radiation (λ = 0.71069 Å), μ(Mo Kα) = 16.43 cm^{-1}, $F(000)$ = 1095.89.

Three-dimensional room-temperature X-ray diffraction data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 diffractometer by the ω-scan method. The 4215 independent reflections for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarization effects and for absorption, by analysis of six azimuthal scans. The structure was solved by conventional Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Hydrogen atoms were placed in calculated positions with isotropic thermal vibrational parameters related to those of the supporting atom. The refinement converged to a final R value of 0.0728 with allowance for the thermal anisotropy of all non-hydrogen atoms. Complex scattering factors were taken from ref 9 and from the SHELXTL program package, which was used for the refinement. Unit weights were used throughout the refinement. Atom coordinates are given in Table V and selected bond distances and angles in Table IV.

Supplementary Material Available: Complete listings of bond lengths and angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors for complex **9c** (4 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

(9) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

Bis(pyridyl)silane and -methanol Ligands. 3. A New Class of Optically Active Ligands Prepared from Readily Available Chiral 2-Bromo-6-alkoxypyridines and Their Application in Rhodium-Catalyzed Hydrosilations and Copper(II)-Catalyzed Cyclopropanations

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Received May 11, 1989

Several chiral 2-bromo-6-alkoxypyridines (**2**) were prepared from the treatment of 2,6-dibromopyridine with the appropriate potassium alkoxide (alkoxides used: methoxide, myrtanoxide, myrtenoxide, isopinocampheoxide, isomenthoxide, fenchoxide, and borneoxide) in dimethylformamide at 80 °C for 30 min. Compound **2** was found to undergo facile halogen–metal exchange with *n*-BuLi in THF at −78 °C to afford the 2-lithio-6-alkoxypyridines (**3**). Treatment of **3** with R_2SiCl_2 resulted in formation of the novel bis(pyridyl)silane compounds $[2\text{-}(6\text{-alkoxypyridyl})]_2SiR_2$ (**4**, R = Me; **5**, R = Ph) in excellent yield. The latter compounds readily chelated to palladium(II) chloride to form air-stable complexes, $\{[2\text{-}(6\text{-alkoxypyridyl})]_2SiR_2\}PdCl_2$ (**6**, R = Me; **7**, R = Ph). The palladium complexes were fully characterized by spectroscopic and analytical data. Oxidative coupling of compounds **3** with copper(I) iodide and oxygen at −78 °C afforded the new 6,6′-dialkoxy-2,2′-bipyridines (**8**) in 34–38% isolated yields. Treatment of **3** with dimethylformamide produced a new series of optically pure 6-alkoxy-2-pyridinecarboxaldehydes (**9**) in greater than 90% isolated yield. Subsequent reaction of **9** with **3** afforded the bis[2-(6-alkoxypyridyl)]methanol ligands (**10**) in excellent yield. Compound **10** was O-alkylated (NaH, DMF) with benzyl chloride to afford **11**. The benzylated compound **11** was complexed to palladium(II) chloride and found by NMR spectroscopy to exist as one of the two possible boat conformations. The energy barriers for rotation about the benzyl–oxygen bond in the latter complexes were found to be dependent upon the chiral alkoxy group on the pyridine ring. Ligand **10** was attached to cross-linked polystyrene beads with 56–74% modification of the chloromethyl sites. Further modification of the remaining chloromethyl reaction sites to hydroxymethyl groups was accomplished by treatment of the polymer with methanolic potassium hydroxide. Complete incorporation of the ligand was achieved by utilizing a lower loading of chloromethyl sites (0.75 mequiv/g) in the starting polymer. Treatment of 2-pyridinecarboxaldehyde with **3** resulted in the two diastereoisomeric products, [2-(6-alkoxypyridyl)](2-pyridyl)methanol (**17**): in the case of R*O = (*1S,2R,4S*)-borneoxy the isomers could not be separated; however, when R*O = (*1R,2R,4S*)-1,3,3-trimethyl-2-norborneoxy the isomers **17(i)** and **17(ii)** were easily separated by column chromatography. Selected ligands prepared in the study were used in the rhodium-catalyzed hydrosilation (Ph_2SiH_2) of acetophenone. Chemical yields were ~85%, and optical yields ranged from 0 to 12.7% for the hydrosilations and 0.5 to 10.0% for the asymmetric cyclopropanation of 2,5-dimethyl-2,4-hexadiene.

Introduction

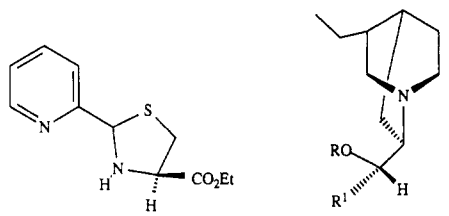
The initial and independent discovery by Horner et al.[1] and Knowles et al.[2] that prochiral alkenes could be catalytically hydrogenated enantioselectively sparked a worldwide effort to develop chiral transition-metal catalysts. The first ligands used in the asymmetric methodology had chiral phosphorus atoms and a later study by Morrison et al.[3] demonstrated that the phosphorus need not be chiral but, rather, the source of chirality could be further removed from the metal center. Two decades of effort by workers in the field of asymmetric catalysis has produced a more rational approach to the design of asymmetric transition-metal catalysts.[4] The very recent

(1) Horner, L.; Siegel, H.; Büthe, H. *Angew. Chem.* **1968**, *80*, 1034; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 942.
(2) Knowles, W. S.; Sabacky, M. J. *Chem. Commun.* **1968**, 1445.
(3) Morrison, J. D.; Burnett, R. E.; Aguiar, A. M.; Morrow, C. J.; Philips, C. *J. Am. Chem. Soc.* **1971**, *93*, 1301.

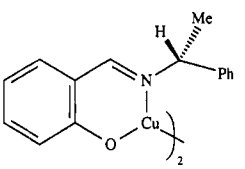
0276-7333/90/2309-0136$02.50/0

work of Noyori and co-workers[5] demonstrates that new ligand designs, variation in the transition metal, and change in the counterion can have a dramatic effect on the efficiency of a catalytic reaction. The ruthenium(II)–BINAP system exploited by Noyori et al. is said to be the beginning of a second generation for asymmetric catalysis.

The development of chiral ligands has clearly centered around bidentate designs containing phosphorus as the coordinating atoms (i.e. P-P type);[6] however, ligands that utilize phosphorus and nitrogen (P-N type)[7] as the coordinating atoms have led to interesting and useful results. Somewhat surprising was the absence of N-N type ligands in the asymmetric catalysis field until the work of Brunner et al.,[8] where ligand I was used in the asymmetric hydrosilation of acetophenone (87% optical yield). Since the initial report the optical yield has been improved to 98% by using the same ligand but different chemical conditions.[9] Nitrogen-based ligands are also crucial for the Sharpless dihydroxylation[10] and the asymmetric cyclopropanation[11] of alkenes (ligands II and III, respectively).

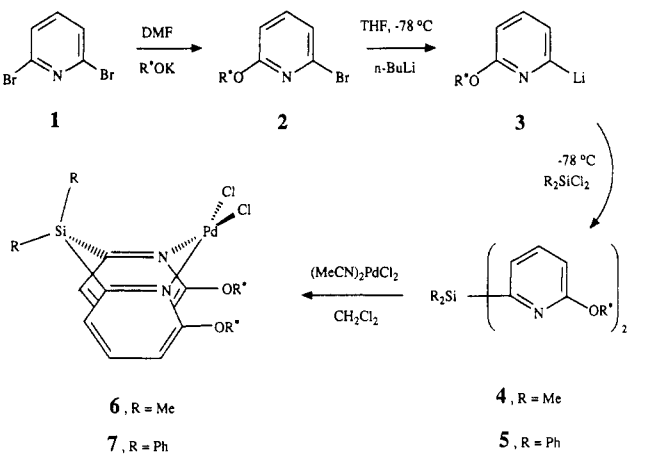


I II



III

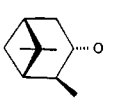
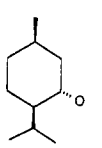
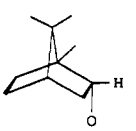
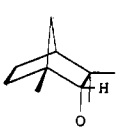
Scheme I



1 2 3

6, R = Me
7, R = Ph
4, R = Me
5, R = Ph

Table I. Yields and Optical Rotations for Compounds 2, 9, and 10

OR*	Compound	Isolated Yield (%)	[α] (c=1, $CHCl_3$)
	2b	88	-4.7°
	2c	85	-25.0°
	2d 9d 10d	81 92 96	52.7° 63.0° 44.3°
	2e 9e 10e	84 92 95	-7.2° 4.4° -16.5°
	2f 9f 10f	84 93 95	-75.0° -79.8° -72.5°
	2g 9g 10g	93 91 95	82.5° 92.5° 107.9°

Recently in our laboratory we developed the synthesis of a series of achiral bis(2-pyridyl)silane ligands and briefly examined their coordination behavior.[12] The ligands form a rigid six-membered chelate ring and exist in a boat conformation with the metal and silicon atoms being out of plane. A consequence of the six-membered chelate ring is that substituents in the 2-position of the pyridine rings are directed toward the metal and under the adjacent ligands. In addition, the substituent on the silicon (in the pseudoaxial position) is in close proximity to the metal center (~3.5 Å).

In this paper we report the synthesis of a new class of optically active 2-bromo-6-alkoxypyridines (2) and facile halogen–metal exchange to the corresponding 2-lithio-6-

(4) For general reviews on asymmetric catalysis see: (a) Brunner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 897. (b) Birch, A. J.; Williamson, D. H. *Org. React.* **1976**, *24*, 74. (c) Morrison, J. D.; Masler, W. F.; Neuberg, M. K. *Adv. Catal.* **1976**, *25*, 81. (d) Ojima, I.; Yamamoto, K.; Kumada, M. *Aspects Homogeneous Catal.* **1977**, *3*, 186. (e) Ojima, I. *Pure Appl. Chem.* **1984**, *56*, 99. (f) Valentine, D., Jr.; Scott, J. W. *Synthesis* **1978**, 329. (g) Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1978**, *10*, 175. (h) Merrill, R. E. *CHEMTECH* **1981**, 118. (i) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106. (j) *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5. (k) Bosnich, B.; Fryzuk, M. D. *Top. Stereochem.* **1981**, *12*, 119. (l) *Asymmetric Catalysis*; NATO ASI Series E103; Martinus Nijhoff: Dordrecht, The Netherlands, 1986. For general mechanistic works on asymmetric hydrogenations see: Halpern, J. *Inorg. Chim. Acta* **1981**, *50*, 11; *Pure Appl. Chem.* **1983**, *55*, 99; *Science* **1982**, *217*, 401.

(5) For the initial ligand synthesis see: Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932. For recent catalytic applications see: Noyori, R.; Ohta, M.; Hsiao, Y.; Kitamura, M.; Ohta, T.; Takaya, H. *J. Am. Chem. Soc.* **1986**, *108*, 7117. For other applications of the $[BINAP]Ru(OAc)_2$ catalyst in asymmetric synthesis see: Kitamura, M.; Hsiao, Y.; Noyori, R.; Takaya, H. *Tetrahedron Lett.* **1987**, *28*, 4829. Takaya, H.; Ohta, T.; Sayo, N.; Kumobayashi, H.; Akutagawa, S.; Inoue, S.-I.; Kasahara, I.; Noyori, R. *J. Am. Chem. Soc.* **1987**, *109*, 1596. Noyori, R.; Takaya, H. *Kagaku* **1988**, *43*, 146.

(6) For an excellent tabulation of optically active ligands see the supplementary material section of ref 4h.

(7) Yamamoto, K.; Tomita, A.; Tsuji, J. *Chem. Lett.* **1978**, 3. Hayashi, T.; Kumada, M. *Fundam. Res. Homogeneous Catal.* **1978**, *2*, 159. Hayashi, T.; Fukushima, M.; Konishi, M.; Kumada, M. *Tetrahedron Lett.* **1980**, 79.

(8) Brunner, H.; Riepl, G.; Weitzer, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 331.

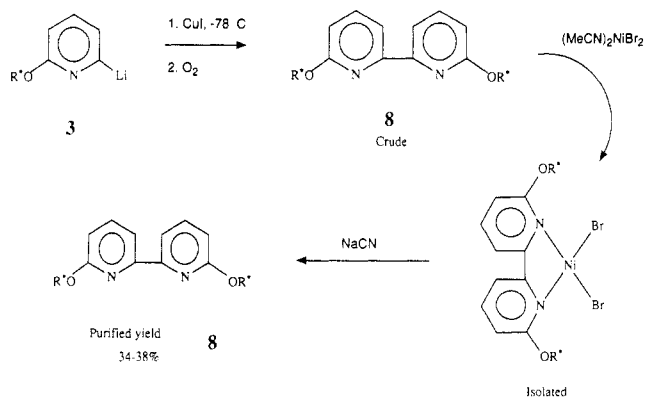
(9) Brunner, H.; Becker, R.; Riepl, G. *Organometallics* **1984**, *3*, 1354.

(10) Jacobsen, E. N.; Markó, I.; Mungall, W. S.; Schröder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968.

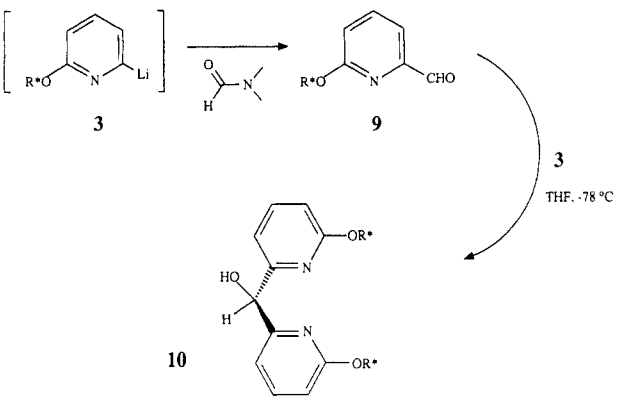
(11) (a) Aratani, T. *Pure Appl. Chem.* **1985**, *57*, 1839. (b) Aratani, T. *J. Synth. Org. Chem., Jpn.* **1985**, *43*, 1134. (c) Aratani, T.; Yoneyoshi, Y.; Nagase, T. *Tetrahedron Lett.* **1975**, *21*, 1707.

