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Synthesis and Coordination Chemistry of the First C_2-Chiral Bisoxazine Ligand

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The ligand 2,5-bis(oxazinyl)-3,4-diethylpyrrole (**4**) was obtained in three reaction steps from the known pyrrole derivative 3,4-diethylpyrrole-2,5-dicarboxylic acid (**1**) which was first coupled with 2 molar equiv of (*S*)-1-benzoxy-3-butylamine to give the corresponding diamide **2** using dicyclohexylcarbodiimide and 1-hydroxybenzitriazole as coupling reagents. Subsequent hydrogenolysis of the benzyl ether functions yielded the dialcohol **3** which was cyclized in high yield after methylsulfonation and treatment with an excess of NaOH giving the target compound 2,5-bis[2-{*(S)*-5-methyloxazinyl}]-3,4-diethylpyrrole (**4**). Lithiation of **4** by reaction with 1 molar equivalent of *n*BuLi at −78°C and addition of [$PdCl_2$(COD)] to the lithium pyrrolide cleanly gave the palladium complex **5** which was fully characterized. Complex **5** is unstable in solution and dimerizes to give a mixture of two diastereomeric helical dinuclear complexes, **6a** and **6b**, which cocrystallized in a 1:1 ratio to give X-ray quality single crystals. Both isomers possess virtual molecular 2-fold symmetry (though no crystallographic rotational symmetry), the molecular C_2-axis being orthogonal to the Pd···Pd vector.

Introduction

Oxazolines and their derivatives have been studied in a wide range of applications in asymmetric catalysis and belong to the basic "tool kit" of ligand design in this field.[1−12] In contrast, the coordination chemistry of the analogous chiral six-member heterocycles, the 4*H*-1,3-oxazines, is barely studied to date.[13−17] One of the main reasons for the paucity of the latter is the lack of natural sources for the chiral 3-aminoalkan-1-ols which are the precursor materials in the synthesis of these heterocycles. This is in contrast to the abundance of the enantiomerically pure 2-aminoalkan-1-ols derived from amino acids, ephedrins, and so forth.

Whereas the oxazoline ring systems are almost planar and possess the rigidity desired for the construction of a well-defined chiral environment in asymmetric catalysis, the six-membered ring systems of the oxazine analogues are much more flexible and may adopt chair and boat type conformations. This problem may be circumvented by ring fusion, a strategy pursued by Evans[13,14] and Kündig[15,16] in their phosphinophenyloxazine derivatives. Both these fused systems **I**[13,14] and **II**[15,16] and a more flexible monocyclic derivative studied by Zehnder et al. (**III**)[17] proved to give high enantioselectivities in a number of chiral catalytic transformations (Chart 1).

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Scheme 1. Three Step Synthesis of the Ligand Precursor 3,4-Diethylpyrrole-2,5-bis[*(S)*-4-methyl-4*H*-1,3-oxazine] (**4**)

