Chiral Oxazoline/Imidazoline-2-ylidene Complexes†

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N-Heterocyclic "carbene" ligands derived from imidazole are alternatives for the well-established phosphines in organometallic catalysis. In contrast to phosphines, they do not easily dissociate from transition metals (e.g., palladium, rhodium) so they seem suited for chiral modifications. This publication reports on the synthesis and coordination chemistry of novel bidentate ligands with both imidazoline-2-ylidene and oxazoline moieties. The synthesis follows straightforward routes, using *N*-functionalized imidazolium salts and 2-amino alcohols. The crystal structures of palladium and rhodium complexes are presented. With rhodium, the ligands show a chelating coordination mode.

Introduction

Metal complexes of imidazoline-2-ylidenes have recently attracted considerable attention as a novel class of homogeneous catalysts.[1,2] For example, complexes of rhodium and palladium show excellent catalytic properties for Heck-olefination, hydroformylation, and isomerization.[3−5] In contrast to the corresponding phosphine complexes, ligand dissociation has never been observed so that these catalysts normally do not depend on an excess of ligand.[6] These properties make them suitable for chiral modifications.[7]

We recently reported on the application of rhodium complexes with *monodentate* chiral imidazoline-2-ylidene ligands derived from enantiomerically pure 1-naphthylethylamine as catalysts for the enantioselective hydrosilylation of acetophenone.[5] *Chelating* chiral ligands are expected to accomplish higher optical inductions in asymmetric reactions. Such ligands can be constructed by the combination of an imidazoline-2-ylidene moiety with a donor-functionalized chiral auxiliary such as a chiral oxazoline (Figure 1).

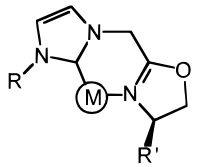

Figure 1. General formula of oxazoline/imidazoline-2-ylidene complexes.

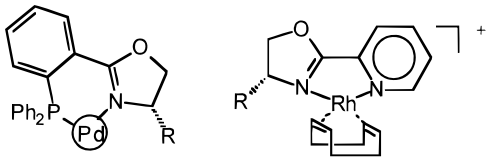

Figure 2. Catalyst-containing oxazoline rings.

Chiral oxazolines are now commonly used in asymmetric catalysis since enantiomerically pure oxazoline derivatives are conveniently accessible from commercially available chiral β-amino alcohols (Figure 2).[8] Oxazoline−phosphines, for example, are useful ligands for palladium-catalyzed asymmetric Heck-olefinations (*A. Pfaltz*),[9] and with pyridine−oxazolines, excellent asymmetric inductions were accomplished in rhodium-catalyzed hydrosilylation reactions (*H. Brunner*).[10]

Imidazoline-2-ylidenes combined with chiral oxazolines (Figure 1) could become interesting alternatives to these established ligand systems. We now report on the synthesis and structures of novel chiral oxazoline/imidazoline-2-ylidene complexes of rhodium and palladium.

Results and Discussion

Synthesis of the Imidazolium Salts. Functionalized imidazoline-2-ylidene complexes are most conve-

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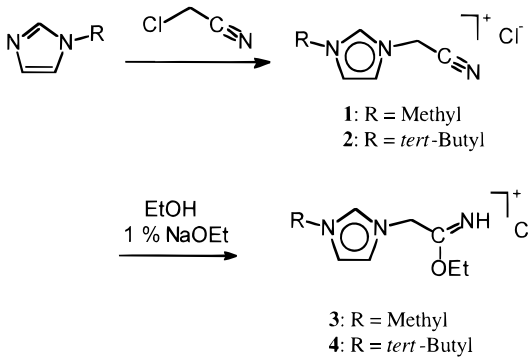
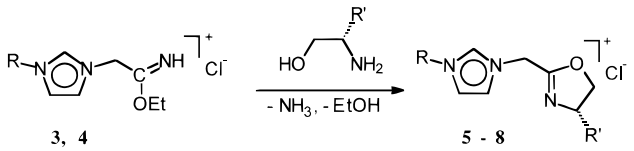
Scheme 1. Synthesis of Imidoester-Substituted Imidazolium Salts



