Inorg. Chem. **2008**, *47*, 10575−10586

Chiral, Hemilabile Palladium(II) Complexes of Tridentate Oxazolidines, Including C_2-Symmetric "Pincers"

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Received June 27, 2008

Two classes of diastereomerically enriched chiral tridentate ligands incorporating either two oxazolidine and one pyridine (**1**) or two pyridine and one oxazolidine (**2a-c**) donor groups have been made in a high-yielding modular fashion from readily available enantiopure amino alcohols and aldehydes. Both ligand classes readily formed metal complexes via 1:1 reactions with *trans*-$PdCl_2(PhCN)_2$. The compounds Pd(**1**)Cl_2 and Pd(**2a-c**)Cl_2 were formed as mixtures of 3 and 2 diastereomers, respectively, owing to indeterminate absolute configuration at the C^2 position of their constituent oxazolidine rings. Within each diastereomeric manifold, the metal complexes existed as equilibrium mixtures of bi- and tridentate isomers in solution, the interconversion between which was very rapid even at −50 °C. The fluxional nature of the compounds was inferred from a combination of ^{1}H and ^{15}N NMR spectroscopic and solution conductivity data. Substitution of one chloride ligand for hexafluorophosphate gave as mixtures of diastereomers the salts [Pd(**1**-$\kappa N,\kappa^2 N'$)Cl]PF_6 (**8**) and [Pd(**2a-c**-$\kappa N,\kappa N',\kappa N''$)Cl]$PF_6$ (**12a-c**) in which the ligands were coordinated through all three N-donors. A single recrystallization of **8** gave in optically pure form the major diastereomer **8**^{maj}, which was characterized crystallographically. Complexes of **2a-c** differed substantially from those of the bis(pyridylmethyl)amine (bpma) ligand family with which they shared direct atom-for-atom connectivity in the coordinating groups. The amines are known to form exclusively the static tridentate complexes [PdCl(bpma-$\kappa N,\kappa^2 N'$)]Cl; the difference was attributed to torsional strain associated with the rigid oxazolidine ring in tricoordinated **2a-c**.

Introduction

The 1,3-oxazolidine ring system is well-known as a chiral auxiliary in asymmetric organic synthesis.[1] It is the annulated condensation product of a β-amino alcohol and an aldehyde and is the fully saturated analogue of the oxazoline (4,5-dihydrooxazole). Although the latter retains a position of privilege in the annals of asymmetric catalysis and has been used as the chiral component of a multitude of ligands that have been applied with exceptional success in a wide variety of metal-catalyzed asymmetric transformations,[2,3] the oxazolidine has seen very little application in this arena. It has instead been used as a stereodirecting group in purely organic transformations such as the preparation of *N*-substituted amino alcohols[4] and β-amino esters,[5] and epoxides.[1]

This contrast is perhaps surprising in light of the fact that the oxazolidine benefits from several of the same advantages that make the oxazoline such an attractive chiral ligand: Both ring systems are easily made in a modular way using essentially quantitative single reactions from readily available enantiopure amino alcohols, and it is trivial to imagine how they could be incorporated into a myriad of chiral ligand

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10.1021/ic8011926 CCC: $40.75
Published on Web 10/18/2008

Scheme 1. Syntheses of Pyridyloxazolines and -Oxazolidines

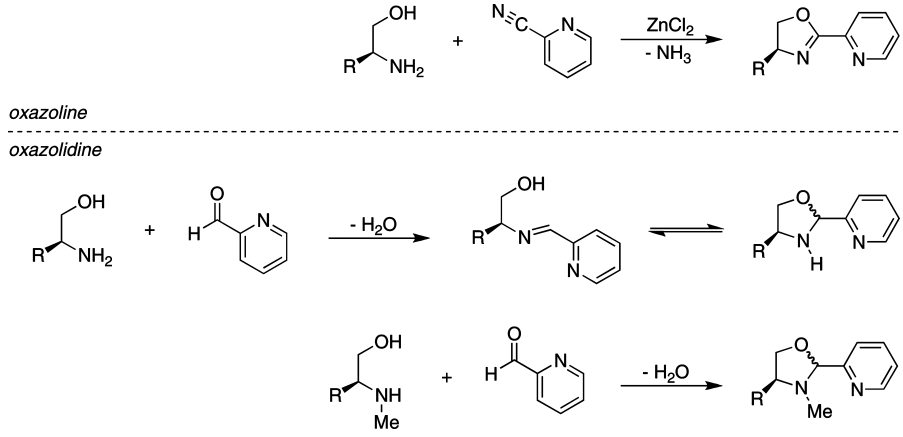
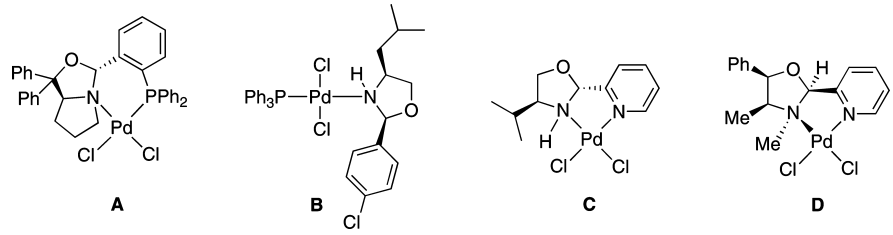


Chart 1. Oxazolidinyl Pd(II) Complexes



frameworks. This latter point is all the more true for the oxazolidine given the pioneering research that has already been done into the synthesis, coordination chemistry, and catalytic applications of the oxazoline.

However, oxazolidines differ from oxazolines in several important respects that have significant ramifications for the potential application of this ring system in asymmetric catalysis. Scheme 1 shows the syntheses of pyridyl derivatives, which are taken as illustrative and relevant examples. Whereas oxazolines are planar, oxazolidines, as a result of being fully saturated, are non-planar and incorporate an sp^3- as opposed to an sp^2-hybridized N-atom. Consequently, oxazolidines are more sterically demanding than oxazolines. Moreover, incorporation of an indeterminate stereocenter at the 2-position leads to diastereomers. When primary amino alcohols are used to make these species, an equilibrium mixture of oxazolidine and imine products results (Scheme 1), but we have shown that the formation of a metal complex can interrupt this reversible process.[6]

Even given the potential limitations, applications of oxazolidines in asymmetric transformations are beginning to emerge. These include the addition of Et_2Zn to aldehydes,[7] epoxidations,[8] allylic alkylations,[9,11] and Diels−Alder reactions.[10] In some cases, very high enantioselectivities have been achieved, for example, up to 98% (and 97% yield) in Pd-catalyzed allylic alkylation reactions.[11] Several examples of metal-oxazolidine (and some closely related thiazolidine) complexes are known, but these have typically been generated *in situ* in catalytic reaction mixtures.[12] With the exception of a few phosphinooxazolidine adducts, for example, **A**[10b] (Chart 1), metal-oxazolidine complexes have generally not been isolated or characterized. Moreover, there are very few reports of structural data. To the best of our knowledge, compound **B**, a closely related Pt(II)-oxazolidine adduct,[13] and our recently reported Pd(II) complex **C**[6] represent the only crystallographically characterized examples of metal-oxazolidine complexes incorporating coordinated NH-groups, that is, bearing oxazolidine ligands derived from primary amines.

This paper addresses the largely unexplored fundamental coordination chemistry of this potentially useful ring system. In a recent report,[6] we disclosed the syntheses and structures of Pd(II) complexes of bidentate pyridyloxazolidine ligands (**C** and **D**, Chart 1). Herein, we extend this early study by describing the syntheses of two new types of chiral tridentate ligands that incorporate both oxazolidinyl and pyridyl rings (Chart 2). Of particular interest to us was the potential for hemilabile coordination of these ligands and a comparison to the oxazoline-based fluxional systems developed primarily

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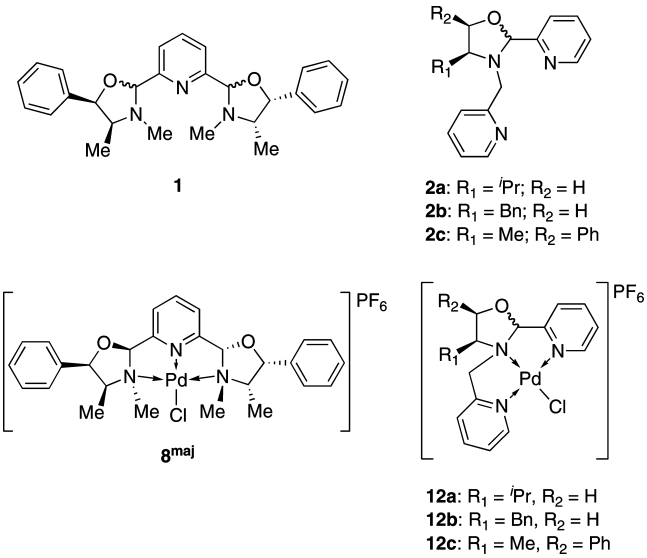
Chart 2. Pyridyloxazolidine Ligands Reported in This Work and Their Tridentate Pd(II) Complexes



by Braunstein.[14] In general, these systems are valuable because they provide the balance of stability and reactivity required for effective catalytic cycles. To the best of our knowledge, hemilabile behavior has not yet been documented for oxazolidine-based ligands.

The first of our new ligands, a bis(oxazolidinyl)pyridine (**1**), is the saturated, oxazolidinyl analogue of the now ubiquitous bis(oxazolinyl)pyridine (pybox) ligand class;[2] the second class (**2a-c**) "inverts" this architecture by attaching two pyridyl rings to a central oxazolidine. We show that in the presence of a coordinating chloride counterion, Pd(II) complexes of these ligands exist as rapidly exchanging $\kappa N,\kappa N'$ and $\kappa N,\kappa N',\kappa N''$ isomers. Exchange for a non-coordinating counterion prevents this fluxionality and leads to the formation of Pd(II) complexes in which the metal center is ligated by all three nitrogen donors (e.g., $\mathbf{8^{maj}}$ and **12a-c**).

Experimental Section

General Considerations. Unless otherwise noted, chemicals were obtained commercially and used as supplied and reactions were done under normal atmosphere. Primary amino alcohols and the Pd(II) precursor *trans*-$PdCl_2(PhCN)_2$ were made according to established literature procedures.[15,16] With the exception of **5b**, the precursors (**4a-d**, **5a,c,d**) to the ligand families **2a-c** and **3a,b** were known compounds and were prepared as previously reported.[6,17,18] The amino alcohol **5b** was prepared analogously to **5a,c,d**.

^1H and $^{13}C\{^1H\}$ NMR spectra were collected using a Varian Mercury 400 spectrometer (400.085 MHz for ^1H and 100.602 MHz for ^{13}C) or a Varian INOVA 400 spectrometer (399.762 MHz for ^1H and 100.520 MHz for ^{13}C). Spectra were recorded at room temperature (r.t.), and residual solvent proton (relative to external $SiMe_4$, δ 0.00) or solvent carbon (relative to external $SiMe_4$, δ 0.00) was used as an internal reference. Coupling constants are given in Hz. Peak multiplicity is reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), and triplet (t). Diastereomeric ratios were calculated from the relative areas of peaks corresponding to the C^2H or the C^5H protons of the oxazolidine ring(s). Heteronuclear multiple bond correlation (HMBC) ^{15}N spectra were collected using a shaped wave pulse on a Varian INOVA 600 spectrometer (599.3906433 MHz for ^1H) and were referenced to CH_3NO_2 (δ 0.00) as an external standard. N-atoms were observed indirectly via coupling with adjacent protons, which is a method that has been used previously by Thompson and co-workers.[19] The ^{15}N NMR signals were assigned as follows: oxazolidinyl N-atom (*ox*N), pyridyl N-atom (*py*N). The resistivity of Pd(II) complexes in CH_2Cl_2 solution was measured with a Biologic MCS-200 modular conductivity system (frequency, 200 000−500 Hz; amplitude, 50 mV; cell constant, 13 cm^{-1}) and used to calculate molar conductivities. High resolution mass spectrometry data were provided by Mr. Doug Hairsine (UWO) and were collected using a Finnigan MAT 8200 instrument. Elemental analyses were provided by Guelph Chemical Laboratories Ltd. Calculations were performed using the Gaussian-03 program suite.[20] Optimized geometries for compounds **9c** and **11c** and the cation of **10c** were calculated at the B3LYP/LANL2DZ level of theory.[21] Thermal analysis was used to verify the vibrational data.

