Stereoselective Synthesis of Chiral Pinene[5,6]bipyridine Ligands and Their Coordination Chemistry

Didier Lötscher,[†] Stefan Rupprecht,[†] Philippe Collomb,[†] Peter Belser,[†] Heiko Viebrock,[†] Alex von Zelewsky,*[,†] and Peter Burger[‡]

Department of Chemistry, University of Fribourg, Pérolles, CH-1700 Fribourg, Switzerland, and Anorganisch-chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Received April 17, 2001

The C_2-symmetric chiral pinene[5,6]bipyridine V (Chart 1) was synthesized according to a procedure published by our group recently (Kolp, B.; Abeln, D.; Stoeckli-Evans, H.; Zelewsky, A. v. *Eur. J. Inorg. Chem.* **2001**, 1207). A series of stereoselectively alkylated derivatives (**Va**−**Vo**) (Table 1) was prepared. The solid-state structures of the compounds **Vc** and **Vk** were determined by single-crystal X-ray diffraction, where both compounds show a transoid conformation of the bipyridine unit and proved to be alkylated stereoselectively from the sterically less hindered side of the pinene moiety. The X-ray structure of the cobalt complex **4** shows the metal ion to be tetrahedrally coordinated by one chiral bipyridine **V** and two chloride ligands. If 2 equiv of ligand **V** was used, 2:1 complexes were obtained with Cu(I), Ag(I), and Co(II) ions.

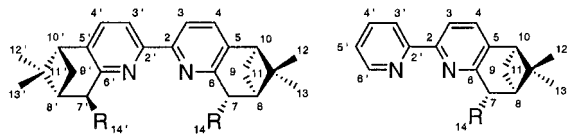
Introduction

Our research interests in the last few years have focused mainly on the synthesis of chiral bipyridine and terpyridine ligands and their coordination chemistry with transition-metal ions.[2−6] These ligands are potentially useful for enantioselective catalysis. As an example, for catalytic zinc-mediated alkylations some ligands yield products of up to 91% enantiomeric excess.[7,8] Recently we published highly enantioselective copper-catalyzed cyclopropanations using the ligands presented in this paper.[9] Kishi and co-workers published the use of these chiral pinene−bipyridine ligands in coupling reactions.[10] The present paper deals with the synthesis of these ligands and their coordination chemistry with transition-metal ions (Chart 1). Very recently Malkov et al. reported another synthetic pathway for ligand **V** and investigated the effect of the latter upon some catalytic reactions.[11]

Results and Discussion

The synthesis of compound **V** was done according to a recently published procedure.[1]

Chart 1. Numbering Scheme for Compounds **V** and **VI**[a]



Va-Vo **VIa**

[a] The numbering is adopted from 2,2′-bipyridine where the nitrogen atom bears the number 1.

Metalation of compound **V** with LDA at the methylene group adjacent to the pyridine ring occurs stereoselectively on the opposite side of the pinene methyl groups. This selectivity is the basis for the preparation of a wide variety of derivatives of **V** with a defined configuration on C(7) (Scheme 2).

Using methyl iodide, ethyl iodide, and *n*-butyl iodide as alkylating agents and LDA (3.3 equiv) as the base, the reaction leads only to the bisalkylated bipyridines **Vf** (61%), **Vi** (79%), and **Vo** (88%). In these alkylations no monosubstituted products were observed. All other reactions using the corresponding alkyl iodides resulted in a mixture of mono- and bisalkylated molecules, with the monoalkylated species as the main products despite the use of excess LDA. No double alkylation at the same pinene ring was observed. Separation of the two species was achieved by column chromatography on silica gel. To confirm the stereochemistry at the carbon atom C(7), a crystal structure determination was carried out for the monoalkylated compound **Vc** and the bisalkylated compound **Vk** (Table 1). Similarly, alkylation of compound **VI** yields the ligand **VIa**. Syntheses of similar ligands have already been published by Chelucci et al.[12]

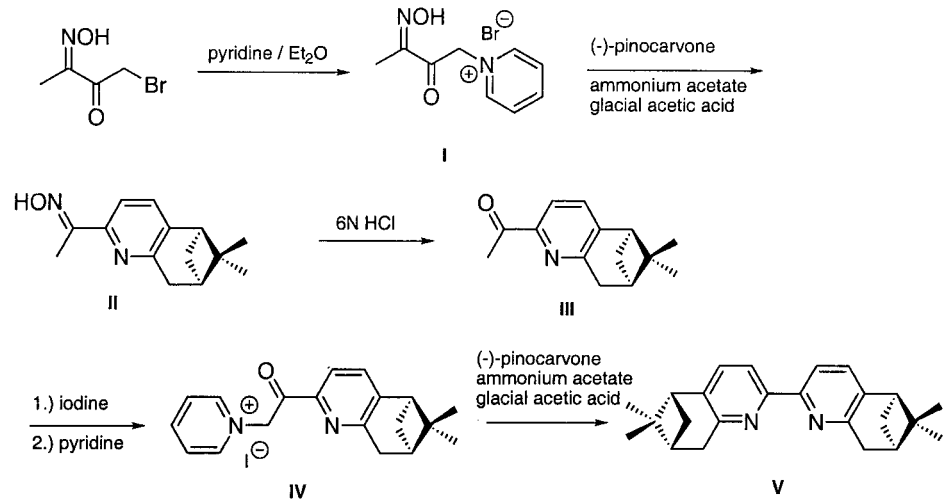
Metal Complexes. The coordination chemistry of the (−)-bispinene[5,6]bipyridines was studied using Ag(I), Cu(I), and Co(II) (Scheme 3). Complexes of ligands **V** and **Vf** with Cu(II) have been published recently by our group.[9] Ligand **V** forms

* To whom correspondence should be addressed. Phone: ++41263008732. Fax: ++41263009738. E-mail: alexander.vonzelewsky@unifr.ch.
[†] University of Fribourg.
[‡] Universität Zürich.

(1) Kolp, B.; Abeln, D.; Stoeckli-Evans, H.; Zelewsky, A. v. *Eur. J. Inorg. Chem.* **2001**, 1207.
(2) Hayoz, P.; Zelewsky, A. v.; Stoeckli-Evans, H. *J. Am. Chem. Soc.* **1993**, *115*, 5111.
(3) Hayoz, P.; Zelewsky, A. v. *Tetrahedron Lett.* **1992**, *33*, 5165.
(4) Knof, U.; Zelewsky, A. v. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 302.
(5) Zelewsky, A. v. *Coord. Chem. Rev.* **1999**, *82*, 811.
(6) Zelewsky, A. v.; Mamula, O. *J. Chem. Soc., Dalton Trans.* **2000**, 219.
(7) Collomb, P.; Zelewsky, A. v. *Tetrahedron: Asymmetry* **1995**, *6*, 2903.
(8) Collomb, P.; Zelewsky, A. v. *Coord. Chem. Rev.* **1998**, *177*, 259.
(9) Lötscher, D.; Rupprecht, S.; Stoeckli-Evans, H.; Zelewsky, A. v. *Tetrahedron: Asymmetry* **2000**, *11*, 4341.
(10) Chen, C.; Tagami, K.; Kishi, Y. *J. Org. Chem.* **1995**, *60*, 5386.
(11) Malkov, A. V.; Baxendale, I. R.; Bella, M.; Langer, V.; Fawcett, J.; Russell, D. R.; Mansfield, D. J.; Valko, M.; Kocovsky, P. *Organometallics* **2001**, *20*, 673.
(12) Chelucci, G.; Pinna, G. A.; Saba, A. *Tetrahedron: Asymmetry* **1998**, *9*, 531.

10.1021/ic010411w CCC: $20.00
Published on Web 09/28/2001

Scheme 1. Synthesis of (−)-Bispinene[5,6]bipyridine **V**



Scheme 2. Alkylation of Compound **V**

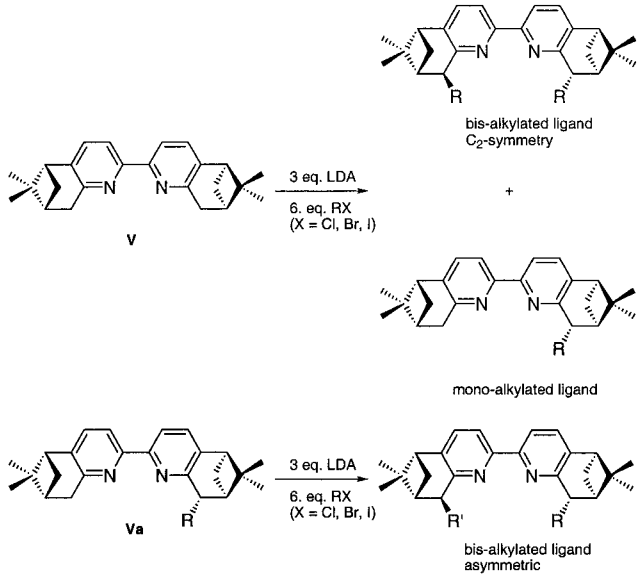


Table 1. Synthesized Compounds[a]

compd	R^1	R^2	yield (%)	de (%)
V	H	H	44	98
Va	H	Me	78	92
Vb	H	Et	72	98
Vc	H	*i*-Pr	43	98
Vd	H	Bn	37	98
Ve	H	TMS	47	84
Vf	Me	Me	61	92
Vg	Me	Et	26	92
Vh	Me	Bn	4	92
Vi	Et	Et	79	98
Vk	*n*-Pr	*n*-Pr	59	98
Vl	*i*-Pr	*i*-Pr	21	98
Vm	Bn	Bn	1.6	98
Vn	TMS	TMS	27	84
Vo	*n*-Bu	*n*-Bu	88	>98
VIa	Me		54	>98