Scheme 2. Synthesis of Oxazoline-Substituted Imidazolium Salts



	R	R '
5	Methyl	Benzyl
6	Methyl	Isopropyl
7	tert-Butyl	Benzyl
8	tert-Butyl	Isopropyl

niently accessible by deprotonation of imidazolium salts in the presence of metal precursors.[11−14] The oxazoline-substituted imidazolium salts required for the desired complexes were synthesized from the corresponding 1-alkylimidazoles in three consecutive steps without workup of the intermediates. The 1-alkylimidazoles were first converted into the corresponding cyanomethyl imidazolium chlorides **1** and **2** by treatment with chloroacetonitrile (Scheme 1). Addition of ethanol to the nitrile groups led to the formation of reactive imidoesters. Due to the high reactivity of the nitrile group, only traces of base were required to catalyze this addition reaction. The imidoester-substituted imidazolium salts **3** and **4**, obtained in about 70% yield, served as the starting material for the construction of the oxazoline-substituted imidazolium salts.

Condensation of the imidoesters **3** and **4** with several commercially available enantiomerically pure β-amino alcohols under acidic conditions efficiently yielded the corresponding chiral oxazoline derivatives **5**−**8** (Scheme 2). During the condensation step only volatile side products (NH_3, EtOH) are formed so that the equilibrium is shifted to the desired products.

Synthesis and Structures of the Rhodium Complexes. The rhodium complexes were synthesized by treatment of the imidazolium salts with bis[(μ-chloro)-(η^4-1,5-cyclooctadiene) rhodium(I)] in the presence of lithium alcoholates following our recently published method (Scheme 3).[14] The chloride was removed by treatment with thallium hexafluorophosphate to ensure a *chelating* coordination of the ligands.

The rhodium complexes were obtained as yellow, air-stable crystals. The ^{13}C NMR spectra show the expected signals for the carbene carbon at around 176 ppm with a characteristic coupling constant $J(^{103}Rh, ^{13}C)$ of 50 Hz. The ^1H NMR spectra of the complexes **5a**−**8a** are very similar, suggesting the same geometry for all compounds. The signals of the two protons at the methylene bridge are detected at significantly different shifts (δ = 5.4 and 4.8 ppm) with a characteristic geminal coupling constant $^2J(HH)$ of 17 Hz. This suggests an angular geometry of the ligands which brings one of the protons closer to the metal center. The mass spectra show strong characteristic signals for the $[M^+ - PF_6]$ fragments, so that a monomeric structure of the complexes is likely.

The crystal structure of **7a** confirms the *monomeric, chelated* structure of the complexes (Figure 3). The rhodium is in a slightly distorted square-planar environment of the COD and the chelating oxazoline/imidazoline-2-ylidene ligand. Both the carbene-to-rhodium distance (d(Rh−C1) = 2.056(5) Å) and the (oxazoline)nitrogen-to-rhodium distance (d(Rh−N12) = 2.115(4) Å) are within the expected range. The distance between rhodium and the COD double bond is slightly longer for the atoms trans to the carbene (d(Rh−C31) = 2.189(6) Å, d(Rh−C32) = 2.213(5) Å) than trans to the oxazoline (d(Rh−C35) = 2.128(6) Å, d(Rh−C36) = 2.157(6) Å). This suggests that the *carbene is a stronger donor than the oxazoline.* The imidazoline and oxazoline rings are in an angle of 119° to each other, so that the *tert*-butyl group is bent into one direction and the bridging methylene group into the other direction out of the coordination plane.