Syntheses. Bis(oxazolidinyl)pyridine Ligand, 1. Method A: Pyridine-2,6-dicarboxaldehyde (0.08 g, 0.59 mmol) and (1*R*,2*S*)-(-)-ephedrine (0.20 g, 1.2 mmol) were combined with benzene (40 mL) in a round-bottomed flask fitted with a Dean−Stark trap and a reflux condenser. The yellow solution was heated to reflux for 3 h and then reduced to a yellow oil by rotatory evaporation. Residual solvent was removed on a high vacuum line. Yield: 0.27 g (100%). Method B: Pyridine-2,6-dicarboxaldehyde (0.08 g, 0.59 mmol) and (1*R*,2*S*)-(-)-ephedrine (0.20 g, 1.2 mmol) were combined in CH_2Cl_2 (20 mL) with activated 4 Å molecular sieves. The mixture was stirred at r.t. for about 17 h. Sieve fragments were removed by vacuum filtration through Celite 545, and the filtrate was reduced by rotatory evaporation to give 0.23 g (93%) of a yellow oil. The two methods produced the desired ligand in 21:4:1 and 77:6:1 diastereomeric ratios, respectively. ^1H NMR ($CDCl_3$)−$\mathbf{1^{maj}}$: δ 0.79 (d, 6H, $C^4(CH_3)$, $^3J_{HH} = 6.4$), 2.29 (s, 6H, NCH_3), 3.04 (m, 2H, C^4H), 4.90 (s, 2H, C^2H), 5.20 (d, 2H, C^5H, $^3J_{HH} = 8.2$); $\mathbf{1^{med}}$, peaks

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corresponding to one of the $C^4H(CH_3)$ methyl groups, and the C^4H and C^5H protons were overlapped with the equivalent peaks arising from **1**^{maj}: δ 0.73 (d, 3H, $C^4(CH_3)$, $^3J_{HH}$ = 6.4), 0.78 (d, 3H, $C^4(CH_3)$, $^3J_{HH}$ = 6.4), 2.33 (s, 3H, NCH_3), 2.36 (s, 3H, NCH_3), 3.72 (m, 1H, C^4H), 4.89 (s, 1H, C^2H), 5.20 (d, 1H, C^5H, $^3J_{HH}$ = 5.2), 5.49 (s, 1H, C^2H), 5.63 (d, 1H, C^5H, $^3J_{HH}$ = 5.2); **1**^{min}, peaks corresponding to C^4H and C^5H were overlapped with one of the equivalent peaks for **1**^{med}: δ 0.74 (d, 6H, $C^4(CH_3)$, $^3J_{HH}$ = 6.7), 2.34 (s, 6H, NCH_3), 5.48 (s, 2H, C^2H). Phenyl and pyridyl peaks could not be assigned unambiguously to the diastereomers. They were: δ 7.28 (m, Ph), 7.35 (m, Ph), 7.47 (m, Ph), 7.68 (m, Ph), 7.85 (m, py) 7.91 (m, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$)−**1**^{maj} and **1**^{med} only, quaternary C-atoms not observed: δ 9.6, 15.2, 33.8, 36.2, 36.3, 61.7, 64.4, 64.6, 83.1, 83.2, 95.7, 98.9, 99.0, 121.8, 122.2, 116.6, 127.5, 128.0, 128.2, 128.3, 128.4, 128.5, 138.0, 138.3, 140.0, 140.1, 157.8. ^{15}N NMR (CD_2Cl_2) − **1**^{maj}: δ −312.8 (*ox*N), −64.9 (*py*N); **1**^{med}: δ −325.0 (*ox*N), −322.5 (*ox′*N), −63.5 (*py*N); **1**^{min} was not detected. HRMS calcd $C_{27}H_{31}N_3O_2$ (found): 429.2416 (429.2398).

Bis(pyridyl)oxazolidine Ligand, 2a. Pyridyloxazolidine **4a**[6] (0.15 g, 0.80 mmol) was dissolved in dry Et_2O (50 mL) and cooled to 0 °C. Solid $LiAlH_4$ (0.091 g, 2.39 mmol) was added in small portions, and the mixture was stirred at 0 °C for 1 h. The mixture was then allowed to warm to r.t. and stirred for an additional hour before being quenched with distilled water (50 mL). The aqueous phase was washed with Et_2O (3 × 50 mL) and the organic fractions were combined, washed with brine (75 mL), dried over $MgSO_4$ and filtered. The filtrate was reduced to dryness by rotatory evaporation to leave 0.085 g (55%) of known amino alcohol **5a**.[18a] The oil **5a** (0.085 g, 0.44 mmol) was combined with 2-pyridinecaboxaldehyde (0.047 g, 0.44 mmol) and benzene (40 mL) in a round-bottomed flask fitted with a Dean−Stark trap and a condenser. The solution was heated to reflux for 3 h. The solvent was removed by rotatory evaporation to leave **2a** as an oil from which the residual C_6H_6 was removed using a high vacuum line. Yield: 0.13 g (54%). ^1H NMR ($CDCl_3$)−**2a**^{maj}: δ 0.86 (m, 6H, $CH(CH_3)_2$), 1.63 (m, 1H, $CH(CH_3)_2$), 3.06 (m, 1H, C^4H), 4.01 (m, 4H, C^5H_2, NCH_2), 5.26 (s, 1H, C^2H), 7.03 (m, py), 7.15 (m, py), 7.44 (m, py), 7.64 (m, py), 8.44 (m, py); **2a**^{min}: δ 0.95 (m, 6H, $CH(CH_3)_2$), 1.84 (m, 1H, $CH(CH_3)_2$), 3.16 (m, 1H, C^4H), 3.44 (m, 1H, C^5H), 3.63 (d, 1H, NCH_2, $^2J_{HH}$ = 14.2), 3.76 (m, 2H, C^5H and NCH_2), 5.56 (s, 1H, C^2H). Pyridyl proton peaks for **2a**^{min} were overlapped with those of **2a**^{maj} and could not be distinguished. $^{13}C\{^1H\}$ NMR ($CDCl_3$)−**2a**^{maj} and **2a**^{min}: δ 17.1, 20.3, 30.3, 58.8, 68.1, 69.2, 98.4, 122.0, 122.3, 123.4, 123.8, 136.0, 136.6, 148.8, 148.9, 159.2, 160.2. HRMS calcd $C_{17}H_{21}N_3O$ (found): 283.1685 (283.1675).

Bis(pyridyl)oxazolidine Ligand, 2b. Reaction of **4b**[6] (1.58 g, 6.60 mmol) with $LiAlH_4$ (0.50 g, 13.2 mmol) using the procedure described for the synthesis of **5a** en route to **2a** gave 1.29 g (81%) of the amino alcohol **5b** as an orange oil. ^1H NMR ($CDCl_3$): δ 2.79 (m, 2H, CH_2Ph), 2.98 (m, 1H, C^4H), 3.40 (dd, 1H, C^5H, $^2J_{HH}$ = 10.8, $^3J_{HH}$ = 5.5), 3.64 (dd, 1H, C^5H, $^2J_{HH}$ = 9.3, $^3J_{HH}$ = 3.6), 3.88 (d, 1H, NCH_2, $^2J_{HH}$ =14.9), 3.99 (d, 1H, NCH_2, $^2J_{HH}$ = 14.9), 7.22 (m, 5H, Ph), 7.62 (m, 3H, py), 8.52 (d, 1H, py, $^3J_{HH}$ = 4.64). ^{13}C NMR ($CDCl_3$): δ 38.6, 52.4, 60.8, 62.9, 122.3, 122.5, 126.5, 128.7, 128.9, 129.4, 136.9, 139.1, 149.3, 160.0. HRMS calcd $C_{15}H_{19}N_2O$, that is, **5b** + H (found): 243.1497 (243.1491). Condensation of **5b** (0.65 g, 2.70 mmol) with 2-pyridinecarboxaldehyde (0.29 g, 2.70 mmol) was carried out at ambient temperature using Method B as described for the synthesis of **1** and gave 0.87 g (98%) of **2b** as a dark red oil. ^1H NMR ($CDCl_3$)−**2b**^{maj}: δ 2.56 (dd, 1H, CH_2Ph, $^2J_{HH}$ = 13.3, $^3J_{HH}$ = 9.6), 2.86 (dd, 1H, CH_2Ph, $^2J_{HH}$ = 13.3, $^3J_{HH}$ = 4.6), 3.45 (m, 1H, C^4H), 4.00 (d, 1H, NCH_2, $^2J_{HH}$ = 14.3), 4.11 (d, 1H, NCH_2, $^2J_{HH}$ = 14.3), 5.29 (s, 1H, C^2H); **2b**^{min}: δ 2.69 (dd, 1H, CH_2Ph, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 10.0), 3.14 (dd, 1H, CH_2Ph, $^2J_{HH}$ = 13.2, $^3J_{HH}$ = 4.6), 3.64 (m, 1H, C^4H), 3.81 (d, 1H, $^2J_{HH}$ = 14.4, NCH_2), 5.62 (s, 1H, C^2H). The peaks corresponding to $C^5H_2{}^{maj}$ (2H), $NCH_2{}^{min}$ (1H) and $C^5H_2{}^{min}$ (1H) appeared as overlapped signals at δ 3.93. The peaks corresponding to the phenyl and pyridyl protons were overlapped and could not be assigned unambiguously to the diastereomers. They were δ 7.08 (m, Ph), 7.23 (m, Ph and py), 7.48 (m, py), 7.54 (m, py), 7.67 (m, py), 8.49 (m, py). $^{13}C\{^1H\}$ NMR (CD_3Cl)−**2b**^{maj}: δ 40.4, 57.5, 36.5, 71.7, 98.2, 122.0, 122.2, 123.6, 124.0, 126.5, 128.6, 129.2, 136.2, 136.8, 138.9, 148.9, 149.1, 158.8, 160.0; **2b**^{min}: δ 39.1, 53.7, 62.7, 70.0, 95.1, 121.9, 122.1, 123.2, 126.4, 128.5, 129.4, 136.5, 137.3, 138.6, 149.0, 149.2. HRMS calcd $C_{21}H_{21}N_3O$ (found): 331.1685 (331.1675).

Bis(pyridyl)oxazolidine Ligand, 2c. Using the procedure described for the synthesis of **5a** en route to **2a**, reaction of the secondary amino alcohol **5c**[18b] (1.3 g, 5.4 mmol) and 2-pyridinecarboxaldehyde (0.57 g, 5.4 mmol) gave 1.7 g (93%) of **2c** as a red oil. ^1H NMR ($CDCl_3$)−**2c**^{maj}: δ 0.62 (d, 3H, $C^4H(CH_3)$, $^3J_{HH}$ = 6.5), 3.46 (m, 1H, C^4H), 3.95 (d, 1H, NCH_2, $^2J_{HH}$ = 14.6), 4.15 (d, 1H, NCH_2, $^2J_{HH}$ = 14.6), 5.23 (d, 1H, C^5H, $^3J_{HH}$ = 7.6), 5.33 (s, 1H, C^2H). **2c**^{min}: δ 0.75 (d, 3H, $C^4H(CH_3)$, $^3J_{HH}$ = 6.7), 3.75 (m, 1H, C^4H), 3.89 (d, 1H, NCH_2, $^3J_{HH}$ = 14.8), 3.97 (d, 1H, NCH_2, $^3J_{HH}$ = 14.6), 5.65 (s, 1H, C^2H), 5.67 (d, 1H, C^5H, $^3J_{HH}$ = 5.3). The phenyl and pyridyl proton peaks could not be assigned unambiguously to the diastereomers. They were: δ 7.29 (m, Ph), 7.39 (m, py), 7.50 (m, py), 7.58 (m, py), 7.72 (m, py), 7.75 (m, py), 7.86 (m, py), 8.45 (m, py), 8.54 (m, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$), both diastereomers, quaternary C-atoms not observed: δ 9.4, 17.2, 52.5, 56.9, 59.3, 62.7, 82.6, 82.7, 94.8, 97.3, 122.1, 122.2, 122.3, 122.4, 123.1, 123.6, 123.7, 123.8, 126.4, 127.5, 127.7, 127.8, 128.2, 128.4, 136.2, 136.6, 137.0, 139.2, 148.9, 149.0, 149.1, 159.2, 159.3, 160.2. ^{15}N NMR (CD_2Cl_2)−**2c**^{maj}: δ −65.0 (C^2Hpy*N*), −67.5 (NCH_2py*N*), −304.1 (*ox*N); **2c**^{min}, *py*N not observed: δ −309.9 (*ox*N). HRMS calcd $C_{21}H_{21}N_3O$ (found): 331.1685 (331.1675).

