio lower (1.3998; 1.3984) than expected (1.4545) for C<sub>32</sub>H<sub>22</sub>PBr, and the mass balance is somewhat short (2.38%) of 100%. The TLC analysis shows that unreacted starting material and the obvious products of side reactions are absent, and the presence of possible binaphthyl derivatives as impurities cannot reasonably account for the excess of H over C and P/Br ratio of ~1.0.<sup>20</sup> It is possible that the crystals have retained some ethanol of crystallization: e.g., C<sub>32</sub>H<sub>22</sub>PBr·1/4 C<sub>2</sub>H<sub>5</sub>O requires C (73.84%), H (4.43%), P (5.85%), Br (15.11%). It is also significant that the white crystals (DPBBN) pick up a distinct yellow coloration on standing for prolonged periods under fluorescent lights, even when sealed in ampules under argon.

Since the analysis is not completely satisfactory, other evidence for the structure and purity was obtained. The high-resolution mass spectrum

showed a base peak (no parent was observed) at *m/e* = 437.1457 (C<sub>32</sub>H<sub>22</sub>P<sup>+</sup> requires 437.1459) and confirms the presence of at least one diphenylphosphino group. Furthermore, no peak near *m/e* = 453 was detectable (<0.01% of base peak) which confirms the absence of C<sub>32</sub>H<sub>22</sub>OP<sup>+</sup>, derivable from the bromophosphine oxide, monophosphine oxide, or bis(phosphine) oxide. No peaks were detectable at *m/e* = 254 (1,1'-binaphthyl), 332 (2-bromo-1,1'-binaphthyl), or 410 (2,2'-dibromo-1,1'-binaphthyl). A major peak at *m/e* = 438.1460 (35.9% of base peak at *m/e* = 437.1457) was observed. C<sub>32</sub>H<sub>22</sub>P (from 2-(diphenylphosphino)-1,1'-binaphthyl) requires *m/e* = 438.1538 (not detectable) while C<sub>31</sub><sup>13</sup>CH<sub>22</sub>P<sup>+</sup> requires *m/e* = 438.1493. Assuming a natural abundance of 1.11% for <sup>13</sup>C, the ratio of the peak at *m/e* = 438.1460 to the peak at *m/e* = 437.1457 should be 35.5% (35.9%, observed). No peak near *m/e* = 242 was detectable (C<sub>16</sub>H<sub>19</sub>P<sup>+</sup>, derived from butyldiphenylphosphine), nor were peaks corresponding to fragments derivable from C<sub>16</sub>H<sub>19</sub>P<sup>+</sup> observed (e.g., *m/e* = 241, 199). The high-resolution mass spectral analysis confirms the TLC analysis that no significant quantities of any obvious diphenylphosphine- or binaphthyl-derived impurities are present. Rast molecular weight determination (calibrated against triphenylphosphine and 2,2'-diiodo-1,1'-binaphthyl) gave *M<sub>r</sub>* = 513 ± 10 (C<sub>32</sub>H<sub>22</sub>PBr requires *M<sub>r</sub>* = 517). The mass spectrum, the molecular weight determination, the molar ratio of P/Br = 1.077 found by elemental analysis, and the starting material (2,2'-dibromo-1,1'-binaphthyl) confirm the identity of the crystals as 2-bromo-2'-(diphenylphosphino)-1,1'-binaphthyl. Unoptimized yield of recrystallized material: 50-60%.

**2,2'-Bis(diphenyloxyphosphino)-1,1'-binaphthyl (BDPOBN).** To a stirring solution of 0.15 g (0.2409 mmol) of BDPBN in 23 mL of *p*-dioxane was added 1 mL (8.8 mmol) of 30% hydrogen peroxide. The reaction was stirred at room temperature until TLC (CH<sub>2</sub>Cl<sub>2</sub> eluant) showed the absence of starting material.

At this point, the dioxane was removed under vacuum at room temperature; the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and chromatographed on silica gel (70-230 mesh) by using 2-5% ethanol/CH<sub>2</sub>Cl<sub>2</sub> (v/v). The chromatographed product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane to give fine, white crystals (mp = 290-292 °C, uncorrected; 305-307 °C, corrected). Low-resolution mass spectrum showed a parent peak at *m/e* = 654 (small). Elemental anal. Calcd for C<sub>44</sub>H<sub>32</sub>O<sub>2</sub>P<sub>2</sub>: C, 80.72%; H, 4.93%; P, 9.46%. Found: C, 80.80%; H, 4.91%; P, 9.35%. IR shows a strong absorption at 1120 cm<sup>-1</sup> (P=O stretch). Under high-resolution conditions, the mass spectrum showed no parent, but gave an ion corresponding to *m/e* = 453.1423 (C<sub>32</sub>H<sub>22</sub>OP<sup>+</sup> requires *m/e* = 453.1409).