Synthesis and Structure of the Palladium Complexes. The imidazolium salts **5**−**8** were converted into the corresponding palladium complexes under similar conditions as those described above. Treatment of the imidazolium salts with palladium acetate in the presence of lithium *tert*-butoxide and sodium iodide in THF was expected to lead directly to the desired palladium complexes (Scheme 4). This modification of the original synthesis for palladium carbene complexes has been used successfully for nonchelating carbene amine palladium complexes.[15] The sodium iodide enhances the solubility of the palladium in THF due to an intermediate formation of sodium tetraiodopalladate, $Na_2[PdI_4]$.

Compounds **5b**−**8b** were obtained as orange, air-stable crystals. In the ^{13}C NMR spectra, characteristic signals at around 149 ppm for the carbene-C atoms give evidence for a successful conversion of the imidazolium salts. The striking feature of the ^1H NMR spectra are again the signal groups arising from the protons at the methylene protons at quite different chemical shifts (δ = 7.67−7.28 ppm vs 4.87−4.68 ppm), with a characteristic geminal coupling constant of 17 Hz. Hence, one of the two protons must be significantly closer to the metal center than the other. The mass spectra indicate a *dimeric* structure for all palladium complexes **5b**−**8b**, because no signals for the monomeric compounds were detected.

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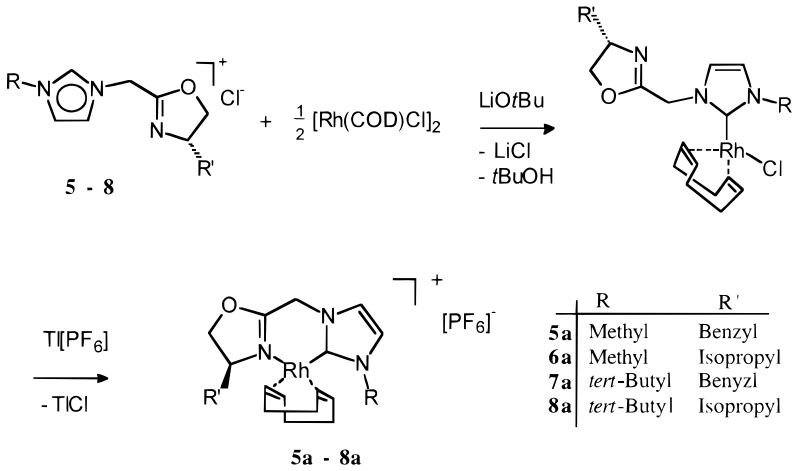
Scheme 3. Synthesis of Oxazoline/Imidazoline-2-ylidene Rhodium Complexes



	R	R'
5a	Methyl	Benzyl
6a	Methyl	Isopropyl
7a	*tert*-Butyl	Benyzl
8a	*tert*-Butyl	Isopropyl

The crystal structure of **6b** confirms the expected dimeric structure of the complexes (Figure 4). Two palladium atoms are coordinated by two bridging oxazoline/imidazoline-2-ylidene ligands and four iodide ions so that each palladium atom is in a slightly distorted square-planar environment with one carbene- and one nitrogen-donor in a *trans* conformation. In both bridging ligands the planes of the oxazoline and the imidazoline heterocycles are bent toward each other (108° and 102°). The bond distances between the palladium and the carbene-carbon (d(Pd1−C1) = 1.943(8) Å) and between the oxazoline-nitrogen and the palladium (d(Pd1−N6) = 2.107(6) Å) are within the expected range.