Pyridyloxazolidine Ligand, 3a. Using the procedure described for the synthesis of **5a** en route **2a**, condensation of **5c**[18b] (0.61 g, 2.7 mmol) with benzaldehyde (0.28 g, 2.7 mmol) gave 0.33 g (57%) of **3a** as a yellow oil. ^1H NMR ($CDCl_3$)−**3a**^{maj}: δ 0.60 (d, 3H, $C^4H(CH_3)$, $^3J_{HH}$ = 6.5), 3.41 (m, 1H, C^4H), 3.84 (d, 1H, NCH_2, $^2J_{HH}$ = 14.7), 3.98 (d, 1H, NCH_2, $^2J_{HH}$ = 14.7), 5.20 (s, 1H, C^2H), 5.21 (d, 1H, C^5H, $^3J_{HH}$ = 5.6), 7.08 (dd, 1H, Ph, $^3J_{HH}$ = 5.4, $^3J_{HH}$ = 6.7), 8.45 (d, 1H, py, $^3J_{HH}$ = 4.7); **3a**^{min}: δ 0.74 (d, 1H, $C^4H(CH_3)$, $^3J_{HH}$ = 6.8), 3.70 (m, 1H, C^4H), 3.76 (d, 1H, NCH_2, $^2J_{HH}$ = 14.8), 3.88 (d, 1H, NCH_2, $^2J_{HH}$ = 14.8), 5.59 (s, 1H, C^2H), 5.62 (d, 1H, C^5H, $^3J_{HH}$ = 5.6), 7.13 (dd, 1H, Ph, $^3J_{HH}$ = 4.8, ^3J = 7.0), 8.48 (d, 1H, py, $^3J_{HH}$ = 4.8). The peaks arising from the remaining phenyl and pyridyl protons could not be assigned unambiguously to the diastereomers. They were: δ 7.33 (m, Ph), 7.54 (m, Ph), 7.62 (d, py, $^3J_{HH}$ = 8.0), 7.68 (d, py, $^3J_{HH}$ = 6.7), 8.09 (d, py, $^3J_{HH}$ = 6.7). ^{13}C NMR ($CDCl_3$), quaternary C-atoms not observed−**3a**^{maj}: δ 17.4, 57.1, 63.0, 82.4, 97.4; **3a**^{min}: δ 9.0, 52.3, 59.0, 82.1, 94.5. Phenyl and pyridyl carbons of the major and minor diastereomers could not be assigned unambiguously. They were: δ 122.1, 123.7, 126.4, 126.8, 127.6, 127.7, 128.2, 128.3, 128.6, 128.7, 129.3, 136.2, 136.3, 139.0, 139.4, 148.8, 148.9, 159.4. ^{15}N NMR (CD_2Cl_2)−**3a**^{maj}: δ −68.0 (*py*N), −303.5 (*ox*N); **3a**^{min}, *py*N not observed: δ −308.7 (*ox*N). HRMS calcd $C_{22}H_{23}N_2O$, that is, for **3a** + H (found): 331.1810 (331.1813).

Pyridyloxazolidine Ligand, 3b. Using the procedure described for the synthesis of **5a** en route to **2a**, condensation of **5d**[17b] (0.26 g, 1.1 mmol) with 2-pyridinecarboxaldehyde (0.11 g, 1.1 mmol) gave 0.38 g (94%) of **3b** as a pale yellow oil. ^1H NMR

($CDCl_3$)−**3a^{maj}**: δ 0.64 (d, 3H, $C^4H(CH_3)$, $^3J_{HH}$ = 6.5), 3.34 (m, 1H, C^4H), 3.97 (d, 1H, NCH_2, $^2J_{HH}$ = 14.1), 5.20 (d, 1H, C^5H, $^3J_{HH}$ = 7.6), 5.26 (s, 1H, C^2H); **3b^{min}**: δ 0.69 (d, 3H, $C^4H(CH_3)$, $^3J_{HH}$ = 6.7), 5.56 (s, 1H, C^2H), 5.62 (d, 1H, C^5H, $^3J_{HH}$ = 5.1). The peak corresponding to one of the NCH_2 protons of **3b^{maj}** was overlapped with both NCH_2 and the C^4H protons of **3b^{min}** (δ 3.71). The phenyl and pyridyl peaks could not be assigned unambiguously to the diastereomers. They were δ 7.29 (m, Ph), 7.76 (m, py), 7.88 (m, py), 8.57 (m, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$), quaternary C-atoms not observed: δ 6.6, 15.4, 47.8, 53.0, 56.1, 60.2, 80.8, 80.9, 92.7, 95.6, 120.2, 120.6, 121.8, 121.9, 124.4, 124.5, 125.2, 125.3, 125.6, 125.8, 125.9, 126.3, 126.4, 126.6, 126.7, 126.9, 127.3, 135.0, 135.2, 136.9, 137.1, 137.3, 147.0, 158.7. ^{15}N NMR (CD_2Cl_2)−**3b^{maj}**: δ −67.5 (pyN), −305.0 (*ox*N); 3b^{min}, *py*N not observed: δ −307.1 (*ox*N). HRMS calcd $C_{22}H_{23}N_2O$, that is, for **3b** + H (found): 331.1810 (331.1800).

Pd(1)Cl$_2$. Ligand **1** (0.10 g, 0.24 mmol) and *trans*-$PdCl_2(PhCN)_2$ (0.093 g, 0.24 mmol) were combined with CH_2Cl_2 (30 mL) to give a yellow solution that was heated to reflux for about 21 h. Following concentration by rotatory evaporation, a beige solid was precipitated by addition of Et_2O (50 mL). Yield: 0.10 g (70%). ^1H NMR (CD_2Cl_2)−**Pd(1^{maj})Cl$_2$**: δ 1.59 (d, 6H, $C^4H(CH_3)$, $^3J_{HH}$ = 6.8), 3.48 (s, 6H, NCH_3), 3.63 (m, 2H, C^4H), 5.65 (d, 2H, C^5H, $^3J_{HH}$ = 4.6), 6.52 (s, 2H, C^2H); **Pd(1^{med})Cl$_2$**, the peak corresponding to one of the C^4H protons was overlapped with the equivalent peak arising from **Pd(1^{maj})Cl$_2$**: δ 0.91 (d, 3H, $C^4H(CH_3)$, $^3J_{HH}$ = 7.0), 1.58 (d, 3H, $C^4H(CH_3)$, $^3J_{HH}$ = 7.0), 3.24 (s, 3H, NCH_3), 3.58 (s, 3H, NCH_3), 4.63 (m, 1H, C^4H), 5.55 (d, 1H, C^5H, $^3J_{HH}$ = 4.7), 6.09 (d, 1H, C^5H, $^3J_{HH}$ = 5.3), 6.47 (s, 1H, C^2H), 6.80 (s, 1H, C^2H); **Pd(1^{min})Cl$_2$**, the peak corresponding to the C^2H proton was overlapped with the equivalent peak arising from **Pd(1^{med})Cl$_2$**: δ 1.06 (d, 6H, $C^4H(CH_3)$, $^3J_{HH}$ = 7.1), 3.00 (s, 6H, NCH_3), 5.01 (m, 2H, C^4H), 5.79 (d, 2H, C^5H, $^3J_{HH}$ = 8.0). The phenyl and pyridyl protons could not be assigned unambiguously to the diastereomers. They were: δ 7.37 (m, Ph), 7.92 (pt, py), 7.98 (m, py), 8.15 (m, py), 8.38 (m, py), 8.47 (m, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$), quaternary C-atoms not observed: δ 10.1, 19.8, 20.0, 23.1, 44.0, 44.2, 52.3, 52.7, 67.1, 68.6, 69.5, 70.0, 80.0, 83.6, 105.0, 107.6, 108.2, 125.8, 126.1, 126.2, 128.7, 128.9, 132.7, 134.3, 134.7, 135.2, 143.1, 157.5, 157.6, 158.1, 159.6, 159.7. ^{15}N NMR (CD_2Cl_2)−**Pd(1^{maj})Cl$_2$**: δ −164.2 (*py*N), −318.7 (*ox*N); **Pd(1^{med})Cl$_2$**: δ −160.6 (*py*N), −323.3 (*ox*N), −324.5 (*ox*′N). HRMS calcd $C_{27}H_{31}N_3O_2ClPd$ (found): 570.1140 (570.1128). Anal. Calcd for $C_{27}H_{31}N_3Cl_2O_2Pd$: C, 53.44; H, 5.15; N, 6.92%; Found: C, 53.70; H, 4.95; N, 6.49%. Molar conductivity, Λ (CH_2Cl_2): 1.18 S cm^2 mol^{-1}.

[Pd(1)Cl][PF$_6$], 8. Pd(**1**)Cl_2 (0.06 g, 0.11 mmol) was dissolved in acetone (15 mL) and solid NH_4PF_6 (0.07 g, 0.42 mmol) was added. The mixture was stirred at r.t. for about 30 min. The solvent was removed by rotatory evaporation to give a paste that was taken up in CH_2Cl_2 (30 mL) and filtered through Celite 545. The resulting yellow solution was concentrated by rotatory evaporation. The product was precipitated by the addition of Et_2O (20 mL), isolated by filtration, and dried in vacuo. Yield: 0.052 g (66%). ^1H NMR (CD_2Cl_2)−**8^{maj}**: δ 1.60 (d, 6H, $C^4H(CH_3)$, $^3J_{HH}$ = 7.0), 3.37 (s, 6H, NCH_3), 3.65 (m, 2H, C^4H), 5.52 (d, 2H, C^5H, $^3J_{HH}$ = 4.6), 5.95 (s, 2H, C^2H); **8^{med}**, peaks corresponding to one of the $C^4(CH_3)$ methyl groups, and the C^4H, and C^2H protons were overlapped with the equivalent peaks arising from **8^{maj}**: δ 0.91 (d, 3H, $C^4H(CH_3)$, $^3J_{HH}$ = 7.05), 3.15 (s, 3H, NCH_3), 3.46 (s, 3H, NCH_3), 4.64 (m, 2H, C^4H), 5.54 (d, 1H, C^5H, $^3J_{HH}$ = 4.7), 6.09 (s, 1H, C^2H), 6.34 (d, 1H, C^5H, $^3J_{HH}$ = 5.4); **8^{min}**: δ 1.00 (d, 6H, $C^4H(CH_3)$, $^3J_{HH}$ = 7.5), 3.05 (s, 6H, NCH_3), 4.75 (m, 2H, C^4H), 6.01 (d, 2H, C^5H, $^3J_{HH}$ = 5.4), 6.16 (s, 2H, C^2H). The phenyl and pyridyl peaks could not be assigned unambiguously to the diastereomers. They were δ 7.37 (m, Ph), 7.82 (m, py), 7.88 (m, py), 8.36 (m, py). $^{13}C\{^1H\}$ NMR (CD_2Cl_2)−**8^{maj}** and **8^{med}** only, quaternary C-atoms not observed: δ 19.5, 19.6, 22.8, 52.1, 67.3, 68.3, 69.9, 70.0, 80.2, 80.4, 84.2, 107.6, 108.0, 125.4, 125.8, 126.0, 126.1, 128.9, 129.0, 133.9, 142.9, 158.1. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 143.5 (h, PF_6^-, $^1J_{PF}$ = 721). ^{15}N NMR (CD_2Cl_2)−**8^{maj}**: δ −163.6 (*py*N), −318.0 (*ox*N). HRMS calcd $C_{27}H_{31}N_3O_2ClPd$ (found): 570.1140 (570.1162). Anal. Calcd for $C_{27}H_{31}ClF_6N_3O_2PPd$: C, 45.27; H, 4.36; N, 5.87%; Found: C, 45.78; H, 4.68; N, 5.88%. Molar conductivity, Λ (CH_2Cl_2): 5.58 S cm^2 mol^{-1}.

Crystals of **8^{maj}**·CH_2Cl_2 suitable for analysis by X-ray diffraction were grown by slow evaporation of a concentrated CH_2Cl_2 solution containing a mixture of the diastereomers.