[a] The de was determined by ^{1}H NMR. If the diastereomer was not detectable, the de was assumed to be at least 98%. Bn = $C_6H_5CH_2$. TMS = $(CH_3)_3Si$.

a 1:1 complex with cobalt(II) chloride in MeOH/MeCN. Crystals of complex **4** suitable for X-ray diffraction were grown by diffusion of hexane into an emerald green solution of the complex in CH_2Cl_2. A homoleptic 2:1 complex of **1** with Cu-$(MeCN)_4ClO_4$ shows the characteristic red color for a 2:1 copper(I) bipyridine complex with an absorption maximum (metal-to-ligand charge transfer) at $\lambda = 445$ nm ($\epsilon = 6200$, in MeCN). The similar reaction between 2 equiv of ligand **V** and $Co(H_2O)_6(ClO_4)_2$ in acetonitrile yields an intensive red complex, **3**, with strong UV−vis bands at $\lambda = 342$ and 275 nm, compared to $\lambda = 312$ and 277 nm for the corresponding copper complex. The relatively weak d−d transitions extend up to 575 nm. The reaction of $AgPF_6$ with 2 equiv of ligand **V** yields the expected 2:1 complex **2**, as confirmed by ^{1}H NMR in [D_3]acetonitrile. Due to the twist of the bipyridine from a transoid to a cisoid conformation upon chelation, the proton H−C(4) shifts from 7.35 ppm in the free ligand to 7.60 ppm in the silver complex. H−C(8) shifts from 2.38 to 2.19 ppm upon complexation, and H−C(7) from 3.08 to 2.95 ppm. The other signals are less affected and show shifts of less than 0.1 ppm.

Structure Determinations. Most of the ligands could be recrystallized from ethanol. Ligands **Vc** and **Vk** both form colorless prisms suitable for X-ray structure determination (Table 2). Crystals of **4** were obtained from CH_2Cl_2/pentane. The raw intensity data were collected on a Siemens P3 or Siemens Nicolet P4 diffractometer and were converted into structure factor amplitudes. Corrections were made for Lorentz and polarization effects and anomalous dispersion. The structures were solved by direct methods using SHELXS86[13] or SIR92[14] (for **Vk**) and refined using SHELXL93.[15] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. Plots were generated by the graphic programs PLUTON[16] and PLATON.[17]

In the solid state the compound **Vc** adopts a trans conformation of the bipyridine rings with a torsional angle N1−C2−C2′∠N1′ of 172.1(3)° (Figure 1). The alkylation at the C(7) position occurs from the sterically less hindered side of the pinene fragment. This can also be seen in the molecular structure of the bisalkylated ligand **Vk** (Figure 2), despite the disorder of one of the propyl substituents. Both alkylations occur from

(13) *SHELXS86, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1986,
(14) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.
(15) Sheldrick, G. M. *SHELXL93, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1994.
(16) Spek, A. L. *PLUTON—Crystal and Molecular graphics program*; University of Utrecht, Utrecht, The Netherlands, 1992.
(17) Spek, A. L. *Acta Crystallogr.* **1994**, *A46*, C34.

Scheme 3. Synthesis of the Metal Complexes of Compound **V**

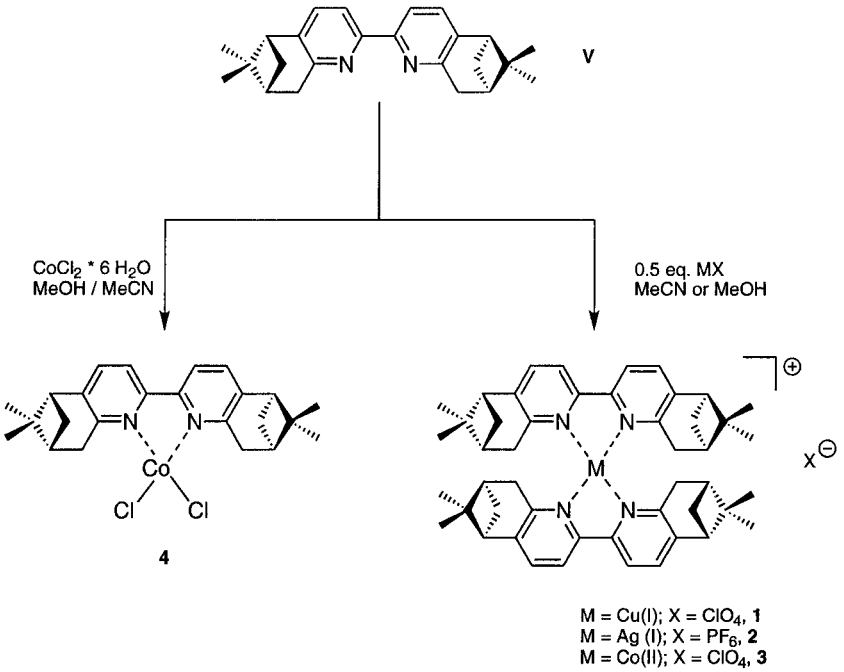


Table 2. Crystal and Data Collection Details[a]

compd	**Vc**	**Vh**	**4**
empirical formula	$C_{27}H_{34}N_2$	$C_{30}H_{40}N_2$	$C_{24}H_{28}N_2Cl_2Co + C_5H_{12}$
fw	386.58	428.64	546.44
temp (K)	293(2)	173(2)	153(2)
cryst size, mm	0.6 × 0.5 × 0.5	0.2 × 0.2 × 0.2	0.5 × 0.5 × 0.4
a (Å)	6.722(4)	8.2230(9)	12.677(3)
b (Å)	13.050(6)	12.959(2)	14.211(2)
c (Å)	26.14(1)	12.577(2)	7.945(2)
β (deg)	90.0	100.200(9)	90.0
V (Å^3)	2293(2)	1319.0(3)	1431.3(5)
space group	$P2_12_12_1$ (no.19)	$P2_1$ (no.4)	$P2_12_12$ (no.18)
Z	4	2	2
d_{calcd} (g/cm^3)	1.120	1.079	1.268
μ (cm^{-1})	0.65	0.62	8.0
diffractometer	Siemens P3	Siemens Nicolet P4	Siemens P3
radiation, wavelength (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
2*θ* range (deg)	4−54	4−54	4−54
reflns measd	$0 \rightarrow +h, +k, +l$ $0 \rightarrow -h, -k, -l$	$+h, +k, \pm l$	$0 \rightarrow +h, +k, +l$ $0 \rightarrow -h, -k, -l$
scan mode	w	w	w
scan speed, deg/min	4.0−29.3	4.0−29.3	4.0−29.3
total no. of data collected	5566	3217	3556
no. of unique data, R_{av} (%)	4704, 4.3	3014, 3.1	3088, 3.1
no. of obsd data [$F_o^2 \geq 2\sigma(F_o^2)$]	3414	1349	2881
R1 (%)	8.33	8.26	7.09
WR2 (%)	17.7	16.3	18.7
GOF	1.16	1.19	1.22
no. of variables	270	299	159

[a] Estimated standard deviations of the last significant digit are given in parentheses.

the same side, leading to only one of the possible three diastereomers.

Figure 3 shows the molecular structure of the cobalt complex **4** where the ligand adopts the cis form and chelates the metal ion. The change of the trans conformation about the C2−C2′ bond in the free ligand to cis in the complex is a known phenomenon.[11] The cobalt atom is situated in the center of a slightly distorted tetrahedron coordinated by two nitrogen and two chloride ligands. A side view shows the chloride ligands to be almost perpendicular to the ligand plane (89.0(2)°), which is different from the corresponding Cu(II) complex, where this angle is 64.12(5)°.[9] The complex has a 2-fold crystallographic axis passing through the cobalt atom. The torsional angle N1−C2−C2′∠N1′ is 0.5(6)° with the cobalt atom in this plane. Compared to the structures of 6,6′-dimethylbipyridine cobalt(II) dichloride[18] (torsional angle 2.0°) and the structure of Bolm's chiral bipyridine cobalt complex[19] (torsional angle 12.9°), this is the most planar bipyridine. The bulky substituents on the bipyridine shield the metal center, so additional coordination leading to an octahedral complex does not occur.