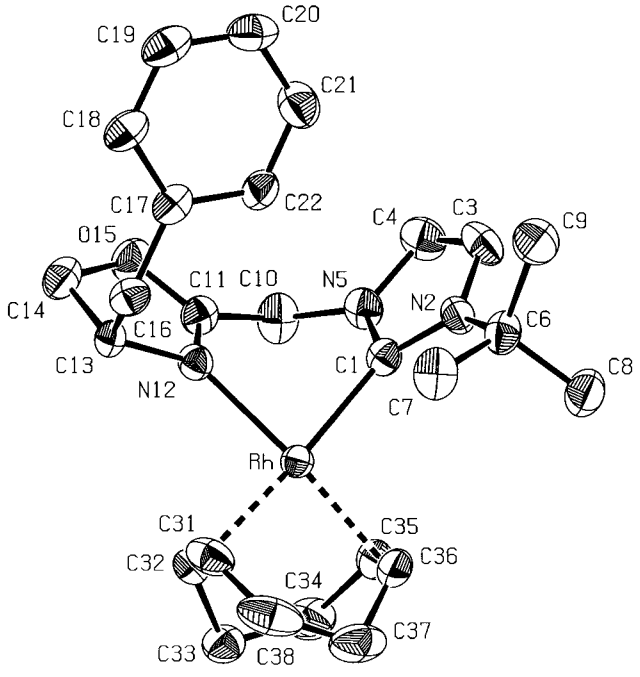


Figure 3. PLATON drawing[16] of the molecular and crystal structure of the cationic complex **7a**. Ellipsoids are drawn at the 50% probability level, and the noncoordinating $[PF_6]^-$ anion and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh−N12 = 2.115(4), Rh−C1 = 2.056(5), Rh−C31 = 2.189(6), Rh−C32 = 2.213(5), Rh−C35 = 2.128(6), Rh−C36 = 2.157(6), N2−C1 = 1.355(7), N2−C3 = 1.390(7), C3−C4 = 1.335(9), N5−C10−C11 = 110.2(4), N12−Rh-C1 = 83.71(18), C31−Rh−C36 = 81.5(2), C32−Rh−C35 = 81.5(2), C1−N2−C3 = 109.2(4), N2−C1−N5 = 104.8(4).

Conclusion

General access to enantiomerically pure oxazoline-substituted imidazolium salts is now available. From these salts, novel metal complexes exhibiting *N*,*N*-chelating ligands of imidazoline-2-ylidene *and* oxazoline moieties can be obtained in good yields. The rhodium compounds were found to be monomeric complexes with a chelating coordination mode of the novel ligands. In contrast, palladium forms dimeric structures with a bridging coordination mode of the ligands. The properties of these complexes as catalysts for asymmetric reactions are presently under investigation in our laboratory.

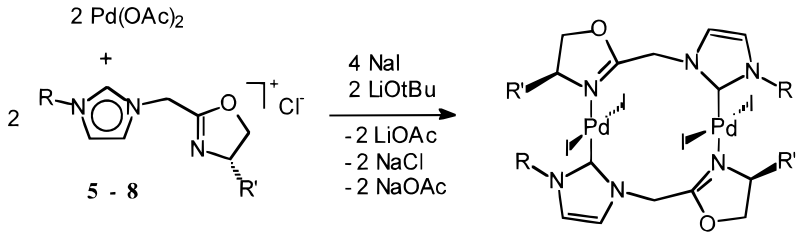
Experimental Section

General Procedures. Oxygen- or moisture-sensitive or hygroscopic materials were handled under purified nitrogen or purified argon using standard Schlenk line techniques. All solvents were degassed and dried using standard procedures unless used for extractions. Dimethyl sulfoxide-d_3 and $CDCl_3$ were stored over 3 Å molecular sieves.

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JMX-GX-400 or Bruker DPX 400 instruments using the solvent resonance as the internal standard. Infrared spectra were obtained using the Perkin-Elmer 1650 Fourier transform IR spectrometer with CaF_2 cells. GC-mass spectra were obtained on a Hewlett-Packard 5890 instrument. All other mass spectra were measured at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 mass spectrometer using either the FAB (xenon/*p*-nitrobenzyl alcohol) or CI (isobutane) technique. All elemental analyses were performed by the TU München Microanalytical Laboratory.