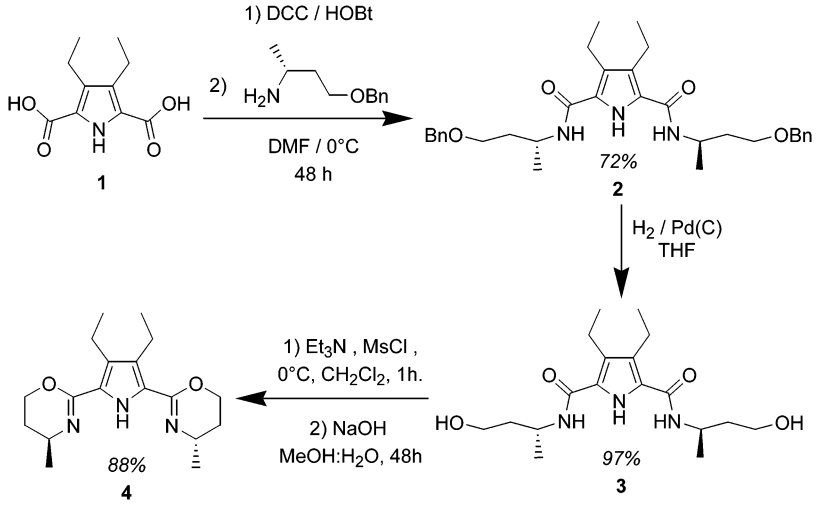


Chart 1

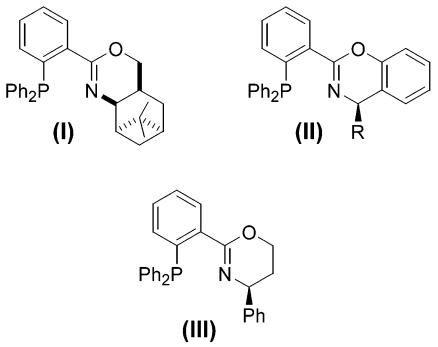
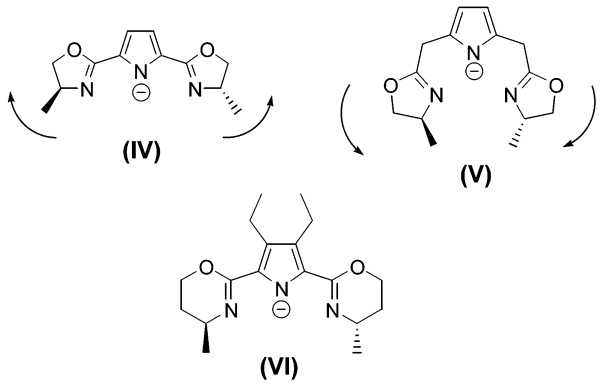


Chart 2



As Kündig pointed out,[15,16] a potential advantage of the replacement of the oxazoline rings by the larger oxazines is the somewhat different orientation of the substituent group at the chiral center adjacent to the N-donor atoms. Moreover, when integrated into a polydentate ligand, the ligating atom points further inward toward a metal center than is the case with the analogous oxazoline derivatives. This was an important consideration in our development of new C_2-chiral tridentate monoanionic ligands such as the bis(oxazolinyl)-pyrroles (**IV**, Chart 2) we recently developed[18,19] which may be viewed as charged analogues to the well-established neutral "pybox" ligands.[5−9]

The arrangement of the three N-donor functions in these ligands proved to be unsuitable for the complexation of a single metal center, yielding instead helical dimeric complexes. To overcome this problem of additional stereochemical complexity, we have modified the arrangement of the donor atoms both by integration of bridging methylene groups linking the heterocycles (**V**)[20] and by increasing the size of the outer chiral heterocycles. In this paper, we report the first example of a C_2-chiral bisoxazine ligand (**VI**) and its complexation to palladium(II).

Results and Discussion

The ligand 2,5-bis(oxazinyl)-3,4-diethylpyrrole (**4**) was obtained in three reaction steps from the known pyrrole derivative 3,4-diethylpyrrole-2,5-dicarboxylic acid (**1**) as is shown in Scheme 1.

Diacid **1** was first coupled with 2 molar equivalents of *(S)*-1-benzoxy-3-butylamine to give the diamide **2** by a well-established coupling protocol using dicyclohexylcarbodiimide and 1-hydroxybenzotriazole in DMF at 0 °C.[21,22] Subsequent hydrogenolysis of the benzyl ether functions yielded dialcohol **3** which was cyclized in high yield after methylsulfonation and treatment with an excess of NaOH.[23,24] After workup, the target compound 2,5-bis[2-{*(S)*-5-methyloxazinyl}]-3,4-diethylpyrrole (**4**) was obtained as a pale yellow oil. Its formulation was confirmed by elemental analysis and the observation of its molecular ion peak at $m/z = 317$ amu in the EI mass spectrum while the molecular structure depicted in Scheme 1 is consistent with the signal patterns in the ^{1}H and ^{13}C NMR spectra. The ν(N−H) and ν(C=N) bands at 3444 and 1641 cm^{-1} are the most characteristic features in the infrared spectrum.

Lithiation of bis(oxazinyl)pyrrole (**4**) by reaction with 1 molar equivalent of *n*BuLi at −78 °C and addition of [$PdCl_2$-(COD)] to the lithium pyrrolide cleanly gave palladium complex **5** which was isolated after chromatographic workup