(12) Wright, M. E. *Tetrahedron Lett.* **1987**, *28*, 2322.

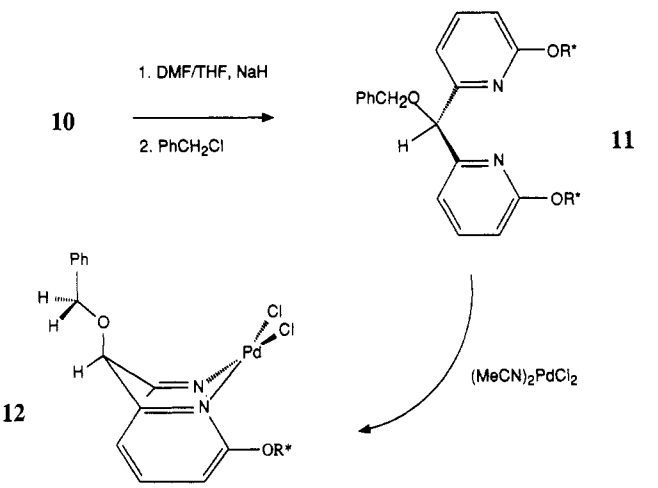
Scheme II



Scheme III



Scheme IV



alkoxypyridines (**3**). The latter compounds were then treated with R_2SiCl_2 to yield a new class of optically active bis[2-(6-alkoxypyridyl)]silane ligands (**4** and **5**). Compound **2** was also converted in high yield to the corresponding 6-alkoxy-2-pyridinecarboxaldehydes (**9**). Treatment of **9** with 1 equiv of **3** produced a new series of chiral bis(2-pyridyl)methanol (**10**) ligands. Selected ligands prepared in this study were evaluated in the rhodium-catalyzed hydrosilation of acetophenone and in certain cases the copper(II)-catalyzed cyclopropanation of 2,5-dimethyl-2,4-hexadiene.

Results and Discussion

Ligand and Palladium Complex Synthesis and Characterization. Utilizing reaction conditions similar to those developed by Testaferri and co-workers,[13] we have prepared a series of chiral 2-bromo-6-alkoxypyridines (**2**) in excellent yield from the treatment of 2,6-dibromopyridine (**1**) with the appropriate chiral potassium alkoxide in *N,N*-dimethylformamide (DMF) (Scheme I). The yields and optical rotations for the preparation of **2** are summarized in Table I. Separation of **2** from unreacted **1** was a relatively simple operation accomplished by chromatography on silica gel; however, the 2,6-dialkoxypyridine byproduct was very difficult to separate from **2** and, hence, an excess of the alkoxide should be avoided. The potassium alkoxides were found to be superior in comparison to the sodium analogues.

The halogen–metal exchange reaction to generate **3** was found to be very efficient in THF but rather sluggish in ether, even at 0 °C. Treatment of **3** with 0.5 mol equiv of R_2SiCl_2 produced compounds **4** and **5** in excellent crude yields.[12] Compound **5f** was obtained in analytically pure form by crystallization from a cold pentane solution. In the other cases, the ligands were obtained in sufficient purity (>90% by NMR spectroscopy) for spectroscopic assignments. The ligand was complexed to palladium(II) chloride, from which air-stable pure yellow solids (**6** and **7**) were isolated (Scheme I). In certain cases the complexes were chromatographed on alumina to separate the desired complex from a reddish palladium-containing byproduct.

The NMR spectra for the complexes showed a doubling of resonances for the pyridine and alkoxy groups consistent with the lack of a mirror plane of symmetry in the complexes. Compounds **6** and **7** would be expected to exist in a boat conformation,[14] and as noted in our related bis(2-pyridyl)silane ligands, the chelate rings are not fluxional.

The chiral 2-lithio-6-alkoxypyridines (**3**) were found to undergo oxidative coupling mediated by copper(I) iodide[15] to afford the new 6,6′-dialkoxy-2,2′-bipyridines (**8**) in modest yield (Scheme II). Purification of the bipyridines was achieved by complexation to $NiBr_2$ and isolation of the Ni(II) complex. Treatment of the nickel(II) complex with sodium cyanide released the bipyridine ligand and after flash column chromatography produced analytically pure product. The nickel complexation–decomplexation purification method was found to be better than 95% efficient on the basis of NMR yields determined on the crude product.

Synthesis of the optically pure aldehydes (**9**) was accomplished in excellent yield by treatment of **3** with DMF (Scheme III). The aldehydes were isolated as colorless oils after flash chromatography on alumina (neutral, nonactivated). Treatment of the 6-alkoxy-2-pyridinecarboxaldehydes (**9**) with 1 mol equiv of **3** furnished the bis[2-(6-alkoxypyridyl)]methanols (**10**) in high yield. A summary of the chemical yields and optical rotations for compounds **9** and **10** can be found in Table I. Similar methodology was previously used in the synthesis of achiral bis(2-pyridyl)methanol[16] and 1,1-bis(2-pyridyl)ethanol compounds.[17]

Compounds **10e** and **10f** were treated with sodium hydride and benzyl chloride in a DMF/THF solution to

(13) Testaferri, L.; Tiecco, M.; Tingoli, M.; Bartoli, D.; Massoli, A. *Tetrahedron* **1985**, *41*, 1373.
(14) Newkome, G. R.; Gupta, V. K.; Taylor, H. C. R.; Fronczek, F. R. *Organometallics* **1984**, *3*, 1549 and references cited therein. Steel, P. J. *Acta Crystallogr., Sect. C* **1983**, *39*, 1623. House, D. A.; Steel, P. J.; Watson, A. A. *Aust. J. Chem.* **1986**, *39*, 1525.
(15) Whitesides, G. M.; SanFilippo, J., Jr.; Casey, C. P.; Panek, E. J. *J. Am. Chem. Soc.* **1967**, *89*, 5302.
(16) Beyerman, H. C.; Bontekoe, J. S. *Recl. Trav. Chim. Pays-Bas* **1955**, *74*, 1395.
(17) Murphy, J.; Bunting, J. W. *Org. Prep. Proced. Int.* **1971**, *3*, 255.

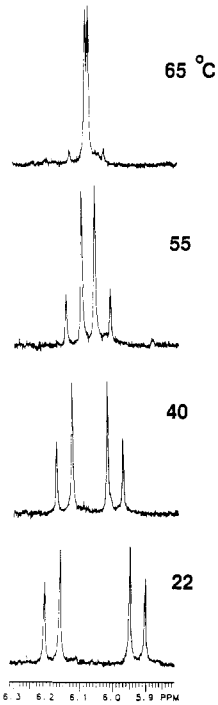


Figure 1. Proton NMR spectra (300 MHz) showing the benzyl proton resonances in complex **12e** at selected temperatures.

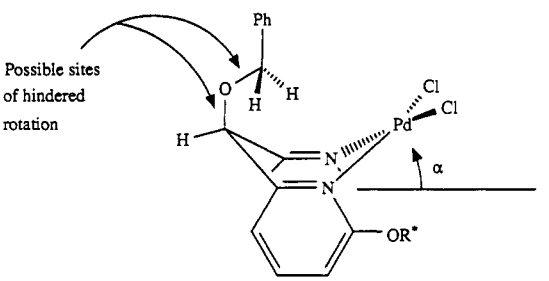


Figure 2. Diagram showing possible steric interactions between the chiral alkoxy group and the palladium metal center in complex **12** that could explain the observed effects on the rotational barrier for the benzyl moiety.

afford the O-benzylated ligands **11e** and **11f**, respectively (Scheme IV). Ligand **11** readily formed yellow air-stable palladium(II) chloride complexes **12e** and **12f** upon treatment with $(MeCN)_2PdCl_2$. The latter compounds were useful for characterizing the ligand's coordination behavior. The proton NMR spectra of the complexes at ambient temperature clearly show only one of the two possible boat conformations for both complexes. The benzylic hydrogens in the complexes show an AB pattern in the proton NMR spectra. Heating a NMR sample of **12e** caused the benzyl proton resonances to approach collapse to a singlet (E_a = ~16 kcal/mol[18]), whereas for **12f**, the resonances remain unchanged up to 65 °C (Figure 1). There was no evidence for interconversion of the boat conformations, as the rest of the resonances in the spectra remained sharp throughout the temperature range studied. This is consistent with previous results from our laboratory concerning related bis(2-pyridyl)silane ligands.[12,19]

On the basis of crystallographic data on related six-membered chelate ring structures it appears a logical assumption to place the larger group in the pseudoaxial position.[20] It is interesting that the chiral alkoxy group

Scheme V

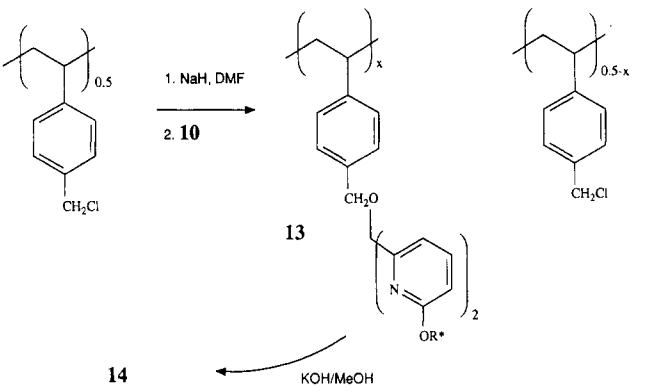


Table II. Results of Polymer Modification with the Bis(6-alkoxypyridyl)methanol Compounds 10[a]

OR*	% modification	% N calcd	% N found
(1*S*,2*S*,3*S*,5*R*)-isopinocampheoxy (**14d**)	60	3.42[b]	3.32
(1*S*,2*R*,5*R*)-isomenthoxy (**14e**)	56	3.06	3.01
(1*S*,2*R*,4*S*)-borneoxy (**14f**)	74	3.57	3.52
(1*R*,2*R*,4*S*)-1,3,3-trimethyl-2-norborneoxy (**14g**)	68	3.57	3.41
polymer **15e**	100	1.56	1.48

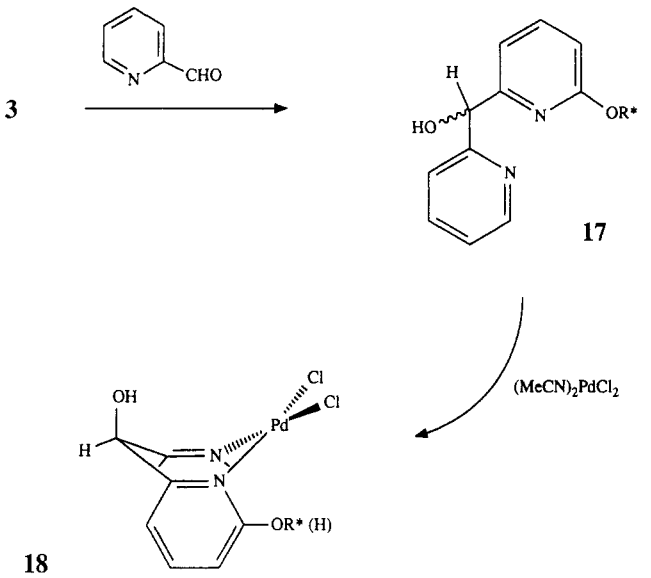
[a] Calculated nitrogen and percent modification values were based upon the observed weight gain for each polymer preparation. Percent modification was calculated by using the equation 100-(x/0.5) = % modification; see Scheme III. [b] Anal. Calcd: C, 81.89; H, 8.05. Found: C, 81.43; H, 8.16.

on the pyridine ring has such an effect on the rotational energy barrier about the oxygen–benzylic carbon bond and strongly suggests that the alkoxy moiety is influencing the coordination sphere of the metal. One might speculate this could be done through pushing the palladium metal center (Figure 2, angle α) further out of plane, thus increasing steric interactions with the axial *O*-benzylic group. Minimizing the number of conformational isomers is a desirable and often important feature in the design of asymmetric catalysts.[21]

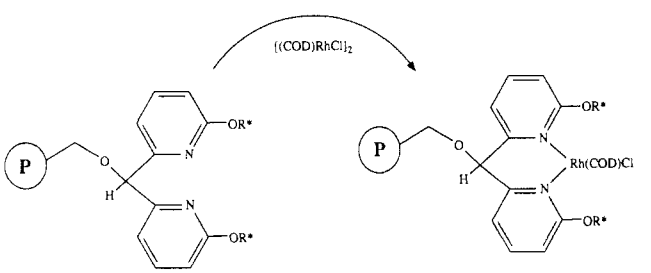
Treatment of chloromethylated polystyrene beads (1% cross-linked, 3.9 mequiv/g, 50% of the phenyl rings modified) with **10** in DMF gave only partial reaction of the chloromethyl sites. The percent modification was dependent upon the chiral alkoxy group and varied between 56 and 74% (Scheme V, Table II). Similar results have been reported with use of the achiral bis(2-pyridyl)-methanol.[22] The unreacted chloromethyl sites were converted to hydroxymethyl groups by treating the polymer with methanolic potassium hydroxide. Polymer **14f** was found to chelate palladium(II) chloride (**16f**) in excellent agreement with the number of ligand sites calculated from a nitrogen analysis of the polymer. When the polymers were treated with $[(COD)RhCl]_2$, only an ~50% weight gain was realized. With the high concentration of ligand sites[23] it appeared that two bis(2-pyridyl)methanol ligands complexed to the rhodium center. The latter polymer-supported rhodium complex was found to be inactive for the hydrosilation of acetophenone.

(18) The energy of activation was calculated from extrapolation to the coalescence temperature (70 °C) and use of the equation $k_c = \pi[(\delta\nu)^2 + 6J_{AB}^2]^{1/2}/2^{1/2}$ from: Alexander, S. *J. Chem. Phys.* **1962**, *37*, 967.
(19) Wright, M. E.; Lowe-Ma, C. K. *Organometallics*, in press.
(20) For crystallographic studies on related bis(pyridyl) and N-N six-membered chelate ring systems see: Steel, P. J. *Acta Crystallogr., Sect. C* **1983**, *39*, 1623. See ref 14.
(21) Calhoun, A. D.; Kobos, W. J.; Nile, T. A.; Smith, C. A. *J. Organomet. Chem.* **1979**, *170*, 175. See also ref 4a, p 898.
(22) Elman, B.; Moberg, C. *J. Organomet. Chem.* **1985**, *294*, 117.
(23) Pittman, C. U., Jr. Polymer Supported Catalysts. In *Comprehensive Organic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Chapter 55, pp 553–611.