(*R,S*)-1-Phenylethylamine was obtained following the procedure of Ingersoll.<sup>21</sup> The proton NMR spectrum of the neat product shows a doublet centered around 1.3 ppm (area = 3), a singlet at 1.4 ppm (area = 2), a quartet at 3.9 ppm (area = 1), and aromatic hydrogens (5) at 7.25 ppm. All proton chemical shifts are downfield relative to Me<sub>4</sub>Si.

(*S*)-(-)-Phenylethylamine was obtained from the racemic form following the method of Ault.<sup>22</sup> [α]<sub>D</sub><sup>25.5</sup> -39.23° (neat); lit.<sup>22</sup> [α]<sub>D</sub><sup>29</sup> -39.4° (neat).

(*S*)-(-)-*N,N*-Dimethyl-1-phenylethylamine was prepared by dimethylation of (*S*)-(-)-1-phenylethylamine following the procedure of Icke and Wisegarver.<sup>23</sup> The proton NMR spectrum of the neat product is similar to the corresponding spectrum of (*R,S*)-1-phenylethylamine, except that the singlet at 1.4 ppm (area = 2) is replaced by a new singlet (area = 6) located about 0.5 ppm downfield from the high-field doublet (area = 3). [α]<sub>D</sub><sup>25.5</sup> -70.27° (neat); lit.<sup>23</sup> [α]<sub>D</sub><sup>24</sup> -68.3° (neat).

μ-(Dichloro)bis(*S*)-*N,N*-dimethyl-(1-phenylethyl)amine-2C,*N*]dipalladium(II) (CDP) was prepared from lithium tetrachloropalladate(II) by the procedure of Cope and Friedrich.<sup>24</sup> Yellow needles (mp = 181

(21) A. W. Ingersoll, "Organic Synthesis", Wiley, New York, 1943, Collect. Vol. II, p 506.

(22) A. Ault "Organic Synthesis", Wiley, New York, 1973, Collect. Vol. V, p 932.

(23) R. N. Icke and B. B. Wisegarver, "Organic Synthesis", Wiley, New York, 1955, Collect. Vol. III, p 723.

(24) A. C. Cope and E. C. Friedrich, *J. Am. Chem. Soc.*, **90**, 909 (1968).

(25) G. R. Clemons and E. C. Dawson, *J. Chem. Soc.*, 1114 (1939).

(26) R. Kuhn and P. Goldfinger, *Justus Liebigs Ann. Chem.*, **470**, 183 (1929).

(27) M. J. O'Connor, R. E. Ernst, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 4561 (1968).

(28) M. P. Cava and J. F. Stucker, *J. Am. Chem. Soc.*, **77**, 6022 (1955).

(29) DBBN is fairly resistant to thermal racemization. Samples in pyridine solution have been left for 1-2 days in sealed polarimeter cells with steam running through the cooling water compartment, and no change in specific rotation was observed. However, DBBN will racemize when melted. Attempts to racemize DIBN in solution or in the melt were not successful, but the aim of these experiments was to determine conditions for crystallization without thermal racemization.

(20) A major problem with attempting to account for the analytical results in terms of contamination by impurities is that the most likely candidates have carbon percentages higher than that for C<sub>32</sub>H<sub>22</sub>BrP. The analytical results for carbon are somewhat low. Three possible impurities that might result in a low analysis for carbon are C<sub>32</sub>H<sub>22</sub>OBrP, C<sub>20</sub>H<sub>13</sub>Br, and C<sub>20</sub>H<sub>12</sub>Br<sub>2</sub>, but these are easily separable by TLC and, if present, could be readily detected. The C/H molar ratio for C<sub>32</sub>H<sub>22</sub>OBrP is identical with that for C<sub>32</sub>H<sub>22</sub>BrP and could not account for the excess of hydrogen over carbon. The mass spectral data (vide infra) does not provide evidence for any significant impurities.

°C dec, uncorrected; 188 °C, corrected; lit.<sup>24</sup> 186–189 °C, dec) were obtained in 45–75% yield.

**2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl[(S)-N,N-dimethyl-(1-phenylethyl)amine-2C,N]palladium(II)** was prepared by separately dissolving equimolar amounts of the dinuclear palladium complex (CDP) (0.180 g) and BDPBN (0.0193 g) in a minimum amount of THF (0.5–2.25 mL); the solutions were mixed and allowed to stand for 0.5–12 h. The THF was evaporated off under a stream of argon to give a yellow solid. The solid was dissolved in CDCl<sub>3</sub>/(CD<sub>3</sub>)<sub>2</sub>CO mixtures (ranging from pure CDCl<sub>3</sub> to 3/1 by volume) for the <sup>31</sup>P NMR analyses. The solid was best dissolved in the CDCl<sub>3</sub> first, followed by dilution with the appropriate amount of (CD<sub>3</sub>)<sub>2</sub>CO.