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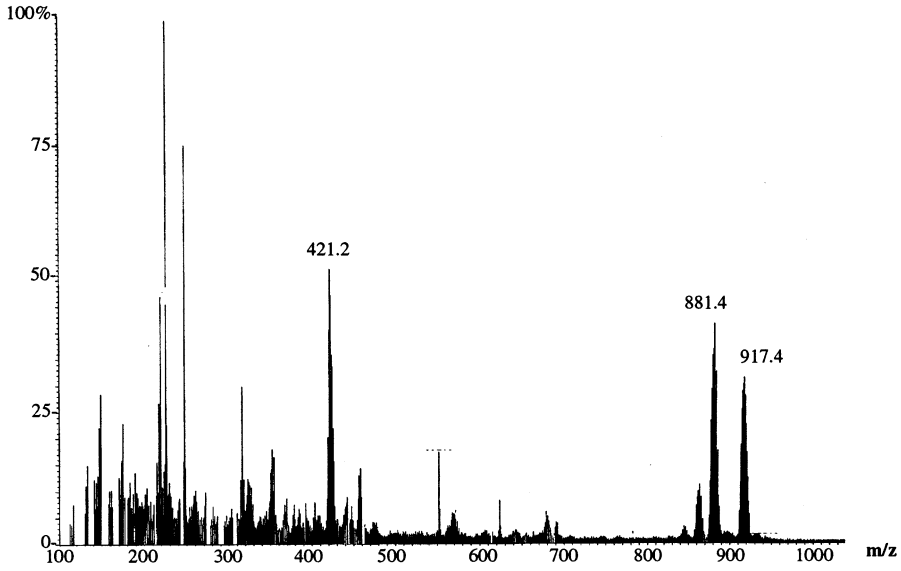
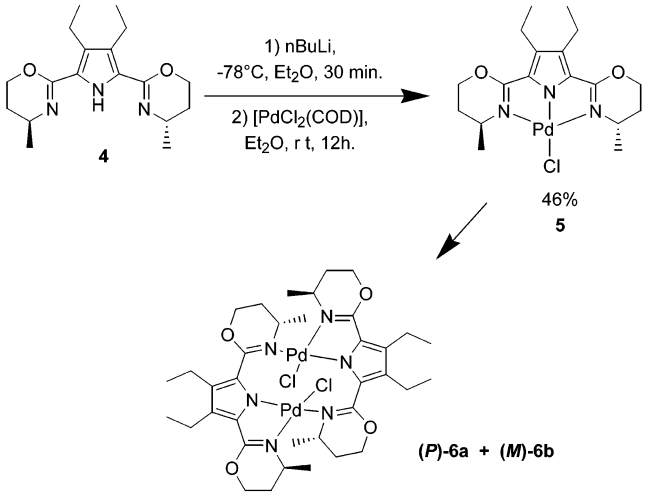


Figure 1. Positive ion FAB mass spectrum of **6a/b** showing the molecular ion (+H) peak at 917 amu for the dinuclear complex, the corresponding {dimer − Cl} ion (881.4) as well as the mononuclear {ligand + Pd}$^+$ at 421 amu.

Scheme 2. Synthesis of Bisoxazine−Palladium Complex **5** and Its Dimerization to Give the Mixture of Helical Diastereomers **6a/b**



(Scheme 2). The signal patterns in the ^{1}H and ^{13}C NMR spectra are consistent with the overall 2-fold symmetry of the C_2-chiral monomeric complex, the individual resonances being shifted with respect to those of ligand precursor **4**. In particular, the ^{13}C NMR signal of the quaternary *C*═N nucleus adjacent to the N-donor atoms in the oxazine rings is shifted from δ 150.1 in **4** to δ 161.1 in **5**.[7,8] The tricoordination of the ligand is supported by the observation of a single ν(C═N) band at 1630 cm^{-1} in the infrared spectrum of **5**.

Complex **5** is unstable in solution and dimerizes over a period of several hours to give a mixture of two diastereomeric helical dinuclear complexes, **6a** and **6b**, analogous to those which were directly and exclusively isolated for the palladium(II) compounds containing the analogous bis(oxazolinyl)pyrrole ligands which we previously studied.[18,19] The dimerization may be directly inferred from the positive ion FAB mass spectrum of the material (Figure 1) obtained after the complete conversion of **5** to **6a/b**, while the CHN analytical data remain unaltered. The molecular ion (+H) peak at 917 amu for the dinuclear complex is associated with the isotopomer distribution of the {dimer − Cl} ion. The mononuclear {ligand + Pd}$^+$ ion is observed at 421 amu.