Conclusion

The new synthesis of the C_2-symmetrical ligand **V** and its alkylated derivatives leads to a versatile chiral bipyridine already tested successfully upon enantioselective catalysis. Alkylation occurs stereoselectively at the C(7) position of the molecule. Double alkylation leads to the C_2-symmetrical ligands **Vf** and **Vi**−**Vn**. Although the free ligands adopt the transoid conformation of the pyridine rings, they are flexible enough to chelate metal ions in the cisoid form. A tetrahedral cobalt complex is formed with $CoCl_2$ and the ligand **V** in a 1:1 ratio. These ligands are also very useful in enantioselective catalysis.[7−9]

Experimental Section

Caution: Perchlorate salts are potentially explosive. They should be handled with care in small quantities. Prolonged drying especially at high temperatures should be avoided.

Apparatus and Chemicals Used. All NMR measurements were recorded using a Varian Gemini 300 (300 MHz for ^{1}H and 75.44 MHz for ^{13}C). Melting points were recorded on a Büchi 520 and are uncorrected. Mass spectra were recorded on a VG Instruments 7070E mass spectrometer equipped with an FAB inlet system. Rotation values have been obtained with a Perkin-Elmer MC 241 polarimeter. The emission spectra were recorded on a Perkin-Elmer luminescence spectrometer LS 50B. $Cu(MeCN)_4ClO_4$[20] was prepared by a literature method. If necessary, the solvents were dried over sodium/benzophenone

(18) Baker, G. L.; Ronczek, F. R.; Kiefer, G. E.; Marston, C. R.; Modenbach, C. L.; Newkome, G. R.; Puckett, W. E.; Watkins, S. F. *Acta Crystallogr.* **1998**, *44*, 1668.
(19) Bolm, C.; Zehnder, M.; Bur, D. *Angew. Chem.* **1990**, *102*, 206.
(20) Hathaway, B. J.; Holah, D. G.; Postlewhaite, J. D. *J. Chem. Soc.* **1961**, 3215.

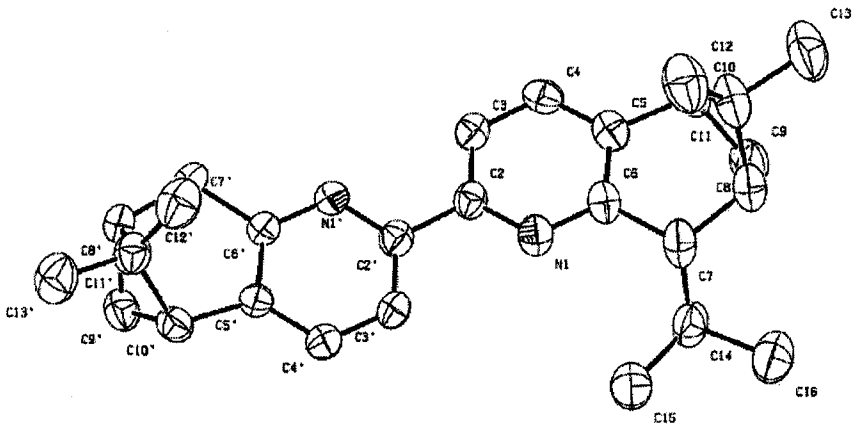


Figure 1. ORTEP drawing of compound **Vc** showing the atomic labeling used in the text. All hydrogen atoms are omitted for clarity.

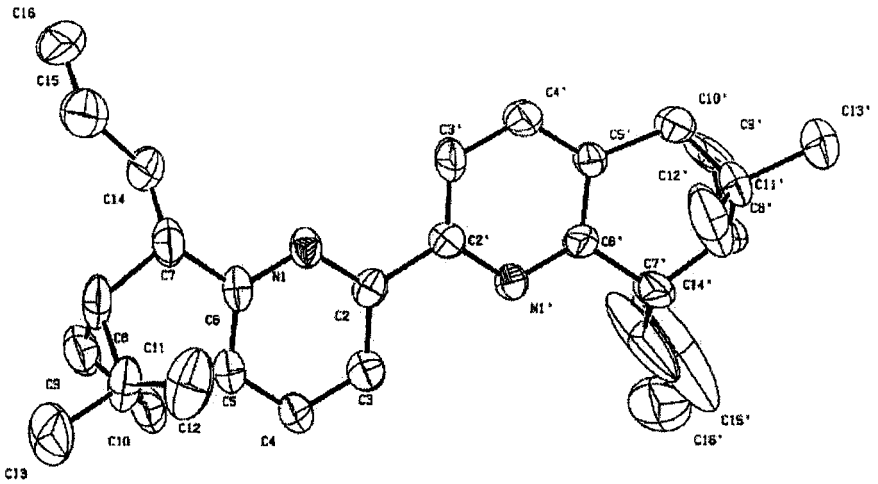


Figure 2. ORTEP drawing of compound **Vk** showing the atomic labeling used in the text. All hydrogen atoms are omitted for clarity.

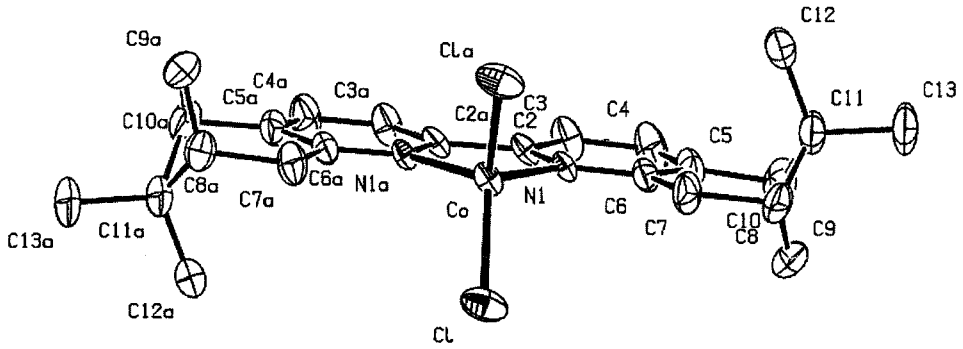


Figure 3. ORTEP drawing of compound **4** (side view) showing the atomic labeling used in the text. All hydrogen atoms and one molecule of pentane are omitted for clarity.

(THF), lithium aluminum hydride (diethyl ether), or calcium hydride (CH_2Cl_2). (−)-α-Pinene (95% ee) was obtained by isomerization of (−)-*β*-pinene (95% ee).[21] The ee of (−)-*β*-pinene was increased similar to a procedure by Jenny et al. from (−)-*β*-pinene (Fluka, puriss).[22]

Preparations. (−)-Bismethyldipinene[5,6]bipyridine Vf. A Schlenk flask was charged with 15 mL of dry THF under argon. At room temperature 0.67 mL (4.79 mmol) of diisopropylamine was added. The reaction mixture was cooled to −40 °C. Then 2.72 mL of *n*-BuLi (1.6 M in hexane, 4.35 mmol) was rapidly added via a syringe. The formed LDA was allowed to warm to 0 °C and was kept for 30 min at this temperature. The system was cooled again to −40 °C, and **V** (500 mg, 1.45 mmol) dissolved in 5 mL of dry THF was added dropwise within 1 h via a syringe pump. Directly after addition of the first drop of this solution, the reaction medium turned to dark blue. After addition of the ligand **V**, the dark blue solution was kept at −40 °C for a further 2 h. Subsequently methyl iodide (659 mg, 4.64 mmol) was added via a syringe pump within 1 h. After this addition the reaction mixture was allowed to warm to room temperature overnight. During this time the dark blue color turned to brown. The mixture was quenched with ca. 2 mL of water and evaporated to dryness. More water was added and the mixture extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and filtered. After removal of the solvent the residue was purified by column chromatography (SiO_2; hexane/ether/TEA, 10:1:0.1). Yield: 328.7 mg (61%) of **Vf**.

The corresponding monomethylated bipyridine **Va** was prepared in the same way using only 1.3 equiv of LDA and 1.4 equiv of methyl iodide (yield 78%).

Data for Compound Va. Mp: 108 °C. TLC (hexane/20% ethyl ether): R_f 0.29. ^{1}H NMR ($CDCl_3$): δ 8.05 (d, 1H, J = 7.8 Hz, H−C(3)), 8.00 (d, 1H, J = 7.9 Hz, H−C(3′)), 7.30 (d, 1H, J = 7.8 Hz, H−C(4)),

(21) Brown, C. A.; Jadhav, P. K. *Org. Synth.* **1987**, *65*, 224.
(22) Jenny, T. A.; Ma, L. *Tetrahedron Lett.* **1987**, *32*, 6101.