Pd(2a)Cl$_2$. The ligand **2a** (0.47 g, 1.66 mmol) and *trans*-$PdCl_2(PhCN)_2$ (0.64 g, 1.66 mmol) were combined with CH_2Cl_2 (20 mL) in a round-bottomed flask fitted with a reflux condenser. The orange solution was brought to reflux for 1 h and then concentrated by rotatory evaporation. The product, a beige solid, was precipitated by the addition of Et_2O (30 mL), isolated by filtration, and dried on a high vacuum line. Yield: 0.57 g (75%). ^1H NMR (DMSO-d_6)−**Pd(2a^{maj})Cl$_2$**: δ 0.70 (d, 3H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.7), 1.10 (d, 3H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.5), 1.53 (m, 1H, $CH(CH_3)_2$), 3.42 (m, 1H, C^4H), 3.57 (pt, 1H, C^5H), 4.50 (dd, 1H, C^5H, $^2J_{HH}$ = 9.9, $^3J_{HH}$ = 7.3), 4.60 (d, 1H, NCH_2, $^2J_{HH}$ = 15.6), 5.68 (d, 1H, NCH_2, $^2J_{HH}$ = 15.6), 6.95 (s, 1H, C^2H); **Pd(2a^{min})Cl$_2$**, peaks due to the C^4H, one C^5H, and the $CH(CH_3)_2$ protons were overlapped with those of **Pd(2a^{maj})Cl$_2$**: δ 0.81 (d, 3H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.6), 0.86 (d, 3H, $CH(CH_3)_2$, $^3J_{HH}$ = 6.8), 4.07 (pt, 1H, C^5H), 4.88 (d, 1H, NCH_2, $^2J_{HH}$ = 16.8), 5.29 (d, 1H, NCH_2, $^2J_{HH}$ = 16.8), 6.87 (s, 1H, C^2H). Peaks corresponding to the pyridyl protons could not be assigned unambiguously to the diastereomers. They were: δ 7.56 (m), 7.66 (m), 7.68 (m), 7.70 (m), 7.80 (m), 7.89 (m), 7.99 (m), 8.21 (m), 8.27 (m), 8.54 (m), 8.58 (m), 8.72 (m). $^{13}C\{^1H\}$ NMR (DMSO-d_6), both diastereomers, quaternary C-atoms not observed: δ 11.3, 15.9, 19.5, 22.6, 26.2, 32.6, 46.8, 61.0, 69.5, 70.2, 71.6, 78.0, 87.8, 100.4, 110.0, 124.8, 125.2, 126.7, 128.0, 130.2, 132.9, 142.5, 143.2, 150.5, 150.9, 156.9, 157.0, 163.4, 164.1. HRMS calcd $C_{17}H_{21}N_3ClOPd$ (found): 422.0413 (422.0398). Anal. Calcd for $C_{17}H_{21}N_3Cl_2OPd$: C, 44.32; H, 4.59; N, 9.12%; Found: C, 44.63; H, 4.70; N, 9.30%.

Pd(2b)Cl$_2$. Ligand **2b** (0.4 g, 1.20 mmol) and *trans*-$PdCl_2(PhCN)_2$ (0.46 g, 1.20 mmol) were combined in CH_2Cl_2 (10 mL) and the solution was stirred at r.t. for about 2 h. Concentration and addition of Et_2O (30 mL) gave 0.53 g (87%) of **Pd(2b)Cl$_2$** as a light brown powder. ^1H NMR (DMSO-d_6)−**Pd(2b^{maj})Cl$_2$**: δ 2.46 (dd, 1H, CH_2Ph, $^2J_{HH}$ = 15.4, $^3J_{HH}$ = 11.4), 2.99 (dd, 1H, CH_2Ph, $^2J_{HH}$ =15.4, $^3J_{HH}$ = 4.1), 3.69 (dd, 1H, C^5H_2, $^2J_{HH}$ = 9.7, $^3J_{HH}$ = 6.4), 4.29 (m, 1H, C^4H), 4.59 (d, 1H, NCH_2, $^2J_{HH}$ = 15.2), 4.69 (dd, 1H, C^5H_2, $^2J_{HH}$ = 9.4, $^3J_{HH}$ = 7.3), 5.53 (d, 1H, NCH_2, $^2J_{HH}$ = 15.2), 6.97 (s, 1H, C^2H), 7.06 (m, 2H, Ph), 7.14 (m, 2H, Ph), 7.40 (m, 1H, py), 7.55 (d, 1H, py, $^3J_{HH}$ = 7.5), 7.66 (d, 1H, py, $^3J_{HH}$ = 7.4), 7.72 (d, 1H, py, $^3J_{HH}$ = 4.5), 7.81 (m, 1H, py), 8.08 (dd, 1H py, $^3J_{HH}$ = 6.3, $^3J_{HH}$ = 14.0), 8.35 (dd, 1H, py, $^3J_{HH}$ = 6.3, $^3J_{HH}$ = 14.0), 8.70 (d, 1H, py, $^2J_{HH}$ = 5.3). **Pd(2b^{min})Cl$_2$**: δ 2.84 (dd, 1H, CH_2Ph, $^2J_{HH}$ = 14.9, $^3J_{HH}$ = 7.7), 3.06 (dd, 1H, CH_2Ph, $^2J_{HH}$ = 14.7, $^3J_{HH}$ = 6.9), 3.99 (pt, 1H, C^5H_2, $^3J_{HH}$ = 16.3), 4.10 (pt, 1H, C^5H_2, $^3J_{HH}$ = 18.0), 4.38 (m, 1H, C^4H), 5.02 (d, 1H, NCH_2, $^2J_{HH}$ = 16.8), 5.37 (d, 1H, NCH_2, $^2J_{HH}$ = 16.8), 6.92 (s, 1H, C^2H). The phenyl and pyridyl peaks of **Pd(2b^{min})Cl$_2$** were overlapped with those of **Pd(2b^{maj})Cl$_2$** and were not distinguishable, except for: δ 8.18 (dd, 1H, py, $^3J_{HH}$ = 7.01, $^3J_{HH}$ = 14.9), 8.28 (dd, 1H, py, $^3J_{HH}$ = 7.5, $^3J_{HH}$ = 14.9), 8.58 (d, 1H, py, $^3J_{HH}$ =

5.2). $^{13}C\{^1H\}$ NMR (DMSO-d_6)−**Pd(2b^{maj})Cl$_2$** only, quaternary C-atoms not observed: δ 15.9, 65.6, 72.1, 99.9, 124.2, 125.2, 125.7, 129.2, 129.3, 129.8, 129.9, 130.2, 132.9, 136.9, 143.1, 150.7, 162.7. HRMS calcd $C_{21}H_{21}N_3ClOPd$ (found): 470.0413 (470.0425). Anal. Calcd for $C_{21}H_{21}N_3Cl_2OPd$: C, 49.58; H, 4.16; N, 8.26%; Found: C, 49.79; H, 3.97; N, 8.24%.

Pd(2c)Cl$_2$. Using the procedure described for the synthesis of **Pd(2b)Cl$_2$**, reaction of **2c** (0.25 g, 0.75 mmol) and *trans*-$PdCl_2(PhCN)_2$ (0.29 g, 0.75 mmol) gave 0.37 g (98%) of the title compound as an orange-brown solid. ^1H NMR (CD_2Cl_2)−**Pd(2c^{maj})Cl$_2$**: δ 1.08 (d, 3H, C^{4}H(CH_3), $^3J_{HH}$ = 7.1), 4.19 (m, 1H, C^4H), 5.79 (d, 1H, NCH_2, $^2J_{HH}$ = 15.3), 6.31 (d, 1H, NCH_2, $^2J_{HH}$ = 15.3), 6.60 (d, 1H, C^5H, $^3J_{HH}$ = 4.8), 7.08 (s, 1H, C^2H), 7.44 (m, 1H, py), 7.75 (d, 1H, py, $^3J_{HH}$ = 8.2), 7.19−7.45 (m, Ph), 8.04 (t, 1H, py, $^3J_{HH}$ = 7.8), 8.17 (t, 1H, py, $^3J_{HH}$ = 8.5), 8.41 (d, 1H, py, $^3J_{HH}$ = 7.7), 8.56 (d, 1H, py, $^3J_{HH}$ = 6.0), 8.73 (m, 2H, py); **Pd(2c^{min})Cl$_2$**, peaks due to phenyl, some pyridyl and the C^2H protons were overlapped with the corresponding peaks of the major diastereomer and could not be distinguished: δ 0.90 (d, 3H, C^{4}H(CH_3), $^3J_{HH}$ = 6.9), 4.30 (m, 1H, C^4H), 4.38 (d, 1H, NCH_2, $^2J_{HH}$ = 16.6), 5.30 (d, 1H, C^5H, $^2J_{HH}$ = 9.4), 6.86 (d, 1H, NCH_2, $^2J_{HH}$ = 16.6), 7.72 (d, 1H, py, $^3J_{HH}$ = 7.8), 7.91 (t, 1H, py, $^3J_{HH}$ = 9.4), 8.12 (m, py), 8.78 (m, py). $^{13}C\{^1H\}$ NMR ($CDCl_3$), both diastereomers, quaternary C-atoms not observed: δ 11.8, 12.5, 19.1, 61.9, 66.2, 68.2, 80.9, 98.3, 98.7, 122.6, 124.9, 125.2, 125.3, 126.0, 126.2, 126.4, 126.6, 127.6, 128.3, 128.6, 129.2, 129.3, 134.7, 135.4, 137.3, 141.4, 141.7, 142.0, 149.5, 150.5, 150.7, 151.0, 163.4, 164.1, 165.7, 166.7. ^{15}N NMR (CD_2Cl_2)−**Pd(2c^{maj})Cl$_2$**: δ −162.1 (NCH$_2$*py*N), −167.2 (C^{2}H*py*N), −293.8 (*ox*N); **Pd(2c^{min})Cl$_2$**−*py*N not observed: δ −301.9 (*ox*N). HRMS calcd $C_{21}H_{21}N_3OClPd$ (found): 472.0408 (472.0407). Anal. Calcd for $C_{21}H_{21}N_3Cl_2OPd$: C, 49.58; H, 4.16; N, 8.26%; Found: C, 49.20; H, 4.49; N, 8.30%. Molar conductivity, Λ (CH_2Cl_2): 1.48 S cm^2 mol^{-1}.

[Pd(2a-κN,κN′,κN″)Cl]PF$_6$, 12a. Solid **Pd(2a)Cl$_2$** (0.075 g, 0.17 mmol) was combined with acetone (30 mL) and the yellow suspension was brought to a boil. Solid NH_4PF_6 (0.11 g, 0.67 mmol) was added, and the mixture was held at reflux for 1.5 h during which time the color changed from yellow to dark orange. The solvent was removed by rotatory evaporation to yield a brown paste, which was further dried on a high vacuum line. This was taken up in hot 1,2-dichloroethane (30 mL) and filtered through Celite 545 to give a deep yellow solution. The solution was concentrated by rotatory evaporation, and the product, a brown solid, was precipitated by the addition of Et_2O (20 mL) and dried in vacuo. Yield: 0.03 g (32%). ^1H NMR (CD_2Cl_2)−**12a^{maj}**: δ 0.84 (d, 3H, CH(CH_3)$_2$, $^3J_{HH}$ = 6.7), 1.29 (d, 3H, CH(CH_3)$_2$, $^3J_{HH}$ = 6.5), 1.65 (m, 1H, CH(CH$_3$)$_2$), 3.41 (m, 1H, C^4H), 3.69 (pt, 1H, C$^5H_2$), 4.66 (pt, 1H, C$^5H_2$), 4.68 (d, 1H, NCH_2, $^2J_{HH}$ = 15.5), 5.50 (d, 1H, NCH_2, $^2J_{HH}$ = 15.5), 6.63 (s, 1H, C^2H), 7.58 (m, py), 7.69 (d, py), 8.11 (pt, py), 8.17 (pt, py), 8.77 (d, py). The minor diastereomer **12a^{min}** was not observed spectroscopically. $^{13}C\{^1H\}$ NMR (CD_2Cl_2) − **12a^{maj}**: δ 19.0, 22.5, 32.8, 44.2, 69.6, 71.0, 78.6, 100.8, 124.3, 124.7, 126.1, 127.4, 142.0, 142.4, 150.8, 151.1, 162.7. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −143.3 (h, PF_6^-, $^1J_{PF}$ = 721). HRMS calcd $C_{17}H_{21}N_3OClPd$ (found): 424.0408 (424.0394). Anal. Calcd for $C_{17}H_{21}N_3ClF_6OPPd$: C, 45.27; H, 4.36; N, 5.87%; Found: C, 45.78; H, 4.36; N, 5.88%.