Scheme VI



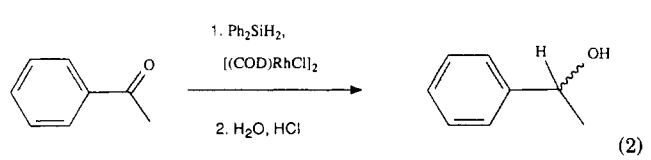
Treatment of chloromethylated polystyrene beads (1% cross-linked, 0.75 mequiv/g, 8.1% of the phenyl rings modified) with **10e** afforded polymer **15e** in a yield consistent with 100% modification of the chloromethyl sites. Treatment of **15e** with $[(COD)RhCl]_2$ produced a weight gain consistent with 90% complexation of the ligand sites in the polymer (eq 1).



(1)

The synthetic methodology developed in Scheme III is easily adapted for the synthesis of unsymmetrical bis(pyridyl)methanol systems (Scheme VI). Reaction of 2-pyridinecarboxaldehyde with compound **3f** or **3g** produced diastereomeric products (**17**) in approximately equal amounts. We have not been able to separate the diastereomeric pair resulting from **3f**; however, the diastereomers **17** prepared from **3g** were efficiently separated by column chromatography. The diastereomers **17(i)** and **17(ii)** have been fully characterized as well as their respective palladium(II) chloride complexes (**18**). To date, we do not have any crystallographic data, so the absolute configuration of the bridging carbon for the diastereomers cannot be assigned.

Asymmetric Hydrosilations. Selected ligands prepared in the study were tested in the rhodium-catalyzed asymmetric hydrosilation of acetophenone (eq 2). The results are presented in Table III for a series of rhodium/substrate and ligand/rhodium ratios.



(2)

Table III. Results for the Hydrosilation of Acetophenone with Use of $[(COD)RhCl]_2$ and Selected Ligands from This Study (−15 °C)

ligand	substrate/Rh	ligand/Rh	optical yield, % ee
4f	200/1	5/1	1.4 (*S*)
	100/1	10/1	7.5 (*S*)
5f	200/1	5/1	3.7 (*S*)
	100/1	10/1	12.7 (*S*)
8f	200/1	5/1	0.0
	100/1	10/1	0.5 (*R*)
	200/1[a]	5/1	0.0
10e	200/1	5/1	1.0 (*S*)
10f	200/1	5/1	9.0 (*S*)
15	200/1	1.0/0.9	0.8 (*S*)
17(i)	200/1	5/1	0.7 (*R*)
Brunner's imine[b,c]	110/1	13/1	29.0 (*R*)

[a] $[Rh(CO)Cl]_2$ used as source of Rh(I). [b] See: Brunner, H.; Riepl, G. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 377 (entry 8, Table I). This reaction was used as a reference to verify the quality of our experimental techniques. Our reaction conditions did vary from those reported previously. [c] After 18 h of reaction at −15 °C the reaction mixture was allowed to warm to ambient temperature; total reaction time 48 h.

The ligand/rhodium ratio was varied for some of the ligands from 5 to 10. From the work of Brunner et al. a general requisite for the N-N ligands to produce high optical yields is a large ligand/rhodium ratio often as high as 13/1. This is in direct contrast to the case for P-P type ligands, where a 1/1 complex is often most efficient and excess ligand typically diminishes or even destroys the catalytic activity of the metal.

The bipyridine ligands afforded virtually no asymmetric induction in the hydrosilation reaction. Notable for the bis(2-pyridyl)silane ligands was the improvement in optical yield by changing from the dimethyl- to the diphenylsilyl bridge. The group on the silicon occupying the pseudoaxial position apparently does exert some influence on the rhodium coordination sphere during the catalytic cycle. This is an important observation to be possibly exploited in second-generation ligand designs. The bis(2-pyridyl)-silane ligands behave as typical N-N type ligands in that an increase of the ligand/rhodium ratio produced an increase in optical yield. The bis(2-pyridyl)silane ligands were found to form rhodium catalysts more reactive than Brunner's chiral imine ligands; however, the former ligands did *not* produce comparable optical yields. It was interesting to find that ligand **17(i)** was less effective than ligand **10f**, thus indicating the need for chiral alkoxy groups on both pyridyl rings.

The results in Table III are not intended to represent an exhaustive survey and optimization of the ligand-catalytic systems possible but, rather, a section of data providing a reasonable evaluation of these first-generation catalysts. Ligands **5f** and **10f** did produce low optical yields, but these results are comparable to those of other recently synthesized chiral ligands that have been employed in the asymmetric hydrosilation of acetophenone.[24]

Asymmetric Cyclopropanations. We have also utilized the bis(6-alkoxy-2-pyridyl)methanol ligands for the synthesis of copper(II) catalysts (Scheme VII). Catalysts **19** were readily synthesized from copper(II) triflate and

(24) For related examples employing Ph_2SiH_2 and Rh(I): *S*-amphos, 27% optical yield; *R*-amphos, 33% optical yield; (+)-diop, 23% optical yield; *S,S*-chiraphos, 4% optical yield; *S*-amars, 0% optical yield (Payne, N. C.; Stephan, D. W. *Inorg. Chem.* **1982**, *21*, 182). For a very recent example of chiral phosphinite ligands see: Vannoorenberghe, Y.; Buono, G. *Tetrahedron Lett.* **1988**, *29*, 3235 (optical yield of 18%).

Scheme VII

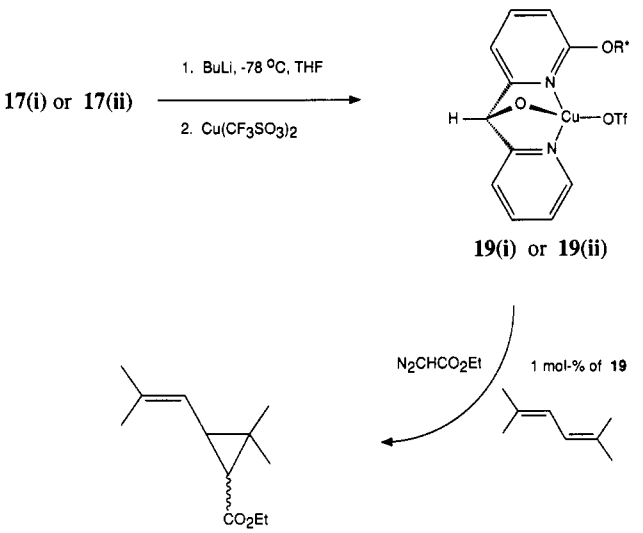


Table IV. Optical Rotations for the Diastereoisomeric Ligands (17) and Copper(II) Complexes (19)

compd	[α] (c = 1, CH_2Cl_2), deg	compd	[α] (c = 1, CH_2Cl_2), deg
17(i)	+78.8	19(i)	+246.0
17(ii)	+64.7	19(ii)	−87.5

Table V. Results for the Cyclopropanation of 2,5-Dimethyl-2,4-hexadiene with Catalysts 19(i), 19(ii), and 19f

Cu(II) catalyst	ester cis/trans	[α] (neat, dm = 1), deg	optical yield,[a] % ee
19(i)	1/1.2	−1.5	~8.5
19(ii)	1/1.3	+1.8	~10.0
19f	1/1.2	+0.1	~0.5

[a] See the Experimental Section for the procedure of determining the optical yield.

the appropriate alkoxide. The catalysts were characterized by their optical rotations (Table IV) and used without purification (analogous to the work of Aratani[11]). In the preparation of **19** it was noted that an excess of ligand generated a blue copper system that was found *not* to catalyze the cyclopropanation reaction, whereas a 1/1 ratio of ligand to copper(II) gave a green complex that was very effective. The results of the asymmetric cyclopropanation of 2,5-dimethyl-2,4-hexadiene with ethyl diazoacetate under copper(II) catalysis are summarized in Table V. Addition of 1 mol equiv of sodium acetate to the copper catalyst **19** generated a less reactive catalyst, which then required a reaction temperature of 40 °C. The latter catalyst produced half the optical yield compared to that for its triflate analogue.

The cyclopropanation results show the diastereomeric ligands to be superior to ligand **10**, whereas for the hydrosilation reaction the latter ligands were unquestionably more efficient. The configuration for the bridging carbon atom in ligand **17** is clearly controlling the chirality of the product and suggests that in the cyclopropanation reaction a lack of C_2 symmetry for the ligand is a desirable feature. This has been apparent in other ligands that have been previously studied by workers in the area of cyclopropanation catalysts.[25]

(25) Matlin, S. A.; Lough, W. J.; Chan, L.; Abram, D. M. H.; Zhou, Z. *J. Chem. Soc., Chem. Commun.* **1984**, 1038. See also ref 11.

In conclusion, the new chiral ligands prepared in the study have been fully characterized as individuals and/or as palladium(II) chloride complexes. Selected examples from each new class of ligands were tested in the rhodium-catalyzed hydrosilation of acetophenone and were found to afford excellent chemical yields but somewhat low optical yields of 1-phenylethanol. Studies are in progress that include the synthesis of other bis(2-pyridyl)dialkylsilane- and bis(2-pyridyl)diarylsilane-based ligands and the examination of additional asymmetric catalytic reactions with the ligands prepared in this study.

Experimental Section

General Considerations. All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents.[26] Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian XL 300; ^{13}C NMR, Varian XL 300 (at 75.4 MHz). NMR chemical shifts are reported in δ vs Me_4Si in ^1H NMR spectroscopy and vs the $CDCl_3$ resonance (assigned at 77.00 ppm) in ^{13}C spectra. Optical rotations were measured on a Perkin-Elmer 241 polarimeter using the sodium lamp. $(MeCN)_2PdCl_2$, $(MeCN)_2NiBr_2$,[27] and $[(COD)RhCl]_2$[28] were prepared by literature methods. Copper(I) iodide (98%), *n*-BuLi (2.5 M in hexane), dimethyldichlorosilane, diphenyldichlorosilane, 2,5-dimethyl-2,4-hexadiene, 2-pyridinecarboxaldehyde, silica gel, and all the optically active alcohols were purchased from Aldrich Chemical Co. and used as received. Acetophenone was distilled from barium oxide, and diphenylsilane and DMF were distilled from CaH_2 prior to use and stored under argon. 2,6-Dibromopyridine was purchased from Lancaster Synthesis and used as received. The alumina used was neutral MPLC grade (nonactivated) purchased from Universal Scientific. Palladium(II) chloride, copper(II) triflate, and nickel(II) bromide were purchased from Alfa. Elemental analyses were performed at Atlantic Microlab Inc., Norcross, GA.

Preparation of Optically Active 6-Alkoxy-2-bromopyridines (2). Potassium alkoxides were generated by treatment of the appropriate alcohol with potassium metal in THF for 48 h under reflux. The potassium alkoxide THF solution was transferred by cannulation to a DMF (60 mL) solution of 2,6-dibromopyridine (4.74 g, 20 mmol) at 85 °C. The mixture was allowed to react for an additional 60 min at 85 °C. The reaction mixture was allowed to cool to ambient temperature, poured onto water, and then extracted with ether (2 × 150 mL). The organic layers were combined and washed with brine and then dried over K_2CO_3. Removal of the solvent under reduced pressure yielded compounds **2b–g** in greater than 90% crude yield. Final purification was achieved by chromatography of the crude products on silica gel with ethyl acetate/hexane (1/9, v/v) as eluent. In each case the desired alkoxybromopyridine eluted first off the column.

2-Bromo-6-[(*1S,2S,5S*)-*trans*-myrtanoxy]pyridine (2b): mp 38–44 °C; ^1H NMR ($CDCl_3$) δ 7.41 (dd, *J* = 9, 7 Hz, 1 H), 7.04 (dd, *J* = 7, 1 Hz, 1 H), 6.67 (dd, *J* = 9, 1 Hz, 1 H), 4.05 (m, 2 H), 2.45 (m, 1 H), 2.11–1.70 (m, 6 H), 1.42 (d, *J* = 10 Hz, 2 H), 1.25 (s, 3 H), 0.90 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.0, 140.3, 138.6, 119.9, 109.4 (pyridine C's), 70.4, 42.5, 40.8, 39.2, 34.5, 26.7, 24.1, 23.5, 20.2, 18.3. Anal. Calcd for $C_{15}H_{20}BrNO$: C, 58.07; H, 6.50. Found: C, 57.99; H, 6.49.

2-Bromo-6-[(*1R*)-myrtenoxy]pyridine (2c): oil; ^1H NMR ($CDCl_3$) δ 7.40 (dd, *J* = 8, 7 Hz, 1 H), 6.93 (dd, *J* = 7, 1 Hz, 1 H), 6.59 (dd, *J* = 8, 1 Hz, 1 H), 5.62 (m, 1 H), 4.68 (m, 2 H), 2.35–2.00 (m's, 6 H), 1.29 (s, 3 H), 0.83 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 143.5, 140.3, 120.9, 120.1, 109.6 (pyridine C's), 69.3, 43.6, 40.8, 38.1, 31.5, 31.3, 26.2, 21.1; always contaminated by dialkoxy byproduct.

2-Bromo-6-[(*1S,2S,3S,5R*)-isopinocampheoxy]pyridine (2d): oil; ^1H NMR ($CDCl_3$) δ 7.40 (dd, *J* = 8.2, 7.5 Hz, 1 H), 7.00

(26) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1972.

(27) Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 216.

(28) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.

(dd, J = 8, 1 Hz, 1 H), 6.64 (dd, J = 8, 1 Hz, 1 H), 5.24–5.18 (m, 1 H), 2.78–2.69 (m, 1 H), 2.36–2.33 (m, 1 H), 2.29–2.24 (m, 1 H), 1.98–1.93 (m, 1 H), 1.89–1.83 (m, 1 H), 1.76–1.69 (dt, J = 14, 3 Hz, 1 H), 1.25 (s, 3 H), 1.17 (d, J = 7 Hz, 3 H), 1.16 (d, J = 10 Hz, 1 H), 1.03 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 163.3, 140.1, 138.5, 119.6, 109.9 (pyridine C's), 76.1, 47.6, 43.9, 41.4, 38.3, 35.9, 33.2, 27.5, 23.9, 20.7. Anal. Calcd for $C_{15}H_{20}BrNO$: C, 58.07; H, 6.50. Found: C, 58.15; H, 6.54.