7.27 (d, 1H, J = 7.9 Hz, H−C(4′)), 3.23 (dd, 1H, J = 7.0,2.4 Hz, H−C(7)), 3.17 (d, J = 2.7 Hz, 2H, H−C(7′)), 2.77 (m, 2H, H−C(10) and H−C(10′)), 2.68 (ddd, 1H, J = 9.3, 5.9, 5.9 Hz, H_b–C(9′)), 2.54 (ddd, J = 9.8, 5.0, 5.0 Hz, 1H, H_b–C(9)), 2.37 (septet, J = 2.9 Hz, 1H, H−C(8′)), 2.15 (ddd, J = 6.0, 6.0, 2.5 Hz, 1H, H−C(8)), 1.45 (d, J = 7.0 Hz, 3H, H−C(14)), 1.40, 1.39 (s, 6H, H−C(13) and H−C(13′)), 1.32 (d, 1H, J = 9.8 Hz, H_a–C(9)), 1.30 (d, 1H, J = 9.4 Hz, H_a–C(9′)), 0.63 (s, 6H, H−C(12) and H−C(12′)). ^{13}C NMR ($CDCl_3$): δ 160.1 (C(6)), 156.1 (C(6′)), 154.3, 153.8 (C(2) and C(2′)), 141.6, 141.4 (C(5) and C(5′)), 133.9 (C(4)), 133.5 (C(4′)), 117.7 (C(3)), 117.6 (C(3′)), 47.1 (C(10)), 46.8 (C(8)), 46.5 (C(10′)), 41.5 C(11)), 40.3 (C(8′)), 39.6 (C(11′)), 38.9 (C(7)), 36.7 (C(7′)), 32.0 (C(9′)), 28.6 (C(9)), 26.3, 26.1 (C(13) and C(13′)), 21.2 (C(12′)), 20.8 (C(12)), 18.3 (C(14)). CI-MS: m/z 359 (100, MH^+), 343 (17, $M^+ - CH_3$). Anal. Calcd for $C_{25}H_{30}N_2$ (358.51): C 83.75, H 8.43, N 7.81. Found: C 83.06, H 8.80, N 7.58.

Data for Compound Vf. TLC (hexane/10% MeOH/20% $CHCl_3$): R_f 0.74. ^{1}H NMR ($CDCl_3$): δ 8.01 (d, 2H, J = 7.7 Hz, H−C(3) and H−C(3′)), 7.27 (d, 2H, J = 7.8 Hz, H−C(4) and H−C(4′)), 3.23 (dq, 2H, J = 7.1,2.4 Hz, H−C(7) and H−C(7′)), 2.76 (dd, 2H, J = 5.7,5.7 Hz, H−C(10) and H−C(10′)), 2.54, (ddd, 2H, J = 9.8, 5.7, 5.7 Hz, H_b–C(9) and H_b–C(9′)), 2.14 (ddd, 2H, J = 5.7, 5.7, 2.5 Hz, H−C(8) and H−C(8′)), 1.44 (d, 6H, J = 7.1 Hz, H−C(14) and H−C(14′)), 1.39 (s, 6H, H−C(13) and H−C(13′)), 1.31 (d, 2H, J = 9.8 Hz, H_a–C(9) and H_a–C(9′)), 0.61 (s, 6H, H−C(12) and H−C(12′)). ^{13}C NMR ($CDCl_3$): δ 160.0, 154.3 (C(2), C(2′) and C(6), C(6′)), 141.3 (C(5), C(5′)), 133.5 (C(4), C(4′)), 117.6 (C(3), C(3′)), 47.1 (C(10), C(10′)), 46.8 (C(8), C(8′)), 41.7 (C(11), C(11′)), 38.9 (C(7), C(7′)), 28.6 (C(9), C(9′)), 26.3 (C(13), C(13′)), 20.8 (C(12), C(12′)), 18.2 (C(14), C(14′)). EI-MS: m/z 372 (46, M^+), 357 (100, $M^+ - CH_3$), 343 (11), 329 (59, $M^+ - C_3H_7$), 299 (14), 285 (14), 271 (23), 259 (11).

(−)-Bisethyldipinene[5,6]bipyridine Vi. A Schlenk flask was charged with 15 mL of dry THF under an inert atmosphere. At room temperature 0.46 mL (3.3 mmol) of diisopropylamine was added. The reaction mixture was cooled to −40 °C. Then 1.87 mL of *n*-BuLi (1.6 M in hexane, 3.0 mmol) was rapidly added via a syringe. The formed LDA was allowed to warm to 0 °C and was kept for 30 min at this temperature. The system was cooled again to −40 °C, and **V (**345 mg, 1.0 mmol) dissolved in 5 mL of dry THF was added dropwise within 1 h via a syringe pump. Directly after addition of the first drop of this solution, the reaction medium turned to dark blue. After addition of the ligand **V**, the dark blue solution was kept at −40 °C for a further 2 h. Subsequently ethyl iodide (500 mg, 3.2 mmol) was added via a syringe pump within 1 h. After this addition the reaction mixture was allowed to warm to room temperature overnight. During this time the dark blue color turned to brown. The mixture was quenched with ca. 2 mL of water and evaporated to dryness. More water was added and the mixture extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and filtered. After removal of the solvent the residue was purified by column chromatography (SiO_2; hexane/ether/TEA, 7:1:0.1). Yield: 316.5 mg (79%) of **Vi**.

The corresponding monoethylated bipyridine **Vb** was prepared in the same way using only 1.3 equiv of LDA and 1.4 equiv of ethyl iodide (yield 72%).

Data for Compound Vb. Mp: 181 °C. TLC (hexane/20% ethyl ether): R_f 0.38. ^{1}H NMR ($CDCl_3$): δ 8.04 (d, 1H, J = 7.8 Hz, H−C(3)), 7.97 (d, 1H, J = 7.7 Hz, H−C(3′)), 7.25 (d, 1H, J = 7.8 Hz, H−C(4)), 7.25 (d, 1H, J = 7.7 Hz, H−C(4′)), 3.14 (br, 2H, H−C(7′)), 2.95 (d br, 1H, J = 9.9 Hz, H−C(7)), 2.75 (dd, 1H, J = 5.5, 5.5 Hz, H−C(10)), 2.74 (dd, 1H, J = 5.5, 5.5 Hz, H−C(10′)), 2.64 (ddd, 1H, J = 9.4, 5.8, 5.8 Hz, H_b–C(9′)), 2.48 (ddd, 1H, H_b–C(9)), 2.44 (m, 1H, H_a–C(14)), 2.32 (m, 1H, H−C(8)), 2.32 (m, 1H, H−C(8′)), 1.49 (m, 1H, H_b–C(14)), 1.38 (s, 3H, H−C(13)), 1.35 (s, 3H, H−C(13′)), 1.28 (d, 1H, J = 9.7 Hz, H_a–C(9)), 1.28 (d, 1H, J = 9.6 Hz, H_a–C(9′)), 1.07 (t, 3H, J = 7.4 Hz, H−C(15)), 0.60 (s, 3H, H−C(12′)), 0.59 (s, 3H, H−C(12)). ^{13}C NMR ($CDCl_3$): δ 159.4 (C(6)), 156.0 (C(6′)), 154.3, 153.8 (C(2) and C(2′)), 141.2, 141.1 (C(5) and C(5′)), 133.6, 133.3 (C(4) and C(4′)), 117.5, 117.4 (C(3) and C(3′)), 46.8 (C(10)), 46.3 (C(10′)), 45.9 (C(7)), 42.8 (C(8)), 41.0 (C(11)), 40.2 (C(8′)), 39.5 (C(11′)), 36.6 (C(7′)), 31.9 (C(9′)), 28.4 (C(9)), 26.4 (C(13)), 26.0 (C(13′)), 25.3 (C(14)), 21.1 (C(12′)), 20.8 (C(12)), 12.4 (C(15)). EI-MS: m/z 371 (94, $M^+ - H$), 357 (29, $M^+ - CH_3$), 43 (100, C_3H_7)). Anal. Calcd for $C_{26}H_{32}N_2$ (372.54): C 83.82, H 8.66, N 7.52. Found: C 83.65, H 9.05, N 6.85.

Data for Compound Vi. TLC (hexane/20% ethyl ether): R_f 0.58. ^{1}H NMR ($CDCl_3$): δ 8.01 (d, 2H, J = 7.7 Hz, H−C(3) and H−C(3′)), 7.25 (d, 2H, J = 7.7 Hz, H−C(4) and H−C(4′)), 2.95 (ddd, 2H, J = 9.9, 3.0, 3.0 Hz, H−C(7) and H−C(7′)), 2.76 (dd, 2H, J = 5.5, 5.5 Hz, H−C(8) and H−C(8′)), 2.50 (ddd, 2H, J = 9.6, 5.8, 5.8 Hz, H_b–C(9) and H_b–C(9′)), 2.45 (m, 2H, H_a–C(14) and H_a–C(14′)), 2.33 (ddd, 2H, J = 6.0, 6.0, 2.5 Hz, H−C(8) and H−C(8′)), 1.50 (m, 2H, H_b–C(14) and H_b–C(14′)), 1.41 (s, 6H, H−C(13) and H−C(13′)), 1.30 (d, 2H, J = 9.6 Hz, H_a–C(9) and H_a–C(9′)), 1.09 (t, 6H, J = 7.4 Hz, H−C(15) and H−C(15′)), 0.60 (s, 6H, H−C(12) and H−C(12′)). ^{13}C NMR ($CDCl_3$): δ 159.6, 154.2 (C(2), C(2′) and C(6), C(6′)), 141.2 (C(5), C(5′)), 133.4 (C(4), C(4′)), 117.6 (C(3), C(3′)), 46.9 (C(10), C(10′)), 46.0 (C(7), C(7′)), 43.0 (C(8), C(8′)), 41.1 (C(11), C(11′)), 28.5 (C(9), C(9′)), 26.5 (C(13), C(13′)), 25.4 (C(14), C(14′)), 20.9 (C(12), C(12′)), 12.5 (C(15), C(15′)). FAB-MS: m/z 401 (100, MH^+), 385 (17, $M^+ - CH_3$), 371 (32, $M^+ - C_2H_5$). Anal. Calcd for $C_{28}H_{36}N_2$ (400.59): C 83.95, H 9.06, N 6.99. Found: C 83.78, H 9.24, N 6.18.