[Pd(2b-κN,κN′,κN″)Cl]PF$_6$, 12b. This compound was made in the same way as **12a**, but hot solvents were not necessary. Thus, reaction of Pd(**2b**)Cl$_2$ (0.30 g, 0.59 mmol) and NH_4PF_6 (0.096 g, 0.59 mmol) gave 0.17 g (47%) of the product as a tan colored powder. ^1H NMR (DMSO-d_6)−**12b^{maj}**: δ 2.39 (dd, 1H, CH_2Ph, $^2J_{HH}$ = 15.5, $^3J_{HH}$ = 11.1), 2.99 (dd, 1H, CH_2Ph, $^2J_{HH}$ = 15.4, $^3J_{HH}$ = 4.0), 3.69 (dd, 1H, C$^5H_2$, $^2J_{HH}$ = 9.5, $^3J_{HH}$ = 6.4), 4.29 (m, 1H, C^4H), 4.59 (d, 1H, NCH_2, $^2J_{HH}$ = 15.3), 4.69 (dd, 1H, C$^5H_2$, $^2J_{HH}$ = 9.4, $^3J_{HH}$ = 7.3), 5.53 (d, 1H, NCH_2, $^2J_{HH}$ = 15.2), 6.98 (s, 1H, C^2H), 7.06 (m, 2H, Ph), 7.13 (m, 3H, Ph), 7.40 (m, 1H, py), 7.54 (d, 1H, py, $^3J_{HH}$ = 8.0), 7.65 (d, 1H, py, $^3J_{HH}$ = 8.2), 7.71 (d, 1H, py, $^3J_{HH}$ = 6.0), 7.81 (m, 1H, py), 8.07 (dd, 1H, py, $^3J_{HH}$ = 15.4, $^3J_{HH}$ = 7.7), 8.35 (dd, 1H, py, $^3J_{HH}$ = 15.7, $^3J_{HH}$ = 7.8), 8.70 (d, 1H, py, $^3J_{HH}$ = 5.5). Because of its low relative abundance, **12b^{min}** was not observed by ^1H or $^{13}C\{^1H\}$ NMR spectroscopy. $^{13}C\{^1H\}$ NMR (DMSO-d_6)−**12b^{maj}**, quaternary C-atoms not observed: δ 69.0, 71.6, 72.1, 100.0, 124.1, 125.2, 125.8, 127.5, 128.0, 129.3, 129.8, 138.9, 141.4, 143.1, 150.7, 150.8, 162.3, 163.3. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −143.2 (h, PF_6, $^1J_{PF}$ = 721). HRMS calcd $C_{21}H_{21}N_3ClOPd$ (found): 470.0413 (470.0410). Anal. calcd for $C_{21}H_{21}N_3ClF_6OPPd$: C, 40.80; H, 3.42; N, 6.80%; Found: C, 41.29; H, 2.90; N, 6.79%.

[PdCl(2c-κN,κN′,κN″)][PF$_6$], 12c. This compound was made in the same way as **12a**, but hot solvents were not necessary. Thus, reaction of Pd(**2c**)Cl$_2$ (0.15 g, 0.29 mmol) and NH_4PF_6 (0.25 g, 1.2 mmol) gave 0.12 g (65%) of the product as a pale brown solid. ^1H NMR (CD_2Cl_2)−**12c^{maj}**: δ 1.17 (d, 3H, C^{4}H(CH_3), $^3J_{HH}$ = 7.0), 3.92 (m, 1H, C^4H), 5.03 (d, 1H, NCH_2, $^2J_{HH}$ = 15.5), 5.43 (d, 1H, NCH_2, $^2J_{HH}$ = 15.5), 5.96 (d, 1H, C^5H, $^3J_{HH}$ = 4.9), 6.49 (s, 1H, C^2H), 7.28−7.45 (m, Ph), 7.53 (m, 2H, py), 7.73 (d, 1H, py, $^3J_{HH}$ = 8.0), 7.81 (d, 1H, py, $^3J_{HH}$ = 7.9), 8.03 (t, 1H, py, $^3J_{HH}$ = 9.4), 8.14 (t, 1H, py, $^3J_{HH}$ = 7.9), 8.61 (d, 1H, py, $^3J_{HH}$ = 5.4), 8.67 (d, 1H, py, $^3J_{HH}$ = 5.6); **12c^{min}**, peaks due to phenyl, some pyridyl and C^5H protons were overlapped with those of **12c^{maj}** and could not be resolved: δ 0.84 (d, 3H, C^{4}H(CH_3), $^3J_{HH}$ = 7.0), 4.25 (m, 1H, C^4H), 4.40 (d, 1H, NCH_2, $^2J_{HH}$ = 16.7), 5.28 (d, 1H, NCH_2, $^2J_{HH}$ = 16.7), 6.83 (s, 1H, C^2H), 7.64 (d, py, $^3J_{HH}$ = 7.8), 7.89 (t, 1H, py, $^3J_{HH}$ = 8.9), 8.10 (t, 1H, py, $^3J_{HH}$ = 7.9), 8.71 (d, 1H, py, $^3J_{HH}$ = 5.8). $^{13}C\{^1H\}$ NMR (CD_2Cl_2), both diastereomers, quaternary C-atoms not observed: δ 12.1, 15.3, 19.2, 62.5, 65.8, 66.1, 68.2, 68.5, 80.9, 99.2, 99.3, 122.4, 124.9, 125.2, 125.6, 126.0, 126.1, 126.3, 126.6, 127.2, 128.9, 129.4, 133.8, 135.0, 142.0, 142.3, 142.4, 149.8, 151.1, 151.3, 158.1, 159.0, 162.0, 162.2, 164.5, 165.6. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −143.2 (h, PF_6, $^1J_{PF}$ = 721). ^{15}N NMR (CD_2Cl_2)−**12c^{maj}**: δ −163.0 (NCH$_2$*py*N), −168.6 (C^{2}H*py*N), −295.0 (*ox*N); **12c^{min}**, *py*N not observed: δ −301.9 (*ox*N). HRMS calcd $C_{21}H_{21}N_3ClOPd$ (found): 470.0413 (470.0403). Anal. Calcd for $C_{21}H_{21}N_3ClF_6OPPd$: C, 40.80; H, 3.42; N, 6.80%; Found: C, 41.09; H, 3.64; N, 7.10%. Molar conductivity, Λ (CH_2Cl_2): 4.29 S cm^2 mol^{-1}.

Pd(3a-κN,κN′)Cl$_2$, 13a. Using the procedure described for the synthesis of **Pd(2b)Cl$_2$**, reaction of **3a** (0.037 g, 0.11 mmol) and *trans*-$PdCl_2(PhCN)_2$ (0.042 g, 0.11 mmol) gave 0.05 g (88%) of **13a** as a beige solid after 2.5 h. ^1H NMR (CD_2Cl_2)−**13a^{maj}**: δ 1.22 (d, 3H, C^{4}H(CH_3), $^3J_{HH}$ = 7.1), 3.94 (d, 1H, NCH_2, $^2J_{HH}$ = 16.6), 4.13 (d, 1H, NCH_2, $^2J_{HH}$ = 16.6), 5.17 (m, 1H, C^4H), 5.44 (d, 1H, C^5H, $^3J_{HH}$ = 9.5), 6.55 (s, 1H, C^2H), 7.19 (m, 1H, py), 8.49 (d, 2H, py, $^3J_{HH}$ = 7.6), 8.94 (d, 1H, py, $^3J_{HH}$ = 5.3); **13a^{min}**: δ 1.78 (d, 3H, C^{4}H(CH_3), $^3J_{HH}$ = 7.5), 3.72 (m, 1H, C^4H), 3.88 (d, 1H, NCH_2, $^2J_{HH}$ = 15.6), 4.19 (d, 1H, NCH_2, $^2J_{HH}$ = 15.6), 5.82 (d, 1H, C^5H, $^3J_{HH}$ = 6.3), 6.94 (s, 1H, C^2H), 7.94 (m, 1H, py), 8.41 (d, 2H, py, $^3J_{HH}$ = 7.3), 9.05 (d, 1H, py, $^3J_{HH}$ = 6.0). The phenyl protons of both diastereomers were observed as overlapping signals at δ 7.28−7.77. ^{15}N NMR (CD_2Cl_2)−**13a^{maj}**: δ −158.9 (*py*N), −308.2 (*ox*N); **13a^{min}**, *py*N not observed: δ −301.1 (*ox*N). HRMS calcd $C_{22}H_{22}Cl_2N_2OPd\cdot Na$ (found): 527.0047 (527.0030). Anal. calcd for $C_{22}H_{22}Cl_2N_2OPd$: C, 52.04; H, 4.37; N, 5.52%; Found: C, 52.02; H, 4.27; N, 5.38%.

Pd(3b-κN,κN′)Cl$_2$, 13b. Using the procedure described for the synthesis of **Pd(2b)Cl$_2$**, reaction of **3b** (0.24 g, 0.73 mmol) with

Table 1. Crystallographic Parameters and Refinement Data for $\mathbf{8}^{\mathbf{maj}}\cdot 0.75CH_2Cl_2$ and $\mathbf{13b}^{\mathbf{maj}}$

	$\mathbf{8}^{\mathbf{maj}}\cdot 0.75CH_2Cl_2$	$\mathbf{13b}^{\mathbf{maj}}$
formula	$C_{27.75}H_{32.5}Cl_{2.5}F_6N_3O_2PPd$	$C_{22}H_{22}Cl_2N_2OPd$
formula mass	780.06	507.72
cryst syst	monoclinic	monoclinic
space group	*C*2	$P2_1$
a, Å	25.8608(16)	7.8400(3)
b, Å	9.9054(6)	14.8979(6)
c, Å	27.5099(17)	9.4679(3)
V, Å^3	6263.2(7)	1073.74
Z	8	2
T, K	193	295(2)
λ, Å	0.71073	0.71073
D_{calcd}, mg/m^{-3}	1.655	1.570
μ, mm^{-1}	0.924	1.128
R_{int}	0.0162	0.0440
$R(F_o)$	0.0343	0.0290
$wR(F_o^2)$	0.0910	0.0545

trans-$PdCl_2(PhCN)_2$ (0.27 g, 0.70 mmol) over 1.5 h gave 0.33 g (93%) of **13b** as an orange solid. ^{1}H NMR (CD_2Cl_2) − $\mathbf{13b}^{\mathbf{maj}}$: δ 1.12 (d, 3H, C^{4}H(C*H*$_3$), $^3J_{HH}$ = 7.1), 3.69 (d, 1H, NC*H*$_2$, $^2J_{HH}$ = 12.2), 4.76 (d, 1H, NC*H*$_2$, $^2J_{HH}$ = 12.2), 5.17 (m, 1H, C^4*H*), 5.78 (s, 1H, C^2*H*), 6.99 (d, 1H, C^5*H*, $^3J_{HH}$ = 5.0), 7.20−7.60 (m, Ph), 7.83 (m, 1H, py), 8.08 (m, 1H, py), 8.49 (m, 1H, py), 8.72 (m, 1H, py); $\mathbf{13b}^{\mathbf{min}}$, peaks due to phenyl and some pyridyl protons were overlapped with those of $\mathbf{13b}^{\mathbf{maj}}$: δ 1.67 (d, 3H, C^{4}H(C*H*$_3$), $^3J_{HH}$ = 7.10), 3.99 (d, 1H, NC*H*$_2$, $^2J_{HH}$ = 12.4), 4.12 (m, 1H, C^4*H*), 5.50 (d, 1H, NC*H*$_2$, $^2J_{HH}$ = 12.2), 5.81 (d, 1H, C^5*H*, $^3J_{HH}$ = 5.4), 6.11 (s, 1H, C^2*H*), 7.99 (m, 1H, py). ^{13}C{^{1}H} NMR (CD_2Cl_2)−$\mathbf{13b}^{\mathbf{maj}}$ only: δ 19.8, 64.3, 69.9, 81.3, 97.6, 123.6, 125.6, 125.9, 128.6, 128.9, 129.4, 130.0, 133.0, 135.4, 140.3, 149.4, 162.8. ^{15}N NMR (CD_2Cl_2)−$\mathbf{13b}^{\mathbf{maj}}$: δ −157.9 (*py*N), −308.0 (*ox*N); $\mathbf{13b}^{\mathbf{min}}$−*py*N not observed: δ −303.9 (*ox*N). HRMS calcd $C_{22}H_{23}ClN_2OPd$, that is, for **13b** +H − Cl, (found): 470.0539 (470.0539). Anal. Calcd for $C_{22}H_{22}Cl_2N_2OPd$: C, 52.04; H, 4.37; N, 5.52%; Found: C, 51.77; H, 4.50; N, 5.49%. Crystals of $\mathbf{13b}^{\mathbf{maj}}$ suitable for analysis by X-ray diffraction were grown by slow diffusion of ^{i}Pr$_2$O into a concentrated CH_2Cl_2 solution containing a mixture of the diastereomers.