In contrast to the helical dinuclear Pd^{II} complexes bearing chiral bis(oxazolinyl)pyrrole ligands,[19] the separation of the diastereomers **6a** and **6b** by chromatography was not possible. To establish the molecular structures of these complexes by X-ray diffraction, their direct crystallization from the product mixture was attempted. Both isomers cocrystallized in a 1:1 ratio to give X-ray quality single crystals. The triclinic crystals (space group *P*1) contain one molecule each of **6a** and **6b** in the unit cell which represent the *P* and the *M* helical isomers, respectively. Their molecular structures are depicted in Figure 2 along with the principal bond lengths and angles which are not affected by the unresolved disorder in the six-membered dihydrooxazine rings of the ligands.

In the two diastereomeric dimers found in the unit cell, one of the oxazinyl units and the anionic pyrrolide occupy two coordination sites in an approximately square planar ligand arrangement at the Pd centers and thus generate an essentially planar unit. The second oxazinyl ring, however, is twisted out of this plane and binds to the second metal center, and it is this twist in the two bridging ligands which is the key structural element in the helical overall arrangement of the compounds. The oxazinyl rings are nonplanar; however, it proved not possible to resolve the disorder between the conformers, as is reflected in the large vibrational ellipsoids. The following structural dicussion is not affected by this deficiency.

Both isomers possess virtual molecular 2-fold symmetry (though no crystallographic rotational symmetry), the molecular C_2-axis being orthogonal to the Pd···Pd vector which implies that the idealized helical arrangement is associated with only one torsion angle between the pyrolide ring and the oxazolinyl unit bound to the second metal center.[25−27] For the complexes **6a** and **6b**, the average twist angles are 33.5° and 31.6°, respectively. This decrease of the torsional