(−)-Bis-n-propyldipinene[5,6]bipyridine Vk. The synthesis of **Vk** was carried out similar to that of **Vf** starting from 327 mg (0.95 mmol) of **V**, 3 equiv of LDA, and 8.0 mmol of *n*-propyl iodide. Column chromatography (40 g SiO_2; hexane/ether, 20:1) yielded 239 mg (59%) of **Vk**. The corresponding monoalkylated compound was not observed.

Data for Compound Vk. Mp: 111 °C. TLC (hexane/20% ethyl ether): R_f 0.61. ^{1}H NMR ($CDCl_3$): δ 8.01 (d, 2H, J = 7.7 Hz, H−C(3) and H−C(3′)), 7.27 (d, 2H, J = 7.7 Hz, H−C(4) and H−C(4′)), 3.05 (br, 2H, H−C(7) and H−C(7′)), 2.77 (dd, 2H, J = 5.7 Hz, H−C(10) and H−C(10′)), 2.53 (ddd, 2H, J = 9.7, 5.5, 5.5 Hz, H_b–C(9) and H_b–C(9′)), 2.35 (m, 2H, H_a–C(14) and H_a–C(14′)), 2.30 (ddd, 2H, J = 6.0, 6.0, 2.5 Hz, H−C(8) and H−C(8′)), 1.6−1.45 (m, 6H, (H_b–C(14), H_b–C(14′) and H−C(15), H−C(15′))), 1.41 (s, 6H, H−C(13) and H−C(13′)), 1.32 (d, 2H, J = 9.8 Hz, H_a–C(9) and H_a–C(9′)), 1.00 (t, 6H, J = 7.1 Hz, H−C(16) and H−C(16′)), 0.61 (s, 6H, H−C(12) and H−C(12′)). ^{13}C NMR ($CDCl_3$): δ 159.7, 154.3 (C(2), C(2′) and C(6), C(6′)), 141.3 (C(5), C(5′)), 133.5 (C(4), C(4′)), 117.6 (C(3), C(3′)), 46.9 (C(10), C(10′)), 44.1 (C(7), C(7′)), 43.5 (C(8), C(8′)), 41.1 (C(11), C(11′)), 34.8 (C(14), C(14′)), 28.5 (C(9), C(9′)), 26.4 (C(13), C(13′)), 21.0 (C(15), C(15′)), 20.9 (C(12), C(12′)), 14.5 (C(16), C(16′)). CI-MS: m/z 429 (100, MH^+), 386 (32, $MH^+ - C_3H_7$), 385 (32, $M^+ - C_3H_7$).

(−)-Bisisopropyldipinene[5,6]bipyridine Vl and Isopropyldipinene-[5,6]bipyridine Vc. A 229 mg (0.66 mmol) sample of **V** was treated with 3 equiv of LDA and 6 equiv of isopropyl iodide similar to the preparation of **Vf**. Column chromatography (70 g SiO_2; hexane/ether, 20:1 gradually to 10:1) yielded 60 mg (21%) of **Vl** and 110 mg (43%) of **Vc**.

Data for Compound Vc. TLC (hexane/20% ethyl ether): R_f 0.43. ^{1}H NMR ($CDCl_3$): δ 8.07, 8.04 (d, 2H, J = 7.9 Hz, H−C(3) and H−C(3′)), 7.29, 7.27 (d, 2H, J = 7.8 Hz, H−C(4) and H−C(4′)), 3.17 (d br, 2H, J = 2.8 Hz, H−C(7′)), 2.95 (dd, 1H, J = 4.7,2.0 Hz, H−C(7)), 2.85 (m, 1H, H_a–C(14)), 2.78 (dd, 1H, J = 5.6,5.6 Hz, H−C(10′)), 2.73 (dd, 1H, J = 5.5, 5.5 Hz, H−C(10)), 2.68 (ddd, 1H, J = 9.6, 6.0, 6.0 Hz, H_b–C(9′)), 2.56 (ddd, 1H, J = 9.6, 5.5, 5.5 Hz, H_b–C(9)), 2.38 (ddd, 1H, J = 5.8, 5.8, 2.7 Hz, H−C(8′)), 2.36 (ddd, 1H, J = 6.0, 6.0, 2.4 Hz, H−C(8)), 1.40 (d, 1H, J = 9.6 Hz, H_a–C(9)), 1.40 (s, 6H, H−C(13) and H−C(13′)), 1.30 (d, 1H, J = 9.4 Hz, H_a–C(9′)), 1.22 (d, 3H, J = 6.9 Hz, H−C(16)), 0.86 (d, 3H, J = 6.9 Hz, H−C(15)), 0.64 (s, 3H, H−C(12′)), 0.60 (s, 3H, H−C(12)). ^{13}C NMR ($CDCl_3$): δ 158.7 (C(6)), 156.1 (C(6′)), 154.3, 153.4 (C(2) and C(2′)), 141.9, 141.3 (C(5) and C(5′)), 133.8, 133.5 (C(4) and C(4′)), 117.7, 117.4 (C(3) and C(3′)), 49.2 (C(7)), 46.8 (C(10)), 46.3 (C(10′)), 42.0 (C(11)), 41.5 (C(8)), 40.3 (C(8′)), 39.6 (C(11′)), 36.7 (C(7′)), 32.0 (C(9′)), 30.4 (C(14)), 29.4 (C(9)), 26.4, 26.1 (C(13), C(13′)) 22.3 (C(16)), 21.3 (C(12′)), 21.0 (C(12)), 20.2 (C(15)). EI-MS: m/z 386 (10, M^+), 371 (12, $M^+ - CH_3$), 343 (100, $M^+ - C_3H_7$).

Data for Compound Vl. TLC (hexane/20% ethyl ether): R_f 0.63. ^{1}H NMR ($CDCl_3$): δ 8.08 (d, 2H, J = 7.7 Hz, H−C(3) and H−C(3′)), 7.28 (d, 2H, J = 7.7 Hz, H−C(4) and H−C(4′)), 2.96 (br, 2H, H−C(7) and H−C(7′)), 2.86 (m, 1H, H−C(14) and H−C(14′)), 2.74 (dd, 2H, J = 5.7 Hz, H−C(10) and H−C(10′)), 2.57 (ddd, 2H, J = 9.6, 5.7, 5.7

Hz, H_b–C(9) and H_b–C(9′)), 2.36 (ddd, 2H, J = 6.0, 6.0, 2.1 Hz, H−C(8) and H−C(8′)), 1.41 (s, 6H, H−C(13) and H−C(13′)), 1.41 (d, 2H, J = 9.6 Hz, H_a–C(9) and H_a–C(9′)), 1.23 (d, 6H, J = 6.9 Hz, H−C(15) and H−C(15′)), 0.87 (d, 6H, J = 6.9 Hz, H−C(16) and H−C(16′)), 0.60 (s, 6H, H−C(12) and H−C(12′)). ^{13}C NMR ($CDCl_3$): δ 158.6, 154.0 (C(2), C(2′) and C(6),C(6′)), 141.9 (C(5), C(5′)), 133.7 (C(4), C(4′)), 117.6 (C(3), C(3′)), 49.1 (C(7), C(7′)), 46.8 (C(10), C(10′)), 42.0 (C(11), C(11′)), 41.5 (C(8), C(8′)), 30.5 (C(14), C(14′)), 29.4 (C(9), C(9′)), 26.4 (C(13), C(13′)), 22.4 (C(15), C(15′)), 21.0 (C(12), C(12′)), 20.2 (C(16), C(16′)). CI-MS: m/z 429 (100, MH^+), 385 (70, $M^+ - C_3H_7$).

(−)-Bisbenzyldipinene[5,6]bipyridine Vm and Benzyl-5,6-dipinene-[5,6]bipyridine Vd. The compound was synthesized from 504 mg (1.46 mmol) of **V** in the same manner as **Vf**, using 1.0 g (6.0 mmol) of benzyl bromide. The first column chromatography run gave 943 mg, which was isolated and dried for 2 days in high vacuum to remove excess benzyl bromide. The second column chromatography run yielded 12 mg of pure **Vm** (1.6%), 68 mg of **Vm** combined with an unknown compound, and 235 mg (37%) of **Vd**.