1-(Cyanomethyl)-3-methylimidazolium Chloride (1). Methylimidazole (4.10 g, 50 mmol) was dissolved in 50 mL of THF, chloroacetonitrile (3.77 g, 50 mmol) was dropwise added, and the mixture was refluxed overnight. During this time, the product precipitated. The solvent was decanted, and the residue was washed twice with THF. After removal of the volatiles in vacuo, **1** was obtained as a white, hygroscopic powder (5.35 g, 68%). ^{1}H NMR (400 MHz, DMSO): δ 9.52 (s, 1H, N_2CH), 7.98 (s, 1H, NCH), 7.85 (s, 1H, NCH), 5.79 (s, 2H, NCH_2), 3.90 (s, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, DMSO): δ 137.8 (N_2CH), 124.3 (NCH), 122.5 (NCH), 114.8 (CN), 36.7 (NCH_2), 36.1 (CH_3). IR (KBr): ν(CN) 2259 cm^{-1}.

Scheme 4. Synthesis of Oxazoline/Imidazoline-2-ylidene Palladium Complexes



	R	R'
5b	Methyl	Benzyl
6b	Methyl	Isopropyl
7b	*tert*-Butyl	Benzyl
8b	*tert*-Butyl	Isopropyl

1-*tert*-Butyl-3-(cyanomethyl)imidazolium Chloride (2). Compound **2** was prepared from 1-*tert*-butylimidazole (5.80 g, 47.0 mmol) and chloroacetonitrile (5.00 g, 66.0 mmol) in the same way as **1**. The product was obtained as a white, hygroscopic powder (5.80 g, 76%), which was directly converted into the imidoester **4**.

3-((Ethoxycarbonimidoyl)methyl)-1-methylimidazolium chloride (3). 1-(Cyanomethyl)-3-methylimidazole (1.50 g, 10.0 mmol) was dissolved in 10 mL of ethanol, and a small aliquot of NaH (ca. 1 mol %) was added. The solution was allowed to stir overnight at room temperature. The progress of the reaction was monitored by IR spectroscopy. After 16 h, the solvent was removed in vacuo and the product was obtained as a white powder, which was used without further workup. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.2 (s, 1H, N_2CH), 8.22 (s, 1H, =NH), 7.61 (s, 1H, NCH), 7.52 (s, 1H, NCH), 5.22 (s, 2H, NCH_2), 4.02 (s, 3H, NCH_3), 3.99 (q, ^3J(HH) = 7 Hz, 2H, OCH_2), 1.17 (t, ^3J(HH) = 7 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.7 (CNHO), 138.4 (NCH), 123.5 (NCH), 123.0 (NCH), 62.1 (NCH_2), 50.9 (OCH_2), 36.7 (NCH_3), 13.8 (CH_3). IR (THF): ν(C=NH) 1679 cm^{-1}.

1-*tert*-Butyl-3-((Ethoxycarbonimidoyl)methyl)imidazolium Chloride (4). Imidoester **4** was prepared using the same procedure as for **3** from 1-*tert*-butyl-3-(cyanomethyl)-imidazolium chloride (**2**; 5.80 g, 38 mmol). The product was obtained as a light brown powder which was used without further workup. ^{1}H NMR (270 MHz, $CDCl_3$): δ 10.36 (s, 1H, N_2CH), 8.24 (s, 1H, =NH), 7.71 (d, ^3J(HH) = 2 Hz, 1H, NCH=), 7.47 (d, ^3J(HH) = 2 Hz, 1H, NCH=), 5.20 (s, 2H, NCH_2), 3.93 (q, ^3J(HH) = 7 Hz, 2H, OCH_2), 1.53 (s, 9H, CCH_3) 1.16 (t, ^3J(HH) = 7 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$): δ 163.0 (CN), 135.8 (N_2CH), 122.9 (NCH=), 119.8 (NCH=), 61.8 (NCH_2), 60.2 (NCR_3), 57.0 (OCH_3), 29.5 (CCH_3), 13.5 (CH_3). IR (THF): ν(C=NH) 1679 cm^{-1}.