2-Bromo-6-[(*1S,2R,5R*)-isomenthoxy]pyridine (2e): oil; ^{1}H NMR ($CDCl_3$) δ 7.37 (dd, J = 8, 7 Hz, 1 H), 6.99 (dd, J = 8, 1 Hz, 1 H), 6.61 (dd, J = 8, 1 Hz, 1 H), 5.28 (m, 1 H), 1.96–1.43 (br m, 8 H), 1.25 (m, 1 H), 1.01 (d, J = 7 Hz, 3 H), 0.96 (d, J = 7 Hz, 3 H), 0.88 (d, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 163.1, 140.2, 138.6, 119.4, 109.7 (pyridine C's), 73.4, 45.2, 35.4, 30.0, 27.5, 26.4, 21.2, 21.0, 20.9, 19.5. Anal. Calcd for $C_{15}H_{22}BrNO$: C, 57.70; H, 7.10. Found: C, 57.77; H, 7.12.

2-Bromo-6-[(*1S,2R,4S*)-borneoxy]pyridine (2f): mp 60–63 °C; ^{1}H NMR ($CDCl_3$) δ 7.41 (dd, J = 8.2, 7.4 Hz, 1 H), 7.03 (dd, J = 7.5, 0.6 Hz, 1 H), 6.68 (dd, J = 8.2, 0.6 Hz, 1 H), 5.01 (ddd, J = 9.5, 3.4, 2.1 Hz, 1 H), 2.50 (m, 1 H), 2.15 (m, 1 H), 1.77 (m, 2 H), 1.31 (m, 2 H), 1.01 (dd, J = 14.0, 3.6 Hz, 1 H), 0.97 (s, 3 H), 0.91 (s, 3 H), 0.90 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.0, 140.1, 138.6, 119.6, 109.6 (pyridine C's), 81.9, 49.0, 47.7, 44.9, 36.8, 28.1, 27.1, 19.8, 19.1, 13.7. Anal. Calcd for $C_{15}H_{20}BrNO$: C, 58.07; H, 6.50. Found: C, 58.28; H, 6.52.

2-Bromo-6-[(*1R,2R,4S*)-1,3,3-trimethyl-2-norborneoxy]pyridine (2g): oil; ^{1}H NMR ($CDCl_3$) δ 7.37 (dd, J = 8.1, 7.5 Hz, 1 H), 6.98 (dd, J = 7.4, 0.7 Hz, 1 H), 6.67 (dd, J = 8.2, 0.6 Hz, 1 H), 4.58 (d, J = 1.7 Hz, 1 H), 1.94 (m, 1 H), 1.70 (m, 3 H), 1.47 (m, 1 H), 1.28 (s, 3 H), 1.26–1.07 (m, 2 H), 1.09 (s, 3 H), 0.72 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.2, 140.1, 138.1, 119.5, 109.4 (pyridine C's), 87.8, 48.8, 48.6, 41.4, 39.9, 29.5, 26.7, 25.9, 20.4, 19.6. Anal. Calcd for $C_{15}H_{20}BrNO$: C, 58.07; H, 6.50. Found: C, 58.17; H, 6.48.

Preparation of Bis(pyridyl)dimethylsilane Ligands (4). A THF (10 mL) solution containing the appropriate 2-bromo-6-alkoxypyridine (5 mmol) at −78 °C was treated with *n*-butyllithium (2 mL, 5 mmol) and the solution stirred at −78 °C for 1 h. Dichlorodimethylsilane (0.30 mL, 2.5 mmol) was then added in one portion, and the reaction mixture was allowed to warm to ambient temperature by removal of the cooling bath. After 1 h at room temperature the reaction mixture was poured into water. The resulting solution was extracted with ether (2 × 100 mL). The organic layers were combined, washed with brine, and then dried over K_2CO_3, and the solvent was evaporated to yield compounds **4a–g** in greater than 85% crude yield. Crude **4a–g** were used in preparing compounds **6a–g** without further purification.

Bis[2-(6-methoxypyridyl)]dimethylsilane (4a): ^{1}H NMR ($CDCl_3$) δ 7.48 (dd, J = 8, 7 Hz, 2 H), 7.19 (dd, J = 7, 1 Hz, 2 H), 6.67 (dd, J = 8, 1 Hz, 2 H), 3.97 (s, 6 H), 0.61 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 162.9, 136.7, 123.6, 110.4 (pyridine C's), 53.1 (OCH_3), −3.8 ($SiCH_3$).

Bis[2-(6-(*1S,2S,5S*)-myrtanoxypyridyl)]dimethylsilane (4b): ^{1}H NMR ($CDCl_3$) δ 7.46 (dd, J = 8, 7 Hz, 2 H), 7.15 (dd, J = 7, 1 Hz, 2 H), 6.64 (dd, J = 8, 1 Hz, 2 H), 4.24–4.10 (m, 4 H), 2.56–2.48 (m, 2 H), 2.12–1.69 (br m, 12 H), 1.44 (d, J = 10 Hz, 4 H), 1.29 (s, 6 H), 0.90 (s, 6 H), 0.60 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 163.4, 162.8, 136.6, 123.3, 110.6 (pyridine C's), 69.0, 42.6, 41.0, 39.2, 34.5, 26.7, 24.2, 23.6, 20.2, 18.4 (myrtanoxy C's), −3.8 ($SiCH_3$).

Bis[2-(6-(*1R*)-myrtenoxypyridyl)]dimethylsilane (4c): ^{1}H NMR ($CDCl_3$) δ 7.43 (dd, J = 8, 7 Hz, 2 H), 7.11 (dd, J = 7, 1 Hz, 2 H), 6.64 (dd, J = 8, 1 Hz, 2 H), 5.58 (m, 2 H), 4.84–4.70 (m, 4 H), 2.41–2.00 (m, 10 H), 1.28 (s, 6 H), 1.21 (d, J = 9 Hz, 2 H), 0.80 (s, 6 H), 0.60 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 163.1, 162.7, 144.6, 136.6, 123.5, 120.0, 110.8 (pyridine C's), 67.8, 43.5, 40.9, 38.1, 31.6, 31.3, 26.2, 21.1 (myrtenoxy C's), −3.8 ($SiCH_3$).

Bis[2-(6-(*1S,2S,3S,5R*)-isopinocampheoxypyridyl)]dimethylsilane (4d): ^{1}H NMR ($CDCl_3$) δ 7.44 (dd, J = 8, 7 Hz, 2 H), 7.16 (dd, J = 7, 1 Hz, 2 H), 6.63 (dd, J = 8, 1 Hz, 2 H), 5.50–5.43 (m, 2 H), 2.80–2.71 (m, 2 H), 2.43–2.39 (m, 2 H), 2.38–2.28 (m, 2 H), 2.00–1.95 (m, 2 H), 1.92–1.86 (m, 2 H) 1.76–1.69 (ddd, J = 14, 5, 3 Hz, 2 H), 1.25 (s, 6 H), 1.16 (d, J = 10 Hz, 2 H), 1.12 (d, J = 7 Hz, 6 H), 1.03 (s, 6 H), 0.59 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 163.1, 162.8, 136.5, 123.1, 111.2 (pyridine C's), 74.5, 47.9, 43.9, 41.7, 38.5, 36.4, 33.8, 27.7, 23.7, 20.9 (isopinocampheoxy C's), −3.7 ($SiCH_3$).

Bis[2-(6-(*1S,2R,5R*)-isomenthoxypyridyl)]dimethylsilane (4e): ^{1}H NMR ($CDCl_3$) δ 7.41 (dd, J = 8, 7 Hz, 2 H), 7.10 (dd, J = 7, 1 Hz, 2 H), 6.58 (dd, J = 8, 1 Hz, 2 H), 5.51 (m, 2 H), 2.02–1.83 (m, 2 H), 1.72–1.44 (m, 14 H), 1.34–1.20 (m, 2 H), 1.03 (d, J = 7 Hz, 6 H), 0.94 (d, J = 7 Hz, 6 H), 0.80 (d, J = 7 Hz, 6 H), 0.65 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 162.9, 162.8, 136.6, 123.0, 111.1 (pyridine C's), 71.0, 45.9, 36.1, 30.4, 27.8, 26.4, 20.8, 20.6, 20.3, 18.9 (isomenthoxy C's), −3.7 ($SiCH_3$).

Bis[2-(6-(*1S,2R,4S*)-borneoxypyridyl)]dimethylsilane (4f): ^{1}H NMR ($CDCl_3$) δ 7.42 (dd, J = 8.4, 7.0 Hz, 2 H), 7.11 (dd, J = 8.4, 0.9 Hz, 2 H), 6.62 (dd, J = 8.4, 0.9 Hz, 2 H), 5.12 (m, 2 H), 2.45 (m, 2 H), 2.18 (m, 4 H), 1.88–1.66 (m, 4 H), 1.28 (m, 4 H), 0.96 (s, 6 H), 0.90 (s, 6 H), 0.88 (s, 6 H), 0.54 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 163.7, 162.8, 136.3, 123.0, 111.0 (pyridine C's), 80.4, 48.8, 47.6, 45.0, 37.4, 28.2, 27.1, 19.8, 19.0, 13.8 (borneoxy C's), −3.7 ($SiCH_3$).

Bis[2-(6-((1*R*,2*R*,4*S*)-1,3,3-trimethyl-2-norborneoxy)-pyridyl)]dimethylsilane (4g): ^{1}H NMR ($CDCl_3$) δ 7.40 (dd, J = 8.4, 7 Hz, 2 H), 7.04 (J = 7, 1 Hz, 2 H), 6.63 (dd, J = 8.4, 1 Hz, 2 H), 4.76 (s, 1 H), 4.75 (s, 1 H), 1.99 (m, 2 H), 1.84 (m, 2 H), 1.78–1.58 (br m, 6 H), 1.45 (m, 2 H), 1.21 (m, 2 H), 1.14 (s, CH_3, 6 H), 1.07 (s, CH_3, 6 H), 0.70 (s, 6 H), 0.56 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 164.3, 162.6, 136.4, 123.3, 110.0 (pyridine C's), 86.1, 48.9, 48.7, 41.6, 39.7, 29.6, 26.8, 25.9, 20.4, 19.8, −3.3 ($SiCH_3$).

Preparation of Bis(pyridyl)diphenylsilane Ligands (5). The diphenylsilane ligands were prepared by using a procedure analogous to that used to prepare the dimethylsilane ligands (**5a–g**), with dichlorodiphenylsilane (0.52 mL, 2.5 mmol) being substituted for dichlorodimethylsilane. The ligands were isolated after water workup as clear, colorless oils, which were later purified by complexation with palladium(II) chloride. In the case of **5f**, the compound was crystallized from pentane at −25 °C to afford analytically pure **5f**.

Bis[2-(6-methoxypyridyl)]diphenylsilane (5a): ^{1}H NMR ($CDCl_3$) δ 7.75 (m, 4 H), 7.51–7.34 (m, 8 H), 7.20 (dd, J = 7, 0.9 Hz, 2 H), 6.72 (dd, J = 8.5, 1 Hz, 2 H), 3.90 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 163.4, 159.6, 136.8, 136.5, 135.5, 129.9, 129.5, 127.7, 127.5, 126.3, 53.3 (OCH_3).

Bis[2-(6-(*1R*)-myrtenoxypyridyl)]diphenylsilane (5c): ^{1}H NMR ($CDCl_3$) δ 7.72 (m, 4 H), 7.50–7.31 (br m, 8 H), 7.13 (dd, J = 7, 0.9 Hz, 2 H), 6.70 (dd, J = 8.4, 0.9 Hz, 2 H), 5.69–5.45 (m, 2 H), 4.71 (m, 4 H), 2.41–2.04 (br m, 8 H), 1.85 (m, 2 H), 1.30–1.12 (m, 2 H), 1.25 (s, 6 H), 0.75 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 163.1, 159.4, 144.3, 136.8, 136.6, 135.0, 130.1, 129.5, 127.8, 127.5, 126.2, 120.2, 111.4, 68.0, 43.5, 40.8, 38.0, 31.5, 31.3, 26.2, 21.0.

Bis[2-(6-(*1S,2S,3S,5R*)-isopinocampheoxypyridyl)]diphenylsilane (5d): ^{1}H NMR ($CDCl_3$) δ 7.77 (m, 4 H), 7.45–7.31 (m, 8 H), 7.16 (dd, J = 7, 0.8 Hz, 2 H), 6.66 (dd, J = 8.3, 0.9 Hz, 2 H), 5.34 (m, 2 H), 2.52–2.19 (br m, 6 H), 1.82 (m, 4 H), 1.60 (ddd, J = 14, 5, 3 Hz, 2 H), 1.27–1.10 (m, 2 H), 1.20 (s, 6 H), 1.02 (d, J = 7.4 Hz, 6 H), 0.88 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 163.1, 159.8, 136.5, 133.9, 129.8, 129.4, 127.5, 125.7, 111.7, 74.6, 47.8, 43.8, 41.6, 38.4, 36.2, 33.8, 27.6, 23.8, 20.7.

Bis[2-(6-(*1S,2R,5R*)-isomenthoxypyridyl)]diphenylsilane (5e): ^{1}H NMR ($CDCl_3$) δ 7.72 (d, J = 6.5 Hz, 4 H), 7.44–7.30 (m, 8 H), 2.10 (d, J = 7 Hz, 2 H), 6.62 (d, J = 8.3 Hz, 2 H), 5.39 (m, 2 H), 1.84 (m, 6 H), 1.60 (m, 6 H), 1.42 (m, 6 H), 1.23 (m, 4 H), 0.96–0.68 (br m, 14 H); ^{13}C NMR ($CDCl_3$) δ 163.0, 159.7, 136.7, 136.5, 135.7, 134.0, 129.3, 127.6, 127.5, 125.6, 111.6, 71.2, 46.1, 36.0, 30.4, 27.7, 26.3, 20.6, 20.5, 19.9, 18.6.