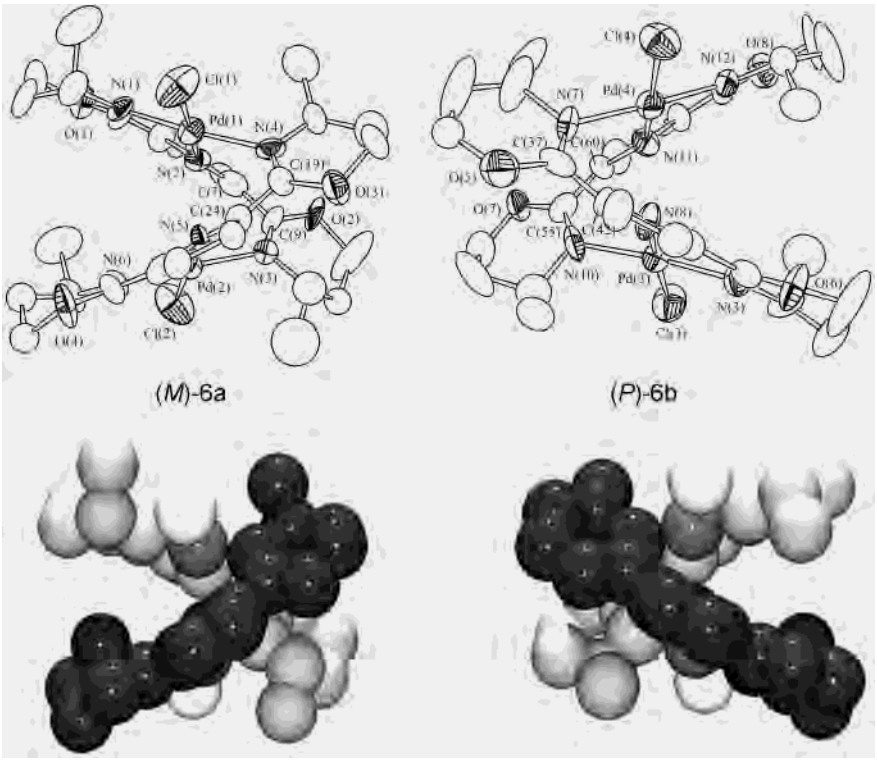


Figure 2. Top: Molecular structures of the two diastereomeric herical palladium complexes cocrystallizing in the same unit cell. Bottom: Comparison of the space filling models of the two helicates. In both cases, diethyl substituents of the pyrrole ring have been omitted for clarity. Selected bond lengths (Å) and interbond angles (deg) follow. **6a**: Pd(1)−Cl(1) 2.28(5), Pd(1)−N(1) 2.03(1), Pd(1)−N(2) 2.07(1), Pd(1)−N(4) 2.09(1), Pd(2)−Cl(2) 2.30(7), Pd(2)−N(3) 2.07(1), Pd(2)−N(5) 1.97(1), Pd(2)−N(6) 2.05(1); Cl(1)−Pd(1)−N(1) 92.4(4), Cl(1)−Pd(1)−N(2) 171.1(4), N(2)−Pd(1)−N(4) 97.2(4), Cl(2)−Pd(2)−N(6) 96.0(3), Cl(2)−Pd(2)−N(5) 174.5(4), N(5)−Pd(2)−N(3) 96.6(5), N(2)−C(7)−C(9)−N(3) 33.0, N(4)−C(19)−C(24)−N(5) 33.9. **6b**: Pd(3)−Cl(3) 2.29(4), Pd(3)−N(9) 2.02(5), Pd(3)−N(8) 2.07(3), Pd(3)−N(10) 2.03(7), Pd(4)−Cl(4) 2.31(2), Pd(4)−N(12) 2.01(6), Pd(4)−N(11) 2.00(1), Pd(4)−N(7) 2.00(5); Cl(3)−Pd(3)−N(9) 92.5(3), Cl(3)−Pd(3)−N(8) 173.3(7), N(8)−Pd(3)−N(10) 97.5(4), Cl(4)−Pd(4)−N(7) 87.2(0), Cl(4)−Pd(4)−N(11) 169.9(8), N(7)−Pd(4)−N(11) 98.1(3), N(7)−C(37)−C(42)−N(8) 29.4, N(10)−C(55)−C(60)−N(11) 33.8.

angle upon going from **6a** to **6b** is associated with a slight increase in the Pd···Pd distance from 3.415 to 3.551 Å.

The principal structural differences between molecular structures of complexes **6a** and **6b** are most readily visualized by comparison of their molecular shapes represented by the space filling models depicted below the ORTEP plots in Figure 2. The most apparent consequence of the two different senses in which the ligands "wrap around" the two Pd centers in the helical isomers is the orientation of the methyl substituents in the oxazine rings vis-à-vis the groove of the helix. In the (*M*)-isomer, **6b**, the methyl groups point inside the groove toward the other helical strand, whereas the (*P*)-isomer, **6a**, displays the opposite orientation. In both structures, there is apparently no significant "interstrand" repulsion between the ligand peripheries [e.g., closest contacts between the alkyl fragments > 4.0 Å]. There is, thus, apparently no energetic preference for one of the diastereomers based on factors related to steric repulsion.

Conclusions

The isolation of a monomeric palladium complex in this first investigation into the coordination chemistry of a bis-(4*H*-1,3-oxazinyl)pyrrole ligand has confirmed the expected effect that a reorientation of the N-donor functions in comparison to those of the oxazoline analogues would have. However, the stabilization of the desired C_2-chiral monomer is as yet insufficient to prevent the slow dimerization of such a complex in solution. We have been able to structurally characterize the two diastereomeric helicates obtained in this aggregation process while being unsuccessful in separating them to date. We are currently varying the periphery of this ligand system. The replacement of the methyl groups at the chiral centers of the oxazine ring by bulkier aryl or alkyl substituents might suppress the dimer formation and make the complexes bearing this type of chiral ligand more adapted to an application in asymmetric catalytic transformations. These ligands would constitute charged alternatives to the chiral "pybox" derivatives[5−9] and thus give access to different coordination geometries in the catalyst precursors.

Experimental Section

Solvents were dried according to the standard procedures and saturated with nitrogen. Solids were separated from suspensions by centrifugation, thus avoiding filtration procedures, using a Hettich Rotina 48 centrifuge equipped with a specifically designed Schlenk tube rotor (Hettich Zentrifugen, Tuttlingen, Germany).[28] The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 300 (^{1}H 300 MHz; ^{13}C{^{1}H} 75 MHz), Bruker AM 400 (^{1}H 400 MHz;

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$^{13}C\{^1H\}$ 100 MHz), and Bruker ARX 500 (^1H 500 MHz; $^{13}C\{^1H\}$ 125 MHz) spectrometers. Infrared spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer and UV spectra on a Varian Cary 05E UV−vis NIC spectrometer. EI mass spectra were recorded on a Shimadzu QP5050-GC/MS system. The elemental analysis were carried out by the Service Commun de Microanalyze de l'Université Louis Pasteur of Strasbourg. 2,5-Dicarboxyl-3,4-diethylpyrrole (**1**)[29−33] and $[PdCl_2(1,5\text{-COD})]$[34] were prepared according to the previously described procedures. *(S)*-1-Benzoxy-3-butylamine was provided by BASF AG (Ludwigshafen, Germany). All other chemicals used as starting materials were obtained commercially and used as received without further purification.