**2-(Hydroxyphenylmethyl)-1,1'-binaphthyl (HPMBN).** (A) **Monolithiation of DIBN with *n*-BuLi at -131 °C.** The general procedure was identical with that followed in the dilithiation of DIBN during the preparation of 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, except that 1.1 equiv of *n*-BuLi and a reaction time of 20 min were used. Benzaldehyde (1.8 equiv) replaced diphenylchlorophosphine. The iodo alcohol, 2-(hydroxyphenylmethyl)-2'-iodo-1,1'-binaphthyl, was isolated in 78% yield (combined yield of both diastereomers). The two iodo alcohol diastereomers were separable by medium-pressure liquid chromatography on silica gel 60 (230–400 mesh, Merck 9385), eluting with 5% ethyl acetate in cyclohexane (v/v). Low-resolution mass spectra of the separated iodo alcohol diastereomers showed a parent at *m/e* = 486 and fragment ions at *m/e* = 359 and 341. The latter two ions correspond to loss of one iodine atom and loss of one iodine atom plus water, respectively. The proton NMR spectrum (200 MHz) of the fast-running diastereomer (IHPMBN-1) showed a doublet (*J* = 3.4 Hz, area = 1) at 5.43 ppm, corresponding to the benzylic hydrogen, and a doublet (*J* = 3.4 Hz, area = 1) at 1.85 ppm, corresponding to the hydroxyl hydrogen. Addition of D<sub>2</sub>O to the sample, thorough mixing, and separation of the CDCl<sub>3</sub> solution led to the collapse of the doublets and to the shift of the upfield signal at 1.85 ppm to a frequency corresponding to that of HOD. The corresponding signals for the slow-running diastereomer (IHPMBN-2) appeared at 5.53 ppm (doublet, *J* = 2.4 Hz) and 2.47 ppm (doublet, *J* = 2.4 Hz).

Treatment of each iodo alcohol with 2.2 equiv of *n*-BuLi under conditions similar to those employed for the monolithiation of DIBN, followed by quenching with methanol, leads to recovery of 2-(hydroxyphenyl)-1,1'-binaphthyl in a yield estimated at ~90%. It was found that the slow-running monoalcohol, HPMBN-2, (TLC, silica gel, 3/1 CH<sub>2</sub>Cl<sub>2</sub>/CCl<sub>4</sub>) was produced from the fast-running iodo alcohol (IHPMBN-1) (TLC, silica gel, 20% ethylacetate/cyclohexane). Each monoalcohol showed a parent ion (*m/e* = 360) in the mass spectrometer and a fragment ion at *m/e* = 342 corresponding to loss of water. HPMBN-1, proton NMR (200 MHz, CDCl<sub>3</sub>): 5.53 (doublet, *J* = 3.6 Hz), 1.98 (doublet, *J* = 3.6 Hz ppm; HPMBN-2: 5.67 (doublet, *J* = 3.6 Hz), 2.05 (doublet, *J* = 3.6) ppm. The monoalcohols were also prepared<sup>17</sup> by lithiating and quenching the mixture of iodo alcohol diastereomers, followed by chromatographic separation on silica gel 60 (230–400 mesh, Merck 9385, Altex column, 15 mm × 500 mm) using 5% ethyl acetate/cyclohexane (v/v) at a flow rate of 9 mL/min and a fraction size of 9 mL. An ISCO Model UA-5 UV absorbance monitor (λ = 280 nm) was used to follow the separation, which was close to base line. The proton NMR spectrum of each separated monoalcohol diastereomer showed chemical shifts and coupling constants for the benzylic and hydroxyl hydrogen signals that were identical with those of the corresponding monoalcohol diastereomer prepared from a single iodo alcohol diastereomer. High-resolution mass spectra of a mixture of monoalcohol diastereomers gave a parent ion corresponding to *m/e* = 360.1530 (C<sub>27</sub>H<sub>20</sub>O<sup>+</sup> requires *m/e* = 360.1514). The highest mass peak detectable was the P + 1 peak at *m/e* = 361.1545 ((P + 1)/P = 0.34, observed; (P + 1)/P = 0.30, theoretical). No peaks were detected (<0.26% of base peak) near *m/e* = 164 (1-phenyl-1-pentanol), 107 (C<sub>6</sub>H<sub>5</sub>CHOH<sup>+</sup>, the major ion observed for 1-phenyl-1-pentanol), 254 (binaphthyl), 380 (iodobinaphthyl), or 106 (benzaldehyde). A P – 2 peak

at *m/e* = 358.1365 was present (1% of the parent) and may derive from 2-benzoyl-1,1'-binaphthyl as an impurity or from fragmentation of the monoalcohol. C<sub>27</sub>H<sub>18</sub>O<sup>+</sup> requires *m/e* = 358.1358.