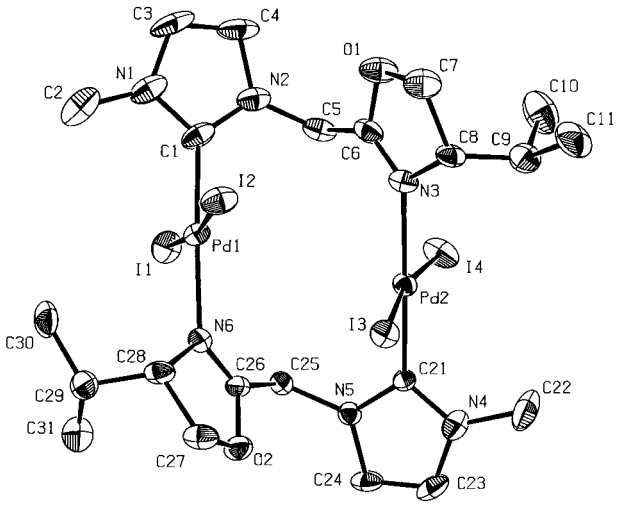


Figure 4. PLATON drawing[16] of the molecular and crystal structure of **6b**. Ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1−I1 = 2.6224(8), Pd1−I2 = 2.6358(9), Pd1−N6 = 2.107(6), Pd1−C1 = 1.943(8), C1−N1 = 1.349(11), N1−C3 = 1.374(14), C3−C4 = 1.347(17), N3−C6 = 1.272(11), N3−C8 = 1.484(10), I1−Pd1−I2 = 170.62(6), I1−Pd1−C1 = 87.5(2), N6−Pd1−C1 = 177.0(3), N1−C1−N2 = 105.6(7), N1−C3−C4 = 107.2(9), C26−N6−C28 = 106.6(6).

1-[(2*S*)-(4-Benzyl-4,5-dihydrooxazolyl)methyl]-3-methylimidazolium Chloride (5). Imidoester **3** (2.04 g, 10.0 mmol) and (*S*)-phenylalaniol (1.52 g, 10.0 mmol) were dissolved in a minimum amount of nitromethane. After the addition of a drop of concentrated hydrochloric acid, the mixture was heated to 80 °C. Nitrogen was slowly bubbled through the solution to remove the volatile products. After 16 h, the mixture was dissolved in ethanol and the product was precipitated out of solution by the addition of diethyl ether. The solvent was decanted, and the residue was washed with small portions of diethyl ether. Removal of the volatiles in vacuo produced **5** (2.10 g, 72%) as a light brown, hygroscopic powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.36 (s, 1H, N_2CH), 7.39 (s, 1H, NCH), 7.32 (s, 1H, NCH), 7.29−7.12 (m, 5H, phenyl-CH), 5.39 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 5.32 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 4.39 (m, 1H, =NCH), 4.29 ("t", J(HH) = 9 Hz, 1H, OCH_2), 4.06 ("t", J(HH) = 9 Hz, 1H, OCH_2), 4.04 (s, 3H, NCH_3), 2.99 (dd, ^2J(HH) = 14 Hz, ^3J(HH) = 6 Hz, 1H, CH_2), 2.67 (dd, ^2J(HH) = 14 Hz, ^3J(HH) = 6 Hz, 1H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.7 (CNO), 139.0 (N_2CH), 137.1 (phenyl-C), 129.3, 128.6 (phenyl-CHs), 126.7 (*p*-phenyl-CH), 123.0 (NCH), 122.8 (NCH), 73.0 (NCH_2), 67.2 (=NCH), 46.1 (OCH_2), 41.1 (CH), 36.8 (NCH_3). MS (FAB): 546 ([M^+ + M − Cl], 2), 256 ([M^+ − Cl], 100).