Bis[2-(6-(*1S,2R,4S*)-borneoxypyridyl)]diphenylsilane (5f): ^{1}H NMR ($CDCl_3$) δ 7.74 (m, 4 H), 7.45–7.29 (br m, 8 H), 7.13 (dd, J = 7, 1 Hz, 2 H), 6.68 (dd, J = 8.4, 1 Hz, 2 H), 5.03 (m, 2 H), 2.18 (m, 2 H), 1.85 (m, 1 H), 1.70 (m, 1 H), 1.57 (m, 4 H), 1.40–1.16 (br m, 4 H), 0.98–0.87 (m, 2 H), 0.86 (s, 6 H), 0.84 (s, 6 H), 0.82 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 163.7, 159.8, 137.0, 136.5, 136.4, 135.49, 135.48, 135.00, 134.99, 130.0, 129.4, 127.7, 127.6, 127.4, 125.6, 123.7, 111.5, 80.5, 48.7, 47.5, 45.9, 37.1, 28.2, 27.1, 19.8, 18.9, 13.7. Anal. Calcd for $C_{42}H_{50}N_2O_2Si$: C, 78.46; H, 7.84. Found: C, 78.37; H, 7.89.

Bis[2-(6-((1*R*,2*R*,4*S*)-1,3,3-trimethyl-2-norborneoxy)-pyridyl)]diphenylsilane (5g): ^{1}H NMR ($CDCl_3$) δ 7.72 (m, 4 H), 7.51–7.29 (br m, 8 H), 7.08 (dd, J = 7, 1 Hz, 2 H), 6.67 (dd, J = 8.4, 1 Hz, 2 H), 4.76 (m, 2 H), 1.96 (m, 2 H), 1.84 (m, 2 H), 1.77–1.36 (br m, 6 H), 1.29–0.97 (br m, 4 H), 1.01 (s, 6 H), 0.71 (s, 6 H), 0.66 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 164.3, 159.5, 136.7, 136.6,

135.6, 135.5, 135.1, 135.0, 133.8, 130.1, 130.0, 129.4, 127.8, 127.7, 127.4, 125.9, 111.5, 85.9, 48.73, 48.66, 41.5, 39.5, 29.1, 26.7, 25.9, 20.3, 19.8.

Preparation of Compounds 6a–g. To a solution of crude compounds **4a–g** (2.5 mmol) in degassed $CHCl_3$ (15 mL) was added $(CH_3CN)_2PdCl_2$ (0.39 g, 1.5 mmol) and the solution stirred for 4 h at room temperature. After 4 h, excess petroleum ether was added and the resulting mixture allowed to stand at −29 °C overnight. The precipitate was filtered and washed with cold petroleum ether (−78 °C) to yield pure **6a–g** in greater than 95% conversion.

{Bis[2-(6-methoxypyridyl)]dimethylsilane}palladium(II) chloride (6a): ^{1}H NMR ($CDCl_3$) δ 7.74 (dd, J = 8.6, 7.1 Hz, 2 H), 7.27 (dd, J = 7.2, 1.1 Hz, 2 H), 6.81 (dd, J = 8.6, 1.1 Hz, 2 H), 4.18 (s, 6 H), 1.81 (s, 3 H), 0.89 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 162.1, 139.8, 124.1, 109.3, 57.4 (OCH_3), −3.7 ($SiCH_3$). Anal. Calcd for $C_{14}H_{18}Cl_2N_2O_2PdSi$: C, 37.23; H, 4.02. Found: C, 37.09; H, 4.02.

{Bis[2-(6-(*1S,2S,5S*)-myrtanoxypyridyl)]dimethylsilane}palladium(II) chloride (6b): $[\alpha]^{20}$ = −6.6° (c = 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.75–7.69 (m, 2 H), 7.23 (d, J = 8 Hz, 2 H), 6.76 (d, J = 8.5 Hz, 2 H), 4.10 (m, 4 H), 2.83 (t, J = 7 Hz, 1 H), 2.71 (t, J = 8 Hz, 1 H), 2.30–1.58 (br m, 12 H), 1.77 (s, 3 H), 1.51 (t, J = 10 Hz, 2 H) 1.25 (s, 3 H), 1.24 (s, 3 H), 0.94 (s, 6 H), 0.86 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.3, 166.2, 162.0, 161.9, 139.6, 123.9, 123.8, 109.7, 109.6 (pyridine C's), 75.2, 42.50, 42.45, 40.8, 39.5, 39.3, 34.6, 34.4, 26.6, 24.2, 24.1, 23.9, 23.8, 20.30, 20.27, 19.05, 19.01 (myrtanoxy C's), 0.8 ($SiCH_3$), −3.6 ($SiCH_3$). Anal. Calcd for $C_{32}H_{46}Cl_2N_2O_2PdSi$: C, 55.21; H, 6.66. Found: C, 55.52; H, 6.80.

{Bis[2-(6-(*1R*)-myrtenoxypyridyl)]dimethylsilane}palladium(II) chloride (6c): $[\alpha]^{20}$ = −3.9° (c = 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.69–7.63 (m, 2 H), 7.20 (apparent t, J = 8 Hz, 2 H), 6.78 (apparent t, J = 8 Hz, 2 H), 5.79 (d, J = 14 Hz, 2 H), 4.85–4.74 (m, 4 H), 2.58–2.25 (br m, 8 H), 2.11 (m, 2 H), 1.81 (s, 3 H), 1.32 (s, 3 H), 1.30 (s, 3 H), 1.19 (d, J = 9 Hz, 1 H), 1.10 (d, J = 9 Hz, 1 H), 0.94 (s, 3 H), 0.88 (s, 3 H), 0.86 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.3, 166.0, 162.1, 162.0, 142.6, 142.58, 139.3, 139.2, 124.0, 123.9, 121.9, 121.2, 110.8, 110.2 (pyridine C's), 73.0, 72.6, 42.8, 42.5, 40.8, 40.7, 38.2, 38.1, 31.6, 31.4, 31.37, 31.3, 26.1, 25.9, 21.3, 21.1 (myrtenoxy C's), 0.8 ($SiCH_3$), −3.6 ($SiCH_3$). Anal. Calcd for $C_{32}H_{42}Cl_2N_2O_2PdSi$: C, 55.53; H, 6.12; Cl, 10.24. Found: C, 54.71; H, 6.20; Cl, 10.31.

{Bis[2-(6-(*1S,2S,3S,5R*)-isopinocampheoxypyridyl)]dimethylsilane}palladium(II) chloride (6d): $[\alpha]^{20}$ = +53.0° (c = 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.71 (dd, J = 8, 7 Hz, 2 H), 7.21 (m, 2 H), 6.74 (dd, J = 8, 5 Hz, 2 H), 4.70 (m, 2 H), 3.17 (m, 1 H), 3.08 (m, 1 H), 2.67 (m, 1 H), 2.47 (m, 4 H), 2.29 (m, 1 H), 1.96 (m, 4 H), 1.89 (d, J = 10 Hz, 1 H), 1.85 (s, 3 H), 1.60 (d, J = 10 Hz, 1 H), 1.31 (s, 3 H), 1.295 (s, 3 H), 1.29 (d, J = 7 Hz, 3 H), 1.22 (d, J = 7 Hz, 3 H), 1.01 (s, 3 H), 0.99 (s, 3 H), 0.88 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 165.3, 164.9, 162.4, 162.2, 139.6, 139.3, 123.4, 109.7, 109.1 (pyridine C's), 80.5, 79.2, 47.2, 47.1, 43.7, 43.6, 41.1, 40.9, 38.1, 36.0, 34.1, 32.6, 32.4, 27.1, 24.1, 23.9, 21.3, 21.2 (isopinocampheoxy C's), 0.7 ($SiCH_3$), −3.7 ($SiCH_3$). Anal. Calcd for $C_{32}H_{46}Cl_2N_2O_2PdSi$: C, 55.21; H, 6.66. Found: C, 55.01; H, 6.69.

{Bis[2-(6-(*1S,2R,5R*)-isomenthoxypyridyl)]dimethylsilane}palladium(II) chloride (6e): $[\alpha]^{20}$ = +12.0° (c = 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.70 (m, 2 H), 7.20 (dd, J = 7, 5 Hz, 2 H), 6.72 (d, J = 9 Hz, 2 H), 4.71 (m, 1 H), 4.67 (m, 1 H), 2.65–2.36 (m, 3 H), 2.17–2.00 (m, 4 H), 2.00–1.50 (m, 12 H), 1.42–1.12 (m, 2 H), 1.04–0.86 (br m, 22 H); ^{13}C NMR ($CDCl_3$) δ 165.2, 165.1, 162.5, 139.3, 123.3, 109.2, 109.1 (pyridine C's), 78.3, 78.1, 44.9, 44.1, 34.9, 33.3, 29.7, 29.2, 27.2, 26.0, 25.98, 25.6, 22.1, 21.4, 21.2, 21.1, 20.9, 20.4, 19.3 (isomenthoxy C's), 0.9 ($SiCH_3$), −3.4 ($SiCH_3$). Anal. Calcd for $C_{32}H_{50}Cl_2N_2O_2PdSi$: C, 54.90; H, 7.20. Found: C, 54.41; H, 7.23.

{Bis[2-(6-(*1S,2R,4S*)-borneoxypyridyl)]dimethylsilane}palladium(II) chloride (6f): $[\alpha]^{20}$ = −6.1° (c = 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.68 (m, 2 H), 7.22 (dd, J = 7, 4 Hz, 2 H), 6.66 (apparent t, J = 9.2 Hz, 2 H), 4.54 (m, 2 H), 3.33 (m, 1 H), 3.10 (m, 1 H), 2.43 (m, 1 H), 2.25 (m, 1 H), 1.80 (m, 4 H), 1.77 (s, 3 H), 1.64–1.34 (m, 4 H), 1.28 (s, 3 H), 1.20 (m, 2 H), 1.07 (s, 3 H), 0.98 (s, 6 H), 0.95 (s, 3 H), 0.86 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.5, 166.4, 162.6, 162.5, 139.4, 139.36, 123.3, 110.1, 109.8 (pyridine C's), 86.5, 85.5, 50.4, 49.4, 48.6, 47.9, 45.1, 45.0, 37.1, 34.6, 28.3, 28.0, 27.5, 19.75, 19.72, 19.00, 18.95, 14.7, 14.0 (borneoxy C's), 1.3 ($SiCH_3$), −3.2 ($SiCH_3$). Anal. Calcd for $C_{32}H_{46}Cl_2N_2O_2PdSi$: C, 55.21; H, 6.66. Found: C, 55.29; H, 6.69.

{Bis[2-(6-((*1R,2R,4S*)-1,3,3-trimethyl-2-norborneoxy)pyridyl)]dimethylsilane}palladium(II) chloride (6g): $[\alpha]^{20}$ = +31.3° (c = 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.67 (m, 2 H), 7.23 (m, 2 H), 6.76 (apparent d, J = 8.6 Hz, 2 H), 4.06 (br s, 1 H), 4.04 (br s, 1 H), 3.08–2.85 (br m, 2 H), 2.10–1.84 (br m, 2 H), 1.79 (s, 3 H), 1.70–1.48 (br m, 6 H), 1.46 (s, 3 H), 1.31 (s, 3 H), 1.28 (s, 3 H), 1.25 (s, 3 H), 1.18 (s, 3 H), 0.88 (s, 3 H), 0.82 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 167.3, 163.0, 139.4, 138.96, 123.3, 123.2, 110.3, 110.0 (pyridine C's), 93.41, 93.39, 50.7, 49.8, 49.6, 49.5, 42.6, 42.0, 41.3, 40.6, 30.8, 30.4, 27.7, 26.7, 26.0, 25.8, 21.8, 21.3, 20.8, 20.5, 1.5 ($SiCH_3$), −2.7 ($SiCH_3$). Anal. Calcd for $C_{32}H_{46}Cl_2N_2O_2PdSi$: C, 55.21; H, 6.66. Found: C, 55.75; H, 6.91.

Preparation of Compounds 7a–g. To a solution of crude compounds **5a–g** (2.5 mmol) in degassed CH_2Cl_2 (15 mL) was added $(CH_3CN)_2PdCl_2$ (0.39 g, 1.5 mmol) and the solution stirred for 4 h at room temperature. After 4 h, excess petroleum ether was added to precipitate the palladium complexes. The precipitates were filtered, washed with petroleum ether and diethyl ether, and dried under vacuum for 24 h.

{Bis[2-(6-methoxypyridyl)]diphenylsilane}palladium(II) chloride (7a): ^{1}H NMR ($CDCl_3$) δ 7.92 (dd, J = 7.9, 1.6 Hz, 2 H), 7.75 (dd, J = 8.6, 7.1 Hz, 2 H), 7.62–7.49 (m, 10 H), 7.18 (dd, J = 7.1, 1.1 Hz, 2 H), 6.92 (dd, J = 8.6, 1 Hz, 2 H), 4.22 (s, OCH_3, 6 H); ^{13}C NMR ($CDCl_3$) δ 167.0, 159.4, 139.3, 136.7, 136.6, 131.2, 131.0, 128.2, 126.6, 109.6, 57.1 (OCH_3). Anal. Calcd for $C_{24}H_{22}Cl_2N_2O_2PdSi$: C, 50.06; H, 3.85. Found: C, 49.94; H, 3.87.

{Bis[2-(6-(*1R*)-myrtenoxypyridyl)]diphenylsilane}palladium(II) chloride (7c): $[\alpha]^{20}$ = −3.3° (c = 1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.90 (m, 4 H), 7.75–7.37 (br m, 8 H), 7.11 (apparent d, J = 7 Hz, 2 H), 6.86 (dd, J = 10.9, 8.7 Hz, 2 H), 5.78 (br s, 2 H), 4.78 (m, 4 H), 2.57–2.08 (br m, 10 H), 1.40–1.08 (br m, 2 H), 1.31 (s, 3 H), 1.27 (s, 3 H), 0.96 (s, 3 H), 0.90 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 167.2, 166.7, 159.7, 159.6, 142.9, 142.6, 139.3, 137.1, 137.0, 135.9, 135.8, 131.4, 131.3, 130.4, 130.0, 128.5, 128.2, 128.1, 128.0, 127.9, 127.0, 126.9, 121.9, 120.9, 111.7, 111.0, 73.6, 72.9, 42.8, 42.5, 40.75, 40.70, 38.14, 38.12, 31.6, 31.41, 31.36, 31.30, 26.1, 25.9, 21.2, 21.1.