Data for Compound Vd. Mp: 85 °C. TLC (hexane/20% ethyl ether): R_f 0.35. ^{1}H NMR ($CDCl_3$): δ 8.15, 8.09 (d, 2H, J = 7.8 Hz, H−C(3) and H−C(3′)), 7.31 (d, 1H, H−C(4′)), 7.31 (m, 4H, H−C(16) and H−C(17)), 7.31 (d, 1H, H−C(4)), 7.24 (br, 1H, H−C(18)), 3.87 (dd, 1H, J = 13.5, 3.7 Hz, H_a–C(14)), 3.41 (d br, 1H, J = 10.9 Hz, H−C(7)), 3.14 (br, 2H, H−C(7′)), 2.80 (m, 1H, H−C(10)), 2.80 (m, 1H, H−C(10′)), 2.75 (m, 1H, H_b–C(14)), 2.72 (m, 1H, H_b–C(9′)), 2.57 (ddd, 1H, J = 9.9, 5.5, 5.5 Hz, H_b–C(9)), 2.40 (m, 1H, H−C(8′)), 2.12 (m, 1H, H−C(8)), 1.45, (d, 1H, J = 10.0 Hz, H_a–C(9′)), 1.42 (s, 3H, H−C(13′)), 1.34 (s, 3H, H−C(13)), 1.33 (d, 1H, J = 9 Hz, H_a–C(9)), 0.68 (s, 3H, H−C(12′)), 0.61 (s, 3H, H−C(12)). ^{13}C NMR ($CDCl_3$): δ 158.4, 156.2 (C(6) and C(6′)), 154.2, 153.9 (C(2) and C(2′)), 141.5 (C(15)), 141.4, 141.1 (C(5) and C(5′)), 133.7, 133.6 (C(4) and C(4′)), 129.3, 128.2 (C(16) and C(17)), 125.7 (C(18)), 117.7, 117.6 (C(3) and C(3′)), 46.8 (C(10)), 46.4 (C(10′)), 46.2 (C(7)), 42.5 (C(8)), 41.1 (C(11)), 40.3 (C(8′)), 39.5 (C(11′)), 38.7 (C(14)), 36.7 (C(7′)), 31.9 (C(9′)), 28.2 (C(9)), 26.2 (C(13)), 26.0 (C(13′)), 21.2 (C(12′)), 20.8 (C(12)). FAB-MS: m/z 435 (100, MH^+), 343 (40, $M^+ - C_7H_7$). Anal. Calcd for $C_{31}H_{34}N_2$ (434.63): C 85.67, H 7.88, N 6.45. Found: C 84.28, H 7.75, N 5.95.

Data for Compound Vm. ^{1}H NMR ($CDCl_3$): δ 8.14 (d, 2H, J = 7.8 Hz, H−C(3) and H−C(3′)), 7.35−7.28 (m, 10H, (H−C(16), H−C(17), H−C(18) and H−C(16′), H−C(17′), H−C(18′)), 7.24 (br, 2H, H−C(4) and H−C(4′)), 3.85 (d, 2H, J = 13.5, 3.7 Hz, H_a–C(14) and H_a–C(14′)), 3.40 (d br, 2H, J = 10.8 Hz, H−C(7) and H−C(7′)), 2.79 (dd, 2H, J = 5.4, 5.4 Hz, H−C(10) and H−C(10′)), 2.56 (ddd, 2H, J = 9.7, 5.8, 5.8 Hz, H_b–C(9) and H_b–C(9′)), 2.10 (ddd, 2H, J = 6.0, 6.0, 2.5 Hz, H−C(8) and H−C(8′)), 1.44 (m, 2H, H_b–C(14) and H_b–C(14′)), 1.44 (d, 2H, J = 9.6 Hz, H_a–C(9) and H_a–C(9′)), 1.34 (s, 6H, H−C(13) and H−C(13′)), 0.60 (s, 6H, H−C(12) and H−C(12′)). ^{13}C NMR ($CDCl_3$): δ 158.5, 154.1 (C(2), C(2′) and C(6), C(6′)), 141.6 (C(15), C(15′)), 141.2 (C(5), C(5′)), 133.8 (C(4), C(4′)), 129.4, 128.3 (C(16), C(16′) and C(17), C(17′)), 125.8 (C(18), C(18′)), 117.9 (C(3), C(3′)), 46.9 (C(10), C(10′)), 46.3 (C(7), C(7′)), 42.6 (C(8), C(8′)), 41.2 (C(11), C(11′)), 38.8 (C(14), C(14′)), 28.3 (C(9), C(9′)), 26.3 (C(13), C(13′)), 20.9 (C(12), C(12′)).

(−)-Bis(trimethylsilyl)dipinene[5,6]bipyridine Ve. Ve was synthesized as shown above from 620 mg (1.8 mmol) of **V** and 870 mg (8.0 mmol) of trimethylsilyl chloride. Column chromatography yielded 355 mg (47%) of a white powder of pure **Ve** and 240 mg (27%) of oily **Vn**. The reduced yield was due to insufficient separation of both compounds.

Data for Compound Ve. Mp: 107 °C. TLC (hexane/20% ethyl ether): R_f 0.48. ^{1}H NMR ($CDCl_3$): δ 8.05, 7.98 (d, 2H, J = 7.7 Hz, H−C(3) and H−C(3′)), 7.29, 7.22 (d, 2H, J = 7.9 Hz, H−C(4) and H−C(4′)), 3.16 (d, 2H, J = 2.8 Hz, H−C(7′)), 2.82 (d, 1H, J = 1.4 Hz, H−C(7)), 2.77 (dd, 1H, J = 5.5, 5.5 Hz, H−C(10′)), 2.73 (dd, 1H, J = 5.5, 5.5 Hz, H−C(10)), 2.68 (ddd, 1H, J = 9.3 Hz, H_b–C(9′)), 2.58 (ddd, 1H, J = 9.3 Hz, H_b–C(9)), 2.37 (m, 2H, H−C(8′)), 2.32 (ddd, 1H, J = 6.0, 6.0, 2.2 Hz, H−C(8)), 1.40 (s, 3H, H−C(13)), 1.37 (s, 3H, H−C(13′)), 1.30 (d, 1H, J = 9.4 Hz, H_a–C(9′)), 1.29 (d, 1H, J = 9.6 Hz, H_a–C(9)), 0.66 (s, 3H, H−C(12)), 0.61 (s, 3H, H−C(12′)), 0.13 (s, 9H, H−C(14)). ^{13}C NMR ($CDCl_3$): δ 159.9, 156.1 (C(6) and C(6′)), 154.5, 153.5 (C(2) and C(2′)), 141.3, 140.6 (C(5) and C(5′)), 133.7, 133.5 (C(4) and C(4′)), 117.3, 115.9 (C(3) and C(3′)), 46.5 (C(10)), 46.4 (C(10′)), 42.7 (C(8)), 40.3 (C(8′)), 39.6, 39.2 (C(11) and C(11′)), 36.7 (C(7′)), 36.6 (C(7)), 32.0 (C(9′)), 29.2 (C(9)), 26.1 (C(13)), 25.9 (C(13′)), 21.3 (C(12)), 21.1 (C(12′)), −0.4 (3C, C(14)). CI-MS: m/z 417 (100, MH^+), 416 (66, M^+). Anal. Calcd for $C_{27}H_{36}N_2Si$ (416.69): C 77.83, H 8.71, N 6.72. Found: C 77.88, H 8.76, N 6.40.

Data for Compound Vn. TLC (hexane/20% ethyl ether): R_f 0.64. ^{1}H NMR ($CDCl_3$): δ 8.02 (d, 2H, J = 7.7 Hz, H−C(3) and H−C(3′)), 7.23 (d, 2H, J = 7.7 Hz, H−C(4) and H−C(4′)), 2.83 (br, 2H, H−C(7) and H−C(7′)), 2.73 (dd, 2H, J = 5.7, 5.7 Hz, H−C(10) and H−C(10′)), 2.59 (m, 2H, H_b–C(9) and H_b–C(9′)), 2.33 (ddd, 2H, J = 6.0, 6.0, 2.2 Hz, H−C(8) and H−C(8′)), 1.38 (s, 6H, H−C(13) and H−C(13′)), 1.29 (d, 2H, J = 9.6 Hz, H_a–C(9) and H_a–C(9′)), 0.61 (s, 6H, H−C(12) and H−C(12′)), 0.15 (s, 18H, H−C(14) and H−C(14′)). ^{13}C NMR ($CDCl_3$): δ 159.7, 153.9 (C(2), C(2′) and C(6), C(6′)), 140.4 (C(5), C(5′)), 133.5 (C(4), C(4′)), 115.8 (C(3), C(3′)), 46.4 (C(10), C(10′)), 42.7 (C(8), C(8′)), 39.2 (C(11), C(11′)), 36.6 (C(7), C(7′)), 29.2 (C(9), C(9′)), 25.9 (C(13), C(13′)), 21.1 (C(12), C(12′)), −0.4 (C(14), C(14′)). FAB-MS: m/z 489 (100, MH^+), 473 (63, $M^+ - CH_3$), 417 (31).