1-[(2*S*)-(4-Isopropyl-4,5-dihydrooxazolyl)methyl]-3-methylimidazolium Chloride (6). Imidoester **3** (2.04 g, 10.0 mmol) and (*S*)-valinol (1.03 g, 10.0 mmol) were mixed in a small Schlenk tube. A drop of concentrated hydrochloric acid was added, and the mixture was heated to 80 °C. To remove the ethanol and ammonia formed during the ring closure, the reaction was performed in a vacuum of ca. 20 mmHg. After 5 h, the gas evolution had ceased. The mixture was then dissolved in ethanol and was precipitated out of solution by the addition of diethyl ether. The solvent was decanted, and the residue was washed with small portions of diethyl ether. Removal of the volatiles in vacuo produced **6** (1.36 g, 68%) as a light brown, hygroscopic powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.56 (s, 1H, N_2CH), 7.46 (s, 1H, NCH), 7.42 (s, 1H, NCH), 5.38 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 5.28 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 4.32 ("t", J(HH) = 9 Hz, 1H, OCH_2), 4.07 (s, 3H, NCH_3), 4.01 ("t", J(HH) = 9 Hz, 1H, OCH_2), 3.86 (m, 1H, =NCH), 1.68 (m, 1H, CH), 0.88 (d, ^3J(HH) = 7 Hz, 3H, CH_3), 0.81 (d, ^3J(HH) = 7 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.9 (CNO), 139.1 (N_2CH), 123.0 (NCH),

122.9 (NCH), 72.3 (NCH_2), 71.6 (=NCH), 46.0 (OCH_2), 36.8 (NCH_3), 32.4 (CH), 18.7 (CH_3), 18.2 (CH_3). MS (FAB) *m*/*z* 208 ([M^+ − Cl], 100).

1-[(2*S*)-(4-Benzyl-4,5-dihydrooxazolyl)methyl]-3-*tert*-butylimidazolium Chloride (7). Compound **7** was prepared using the same procedure as for **5** from imidoester **4** (1.90 g, 7.7 mmol) and (*S*)-phenylalaniol (0,80 g, 7.7 mmol). The product was obtained as a light brown, hygroscopic powder (1.12 g, 64%). ^{1}H NMR (400 MHz, 25 °C, $CDCl_3$): δ 10.75 (s, 1H, N_2CH), 7.44 (d, ^3J(HH) = 2 Hz, 1H, NCH), 7.34 (d, ^3J(HH) = 2 Hz, 1H, NCH), 7.23 (m, 5H, phenyl-CH), 5.46 (d, ^2J(HH) = 17.0 Hz, 1H, NCH_2), 5.11 (d, ^2J(HH) = 17.0 Hz, 1H, NCH_2), 4.41 (m, 1H, =NCH), 4.30 (dd, ^2J(HH) = 8.0 Hz, ^3J(HH) = 1.5 Hz, 1H, OCH_2), 4.07(dd, ^2J(HH) = 8.0 Hz, ^{3}J (HH) = 1.5 Hz, 1H, OCH_2), 3.11 (dd, ^2J(HH) = 7.0 Hz, ^3J(HH) = 1 Hz, 1H, CH_2), 2.87 (dd, ^2J(HH) = 7.0 Hz, ^3J(HH) = 1 Hz, 1H, CH_2), 1.65 (s, 9H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.1 (CNO), 139.3 (N_2CH), 136.9 (phenyl-C), 129.1, 128.4 (phenyl-CHs), 126.2 (*p*-phenyl-CH), 123.3 (NCH), 122.4 (NCH), 73.2 (NCH_2), 67.0 (=NCH), 60.1 (NCR_3), 46.4 (OCH_2), 41.1 (CH), 29.3 ((CH_3)$_3$). MS (FAB): *m*/*z* 298 ([M^+ − Cl], 100).