Preparation of the Compounds. 3,4-Diethylpyrrole-2,5-bis-[(*S*)-1-benzoxy-3-butyl]carboxamide (2). To a solution of 3,4-diethylpyrrole-2,5-dicarboxylic acid (0.5 g, 2.37 mmol) in 75 mL of DMF were added 1.075 g of DCC (5.21 mmol) and 0.704 g of HOBt (5.21 mmol) at 0 °C. After 30 min, 0.919 g of (*S*)-1-benzyloxy-3-butylamine (5.21 mmol) was added portionwise. The resulting mixture was then stirred for 48 h under a nitrogen atmosphere at room temperature. The reaction mixture was filtered and washed with DMF and the solvent removed under vacuum. The mixture is retaken in EtOAc and washed several times with a satured $NaHCO_3$ aqueous solution, and the combined aqueous layer was extracted with EtOAc. The combined organic layers were washed successively with brine and water and then dried over anhydrous Na_2SO_4. After chromatographic work-up (SiO_2; hexanes−EtOAc 2:1), the product was isolated as a pale off-white solid (0.911 g, 1.71 mmol, 72% yield). ^1H NMR (300 MHz, $CDCl_3$, 295 K): 10.5 (broad s, 1H, NH_{pyrr}); 7.28 (m, 10H, Ph); 6.70 (d, 2H, NHC═O, ^3J = 7.9 Hz); 4.46 (s, 4H, C*H*$_2$Ph); 4.35 (m, 2H, NC*H*); 3.56 (m, 4H,C*H*$_2$O); 2.53 (q, 4H, $CH_{2\ pyrr}$); 1.88 (m, 2H, C*H*H,-CH_2O); 1.76 (m, 2H, CH*H*,CH_2O); 1.21 (d, 6H, CH_3, ^3J = 6.6 Hz); 1.11 (s, 6H, CH_{3pyrr}).

$\{^1H\}^{13}C$ NMR (75 MHz, $CDCl_3$, 295 K): 160.9 ($C_{3/4pyrr}$); 137.9 (NH*C*═O); 128.3 (C_{Ar}); 127.9 (C_{Ar}); 127.7 (C_{Ar}); 127.6 (C_{Ar}); 123.5 ($C_{2/5pyrr}$); 73.3 (OCH_2); 67.2 (CH_2); 43.5 (CH); 35.7 (CH_2); 20.1 (CH_3); 17.5 ($CH_{2\ pyrr}$); 15.9 (CH_{3pyrr}). IR (KBr disk): 3414 (w), 2931 (m), 1707 (w), 1634 (m), 1552 (m), 1459 (m), 1420 (m), 1098 (m), 896 (m). Anal. Calcd for $C_{32}H_{43}N_3O_4$ (533.70): C, 72.01; H, 8.12; N, 7.87. Found: C, 71.97; H, 8.04 N, 7.99.

3,4-Diethylpyrrole-2,5-bis[{*(S)*-1-hydroxyl-3-butyl}-carboxamide] (3). Compound **2** (3 g) was dissolved in 25 mL of THF, and activated palladium on charcoal (4.1 equiv) was added. The mixture was stirred under an hydrogen atmosphere (1 bar) for 2 h, then filtered, and washed several times with THF. After removal of the solvent, the product diol **3** was isolated as a pale yellow oil (1.927 g, 97% yield). ^1H NMR (300 MHz, $CDCl_3$, 295 K): 10.8 (broad s, 1H, NH_{pyrr}); 6.49 (d, 2H, NHC═O, ^3J = 8.4 Hz); 4.34 (m, 2H, CH); 3.99 (s broad, 2H, OH); 3.62 (m, 4H,C*H*$_2$O); 2.67 (q, 4H, CH_{2pyrr}); 1.85 (m, 2H, C*H*H,CH_2O); 1.24 (d, 6H, CH_3, ^3J = 6.7 Hz); 1.15 (s, 6H, CH_{3pyrr}). $\{^1H\}^{13}C$ NMR (75 MHz, $CDCl_3$, 295 K): 161.9 ($C_{3/4pyrr}$); 128.5 (NH*C*═O); 122.3 ($C_{2/5pyrr}$); 58.7 (CH_2); 42.4 (CH); 39.9 (CH_2); 21.0 (CH_3); 17.8 (CH_{2pyrr}); 15.8 (CH_{3pyrr}). IR (KBr disk): 3426 (w), 1720 (m), 1612 (m), 1516 (m), 1422 (m), 1096 (s), 973 (s), 895 (s). Anal. Calcd for $C_{18}H_{31}N_3O_4$ (353.46): C, 61.17; H, 8.84; N, 11.89. Found: C, 61.01; H, 8.97; N, 11.55.