(−)-Bisbutyldipinene[5,6]bipyridine Vo. This compound was synthesized according to the procedure for ligands **Vf** and **Vi**. A Schlenk flask was charged with 15 mL of dry THF under an inert atmosphere. At room temperature 0.41 mL (2.87 mmol) of diisopropylamine was added. The reaction mixture was cooled to −40 °C. Then 1.7 mL of *n*-BuLi (1.6 M in hexane, 2.7 mmol) was rapidly added via a syringe. The formed LDA was allowed to warm to 0 °C and was kept for 30 min at this temperature. The system was cooled again to −40 °C, and **V (**300 mg, 0.871 mmol) dissolved in 5 mL of dry THF was added dropwise within 1 h via a syringe pump. Directly after addition of the first drop of this solution, the reaction medium turned to dark blue. After addition of the ligand **V**, the dark blue solution was kept at −40 °C for a further 2 h. Subsequently *n*-butyl iodide (513 mg, 2.787 mmol) was added via a syringe pump within 1 h. After this addition the reaction mixture was allowed to warm to room temperature overnight. During this time the dark blue color turned to brown. The mixture was quenched with ca. 2 mL of water and evaporated to dryness. More water was added and the mixture extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and filtered. After removal of the solvent the residue was purified by column chromatography (SiO_2; hexane/EtOAc/TEA, 10:1:0.1). Yield: 357.2 mg (88%) of **Vo** as an oily product.

Data for Compound Vo. ^{1}H NMR ($CDCl_3$): δ 8.02 (d, 2H, J = 7.7 Hz, H−C(3) and H−C(3′)), 7.25 (d, 2H, J = 7.7 Hz, H−C(4) and H−C(4′)), 3.05 (br, 2H, H−C(7) and H−C(7′)), 2.73 (dd, 2H, J = 5.7,5.7 Hz, H−C(10) and H−C(10′)), 2.59 (m, 2H, H_b–C(9) and H_b–C(9′)), 2.35 (m, 2H, H_a–C(14) H_a–C(14′)) 2.33 (ddd, 2H, J = 6.0, 6.0, 2.2 Hz, H−C(8) and H−C(8′)), 1.48 (m, 10H H_2–C(15), H_2–C(15′), H_2–C(16), H_2–C(16′), H_b–C(14) H_b–C(14′)), 1.38 (s, 6H, H−C(13) and H−C(13′)), 0.94 (t, 6H, H_3–C(17), H_3–C(17′)) 1.29 (d, 2H, J = 9.6 Hz, H_a–C(9) and H_a–C(9′)), 0.61 (s, 6H, H−C(12) and H−C(12′)), 0.15 (s, 18H, H−C(14) and H−C(14′)). ^{13}C NMR ($CDCl_3$): 159.8, 154.3 (C(2), C(2′) and C(6), C(6′)), 141.3 (C(5), C(5′)), 133.5 (C(4), C(4′)), 117.6 (C(3), C(3′)), 47.0 (C(10), C(10′)), 44.0 (C(8), C(8′)), 43.57 (C(14) C(14′)), 41.2 (C(11), C(11′)), 32.4 (C(7), C(7′)), 30.27 (C(15), C(15′)), 28.6 (C(9), C(9′)), 26.3 (C(13), C(13′)), 23.13 (C(16), C(16′)), 20.8 (C(12), C(12′)), 14.3 (C(17), C(17′)). FAB-MS: m/z 457 (100, MH^+), 399 (24, $M^+ - CH_2CH_2CH_3$), 357 (20).

(−)-Methylethyldipinene[5,6]bipyridine Vg. Vg was synthesized from 91 mg (0.255 mmol) of **Va** by metalation with 0.26 mL (0.38 mmol) LDA at −40 °C. After 3 h at this temperature 193 mg (1.24 mmol) of ethyl iodide was added. After workup as shown above the crude mixture was purified by column chromatography. Yield: 25 mg (26%). A 16 mg yield of a dimeric compound and 22 mg of a structurally unknown compound were isolated as well.

Data for Compound Vg. TLC (hexane/20% ethyl ether): R_f 0.54. ^{1}H NMR ($CDCl_3$): δ 8.02 (d, 2H, J = 7.5 Hz, H−C(3) and H−C(3′)), 7.27 (d, 2H, J = 7.8 Hz, H−C(4) and H−C(4′)), 3.24 (br, 1H, H−C(7′)), 2.95 (m, 1H, H−C(7)), 2.77 (ddd, 2H, J = 5.6, 5.6, 2.2 Hz, H−C(10) and H−C(10′)), 2.54 (m, 2H, H_b–C(9) and H_b–C(9′)), 2.46 (m, 1H, H_a–C(14)), 2.34 (ddd, 1H, J = 6.0, 6.0, 2.6 Hz, H−C(8)),

2.15 (ddd, 1H, $J = 6.0, 6.0, 2.6$ Hz, H−C(8′)), 1.49 (m, 1H, H_b–C(14)), 1.45 (d, 3H, $J = 7.0$ Hz, H−C(14′)), 1.42, 1.40 (s, 6H, H−C(13) and H−C(13′)), 1.32, 1.31 (d, 2H, $J = 9.7$ Hz, H_a–C(9) and H_a–C(9′)), 1.09 (t, 3H, $J = 7.5$ Hz, H−C(15)), 0.62, 0.61 (s, 6H, H−C(12) and H−C(12′)). ^{13}C NMR ($CDCl_3$): δ 160.0, 159.6, 154.2, 154.1 (C(2), C(6), C(2′), C(6′)), 141.3 (C(5) and C(5′)), 133.6, 133.5 (C(4) and C(4′)), 117.7, 117.6 (C(3) and C(3′)), 47.1 (C(10′)), 46.9 (C(10)), 46.8 (C(8′)), 46.0 (C(7)), 42.9 (C(8)), 41.5, 41.1 (C(11) and C(11′)), 38.9 (C(7′)), 28.6, 28.5 (C(9) and C(9′)), 26.5, 26.3 (C(13) and C(13′)), 25.4 (C(14)), 20.9, 20.8 (C(12) and C(12′)), 18.3 (C(15)), 12.5 (C(14′)). CI-MS: *m*/*z* 387 (100, MH^+), 371 (13, $M^+ - CH_3$), 357 (11, $M^+ - C_2H_5$).

(−)-Methylbenzyldipinene[5,6]bipyridine Vh. Vh was synthesized according to the procedure for **Vg** from 72 mg (0.20 mmol) of **Va** with 107 mg (0.84 mmol) of benzyl chloride. Yield: 3 mg (4%).

Data for Compound Vh. ^{1}H NMR ($CDCl_3$): δ 8.08 (br, 2H, H−C(3) and H−C(3′)), 7.4−7.2 (m, 7H, H−C(4), H−C(4′), H−C(16), H−C(17), H−C(18)), 3.84 (dd, 1H, $J = 13.7, 4.0$ Hz, H_a–C(14)), 3.39, 3.27 (br, 2H, H−C(7′) and H−C(7)), 2.8 (br, 2H, H−C(10) and H−C(10′)), 2.56 (ddd, 2H, $J = 10.2, 4.9, 4.9$, H_b–C(9) and H_b–C(9′)), 2.16 (ddd, 1H, $J = 6.0, 6.0, 2.6$ Hz, H−C(8′)), 2.08 (ddd, 1H, $J = 6.0, 6.0, 2.6$ Hz, H−C(8)), 1.46 (m, 4H, H_b–C(14), H_a–C(9) and H−C(14′)), 1.41, 1.33 (s, 6H, H−C(13) and H−C(13′)), 1.34 (d, 1H, $J = 8.5$ Hz, H_a–C(9′)), 0.65, 0.58 (s, 6H, H−C(12) and H−C(12′)). ^{13}C NMR ($CDCl_3$): δ 160.0, 158.5, 154.0 (C(2), C(6), C(2′), C(6′)), 141.5 (C(5) and C(5′)), 141.1 (C(15)), 133.9 (C(4) and C(4′)), 129.4, 128.3 (4C, C(16) and C(17)), 125.8 (C(18), 117.8 (C(3) and C(3′)), 47.1 (C(10′)), 46.9 (C(10)), 46.8 (C(8′)), 46.2 (C(7)), 42.6 (C(8)), 41.5, 41.2 (C(11) and C(11′)), 38.8 (C(7′) and C(14)), 28.6, 28.2 (C(9) and C(9′)), 26.33, 26.28 (C(13) and C(13′)), 20.9, 20.8 (C(12) and C(12′)), 18.4 (C(14′)). CI-MS: *m*/*z* 449 (100, $M^+ - H$), 371 (15, $M^+ - C_6H_5$), 357 (23, $M^+ - C_7H_7$).

(−)-Ethylpinene[5,6]bipyridine VIb. To a solution of 4.4 mmol of LDA in THF, made from 4.4 mmol of *n*-butyllithium and 4.8 mmol of diisopropylamine, was added at −40 °C a solution of 4.0 mmol of **VI** in 20 mL of dry THF. The reaction mixture was kept at −40 °C for 2 h, and then 8.0 mmol of ethyl iodide was added. The reaction mixture was stirred at room temperature overnight. Most of the solvent of the quenched mixture was removed, a few milliliters of water was added, and the remaining aqueous phase was extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$ and filtered and the solvent removed. **VIb** was purified by column chromatography (80 g SiO_2; hexane/EtOAc/TEA, 8:1:1). Yield: 603 mg (54%) of pure **VIb**. Recrystallization from ethanol gave colorless crystals.