Crystallography. The crystallographic parameters and refinement data for $\mathbf{8}^{\mathbf{maj}}\cdot 0.75CH_2Cl_2$ and $\mathbf{13b}^{\mathbf{maj}}$ are given in Table 1. ORTEP representations of the Pd-containing portions of these structures, along with selected bond lengths and angles, are given in Figures 1 and 4, respectively.

For $\mathbf{8}^{\mathbf{maj}}\cdot 0.75CH_2Cl_2$, a Bruker PLATFORM/SMART 1000 CCD diffractometer was used. Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker. Attempts to refine peaks of residual electron density as disordered or partial-occupancy solvent CH_2Cl_2 Cl- or C-atoms were unsuccessful. The data were corrected for disordered electron density through use of the SQUEEZE procedure[28] as implemented in PLATON.[29] A total solvent-accessible void volume of 675.0 A^3 with a total electron count of 263 (consistent with six molecules of solvent dichloromethane, or 0.75 molecule per formula unit of the palladium complex ion) was found in the unit cell. Distances involving disordered 1,3-oxazolidin-2-yl oxygen atoms were constrained to be equal (within 0.05 Å) during refinement: *d*(O20A−C21A) = *d*(O21A−C21A); *d*(O20A−C22A) = *d*(O21A−C22A); *d*(O20B−C21B) = *d*(O21B−C21B); *d*(O20B−C22B) = *d*(O21B−C22B). The disordered phenyl groups were refined as ideal regular hexagons with *d*(C−C) = 1.39 Å.

For $\mathbf{13b}^{\mathbf{maj}}$, a Nonius Kappa-CCD diffractometer running the COLLECT software was used. Crystal cell refinement and data reduction were carried out using HKL2000 DENZO-SMN. Absorption correction was applied using HKL2000 DENZO-SMN (SCALEPACK). The SHELXTL/PC V6.14 suite of programs was used to solve the structure by direct methods. Subsequent difference Fourier syntheses allowed the remaining atoms to be located.

Results and Discussion

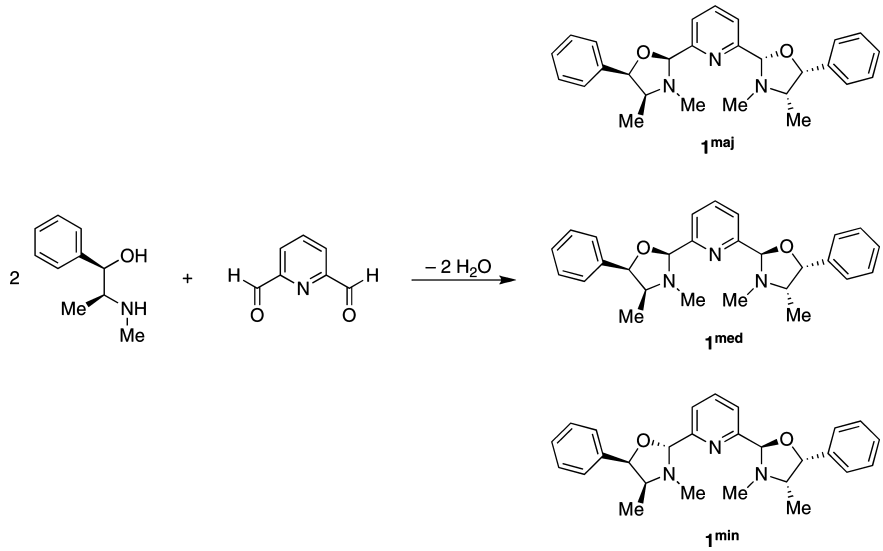
1. Ligands. The tridentate bis(oxazolidinyl)pyridine ligand **1** was made quantitatively according to Scheme 2. Here, 2 equiv of (1*R*,2*S*)-(-)-ephedrine were condensed with 1 equiv of pyridine-2,6-dicarboxaldehyde; product H_2O was driven off by azeotropic distillation from benzene. The ligand was produced as a mixture of three diastereomers, and gave rise to three distinct sets of peaks in the resulting ^{1}H NMR spectrum. The singlets due to the oxazolidinyl C^{2}H protons were not overlapped and allowed determination of the relative abundances of the diastereomers, which were present in a 21:4:1 ratio. The configuration of the major diastereomer was assigned as $\mathbf{1}^{\mathbf{maj}}$ based on X-ray crystallographic data for metal complexes of related ligand systems[6] and on accepted NOE spectroscopic evidence.[22] The substituents at the C^2- and C^4-positions on the oxazolidinyl rings of $\mathbf{1}^{\mathbf{maj}}$ had the expected syn orientation, and the compound was therefore C_2-symmetric and gave rise to a single peak corresponding to homotopic C^2*H* protons (δ 4.90). The next most abundant diastereomer was assigned as $\mathbf{1}^{\mathbf{med}}$ based on its unique C_1-symmetry and gave rise to two distinct sets of peaks corresponding to its two diastereotopic oxazolidinyl rings (δ 4.89 and 5.49 for C^{2}H). Finally, the remaining set of peaks was assigned by elimination to the C_2-symmetric, least abundant diastereomer $\mathbf{1}^{\mathbf{min}}$ (δ 5.48 for C^{2}H).

We found that the diastereomeric distribution in the products was significantly impacted by the conditions under which the reaction was conducted. The ratio of $\mathbf{1}^{\mathbf{maj}}/\mathbf{1}^{\mathbf{med}}/\mathbf{1}^{\mathbf{min}}$ was improved to 77:6:1 by performing the reaction at r.t. over activated 4 Å molecular sieves (see Experimental Section, Method B). The slower removal of water in the r.t. synthesis allowed this reversible reaction to proceed toward a product distribution that was closer to the thermodynamically favored one (vide infra). Presumably, a very small concentration of water was maintained in solution when molecular sieves were used, which facilitated the interconversion of diastereomers. However, rapid and irreversible removal of water via azeotropic distillation by contrast trapped the diastereomers in their kinetic distribution.

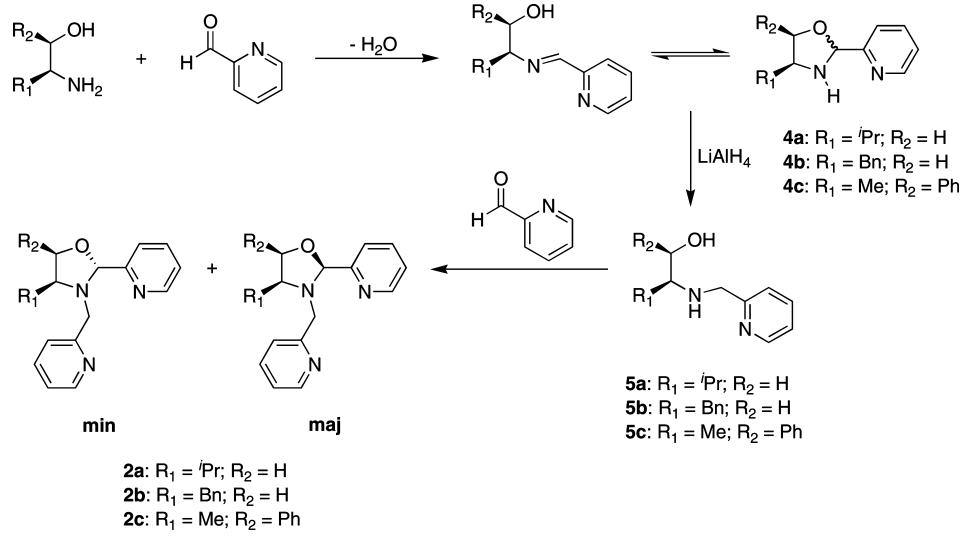
Ligand family **2a-c** was made according to Scheme 3. The first step, condensation of the appropriate primary β-aminoalcohol and 2-pyridinecarboxaldehyde, was identical in principle to that previously reported[6,17] for the synthesis of bidentate *N,N*′-chelating ligands and gave the expected equilibrium mixture of the imine and oxazolidine products (**4a-c**). Reduction of this mixture with $LiAlH_4$ gave secondary amino alcohols (**5a-c**),[18] which were condensed with a second equivalent of 2-pyridinecarboxaldehyde to furnish the target ligands (**2a-c**) in 29%, 66%, and 68% overall yields. In these cases, the second condensation reaction, which installed the indeterminate stereocenter in the resulting

(22) (a) Agami, C.; Ritzk, T. *Tetrahedron* **1985**, *41*, 537–540. (b) Agami, C.; Rizk, T. *J. Chem. Soc., Chem. Commun.* **1983**, 1485–1486.

Scheme 2. Synthesis of Ligand **1** and Configurations of the Product Diastereomers



Scheme 3. Synthesis of Ligand Family **2a-c**



oxazolidinyl ring, was conducted at r.t. in CH_2Cl_2 in the presence of activated 4 Å molecular sieves. Isolated product mixtures had major/minor diastereomeric ratios of 18:1, 1:1, and 6:1 for **2a-c**, respectively.

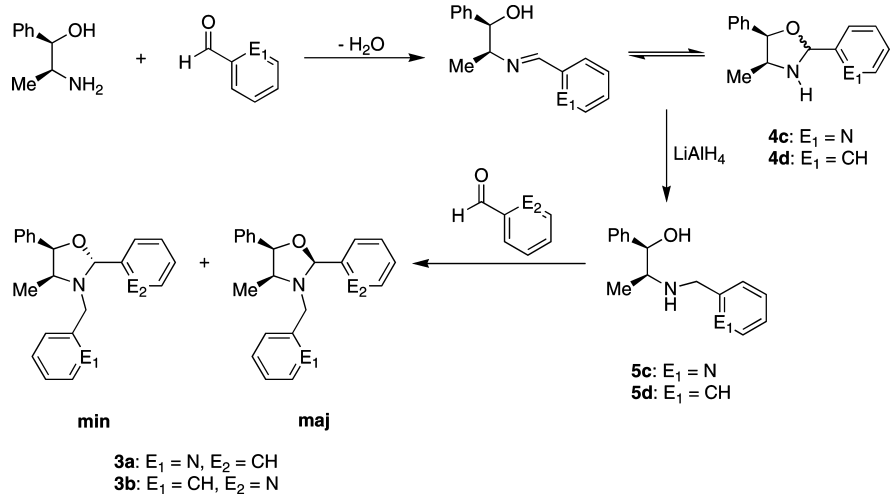
When 10 mol % H_2O was added to a CH_2Cl_2 solution containing isolated **2b**, and the mixture was stirred at r.t. overnight, improvement in the $\mathbf{2b^{maj}/2b^{min}}$ ratio was dramatic (from 1:1 to 6:1). This experiment confirmed that aggressive removal of product H_2O in the condensation reactions was detrimental from the point of view of generating diastereomerically pure material. An inferred planar iminium intermediate in the cyclization reaction may collapse to either of the two oxazolidinyl diastereomers[23] (see Supporting Information, Scheme S2). Presumably, when H_2O was removed quickly in the synthesis of **2b**, the oxazolidine products were trapped in their kinetic distribution, which, relative to the thermodynamic distribution, favored the minor diastereomer.

The "cassette-based" approach outlined in Scheme 3 also lent itself to substantial variation. For example, we made two further pseudoephedrine-derived ligands, **3a** and **3b**, that differed from **2c** by having a single as opposed to two pyridyl rings. The location of this pyridyl substituent could easily be switched between the N- and C^2-positions of the oxazolidinyl ring simply by substituting benzaldehyde for 2-pyridinecarboxaldehyde in either the first or the second condensation step, respectively (Scheme 4).

2. Palladium Complexes. Diastereomeric Pd(II) complexes were easily made by the equimolar reaction between a mixture of the diastereomers of **1** and *trans*-$PdCl_2(PhCN)_2$ in CH_2Cl_2 solution. The isolated solid was a dull brown, air- and moisture-stable microcrystalline powder that was partially soluble in chlorinated organic solvents and insoluble in Et_2O and hexanes. Despite many attempts, it proved to be impossible to grow crystals of the requisite quality for structural determination by X-ray diffraction. By combustion analysis, however, the empirical formula was unequivocally given by Pd(**1**)Cl_2. Proton NMR spectroscopy showed that

(23) Juhász, M.; Lázár, L.; Fülöp, F. *J. Heterocyclic Chem.* **2007**, *44*, 1465–1473.