(B) **Monolithiation of DBBN with *n*-BuLi at -44 °C.** The procedure used for the monolithiation of 2,2'-dibromo-1,1'-binaphthyl (DBBN) in the synthesis of 2-bromo-2'-(diphenylphosphino)-1,1'-binaphthyl was employed for the synthesis of 2-(hydroxyphenylmethyl)-1,1'-binaphthyl from DBBN and benzaldehyde. The sequence of reactions is analogous to that outlined above for DIBN. The intermediate bromo alcohol diastereomers have been characterized by mass spectrometry and NMR spectroscopy.<sup>17</sup> Conversion<sup>17</sup> of the bromo alcohol diastereomers to HPMBN, followed by separation of HPMBN-1 and HPMBN-2, led to the same products as were obtained from the corresponding reactions initiated with DIBN. Furthermore, the sequence—monolithiation, quenching with methanol, monolithiation, reaction with benzaldehyde—led to the same products as when the quenching step and “benzaldehyde” step were reversed in order.

**Determination of the Optical Purity of HPMBN.** The two diastereomers, HPMBN-1 and HPMBN-2, were separated by medium pressure liquid chromatography, as described in the synthesis section (vide supra). Several chiral NMR shift reagents were observed to complex with the two monoalcohols, and it was found that tris(*d,d*-dicampholy-methanato)europium(III) [i.e., (Eu(dcm)<sub>3</sub>, Alfa]<sup>16</sup> gave the best separation of the benzylic hydrogen signals with HPMBN-1 in 33% CDCl<sub>3</sub>/CCl<sub>4</sub> at temperatures between 0 to 10 °C. The general procedure was to monitor the chemical shift and separation of the benzylic hydrogen signals (200 MHz <sup>1</sup>H NMR) in the diastereomeric complexes of (*R*)-HPMBN-1-Eu(dcm)<sub>3</sub> and (*S*)-HPMBN-1-Eu(dcm)<sub>3</sub> as increments of the shift reagent were added to the alcohol samples. An increase in shift reagent concentration or a decrease in temperature resulted in larger overall shifts (Δδ) and in larger relative shifts (ΔΔδ) for the benzylic hydrogens until broadening of the signals negated these increases. Because Eu(dcm)<sub>3</sub> slowly decomposes upon standing in solution, all analyses were carried out in a single day on freshly prepared solutions.

Optically active samples of DIBN and DBBN with varying specific rotations were separately converted to HPMBN as described above, small amounts of HPMBN-1 were isolated by medium-pressure liquid chromatography, and the optical purity of the latter was determined<sup>16</sup> by using Eu(dcm)<sub>3</sub>.

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**Registry No.** (±)-DIBN, 86632-29-3; (*R*)-DIBN, 86688-06-4; (*S*)-DIBN, 86688-07-5; (±)-BDPBN, 76144-87-1; (*R*)-BDPBN, 76189-55-4; (*S*)-BDPBN, 76189-56-5; (*R*)-DLBN, 86632-30-6; (*S*)-DLBN, 86632-31-7; (*R*)-DBBN, 86688-08-6; (*R*)-DPBBN, 86632-32-8; (±)-BDPOBN, 86632-33-9; (*S*)-IHPMBN (isomer 1), 86632-34-0; (*S*)-IHPMBN (isomer 2), 86688-09-7; (*R*)-HPMBN (isomer 1), 86632-35-1; (*R*)-HPMBN (isomer 2), 86688-10-0; (*S*)-HPMBN (isomer 1), 86688-11-1; (*S*)-HPMBN (isomer 2), 86688-12-2; CDP, 34424-15-2; 2,2'-bis(diphenylphosphino)-(R)-1,1'-binaphthyl[(S)-N,N-dimethyl-(1-phenylethyl)amine-2C,N]palladium(II) chloride, 86688-13-3; 2,2'-bis(diphenylphosphino)-(S)-1,1'-binaphthyl[(S)-N,N-dimethyl-(1-phenylethyl)amine-2C,N]palladium(II) chloride, 86688-14-4; diphenylchlorophosphine, 1079-66-9; benzaldehyde, 100-52-7.

**Supplementary Material Available:** Full experimental details of preparation and resolution of compounds (7 pages). Ordering information is given on any current masthead page.