{Bis[2-(6-(*1S,2S,3S,5R*)-isopinocampheoxypyridyl)]diphenylsilane}palladium(II) chloride (7d): $[\alpha]^{20}$ = +41.0° (c = 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.91 (dd, J = 7.6, 1.4 Hz, 2 H), 7.68–7.44 (br m, 10 H), 7.08 (dd, J = 7.1, 1.0 Hz, 2 H), 7.06 (dd, J = 7.1, 1.0 Hz, 2 H), 6.77 (apparent t, J = 8.7 Hz, 2 H), 4.70 (m, 2 H), 3.16 (m, 1 H), 3.06 (m, 1 H), 2.67 (m, 1 H), 2.53–2.27 (br m, 3 H), 2.01–1.84 (m, 4 H), 1.56 (m, 2 H), 1.23 (m, 14 H), 0.98 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 166.0, 165.7, 160.3, 160.2, 139.2, 138.9, 137.3, 136.9, 131.6, 131.2, 130.6, 128.6, 128.4, 128.3, 126.4, 126.3, 110.3, 109.7, 80.6, 79.6, 47.2, 43.6, 43.5, 41.1, 41.0, 38.3, 38.2, 36.1, 34.2, 32.5, 32.4, 27.2, 24.2, 24.0, 21.4, 21.3. Anal. Calcd for $C_{42}H_{50}Cl_2N_2O_2PdSi$: C, 61.50; H, 6.14. Found: C, 61.58; H, 6.17.

{Bis[2-(6-(*1S,2R,5R*)-isomenthoxypyridyl)]diphenylsilane}palladium(II) chloride (7e): $[\alpha]^{20}$ = +10.0° (c = 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.90 (dd, J = 8.7, 1.5 Hz, 2 H), 7.66–7.44 (m, 10 H), 7.07 (dd, J = 7.1, 1.0 Hz, 1 H), 7.06 (dd, J = 7.1, 1.0 Hz, 1 H), 6.77 (apparent d, J = 8.9 Hz, 2 H), 4.75 (br s, 1 H), 4.70 (br s, 1 H), 2.58 (m, 1 H), 2.35 (m, 2 H), 2.27–2.05 (m, 4 H), 2.01–1.55 (br m, 10 H), 1.43–1.12 (br m, 4 H), 1.05–0.88 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ 166.0, 165.9, 160.4, 139.0, 137.3, 137.0, 135.2, 131.3, 131.1, 130.8, 129.6, 128.5, 128.43, 128.38, 127.4, 126.3, 109.6, 109.5, 78.5, 78.4, 45.0, 44.2, 35.0, 33.5, 29.8, 29.2, 27.4, 26.2, 26.1, 25.6, 22.0, 21.9, 21.5, 21.2, 21.1, 21.0, 20.9, 20.6, 20.3, 19.2. Anal. Calcd for $C_{42}H_{54}Cl_2N_2O_2PdSi$: C, 61.20; H, 6.60. Found: C, 61.43; H, 6.77.

{Bis[2-(6-(*1S,2R,4S*)-borneoxypyridyl)]diphenylsilane}palladium(II) chloride (7f): $[\alpha]^{20}$ = −1.2° (c = 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.87 (m, 2 H), 7.66–7.41 (br m, 10 H), 7.11 (d, J = 7.1 Hz, 1 H), 7.07 (d, J = 7.1 Hz, 1 H), 6.73 (d, J = 8.0 Hz, 1 H), 6.70 (d, J = 8.0 Hz, 1 H), 4.57 (m, 2 H), 3.33 (m, 1 H), 3.10 (m, 1 H), 2.44 (m, 1 H), 2.24 (m, 1 H), 1.87–1.72 (m, 4 H), 1.60–1.36 (br m, 4 H), 1.28–1.19 (m, 2 H), 1.26 (s, 3 H), 1.09 (s, 3 H), 0.97 (s, 6 H), 0.95 (s, 3 H), 0.93 (s, 3 H). Anal. Calcd for $C_{42}H_{50}Cl_2N_2O_2PdSi$: C, 61.50; H, 6.14. Found: C, 61.53; H, 6.08.

{Bis[2-(6-((*1R,2R,4S*)-1,3,3-trimethyl-2-norborneoxy)-pyridyl)]diphenylsilane}palladium(II) chloride (7g): $[\alpha]^{20}$ = +32.8° (*c* = 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 7.84 (dd, *J* = 7.5, 1.5 Hz, 2 H), 7.72–7.40 (br m, 10 H), 7.09 (apparent t, *J* = 7 Hz, 2 H), 6.83 (apparent d, *J* = 7 Hz, 2 H), 4.09 (m, 2 H), 2.92 (m, 1 H), 1.97 (m, 1 H), 1.80–1.46 (br m, 12 H), 1.42 (s, 3 H), 1.32 (s, 3 H), 1.30 (s, 3 H), 1.26 (s, 3 H), 1.20 (s, 3 H), 0.86 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 167.79, 167.77, 160.7, 160.6, 138.8, 138.7, 137.3, 136.9, 135.86, 135.83, 131.18, 131.11, 131.07, 128.8, 128.4, 127.9, 126.6, 126.4, 110.8, 110.7, 93.6, 93.2, 50.6, 49.8, 49.49, 49.45, 42.5, 41.9, 41.1, 40.6, 30.7, 30.4, 27.6, 26.7, 26.1, 25.8, 22.0, 21.4, 20.9, 20.5. Anal. Calcd for $C_{42}H_{50}Cl_2N_2O_2PdSi$: C, 61.50; H, 6.14. Found: C, 61.56; H, 6.42.

Preparation of Optically Active Bipyridine Ligands (8). To compounds **2c–g** (5 mmol) in THF (20 mL) at −78 °C was added *n*-butyllithium (2 mL of 2.5 M *n*-BuLi, 5 mmol) and the solution stirred under N_2 for 1 h. Copper(I) iodide (2.5 mmol) was then added. The resulting mixture was stirred at −78 °C for 12 h. After 12 h, air was bubbled through the reaction mixture at −78 °C for 1 h. The reaction mixture was then allowed to warm to room temperature while air was still bubbled. The resulting solution was diluted with diethyl ether and then washed with two equal volumes of 10% NaCN, dried over K_2CO_3, and evaporated to yield crude compounds **8c–g**. To a stirred solution of **8c–g** in degassed $CHCl_3$ (15 mL) was added $(CH_3CN)_2NiBr_2$ (0.75 g, 2.5 mmol) and the solution stirred at ambient temperature for 4 h under N_2. After 4 h the resulting solution was passed through Celite to remove excess $(CH_3CN)_2NiBr_2$. The resulting nickel(II) bromide complexes were precipitated by addition of petroleum ether. The precipitates were allowed to cool at −29 °C overnight. The cooled precipitates were then filtered and washed with cold petroleum ether (−78 °C). The washed precipitates were dissolved in $CHCl_3$ and extracted twice with equal volumes of 10% NaCN. The $CHCl_3$ layer was washed with brine and dried over K_2CO_3 and the solvent removed under reduced pressure to yield pure **8c–g** in 34–38% yield.

6,6′-Bis[(*1R*)-myrtenoxy]-2,2′-bipyridine (8c): $[\alpha]^{20}$ = −43.0° (*c* = 1, $CHCl_3$); mp 97–109 °C; 34%; ^1H NMR ($CDCl_3$) δ 7.99 (dd, *J* = 7, 1 Hz, 1 H), 7.69 (dd, *J* = 8, 7 Hz, 1 H), 6.77 (dd, *J* = 8, 1 Hz, 1 H), 5.68 (t, *J* = 1.5 Hz, 1 H), 4.86 (apparent t, *J* = 1 Hz, 2 H), 2.46 (m, 2 H), 2.32 (m, 2 H), 2.15 (m, 1 H), 1.33 (s, 3 H), 1.28 (d, *J* = 8 Hz, 1 H), 0.88 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 163.1, 153.3, 144.4, 139.1, 120.1, 113.5, 111.2, 68.2, 43.6, 40.9, 38.1, 31.6, 31.3, 26.2, 21.1. Anal. Calcd for $C_{30}H_{36}N_2O_2$: C, 78.91; H, 7.95. Found: C, 78.81; H, 7.98.

6,6′-Bis[(*1S,2S,3S,5R*)-isopinocampheoxy]-2,2′-bipyridine (8d): $[\alpha]^{20}$ = +91° (*c* = 1, $CHCl_3$); mp 176–178 °C; 37%; ^1H NMR ($CDCl_3$) δ 7.97 (dd, *J* = 7, 1 Hz, 1 H), 7.71 (dd, *J* = 8, 7 Hz, 1 H), 6.76 (dd, *J* = 8, 1 Hz, 1 H), 5.51 (m, 1 H), 2.92 (m, 1 H), 2.41 (m, 2 H), 2.10–1.81 (m, 4 H), 1.32 (s, 3 H), 1.23 (d, *J* = 7 Hz, 3 H), 1.16 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 163.1, 153.6, 139.1, 113.1, 111.6, 74.8, 47.8, 44.0, 41.6, 38.5, 36.4, 33.6, 27.6, 23.9, 21.0. Anal. Calcd for $C_{30}H_{40}N_2O_2$: C, 78.22; H, 8.75. Found: C, 78.06; H, 8.80.

6,6′-Bis[(*1S,2R,5R*)-isomenthoxy]-2,2′-bipyridine (8e): $[\alpha]^{20}$ = −5.0° (*c* = 1, $CHCl_3$); mp 96–98 °C; 34%; ^1H NMR ($CDCl_3$) δ 7.92 (dd, *J* = 7, 1 Hz, 2 H), 7.65 (dd, *J* = 8, 7 Hz, 2 H), 6.69 (dd, *J* = 8, 1 Hz, 2 H), 5.54 (m, 2 H), 2.10–1.84 (m, 4 H), 1.82–1.60 (m, 6 H), 1.60–1.42 (m, 6 H), 1.38–1.22 (m, 2 H), 1.06 (d, *J* = 3 Hz, 6 H), 1.04 (d, *J* = 2 Hz, 6 H), 0.88 (d, *J* = 7 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 162.8, 153.6, 139.0, 112.9, 111.4, 71.5, 45.8, 35.8, 30.3, 27.6, 26.3, 21.0, 20.8, 20.4, 19.1. Anal. Calcd for $C_{30}H_{44}N_2O_2$: C, 77.54; H, 9.54. Found: C, 77.39; H, 9.56.

6,6′-Bis[(*1S,2R,4S*)-borneoxy]-2,2′-bipyridine (8f): $[\alpha]^{20}$ = −110.3°; mp 178–180 °C; 36%; ^1H NMR ($CDCl_3$) δ 7.88 (dd, *J* = 8.2, 0.8 Hz, 2 H), 7.64 (dd, *J* = 8.2, 7.5 Hz, 2 H), 6.72 (dd, *J* = 8.1, 0.8 Hz, 2 H), 5.18 (ddd, *J* = 10, 4, 2 Hz, 2 H), 2.59 (m, 2 H), 2.22 (m, 2 H), 1.74 (m, 4 H), 1.32 (m, 4 H), 1.11 (dd, *J* = 14, 4 Hz, 2 H), 1.05 (s, 6 H), 0.94 (s, 6 H), 0.93 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 163.7, 153.6, 138.9, 112.9, 111.4, 80.7, 48.9, 47.7, 45.0, 37.3, 28.2, 27.2, 19.8, 19.2, 13.8. Anal. Calcd for $C_{30}H_{40}N_2O_2$: C, 78.22; H, 8.75. Found: C, 78.12; H, 8.82.

6,6′-Bis[(*1R,2R,4S*)-1,3,3-trimethyl-2-norborneoxy]-2,2′-bipyridine (8g): $[\alpha]^{20}$ = +144.2° (*c* = 1, $CHCl_3$); mp 127–132 °C; 38%; ^1H NMR ($CDCl_3$) δ 7.94 (dd, *J* = 7.4, 1 Hz, 2 H), 7.63 (dd, *J* = 8.4, 7.6 Hz, 2 H), 6.72 (dd, *J* = 8, 1 Hz, 3 H), 4.92 (s, 1 H), 4.91 (s, 1 H), 2.03 (m, 2 H), 1.75 (m, 6 H), 1.49 (m, 4 H), 1.31 (s, 6 H), 1.24 (dd, *J* = 10, 1 Hz, 2 H), 1.12 (s, 6 H), 0.78, 0.76 (s, s, CH_3, 6 H); ^{13}C NMR ($CDCl_3$) δ 164.2, 153.4, 138.9, 113.2, 111.3, 86.1, 48.9, 48.8, 41.6, 40.1, 30.2, 26.8, 26.0, 20.5, 19.8. Anal. Calcd for $C_{30}H_{40}N_2O_2$: C, 78.22; H, 8.75. Found: C, 78.15; H, 8.77.

Preparation of Optically Active 6-Alkoxy-2-pyridinecarboxaldehydes (9). To a chilled (−78 °C) THF (30 mL) solution containing the appropriate 6-alkoxy-2-bromopyridine **2** (6.4 mmol) was added *n*-BuLi (2.8 mL, 2.5 M solution in hexane) dropwise by syringe. The mixture was stirred at −78 °C for 50 min, and then DMF (0.6 g, 8.2 mmol) was slowly added. The mixture was allowed to warm to room temperature and then diluted with ether (150 mL) and H_2O (30 mL). The solution was stirred for 5 min. The solution was washed with H_2O (150 mL) and then brine (100 mL). The organic layer was dried (K_2CO_3), and the solvents were removed under reduced pressure to afford crude **9d–g**. Purification of crude **9** was achieved by flash chromatography on neutral alumina (4 × 5 cm) with 5% ethyl acetate in hexane (v/v) to give pure **9d–g** in greater than 90% yield.

6-[(*1S,2S,3S,5R*)-Isopinocampheoxy]-2-pyridinecarboxaldehyde (9d): oil; ^1H NMR ($CDCl_3$) δ 9.93 (s, 1 H), 7.70 (t, *J* = 9.0 Hz, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 6.94 (d, *J* = 9.2 Hz, 1 H), 5.39 (m, 1 H), 2.81 (m, 1 H), 2.46–2.26 (m, 2 H), 1.98 (m, 1 H), 1.89 (m, 1 H), 1.75 (dt, *J* = 7.5, 2.8 Hz, 1 H), 1.26 (s, 3 H), 1.18 (d, *J* = 7.4 Hz, 4 H), 1.05 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 193.5, 164.0, 150.4, 138.9, 116.9, 114.7, 75.6, 47.6, 43.9, 41.5, 38.4, 36.2, 33.4, 27.5, 23.9, 20.8. Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16. Found: C, 74.21; H, 8.20.