3,4-Diethylpyrrole-2,5-bis[(*S*)-4-methyl-4*H*-1,3-oxazine] (4). To an ice cold solution of **3** (2.0 g, 5.66 mmol) and Et_3N (25.0 mmol) in 20 mL of dichloromethane was slowly added 3.5 mL of MsCl (14.2 mmol). The mixture was allowed to warm to room temperature and reacted for 1 h. After washing with water (5 mL), the organic phase was dried with Na_2SO_4, and the volatiles were removed in vacuo to give a yellow oil which was used in the next step without purification. The bis-mesylated compound was treated with NaOH (0.228 g, 5.7 mmol) in 25 mL of a MeOH/H_2O mixture (5:1). The reaction mixture was stirred at room temperature for 3 days, then washed with water, and dried over Na_2SO_4. The solvents were removed to give **4** as a pale yellow oil in 88% yield (1.581 g).

^1H NMR (300 MHz; $CDCl_3$): 10.1 (br s, 1H, NH_{pyrr}); 4.25 (m, 4H, OCH_{2oxa}); 3.56 (m, 2H, CH_{oxa}); 2.66 (q, 4H, CH_{2pyrr}); 1.95 (m, 2H, C*H*H $_{oxa}$); 1.61 (m, 2H, CH*H*$_{oxa}$); 1.20 (d, 6H, CH_3, ^3J = 6.8 Hz); 1.07 (t, 6H, CH_{3oxa}). $\{^1H\}^{13}C$ NMR (75 MHz, $CDCl_3$, 295 K): 150.1 (C═N_{oxa}); 127.9 ($C_{2/5pyrr}$); 121.8 ($C_{3/4pyrr}$); 63.4 (CH_2); 47.6 (CH); 30.4 (CH_2); 24.1 (CH_3); 18.7 (CH_{2pyrr}); 17.0 (CH_{3pyrr}). IR (CH_2Cl_2): 3444 (m); 2966 (s), 1641 (s), 1523 (w), 1452 (w), 1314 (m), 1258 (s), 909 (w), 805 (w) cm^{-1}. Anal. Calcd for $C_{18}H_{27}N_3O_2$ (317.43): C, 68.11; H, 8.57; N, 13.24. Found: C, 67.92; H, 8.44 N, 13.20.

[(Bisoxazine)PdCl] (5). A solution of **4** (0.1 g; 0.32 mmol) in 20 mL of Et_2O was cooled under a nitrogen atmosphere to −78 °C. A 1.6 M solution of ^{n}BuLi in hexanes (0.20 mL) was added and the mixture stirred at this temperature for half an hour and warmed to room temperature. A suspension of $[PdCl_2(1,5\text{-COD})]$ (0.100 g, 0.35 mmol) in 15 mL of diethyl ether was then added via a cannula. After the addition was completed, the reaction mixture was stirred for 8 h. The reaction mixture was filtered over a pad of Celite and the solvent removed in vacuo. The orange residue was subjected to a rapid flash column chromatography (silica gel; hexanes−EtOAc 1:6). ^1H NMR (300 MHz; $CDCl_3$): 4.35 (m, 4H, OCH_{2oxa}); 3.58 (m, 2H, CH_{oxa}); 2.33 (q, 4H, CH_{2pyrr}); 2.20 (m, 2H, C*H*H$_{oxa}$); 1.17 (m, 2H, CH*H*$_{oxa}$); 1.38 (d, 6H, CH_3, ^3J = 6.7 Hz); 1.05 (t, 6H, CH_{3oxa}). $\{^1H\}^{13}C$ NMR (75 MHz, $CDCl_3$, 295 K): 161.1 (C═N_{oxa}); 128.3 ($C_{2/5pyrr}$); 106.3 ($C_{3/4pyrr}$); 62.8 (CH_2); 48.7 (CH); 29.7 (CH_2); 27.5 (CH_3); 17.4 (CH_{3pyrr}); 16.6 (CH_{2pyrr}). IR (KBr): 2924 (s), 1630 (s), 1585 (s), 1556 (s), 1456 (s), 1260 (s), 1098 (s), 1018 (s), 870 (m), 799 (s), 392 (m), 338 (w). Anal. Calcd for $C_{18}H_{26}ClN_3O_2Pd$ (458.29): C, 47.17; H, 5.72; N, 9.17. Found: C, 46.86; H, 5.59; N, 9.09.