Data for Compound VIb. Mp: 69 °C. TLC (hexane/20% ethyl ether): R_f 0.16. ^{1}H NMR ($CDCl_3$): δ 8.59 (ddd, 1H, $J = 4.8, 1.8, 1.0$ Hz, H−C(6′)), 8.41 (dd, 1H, $J = 8.0, 1.0$ Hz, H−C(3′)), 8.05 (d, 1H, $J = 7.8$ Hz, H−C(3)), 7.71 (ddd, 1H, $J = 8.0, 8.0, 1.8$ Hz, H−C(4′)), 7.25 (d, 1H, $J = 7.8$ Hz, H−C(4)), 7.17 (ddd, 1H, $J = 7.5, 4.8, 1.2$ Hz, H−C(5′)), 2.92 (d, 1H, $J = 10.2$ Hz, H−C(7)), 2.73 (dd, 1H, $J = 5.8, 5.8$ Hz, H−C(10), 2.55−2.35 (m, 2H, H_b–C(9) and H−C(14)), 2.31 (ddd, 1H, $J = 6.0, 6.0, 2.6$ Hz, H−C(8)), 1.48 (m, 1H, H−C(14)), 1.38 (s, 3H, H−C(13)), 1.26 (d, 1H, $J = 9.7$ Hz, H_a–C(9)), 1.07 (t, 3H, $J = 7.5$ Hz, H−C(15)), 0.61 (s, 3H, H−C(12)). ^{13}C NMR ($CDCl_3$): δ 159.6, 156.8, 153.1 (C(2), C(6), C(2′)), 148.8 (C(6′)), 141.9 (C(5)), 135.5 (C(4′)), 133.3 (C(4)), 122.8 (C(5′)), 120.6 (C(3′)), 117.6 (C(3)), 46.8 (C(10)), 45.9 (C(7)), 42.8 (C(8)), 40.9 (C(11)), 28.3 (C(9)), 26.3 (C(13)), 25.3 (C(14)), 20.8 (C(12)), 12.4 (C(15)). EI-MS: *m*/*z* 278 (15, M^+), 263 (22, $M^+ - CH_3$), 249 ($M^+ - C_2H_5$), 235 (95), 207 (100). Anal. Calcd for $C_{19}H_{22}N_2$ (278.40): C 81.97, H 7.97, N 10.06. Found: C 81.82, H 8.01, N 10.09.

[Cu^I((−)-V)$_2$]ClO_4 (1). A 10 mL round-bottom flask was charged with 100 mg (0.29 mmol) of **V** and 48 mg (0.145 mmol) of **[**$Cu(MeCN)_4$**]**ClO_4. A 5 mL sample of methanol was added, and the mixture was stirred at room temperature for 30 min. The deep-red solution was allowed to evaporate. After 3 days white crystals of starting material **V** precipitated and were filtered. The solvent of the filtrate was evaporated and the residue redissolved in CH_2Cl_2. Crystallization from methanol yielded red crystals. Yield: 115 mg (93%).

Data for Compound 1. Mp: 195 °C. ^{1}H NMR (d_6-DMSO): δ 8.35 (d, 4H, $J = 8.0$ Hz, H−C(3) and H−C(3′)), 7.78 (d, 4H, $J = 8.0$ Hz, H−C(4) and H−C(4′)), 3.33 (m, 8H, H−C(7) and H−C(7′)), 2.96 (dd, 4H, $J = 5.4, 5.0$ Hz, H−C(10) and H−C(10′)), 2.63 (m, 4H, H_b–C(9) and H_b–C(9′)), 2.09 (m, 4H, H−C(8) and H−C(8′)), 1.30 (s, 12H, H−C(13) and H−C(13′)), 1.10 (d, 4H, $J = 9.6$ Hz, H_a–C(9) and H_a–C(9′)), 0.45 (s, 12H, H−C(12) and H−C(12′)). ^{13}C NMR (CD_3CN): δ 156.4, 150.7 (C(2), C(2′) and C(6), C(6′)), 145.7 (C(5), C(5′)), 135.4 (C(4), C(4′)), 119.3 (C(3), C(3′)), 46.9 (C(10), C(10′)), 40.5 (C(8), C(8′)), 40.1 (C(11), C(11′)), 37.9 (C(7), C(7′)), 32.5 (C(9), C(9′)), 25.8 (C(13), C(13′)), 21.6 (C(12), C(12′)). FAB-MS: *m*/*z* 751 (68, [Cu(**V**)$_2$]$^+$), 407 (100, [Cu(**V**)]$^+$). Anal. Calcd for $C_{48}H_{56}N_4O_4ClCu$ (852.0): C 67.67, H 6.62, N 6.57. Found: C 67.30, H 6.59, N 6.33. Optical rotation: $[\alpha]_D = -315°$ ($c = 1.55$ mM in MeCN, 20 °C). UV−vis (MeCN, nm (ϵ)): 276 (50000), 310 (45000), 445 (6200). CD (MeCN, nm ($\Delta\epsilon$)): 283 (−7.0), 311 (−12.2), 331 (2.8), 347 (−3.2), 451 (−2.02).

[Ag^I((−)-V)$_2$]PF_6 (2). A 253 mg (0.1 mmol) sample of $AgPF_6$ was dissolved in 2 mL of MeOH and treated with 3 mL of a solution of 69 mg (0.2 mmol) of **V** in acetone. The colorless solution was stirred for 30 min in the dark, and then the solvent was evaporated. Crystallization was unsuccessful.

Data for Compound 2. ^{1}H NMR (CD_3CN): δ 8.03 (d, 4H, $J = 8.0$ Hz, H−C(3) and H−C(3′)), 7.60 (d, 4H, $J = 8.0$ Hz, H−C(4) and H−C(4′)), 3.0−2.9 (m, 12H, (H−C(7), H−C(7′) and H−C(10), H−C(10′)), 2.68 (m, 4H, H_b–C(9) and H_b–C(9′)), 2.19 (septet, 4H, $J = 5.8$ Hz, H−C(8) and H−C(8′)), 1.34 (s, 12H, H−C(13) and H−C(13′)), 1.18 (d, 4H, $J = 9.8$ Hz, H_a–C(9) and H_a–C(9′)), 0.56 (s, 12H, H−C(12) and H−C(12′)). ^{13}C NMR (CD_3CN): δ 156.7, 150.4 (C(2), C(2′) and C(6), C(6′)), 145.3 (C(5), C(5′)), 136.6 (C(4), C(4′)), 119.9 (C(3), C(3′)), 46.8 (C(10), C(10′)), 40.8 (C(8), C(8′)), 40.2 (C(11), C(11′)), 39.1 (C(7), C(7′)), 32.4 (C(9), C(9′)), 25.9 (C(13), C(13′)), 21.5 (C(12), C(12′)).

[Co^{II}((−)-V)$_2$]ClO_4 (3). A 203 mg (0.59 mmol) sample of **V** was suspended in 20 mL of acetonitrile and treated with a pink solution of 108 mg (0.295 mmol) of $[Co(H_2O)_6](ClO_4)_2$ in acetonitrile. On addition the reaction mixture turned red and the solid ligand dissolved. After additional stirring at room temperature for 30 min the solvent was removed at room temperature. Attempts to crystallize the complex failed. Complex **3** is soluble in CH_2Cl_2, MeCN, and MeOH and insoluble in hexane.

Data for Compound 3. FAB-MS: *m*/*z* 846 (43, [Co(**V**)$_2$]ClO_4^+), 747 (41, [Co(**V**)$_2$]$^+$), 502 (77, [Co(**V**)]ClO_4^+), 403 (100, [Co(**V**)]$^+$), 345 (94, $C_{24}H_{29}N_2$). UV−vis (MeCN, nm (ϵ)): 277 (30000), 332 (26000), 444 (940), 475 (730), 575 (280). CD (MeCN, nm ($\Delta\epsilon$)): 299 (1.1), 352 (−12.7), 642 (−0.5).

[Co^{II}((−)-V)]Cl_2 (4). A 368 mg (1.07 mmol) sample of **V** was mostly dissolved in 60 mL of MeOH/30% MeCN. To this solution was added 30 mL of a solution of $CoCl_2 \cdot 6H_2O$ in the same solvent mixture. On addition a deep-green solution formed immediately. The solvent was allowed to evaporate at room temperature over a period of 7 days. The crystals were collected and dried. Yield: 335 mg (66%). Crystals suitable for X-ray diffraction were obtained from a CH_2Cl_2 solution, covered by pentane.

Data for Compound 4. FAB-MS: *m*/*z* 473 (5, [Co(**V**)]Cl_2), 438 (100, [Co(**V**)]Cl^+). Anal. Calcd for $C_{24}H_{28}N_2Cl_2Co$ (474.29): C 60.77, H 5.95, N 5.91. Found: C 60.40, H 6.05, N 5.57. Optical rotation: $[\alpha]_D = -148°$ ($c = 1.0$ mM in CH_2Cl_2, 25 °C).

Acknowledgment. We thank Dr. Catherine Goujon-Ginglinger for her help with the preparation of the manuscript. This work was supported by the Swiss National Science Foundation.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010411W