6-[(*1S,2R,5R*)-Isomenthoxy]-2-pyridinecarboxaldehyde (9e): oil; ^1H NMR ($CDCl_3$) δ 9.89 (s, 1 H), 7.68 (t, *J* = 6.4 Hz, 1 H), 7.50 (d, *J* = 8.1 Hz, 1 H), 6.90 (d, *J* = 9.1 Hz, 1 H), 5.50 (m, 1 H), 2.06–1.42 (m, 8 H), 1.32–1.16 (m, 1 H), 1.09 (d, *J* = 7 Hz, 3 H), 0.97 (d, *J* = 7 Hz, 3 H), 0.86 (d, *J* = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 193.5, 163.9, 150.5, 139.0, 116.8, 114.4, 72.7, 45.4, 35.6, 30.1, 27.6, 26.4, 21.1, 21.0, 20.7, 19.4. Anal. Calcd for $C_{16}H_{23}NO_2$: C, 73.52; H, 8.87. Found: C, 73.62; H, 8.89.

6-[(*1S,2R,4S*)-Borneoxy]-2-pyridinecarboxaldehyde (9f): oil; ^1H NMR δ 9.91 (s, 1 H), 7.70 (t, *J* = 8.1 Hz, 1 H), 7.53 (d, *J* = 8.1 Hz, 1 H), 6.96 (d, *J* = 9.0 Hz, 1 H), 5.16 (ddd, *J* = 4.1, 1.5, 1.5 Hz, 1 H), 2.53 (m, 1 H), 2.18 (m, 1 H), 1.75 (m, 2 H), 1.31 (m, 2 H), 1.02 (m, 1 H), 1.01 (s, 3 H), 0.92 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 193.6, 164.7, 150.5, 138.8, 116.7, 114.6, 81.5, 49.0, 47.7, 45.0, 37.2, 28.1, 27.1, 19.8, 19.1, 13.8. Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16. Found: C, 74.11; H, 8.20.

6-[(*1R,2R,4S*)-1,3,3-Trimethyl-2-norborneoxy]-2-pyridinecarboxaldehyde (9g): oil; ^1H NMR δ 9.90 (s, 1 H), 7.69 (t, *J* = 9.1 Hz, 1 H), 7.50 (d, *J* = 8.1 Hz, 1 H), 6.98 (d, *J* = 7.3 Hz, 1 H), 4.77, 4.78 (s, s, 1 H), 1.98 (m, 1 H), 1.72 (m, 3 H), 1.49 (m, 1 H), 1.17 (s, 3 H), 1.15 (m, 2 H), 1.12 (s, 3 H), 0.75 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 193.2, 165.1, 150.3, 138.9, 116.6, 114.8, 87.4, 48.8, 48.7, 41.5, 39.8, 29.5, 26.7, 25.8, 20.4, 19.7. Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.10; H, 8.16. Found: C, 73.97; H, 8.18.

Preparation of Optically Active Bis[2-(6-alkoxypyridyl)]methanols (10). A chilled (−78 °C) THF solution (10 mL) of **3** (0.4 mmol) was cannulated into a THF (30 mL) solution containing **9** (0.4 mmol), prepared as above. The cooling bath was removed and the mixture allowed to warm to ambient temperature. The mixture was diluted with ether (150 mL) and washed with H_2O (120 mL) and with brine (100 mL). The organic layer was dried (K_2CO_3), and the solvents were removed under reduced pressure. The residue was chromatographed on neutral alumina (4 × 8 cm) with an eluent gradient of 0–5% ethyl acetate in hexane to give pure **10d–g** in greater than 90% yield.

Bis{2-(6-[(*1S,2S,3S,5R*)-isopinocampheoxy]pyridyl)}-methanol (10d): mp 44–46 °C; ^1H NMR ($CDCl_3$) δ 7.51 (t, *J* = 8.0 Hz, 2 H), 7.04 (dd, *J* = 4.7, 2.6 Hz, 2 H), 6.57 (d, *J* = 8.1 Hz, 2 H), 5.66 (d, *J* = 5.8 Hz, 1 H), 5.31 (d, *J* = 5.8 Hz, 1 H), 5.28 (m, 2 H), 2.51 (m, 2 H), 2.34–2.14 (m, 4 H), 1.95 (m, 2 H), 1.86 (m, 2 H), 1.74 (dt, *J* = 11.6, 2.5 Hz, 2 H), 1.25 (s, 6 H), 1.13 (dd, *J* = 5.8, 1.7 Hz, 6 H), 1.04 (s, 6 H), 0.87 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 162.8, 162.8, 158.7, 158.4, 139.0, 139.0, 113.1, 113.0, 110.0, 110.0, 75.2, 74.9, 74.6, 47.6, 44.0, 43.9, 43.9, 41.5, 41.4, 38.4, 38.3, 36.4, 36.4, 33.5, 33.3, 27.5, 27.5, 23.9, 20.9. Anal. Calcd for $C_{31}H_{42}N_2O_3$: C, 75.88; H, 8.63. Found: C, 75.66; H, 8.67.

Bis{2-(6-[(*1S,2R,5R*)-isomenthoxy]pyridyl)}methanol (10e): mp 84–86 °C; ^{1}H NMR ($CDCl_3$) δ 7.49 (t, J = 7.8 Hz, 2 H), 7.04 (dd, J = 4.3, 3.6 Hz, 2 H), 6.54 (d, J = 8 Hz, 2 H), 5.63 (d, J = 5.6 Hz, 1 H), 5.35 (m, 2 H), 5.26 (d, J = 6.9 Hz, 1 H), 2.07–1.40 (m, 16 H), 1.38–1.15 (m, 2 H), 1.00 (t, J = 5.9 Hz, 12 H), 0.83 (dd, J = 3.9, 2.8 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 162.7, 162.6, 158.7, 139.2, 139.1, 112.8, 112.7, 109.9, 109.9, 74.7, 72.0, 71.8, 45.6, 45.5, 35.9, 35.8, 30.1, 27.6, 26.4, 26.3, 21.0, 20.9, 20.9, 20.6, 20.6, 19.2. Anal. Calcd for $C_{31}H_{46}N_2O_3$: C, 75.25; H, 9.37. Found: C, 75.30; H, 9.43.

Bis{2-(6-[(*1S,2R,4S*)-borneoxy]pyridyl)}methanol (10f): mp 81–83 °C; ^{1}H NMR ($CDCl_3$) δ 7.49 (t, J = 7.9 Hz, 2 H), 7.02 (dd, J = 5.2, 2.1 Hz, 2 H), 6.60 (d, J = 8.2 Hz, 2 H), 5.63 (d, J = 5.8 Hz, 1 H), 5.37 (d, J = 5.8 Hz, 1 H), 5.00 (m, 2 H), 2.40 (m, 2 H), 2.17 (m, 2 H), 1.72 (m, 4 H), 1.28 (m, 4 H), 1.03 (m, 2 H), 0.98 (s, 6 H), 0.91 (s, 6 H), 0.89 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 163.4, 158.8, 158.4, 139.0, 138.9, 112.9, 112.8, 109.8, 109.7, 81.1, 80.9, 74.4, 49.0, 48.9, 47.6, 45.0, 45.0, 37.4, 37.3, 28.1, 27.0, 27.0, 19.8, 19.1, 19.0, 13.8. Anal. Calcd for $C_{31}H_{42}N_2O_3$: C, 75.88; H, 8.63. Found: C, 75.15; H, 8.57.

Bis{2-(6-[(*1R,2R,4S*)-1,3,3-trimethyl-2-norborneoxy]-pyridyl)}methanol (10g): mp 93–95 °C; ^{1}H NMR ($CDCl_3$) δ 7.49 (dd, J = 7.3, 0.9 Hz, 2 H), 6.96 (dd, J = 6.6, 0.6 Hz, 2 H), 6.61 (d, J = 8.1 Hz, 2 H), 5.64 (d, J = 5.5 Hz, 1 H), 5.24 (d, J = 5.5 Hz, 1 H), 4.71 (m, 2 H), 1.97 (m, 2 H), 1.78–1.55 (m, 6 H), 1.47 (m, 4 H), 1.23, 1.19 (s, s, 6 H), 1.26–1.13 (m, 2 H), 1.09, 1.07 (s, s, 6 H), 0.76, 0.68 (s, s, 6 H); ^{13}C NMR ($CDCl_3$) δ 163.9, 158.5, 158.4, 139.0, 139.1, 113.2, 113.0, 109.9, 109.8, 109.7, 86.8, 86.6, 75.1, 48.9, 48.8, 48.7, 41.5, 39.8, 39.8, 30.0, 29.9, 29.9, 29.8, 26.7, 25.9, 20.5, 20.4, 20.4, 19.8. Anal. Calcd for $C_{31}H_{42}N_2O_3$: C, 75.88; H, 8.63. Found: C, 75.79; H, 8.66.

Preparation of Bis[2-(6-alkoxypyridyl)]methyl Benzyl Ether (11). To a solution of **4** (2.0 mmol) in DMF (20 mL) was added NaH (48 mg, 2.0 mmol). The mixture was stirred at 0 °C for 15 min, and then benzyl chloride (0.25 g, 2.0 mmol) was added. The mixture was allowed to react for 2 h at ambient temperature. The mixture was diluted with H_2O (30 mL) and Et_2O (100 mL). The organic layer was separated and then washed with H_2O (2 × 100 mL) and brine (50 mL). The organic layer was dried (K_2CO_3) and filtered, and the solvents were removed under reduced pressure. The residue was chromatographed on neutral alumina (4 × 10 cm) with an eluent gradient of 0–3% ethyl acetate in hexane to give pure **11**.

Bis[2-(6-(*1S,2R,5R*)-isomenthoxypyridyl)]methyl benzyl ether (11e): $[\alpha]^{20}$ = 15.8° (c = 1, CH_2Cl_2); oil; ^{1}H NMR ($CDCl_3$) δ 7.49 (dt, J = 2.5, 1.0 Hz, 2 H), 7.35 (m, 2 H), 7.06 (m, 3 H), 6.95 (m, 2 H), 6.50 (ddd, J = 4.8, 4.0, 0.8 Hz, 2 H), 5.86 (s, 1 H), 5.28 (m, 2 H), 3.61 (d, J = 3.2 Hz, 2 H), 1.84 (m, 3 H), 1.58 (m, 4 H), 1.41 (m, 8 H), 1.22 (m, 3 H), 0.90 (m, 12 H), 0.73 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 162.0, 161.9, 160.7, 160.4, 139.1, 139.1, 137.3, 130.6, 127.4, 126.0, 113.1, 113.0, 109.5, 109.5, 78.1, 71.9, 71.7, 47.9, 46.0, 45.7, 36.1, 35.9, 31.6, 30.3, 30.2, 27.7, 26.4, 26.4, 22.7, 20.9, 20.8, 20.8, 20.6, 20.4, 20.2, 19.0, 18.9, 14.1. Anal. Calcd for $C_{38}H_{52}N_2O_3$: C, 78.07; H, 8.90. Found: C, 78.12; H, 9.03.

Bis[2-(6-(*1S,2R,4S*)-Borneoxypyridyl)]methyl benzyl ether (11f): $[\alpha]^{20}$ = −73.8° (c = 1, CH_2Cl_2); oil; ^{1}H NMR ($CDCl_3$) δ 7.50 (m, 2 H), 7.37 (dd, J = 7.5, 0.8 Hz, 1 H), 7.25 (m, 1 H), 7.21 (m, 3 H), 6.95 (m, 2 H), 6.58 (dd, J = 4.3, 0.8 Hz, 2 H), 6.56 (dd, J = 4.3, 0.8 Hz, 1 H), 5.00 (d, J = 4.2 Hz, 1 H), 4.83 (d, J = 4.5 Hz, 1 H), 3.57 (q, J = 13.4 Hz, 2 H), 2.52 (m, 1 H), 2.39 (m, 1 H), 2.14 (m, 2 H), 1.76 (m, 4 H), 1.22 (m, 4 H), 0.98 (m, 2 H), 0.96 (s, 6 H), 0.90 (s, 6 H), 0.89 (s, 6 H), 0.8 (d, J = 6.1 Hz, 3 H), 0.71 (t, J = 2.8 Hz, 3 H), 0.69 (s, 3 H). ^{13}C NMR ($CDCl_3$) δ 162.8, 162.6, 160.7, 160.5, 138.9, 138.9, 137.3, 130.6, 127.4, 125.9, 113.3, 113.0, 109.4, 109.3, 81.2, 81.0, 77.9, 48.9, 48.8, 47.9, 47.6, 47.5, 45.0, 37.6, 37.3, 28.1, 28.1, 27.0, 19.8, 19.0, 19.0, 13.8, 13.8. Anal. Calcd for $C_{38}H_{48}N_2O_3$: C, 78.53; H, 8.27. Found: C, 78.68; H, 8.36.

Preparation of {[Bis(6-alkoxypyridyl)]methyl benzyl ether}palladium(II) Chloride (12). A CH_2Cl_2 solution (20 mL) containing **11** (3.0 mmol) and $(CH_3CN)_2PdCl_2$ (0.70 g, 2.7 mmol) was allowed to react for 1 h with stirring. The palladium complex was precipitated with pentane (60 mL), filtered, and washed with pentane. The complex was dried under reduced pressure to yield **12** as a light yellow powder in quantitative yield.

{Bis[2-(6-((*1S,2R,5R*)-isomenthoxy)pyridyl)]methyl benzyl ether}palladium(II) Chloride (12e): ^{1}H NMR ($CDCl_3$) δ 7.59 (m, 2 H), 7.26 (m, 5 H), 6.54 (m, 2 H), 5.80 (q, J = 3.7 Hz, 2 H), 4.75 (m, 2 H), 4.75 (m, 2 H), 3.85 (s, 1 H), 2.72 (m, 2 H), 2.42–1.56 (m, 18 H), 0.90 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 164.5, 164.4, 158.7, 158.7, 158.6, 141.4, 134.3, 131.3, 131.2, 128.1, 127.8, 127.2, 115.7, 107.2, 107.1, 82.5, 79.0, 78.9, 49.1, 44.0, 43.0, 33.7, 33.6, 29.4, 29.2, 27.0, 26.5, 26.1, 26.1, 25.9, 22.3, 22.1, 22.1, 21.9, 21.3, 21.2, 20.6, 20.6. Anal. Calcd for $C_{38}H_{52}Cl_2N_2O_3Pd$: C, 59.68; H, 6.82. Found: C, 58.84; H, 6.86.