Selected Spectroscopic Data for the Mixture of Diastereomers 6a/b. ^1H NMR (300 MHz; $CDCl_3$): 4.6−4.2 (m, OCH_{2oxa}); 3.5−3.7 (m, CH_{oxa}); second-order spectra between 0.87 and 2.70 ppm (CH_{2pyrr}, CH_{2oxa}, CH_3, CH_{3oxa}). $\{^1H\}^{13}C$ NMR (50 MHz, $CDCl_3$, 295 K): 164.5, 163.9, 163.4, and 162.1 (C═N_{oxa}); 130.8, 130.1, 129.1, and 128.3 ($C_{2/5pyrr}$); 101.3 and three other peaks not detected ($C_{3/4pyrr}$); 65.0, 62.9, 62.8, and 62.2 (CH_2); 51.9, 49.0, 48.7, and 46.9 (CH); 33.9, 29.0, 27.5, and 27.1 (CH_2); 25.7, 25.3 (2 peaks), and 25.0 (CH_3); 22.7, 21.9, 21.5, and 20.4 (CH_{3pyrr}); 18.8, 18.3, 17.4, and 16.6 (CH_{2pyrr}). IR (CH_2Cl_2): 2967 (m), 2926 (m), 1614 (s), 1608 (s), 1600 (s), 1525 (m), 1470(m), 1400 (s), 1281 (s), 1177 (s), 341 (w). Elemental analysis identical to that of **5**.

X-ray Crystallographic Study of 6a/b. Suitable crystals of cocrystallized compound **6a/b** were obtained by layering concentrated solutions of the compounds in dichloromethane with hexanes and allowing slow diffusion at room temperature. The crystal data were collected on a Nonius Kappa CCD diffractometer at −100 °C and transferred to a DEC Alpha workstation; for all subsequent

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Table 1. X-ray Experimental Data of Compound **6a/b**

	6a/b
formula	$C_{36}H_{52}Cl_2N_6O_4Pd_2$/ $C_{36}H_{52}Cl_2N_6O_4Pd_2$
molecular weight	916.56
cryst syst	triclinic
space group	*P*1
a (Å)	9.8399(3)
b (Å)	13.7785(7)
c (Å)	15.9563(5)
α (deg)	78.859(5)
β (deg)	72.529(5)
γ (deg)	72.664(5)
V (Å^3)	1957.0(1)
Z	1
ρ_{calcd} (g cm^{-3})	1.56
*F*000	936
μ (mm^{-1})	1.101
T (K)	294
wavelength (Å)	0.71073
radiation	Mo Kα
no. data measured	11386
no. data with $I > 3\,\sigma(I)$	7215
no. variables	886
R	0.042
wR_2	0.056
GOF	1.133

calculations, the Nonius OpenMoleN package was used.[35] The structure was solved using direct methods with absorption corrections being part of the scaling procedure of the data reductions. After refinement of the heavy atoms, difference Fourier maps revealed the maxima of residual electron density close to the positions expected for the hydrogen atoms; they were introduced as fixed contributors in the structure factor calculations with fixed coordinates (C−H: 0.95 Å) and isotropic temperature factors (B(H) = $1.3B_{eqv}$(C) Å^2) but not refined. Full least-squares refinements on F^2. A final difference map revealed no significant maxima of electron density. The scattering factor coefficients and the anomalous dispersion coefficients were taken from ref 36. Crystal data and experimental details for the crystals of **6a/b** are given in Table 1.

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Supporting Information Available: Details of the structure determination, tables of crystallographic data, and the positional and thermal parameters and interatomic distances and angles for **6a/b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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