Scheme 4. Synthesis of "Mixed" Ligands **3a** and **3b**



like the free ligand **1**, the complex existed in solution as two C_2- and one C_1-symmetric diastereomers. Static, or only slowly exchanging, *N,N′*-bidentate coordination modes, as in the putative complexes Pd(**1**-$\kappa N,\kappa N'$)Cl_2 (**6** in Scheme 5a), were ruled out on the basis of symmetry: in this conformation, complexes of the C_2-symmetric ligands $\mathbf{1}^{maj}$ and $\mathbf{1}^{min}$ would each give rise to two sets of peaks due to oxazolidinyl protons, one for the coordinated ring, the other for the free (only a single set was observed for each), while that of the C_1-symmetric $\mathbf{1}^{med}$ would give rise to four, one for each of the pair of diastereomeric coordinated rings, and one for each of the pair of free rings (two sets of equal intensity were observed). The identity of Pd(**1**)Cl_2 in solution could not be rationalized in terms of a single, static structure, but was better described as diastereomeric equilibrium mixtures of *N,N′*- (**6**) and N^2,*N′*-chelated (**7**) species that were rapidly interconverting on the NMR time scale (Scheme 5a). The evidence for this assignment was as follows: (*i*) The r.t. ^{1}H NMR spectrum of Pd(**1**)Cl_2 had the same number of peaks and splitting patterns as that of the free ligand **1** (but different chemical shifts, see Table 2), that is, the complexity of the spectrum did not increase upon coordination, and the individual oxazolidinyl rings within Pd(**1**)Cl_2 were not differentiated on the basis of being coordinated or free. This indicated either a static tridentate coordination as in **7**, or a rapid **6**⇆**7** equilibrium. (*ii*) The ^{15}N NMR data clearly indicated (by ca. 100 ppm downfield shifts for the complexes relative to the free ligand, see Table 2) that the pyridyl N-atom was coordinated; smaller chemical shift differences were observed for *both* of the oxazolidinyl N-atoms, which remained chemically equivalent in the case of the C_2-symmetric diastereomers (Table 2). While this eliminated **6** as a static structure, it did not rule out the possibility of a rapid equilibrium. (*iii*) Reaction with the mild halide-abstracting reagent NH_4PF_6 in acetone gave a mixture of three diastereomers of [Pd(**1**-$\kappa^2 N,\kappa N'$)Cl]PF_6 (**8**), of which the major diastereomer was structurally characterized by X-ray crystallography (Figure 1). The ^{1}H NMR spectrum of a mixture of the diastereomers of **8** was significantly different from that of the parent dichloride (Table 2), which indicated coordination changes that could not be explained by simple exchange of non-coordinating halide. This eliminated **7** as a single static structure (chloride and hexafluorophosphate salts of which would be expected to have identical ^{1}H NMR spectra). (*iv*) The molar conductivity of Pd(**1**)Cl_2 in CH_2Cl_2 solution was 1.18 S cm^2 mol^{-1}, which was less than that of the 1:1 electrolyte, ^{n}Bu$_4$NBr (6.58 S cm^2 mol^{-1}) but significantly higher than that of neat CH_2Cl_2 (0.01 S cm^2 mol^{-1}). Moreover, the molar conductivity of Pd(**1**)Cl_2 was about 20% that of **8** (5.58 S cm^2 mol^{-1}). This once again indicated that **7** was not a viable exclusive description of

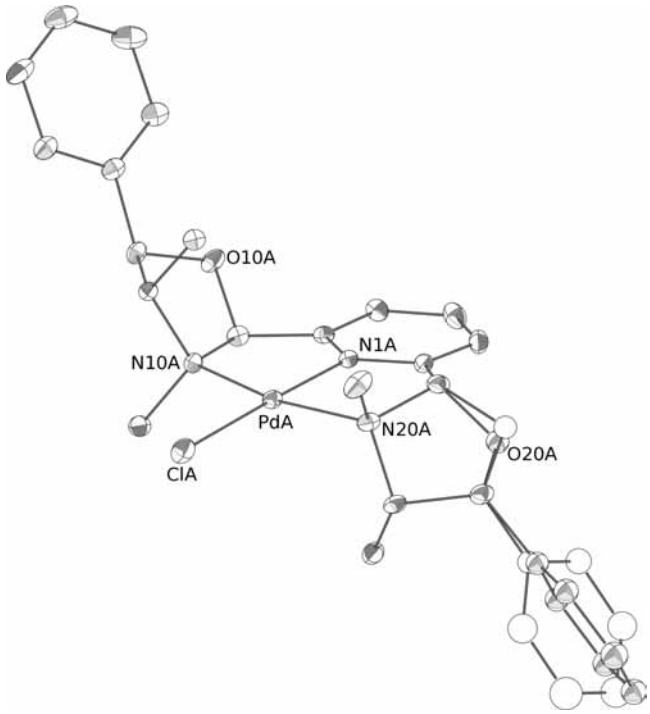
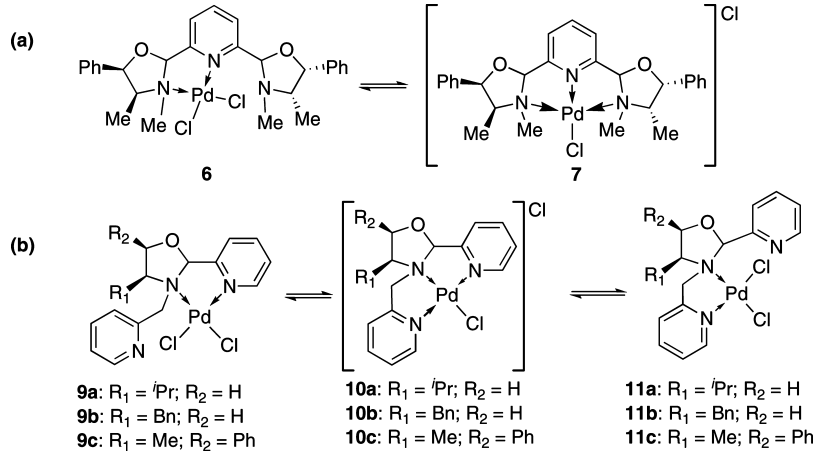


Figure 1. ORTEP representation of the molecular structure of the cation of $\mathbf{8}^{maj}$ with thermal ellipsoids shown at 30% probability. Disorder in one of the oxazolidinyl and phenyl rings is indicated by open circles. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg), with standard deviations in parentheses: PdA-N1A 1.955(3), PdA-N10A 2.073(2), PdA-N20A 2.077(3), PdA-ClA 2.3109(9), N20A-PdA-N10A 167.45(11), N1A-PdA-ClA 178.34(8), N1A-PdA-N10A 83.50(11), N10A-PdA-ClA 96.84(8), N20A-PdA-ClA 95.53(9).

Scheme 5. Solution Phase Equilibria Involving Isomers of (a) Pd(**1**)Cl_2 (**6** and **7**) and (b) Pd(**2a-c**)Cl_2 (**9a-c**, **10a-c**, **11a-c**)[a]



[a] In each case, parallel diastereomeric equilibria are at play.

Table 2. Summary of ^1H and ^{15}N NMR Data for Ligand **1** and Its Pd(II) Complexes, Pd(**1**)Cl_2 and [Pd(**1**-$\kappa N,\kappa^2 N'$)Cl]PF_6 (**8**)

	major C_2-symmetric diastereomer (δ)			C_1-symmetric diastereomer (δ)[a]			minor C_2-symmetric diastereomer (δ)		
	$\mathbf{1}^{maj}$	Pd($\mathbf{1}^{maj}$)Cl_2	$\mathbf{8}^{maj}$	$\mathbf{1}^{med}$	Pd($\mathbf{1}^{med}$)Cl_2	$\mathbf{8}^{med}$	$\mathbf{1}^{min}$	Pd($\mathbf{1}^{min}$)Cl_2	$\mathbf{8}^{min}$
C^2H	4.90	6.52	5.95	4.89, 5.49	6.47, 6.80	5.94,[b] 6.09	5.48	6.81[b]	6.16
C^4H	3.04	3.63	3.65	3.06,[b] 3.72	3.63,[b] 4.63	3.65,[b] 4.64	3.72[b]	5.01	4.75
C^5H	5.20	5.65	5.52	5.20,[b] 5.63	5.55, 6.09	5.54, 6.33	5.62[b]	5.79	6.01
NCH_3	2.29	3.48	3.37	2.33, 2.36	3.24, 3.58	3.15, 3.46	2.34	3.00	3.05
C^4HCH_3	0.79	1.59	1.60	0.73, 0.78[b]	0.91, 1.58	0.91, 1.60[b]	0.74	1.06	1.00
ox*N*	−312.8	−318.7	−318.0	−322.5, −325.0	−323.3, −324.5	*c*	*c*	*c*	*c*
py*N*	−64.9	−164.2	−163.6	−63.5	−160.6	*c*	*c*	*c*	*c*

[a] The oxazolidinyl rings in this diastereomer are chemically inequivalent and give rise to two sets of peaks. [b] Overlapped with the equivalent peaks arising from the next most abundant diastereomer. [c] Low abundance prevented detection.

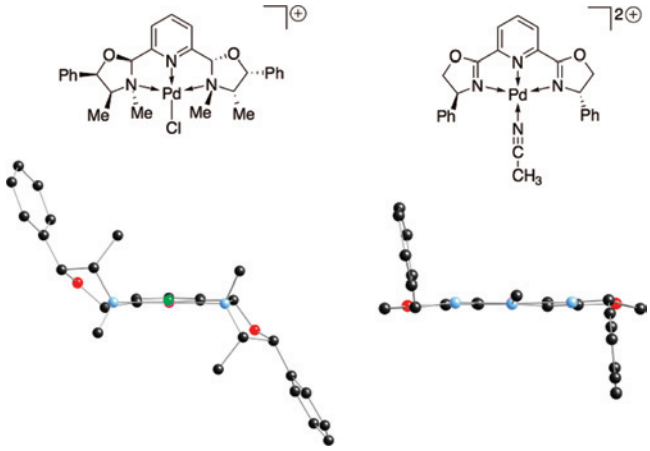


Figure 2. Structural comparison of the cations of $\mathbf{8}^{maj}$ (disorder removed for clarity) and a representative Pd(II)-pybox complex.[24] The ball-and-stick models are oriented such that the coordination plane of the metal is perpendicular to the page, and the ligand trans to the pyridyl donor points toward the reader. The carbon atoms of the CH_3CN ligand in the pybox complex are eclipsed. Carbon atoms are shown in black, nitrogen in blue, oxygen in red, palladium in pink, and chlorine in green.

Pd(**1**)Cl_2 in solution, but was rather a minor contributor to a rapid equilibrium mixture. (*v*) NH_4PF_6, even in excess, is generally not capable of stripping chloride from the inner coordination sphere of Pd(II). This implied that while **7** was not alone an adequate description of Pd(**1**)Cl_2, **8** was almost certainly formed through it. (*vi*) Low temperature NMR measurements to −50 °C did not give rise to more complicated spectra, as may have been expected, but only to slight peak broadening. Presumably, this meant that the proposed equilibrium was rapid even at low temperatures.

A single recrystallization of [Pd(**1**-$\kappa^2 N,\kappa N'$)Cl]PF_6 gave the major diastereomer ($\mathbf{8}^{maj}$) in pure form. An ORTEP representation of the molecular structure of the cation is shown in Figure 1. As expected, the metal center adopted an approximately square coordination, and there was a rough C_2-axis of symmetry coincident with the Pd−Cl bond. The pyridyl ring was essentially coplanar with the coordination plane. The N_{ox}−Pd−N_{py} angles were less than 90 ° (83.50(11)° and 84.19(11)°) on account of steric requirements of the ligand, while the N_{ox}−Pd−Cl angles were greater (95.53(9)° and 96.84(8)°). All of these characteristics were held in common with the known structures of analogous Pd(II)-pybox derivatives.[24] However, the latter were essentially planar except for their C^4-substituents that projected above and below the plane defined by the metal and the ligand, whereas the oxazoldinyl rings in $\mathbf{8}^{maj}$ were substantially buckled. Figure 2 shows a side-by-side comparison of the structures of the cations of $\mathbf{8}^{maj}$ and a representative Pd(II)-pybox complex.[24] In contrast to the oxazoline complex, the metal center in $\mathbf{8}^{maj}$ was crowded above and below the coordination plane by the methyl groups at the C^4-positions of the oxazolidine rings. In principle, these structural differences may lead to significant activity and selectivity differences in asymmetric catalytic reactions catalyzed by

(24) Nesper, R.; Pregosin, P.; Puentener, K.; Woerle, M.; Albinati, A. *J. Organomet. Chem.* **1996**, *507*, 85–101.