{Bis[2-(6-((*1S,2R,4S*)-borneoxy)pyridyl)]methyl benzyl ether}palladium(II) Chloride (12f): ^{1}H NMR ($CDCl_3$) δ 7.65 (m, 2 H), 7.27 (m, 7 H), 6.59 (d, J = 8.5 Hz, 1 H), 6.54 (d, J = 8.0 Hz, 1 H), 6.25 (d, J = 14.0 Hz, 1 H), 5.74 (d, J = 14.4 Hz, 1 H), 4.59 (m, 1 H), 4.50 (m, 1 H), 3.51 (s, 1 H), 3.30 (m, 1 H), 3.16 (m, 1 H), 2.37 (m, 2 H), 1.80 (m, 4 H), 1.59 (m, 2 H), 1.30 (m, 6 H), 0.98 (m, 12 H), 0.87 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 165.6, 165.2, 158.6, 158.4, 141.5, 141.3, 133.9, 131.1, 128.6, 127.6, 115.7, 115.6, 108.2, 107.6, 86.1, 85.7, 82.3, 50.4, 49.8, 49.5, 48.6, 47.9, 45.1, 44.9, 36.8, 34.7, 28.2, 28.0, 27.7, 27.2, 22.3, 19.8, 19.1, 19.0, 14.6, 14.1, 14.0. Anal. Calcd for $C_{38}H_{48}Cl_2N_2O_3Pd$: C, 60.15; H, 6.33. Found: C, 59.50; H, 6.10.

Preparation of Polymer-Bound Bis[2-(6-alkoxypyridyl)]methanols (14). To a solution of **10** (1.2 mmol) in DMF (20 mL) was added NaH (29 mg, 1.2 mmol). The mixture was stirred at room temperature for 15 min, and then the chloromethylated polystyrene beads (0.25 g, 3.90 mequiv/g) were added. The mixture was allowed to react for 6 h, quenched with H_2O (15 mL), and stirred for an additional 5 min. The DMF/water mixture was removed by filtration on a glass frit, and the beads were washed with methanol (2 × 50 mL), CH_2Cl_2 (2 × 50 mL), and finally with ether (2 × 50 mL). Polymer **13** was treated with excess KOH in methanol to yield polymer **14**. The beads were washed with methanol (3 × 50 mL) and then dried under reduced pressure at 65 °C for 24 h. The percent incorporation for each ligand was determined by weight gain and verified by elemental analysis for each polymer. See Table II for analytical data showing the calculated and found percent nitrogen data.

Polymer **15e** was prepared in a similar manner except that polystyrene beads containing 0.75 mequiv/g of chloromethyl sites were utilized. See Table II for analytical data.

Preparation of Polymer-Bound {Bis[2-(6-((*1S,2R,4S*)-borneoxy)pyridyl)]methanol}palladium(II) Chloride (16f). A CH_2Cl_2 solution (30 mL) containing **14f** (1.3 mequiv) and $(CH_3CN)_2PdCl_2$ (0.36 g, 1.4 mmol) was allowed to react with stirring for 4 h. The polymer was isolated on a glass frit, washed with hot CH_3CN and CH_2Cl_2, and then dried under reduced pressure at 65 °C for 24 h to yield **16f**. Anal. Calcd for **16f** (100% complexation): Cl, 7.30. Found: Cl, 7.43.

Preparation of {2-[6-((*1R,2R,4S*)-1,3,3-Trimethyl-2-norborneoxy)]pyridyl}(2-pyridyl)methanol (17). To a chilled (−78 °C) THF (30 mL) solution containing 6-[(*1R,2R,4S*)-1,3,3-trimethyl-2-norborneoxy]-2-bromopyridine (**2g**; 4.00 g, 12.9 mmol) was added *n*-BuLi (5.2 mL, 2.5 M solution in hexanes) dropwise by syringe. The mixture was stirred at −78 °C for 50 min, and then a chilled (−78 °C) THF solution (10 mL) containing 2-pyridinecarboxaldehyde (1.38 g, 12.9 mmol) was cannulated into the mixture. The mixture was allowed to warm to room temperature for 1.5 h and then diluted with ether (150 mL). The mixture was washed with H_2O (120 mL) and then brine (100 mL). The organic layer was dried over K_2CO_3. Removal of the solvent under reduced pressure yielded two desired diastereoisomers. Separation was achieved by chromatography on silica gel (3 × 70 cm) with 45% ethyl acetate in hexane eluent to afford **17(i)** and **17(ii)** (**17(i)**/**17(ii)** = 4/3) in 76% yield. **17(i)**: $[\alpha]^{20}$ = +78.8° (c = 1, CH_2Cl_2); mp 81–83 °C; ^{1}H NMR ($CDCl_3$) δ 8.54 (ddd, J = 5.0, 1.8, 1.0 Hz, 1 H), 7.65 (dt, J = 6.1, 1.8 Hz, 1 H), 7.51 (m, 2 H), 7.19 (ddd, J = 7.6, 5.0, 1.0 Hz, 1 H), 7.03 (dd, J = 6.5, 0.8 Hz, 1 H), 6.62 (d, J = 8.2, 1 H), 5.76 (d, J = 5.2 Hz, 1 H), 5.52 (d, J = 5.2 Hz, 1 H), 4.69 (d, J = 1.8 Hz, 1 H), 2.00 (m, 1 H), 1.75 (m, 3 H), 1.48 (m, 1 H), 1.22 (s, 3 H), 1.15 (m, 2 H), 1.09 (s, 3 H), 0.69 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 163.9, 160.9, 158.1, 147.9, 139.1, 136.5, 122.3, 120.9, 112.9, 109.9, 86.7, 75.0, 48.8, 48.6, 41.4, 39.8, 29.7, 26.6, 25.8, 20.3, 19.7. **17(ii)**: $[\alpha]^{20}$ = +64.7° (c = 1, CH_2Cl_2); mp 76–77 °C; ^{1}H NMR ($CDCl_3$) δ 8.56 (ddd, J = 3.7, 1.8, 0.9 Hz, 1 H), 7.65 (dt, J = 5.9, 1.8 Hz, 1 H), 7.49 (m, 2 H), 7.21 (ddd, J = 7.4, 4.7, 1.1 Hz, 1 H), 6.96 (d, J = 7.4 Hz, 1 H), 6.62 (d, J = 8.1 Hz, 1 H), 5.77 (d, J = 5.1 Hz, 1 H), 5.42 (d, J = 5.1 Hz, 1 H),

4.73 (d, J = 1.7 Hz, 1 H), 1.98 (m, 1 H), 1.74 (m, 3 H), 1.48 (m, 1 H), 1.23 (s, 3 H), 1.50 (m, 2 H), 1.08 (s, 3 H), 0.77 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 164.0, 161.1, 158.1, 148.2, 139.2, 136.6, 122.5, 121.2, 113.1, 110.0, 86.7, 75.3, 48.9, 48.8, 41.5, 39.7, 30.0, 26.7, 25.9, 20.5, 19.8. Anal. Calcd for $C_{21}H_{26}N_2O_2$: C, 74.45; H, 7.68. Found: C, 74.52; H, 7.75.

Preparation of {[2-(6-((*1R,2R,4S*)-1,3,3-Trimethyl-2-norborneoxy)pyridyl)](2-pyridyl)methanol}palladium(II) Chloride (18). A CH_2Cl_2 (20 mL) solution containing **17** (0.40 g, 1.2 mmol) and $(CH_3CN)_2PdCl_2$ (0.36 g, 1.4 mmol) were allowed to react with stirring for 1 h. The palladium complex was precipitated with cold pentane (60 mL), filtered, and then washed with cold pentane. The product was dried under reduced pressure to afford **18** as a light brown powder in quantitative yield. **18(i)**: ^{1}H NMR ($CDCl_3$) δ 8.66 (dd, J = 4.9, 0.9 Hz, 1 H), 7.93 (dt, J = 6.4, 0.8 Hz, 1 H), 7.77 (m, 2 H), 7.70 (t, J = 6.5 Hz, 1 H), 7.54 (d, J = 7.7 Hz, 1 H), 7.16 (m, 1 H), 6.66 (d, J = 8.1 Hz, 1 H), 5.91 (d, J = 8.1 Hz, 1 H), 4.20 (s, 1 H), 2.91 (m, 1 H), 2.00 (m, 1 H), 1.75 (t, J = 3.2 Hz, 2 H), 1.61 (m, 1 H), 1.30 (s, 3 H), 1.35-1.25 (m, 2 H), 1.05, 0.99, 0.88, 0.85 (s, s, s, s, 6 H); ^{13}C NMR ($CDCl_3$) δ 165.5, 159.5, 158.2, 151.7, 142.2, 139.3, 123.9, 123.0, 114.4, 107.6, 93.0, 75.3, 49.8, 48.8, 41.7, 41.0, 30.7, 26.7, 26.0, 21.3, 20.1. **18(ii)**: ^{1}H NMR ($CDCl_3$) δ 8.62 (d, J = 5.9 Hz, 1 H), 7.94 (d, J = 7.5 Hz, 1 H), 7.73 (m, 2 H), 7.85 (m, 1 H), 7.56 (d, J = 7.7 Hz, 1 H), 7.13 (dt, J = 5.8, 1.5 Hz, 1 H), 6.55 (d, J = 7.9 Hz, 1 H), 5.97 (m, 1 H), 3.83 (s, 1 H), 3.10 (m, 1 H), 1.97 (m, 1 H), 1.81 (m, 1 H), 1.56 (m, 2 H), 1.31 (m, 2 H), 1.24 (s, 3 H), 1.19 (s, 3 H), 0.97 (s, 3 H); ^{13}C NMR ($CDCl_3$): δ 165.7, 159.7, 158.1, 151.7, 142.3, 139.1, 123.8, 123.1, 114.5, 108.0, 95.0, 75.3, 50.1, 49.5, 41.3, 40.4, 30.5, 27.6, 25.5, 21.0, 20.2. Anal. Calcd for $C_{21}H_{26}Cl_2N_2O_2Pd$: C, 48.86; H, 5.04. Found: C, 48.41; H, 5.12.

Hydrosilation of Acetophenone. A Schlenk tube was charged with acetophenone (0.6 g, 5 mmol), $[(COD)RhCl]_2$ (12.3 mg, for 100/1 substrate/Rh mol ratio), the appropriate ligand **4**, **5**, or **8**, and dichloromethane (3 mL). The mixture was degassed by three consecutive freeze-pump-thaw cycles. A separate Schlenk tube was changed with diphenylsilane (1.3 mL, 7 mmol) and dichloromethane (1 mL) and degassed as above. The latter solution was cannulated into the acetophenone mixture and allowed to react at -15 °C until the carbonyl band in the infrared spectrum (1685 cm^{-1}) disappeared. The mixture was then diluted with acetone (5 mL) and 10% hydrochloric acid (10 mL) and stirred vigorously for 4 h. The mixture was extracted with ether and the organic layer dried over K_2CO_3. The ether was removed and the crude product purified by bulb-bulb distillation. Contamination by acetophenone in the samples was taken into account and calculated by using the proton NMR spectrum for the purified product. The spectroscopically determined weight of acetophenone in each sample was subtracted out for optical yield calculations.

Asymmetric Cyclopropanation Reactions. To a cool (5 °C) THF (1 mL) solution of 2,5-dimethyl-2,4-hexadiene (3.0 g, 27.2 mmol) was slowly added ethyl diazoacetate (1.0 g, 8.8 mmol) in the presence of catalyst **19(i)** (1 mol %). After nitrogen gas evolution had ceased, the mixture was fractionally distilled under reduced pressure to afford (-)-ethyl chrysanthemate (cis and trans mixture, $[\alpha]$ = -1.5°, neat, dm = 1) in 59% chemical yield. A comparison of these data with that of Aratani and co-workers[11c] (Table I, entry 6, 50% optical yield) affords an estimated optical yield of 8.5%. This is based on the assumption that we are observing approximately the same asymmetric induction in the cis and trans isomers as Aratani.

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Synthesis of the Monomeric $HBTrip_2$ (Trip = 2,4,6-*i*-$Pr_3C_6H_2$) and the X-ray Crystal Structures of $[HBMes_2]_2$ (Mes = 2,4,6-$Me_3C_6H_2$) and $HBTrip_2$

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The synthesis and spectroscopic properties of $HBTrip_2$ (**1**) and the X-ray crystal structures of **1** and the dimeric species $[HBMes_2]_2$ (**2**) are described. The synthesis of **1** was carried out by treatment of $Me_2S{\cdot}BHCl_2$ with 2 equiv of TripMgBr in THF solution. Standard workup gave **1** as a colorless crystalline material that exhibited a broad singlet at 73.5 ppm downfield in the ^{11}B NMR spectrum. X-ray data confirmed a monomeric structure with a planar boron center and a wide CBC angle of 128.0 (4)°. The less sterically encumbered **2** was prepared according to a literature procedure. The X-ray crystal structure reveals a dimeric structure with the expected bridging hydrogens. The compounds of **1** and **2** are the first diorganoboranes to be structurally characterized by X-ray crystallography. In addition, the structure of **1** represents the first structural characterization of a monomeric diorganoborane. Crystal data at 225 K for **1** or 140 K for **2**, with Mo Kα (λ = 0.710 69 Å) radiation: **1**, monoclinic, a = 11.116 (4) Å, b = 14.869 (5) Å, c = 17.321 (6) Å, β = 100.19 (3)°, Z = 4, space group $P2_1/c$, R = 0.093; **2**, monoclinic, a = 12.254 (6) Å, b = 7.768 (2) Å, c = 16.785 (6) Å, β = 109.43 (3)°, Z = 2, space group $P2/n$, R = 0.047.

Introduction

The use of steric effects in order to achieve regiospecificity in the reactions of organoboranes has been a feature of organoboron chemistry for many years.[1] For example, crowded HBR_2 species such as dicyclohexylborane[2] and 9-borabicyclo[3.3.1]nonane (9-BBN)[3] are extremely useful reagents for the hydroboration of less hindered alkenes. In addition, dimesitylborane[4] has proved an especially selective reagent for the hydroboration of alkynes.[5] For

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