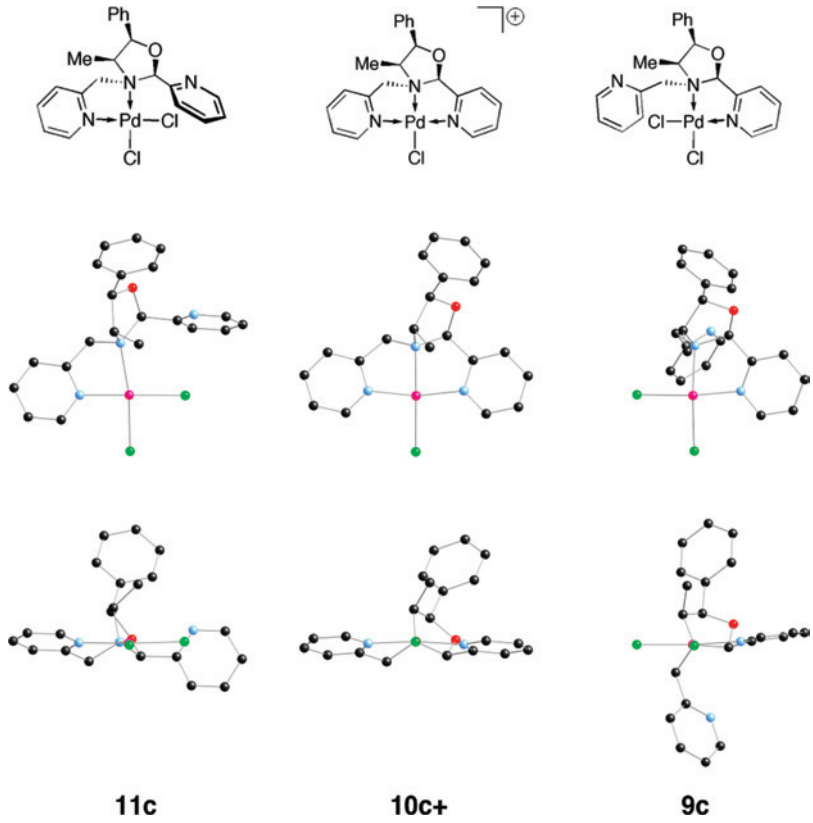


Figure 3. Calculated structures (B3LYP/LANL2DZ) of the major diastereomers of **9c** and **11c** and the cation of **10c**. In the top row, the ball-and-stick models are oriented such that the coordination plane of the metal is parallel to the page; in the bottom, it is perpendicular. The chloride ligand trans to the oxazolidinyl donor points toward the reader. Carbon atoms are shown in black, nitrogen in blue, oxygen in red, palladium in pink, and chlorine in green.

these two classes of compounds, and these studies are currently under investigation.

Palladium(II) complexes of the bis(pyridyl)oxazolidine ligands were made by 1:1 reaction of mixtures of the diastereomers of **2a-c** and *trans*-$PdCl_2(PhCN)_2$ in CH_2Cl_2 to give Pd(**2a-c**)Cl_2. As in the case of ligand **1**, the identity of the complexes in solution could not be rationalized in terms of single, static structures, but rather were best described in each case as two diastereomeric equilibrium mixtures of *N,N′*- (**9a-c**), *N,N′,N″*- (**10a-c**), and *N′,N″*-chelated (**11a-c**) species that were rapidly interconverting on the NMR time scale (Scheme 5b). The evidence for and rationale behind this assignment, combustion analyses, low and r.t. ^1H and ^{15}N NMR spectroscopic data, reactions with NH_4PF_6, and solution molar conductivities, were very similar to those discussed above for the **6**⇆**7** equilibrium, but in this case, three distinct isomers were possible, each of which had two diastereomers (see Supporting Information for the explicit rationale). All of the compounds resisted solid-state characterization by X-ray crystallography, but calculated structures for the major diastereomers of **9c**, **11c**, and the cation of **10c** are given in Figure 3. Isomer **11c** was calculated to be about 17 kcal mol^{-1} less stable than **9c**.

Reaction of equilibrium mixtures of isomers of Pd(**2a-c**)Cl_2 with NH_4PF_6 in acetone gave the hexafluorophosphate salts, [Pd(**2a-c**-$\kappa N,\kappa N',\kappa N''$)Cl]$PF_6$ (**12a-c**) in which the ligands were bound exclusively through all three N-donors.

The bi-to-tridentate fluxionality observed for Pd(II) complexes of oxazolidine-based ligands **1** and **2a-c** (Scheme 5) has literature precedent in the fluxionality observed by Braunstein and co-workers in Pd(II) complexes of tridentate ligands incorporating a phosphite and two oxazoline donors (the "NOPON" ligand system).[25] These researchers identified an equilibrium mixture of PdI_2(NOPON-$\kappa P,\kappa N$) and [PdI(NOPON-$\kappa P,\kappa^2 N$)]I isomers at 172 K by solution NMR

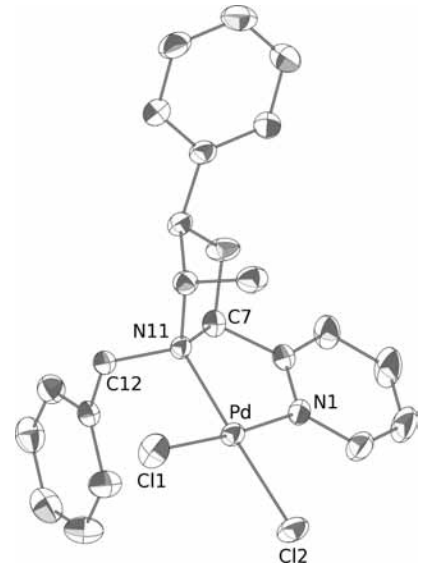
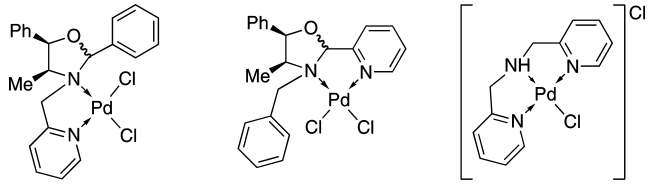


Figure 4. ORTEP representation of the molecular structure of **13b**^{maj} with thermal ellipsoids shown at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg), with standard deviations in parentheses: Pd1−N1 2.022(3), Pd1−N11 2.073(3), Pd1−Cl1 2.2938(10), Pd1−Cl2 2.2865(12), N1−Pd1−Cl2 94.86(10), N1−Pd1−N11 82.96(12), N11−Pd1−Cl1 92.77(8), Cl1−Pd1−Cl2 89.41(5).

Chart 3. Pd(**3a,b**-$\kappa N,\kappa N'$)Cl_2 (**13a,b**) and [PdCl(bpma-H-$\kappa^2 N,\kappa N'$)]Cl



spectroscopy. The tricoordinated complex was the minor isomer in solution (10%) at this temperature but could be isolated quantitatively as its PF_6^- salt by reaction of the equilibrium mixture with NH_4PF_6, just as we found for our oxazolidine-based systems, Pd(**1**)Cl_2 and Pd(**2a-c**)Cl_2. Braunstein and co-workers also invoked tricoordinated NOPON ligands as intermediates in exchange of equivalent oxazoline "arms" in $PdCl_2$(NOPON) complexes, which are analogous to **7** (Scheme 5); however, these were postulated to be neutral, 5-coordinate $PdCl_2$(NOPON-$\kappa P,\kappa^2 N$) species formed through an associative route and not the 4-coordinate cation [Pd(**1**-$\kappa N,\kappa^2 N'$)Cl]$^+$ we envisage.

The coordination of bis(pyridyl)oxazolidines **2a-c** differed substantially from the well-known bis(2-pyridylmethyl)amine ligand family, $NR(CH_2(py))_2$ (R = H (bpma-H),[26] Me (bpma-Me)[27]) with which they could in principle share atom-for-atom connectivity in chelated rings. Thus, while $PdCl_2$ adducts of **2a-c** were highly fluxional, the compound whose empirical formula is $PdCl_2$(bpma-H) has been shown by crystallography to be the salt [PdCl(bpma-H-$\kappa^2 N,\kappa N'$)]Cl wherein the ligand was bound through both pyridyl as well as the amine N-atoms (Chart 3); closely related derivatives showed the same coordination.[26] We believe that the geometrical constraints associated with the oxazolidinyl ring in Pd(**2**)Cl_2 make tridentate coordination of the ligand less favorable than in complexes of the bpma family, in which flexible methylene groups bridge the amine and pyridyl donors.

This hypothesis was borne out by structural studies. Reactions of **3a,b** and *trans*-$PdCl_2(PhCN)_2$ produced the expected *N,N′*-chelated complexes Pd(**3a,b**-$\kappa N,\kappa N'$)Cl_2 (**13a** and **13b**; Chart 3). These compounds were the direct analogues of the *N,N′*-coordinated complexes **11c** and **9c**, respectively, but did not display isomerism in solution and were accordingly easier to crystallize. The solid-state structure of **13b**^{maj} was determined (Figure 4). In this and every other known structure of Group 10 coordination complexes of *N*-alkyl oxazolidines,[6,10] the substituent at the C^2 position of the ring (C7 in Figure 4) and that on the N-atom had an anti relationship. This ensured that the N1−Pd−N11−C7 torsion angle in **13b**^{maj}(ca. 7.8 °) was necessarily much smaller than that of Cl1−Pd−N11−C12 (ca. 51.9 °) because of coordination of the pyridyl ring pendant from C^2 of the oxazoldinyl ring. By extension to complexes of ligands **2a-c**, this meant that coordination of the pyridylmethyl groups bonded to the oxazolidinyl N-atoms in the proposed cations of **10a-c** (Scheme 5) was disfavored with respect to simple chloride coordination (i.e., to generate **9a-c**) on account of ring strain. Specifically, Figure 3 shows clearly that substitution of the pyridylmethyl group in the cation of **10c** by Cl^- (i.e., to give **9c**) would have the dual effect of lowering the calculated intrachelate $N_{py}-Pd-N_{ox}-C^2$ torsion angle from about 20.9 ° to 8.1 °, and relaxing the $E-Pd-N_{ox}-CH_2$ torsion angle (E = N_{py} for **10c**, Cl for **9c**) from about 33.1° to about 54.9°. These perturbations gave calculated angles in **9c** that were similar to the analogous angles observed in the solid state of **13b**^{maj}, as expected. By comparison, the two intrachelate torsion angles in [PdCl(bpma-H-$\kappa^2 N,\kappa N'$)]$^+$ were approximately 19.8° and 28.8°.

These observations were consistent with the measured molar conductivities of Pd(**2c**)Cl_2 (1.48 S cm^2 mol^{-1}) and **12c** (4.29 S cm^2 mol^{-1}) in CH_2Cl_2 solution, which demonstrated that the putative 1:1 electrolyte **10c**, being disfavored on steric grounds, was a minor contributor to the equilibrium distribution of isomers.

Conclusions

Structurally diverse and potentially tridentate pyridyloxazolidine ligands may be synthesized in a modular fashion using simple, high-yielding reactions. Diastereomeric product distributions are sensitive to the conditions under which the condensation reactions are performed: the thermodynamically preferred major diastereomer of the oxazolidine, in which the substituents at the C^2 and C^4 positions are syn, is favored when product water is removed slowly. The ligands form 1:1 adducts with Pd(II), but geometrical constraints imposed by the oxazolidine ring render the complexes fluxional in the presence of chloride. Substitution of Cl^- for PF_6^- gives salts in which the ligands are bound exclusively in tridentate coordination modes. The diastereomeric ratio of the salts could be improved by recrystalization. In some cases, for example, **8** and **12b**, optical purity was achieved using only a single recrystalization. We are currently investigating these compounds as catalysts for asymmetric transformations.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for a Discovery Grant (to N.D.J.). We acknowledge useful discussion with Profs. Robert Hudson and Michael Kerr of the UWO Chemistry Department.

Supporting Information Available: Explicit evidence and rationale for the equilibrium **9a-c**⇆**10a-c**⇆**11a-c**; table of ^{1}H and ^{15}N NMR data for **2c**, Pd(**2c**)Cl_2, and **12c**; comparative ^{1}H NMR spectra of Pd(**1**)Cl_2 and **8**, and of Pd(**2c**)Cl_2 and **12c**; X-ray crystallographic data for **8**^{maj} and **13b**^{maj} in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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