3-*tert*-Butyl-1-[(2*S*)-(4-Isopropyl-4,5-dihydrooxazolyl)-methyl]imidazolium Chloride (8). Compound **8** was prepared in the same way as **6** from imidoester **4** (2.04 g, 10.0 mmol) and (*S*)-phenylalaniol (1.52 g, 10.0 mmol). The product was obtained as a light yellow powder (1.5 g, 68%). ^{1}H NMR (270 MHz, $CDCl_3$): δ 10.05 (s, 1H, N_2CH), 7.53 (s, 1H, NCH), 7.38 (s, 1H, NCH), 5.56 (d, ^2J(HH) = 17.0 Hz, 1H, NCH_2), 5.39 (d, ^2J(HH) = 17.0 Hz, 1H, NCH_2), 4.35 (dd, ^2J(HH) = 12.5, ^3J(HH) = 2.5 Hz, 1H, OCH_2), 4.15 (dd, ^2J(HH) = 12.5, ^3J(HH) = 2.5 Hz, 1H, OCH_2), 3.67 (m, 1H, =NCH), 2.49 (m, 1H, CH), 1.63 (s, 9H, $C(CH_3)_3$), 1.15 (m, 6H, CH_3). ^{13}C{^{1}H} NMR (68 MHz, $CDCl_3$): δ 157.6 (CNO), 138.5 (N_2CH), 123.9 (NCH), 122.3 (NCH), 72.0 (NCH_2), 71.2 (=NCH), 59.6 (NCR_3), 46.4 (OCH_2), 32.1 (CH), 18.4 (CH_3), 18.1 (CH_3), 29.8 ((CH_3)$_3$). MS (FAB): *m*/*z* 250 ([M^+ − Cl], 100).

(η^4-1,5-Cyclooctadiene)(1-[(2*S*)-(4-benzyl-4,5-dihydrooxazolyl)methyl]-3-methylimidazolin-2-ylidene)rhodium-(I) Hexafluorophosphate (5a). $(RhCODCl)_2$ (200 mg, 0.41 mmol) was dissolved in 10 mL of THF. Under intense stirring, *t*-BuOLi (79 mg, 1.00 mmol) was added. After 10 min at room temperature, the imidazolium salt **5** (233 mg, 0.80 mmol) was added and the resulting slurry was allowed to stir overnight. The progress of the reaction was monitored by TLC. After 16 h, the solvent was removed in vacuo and the product was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH). After the removal of the solvents, the product was dissolved in 10 mL of THF, and Tl[PF_6] (300 mg, 0.86 mmol) was added. Immediately, the formation of a white precipitate was observed. After 20 min, the solvent was removed in vacuo and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH) and crystallized from CH_2Cl_2/diethyl ether as yellow crystals (259 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$/CD_3OD): δ 7.42 (m, 3H, phenyl-CH, NCH), 7.08 (m, 3H, phenyl-CH, NCH), 5.32 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 4.89 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 4.76 (m, 1H, =NCH), 4.67 (m, 2H, OCH_2), 4.20 (m, 4H, COD-CH), 3.99 (s, 3H, CH_3), 2.89 (m, 1H, CH_2), 2.64 (m, 1H, CH_2), 2.21 (m, 4H, COD-CH_2), 2.10 (m, 4H, COD-CH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$/CD_3OD): δ 176.5 (d, $^1J(^{103}Rh^{13}C)$ = 50 Hz, CN_2), 165.8 (CNO), 137.8, 128.4, 128.1, 126.7 (phenyl-C), 122.6 (NCH), 121.4 (NCH), 96.8 (d, $^1J(^{103}Rh^{13}C)$ = 9 Hz, COD-CH), 91.9 (d, $^1J(^{103}Rh^{13}C)$ = 8 Hz, COD-CH), 79.7 (d, $^1J(^{103}Rh^{13}C)$ = 13 Hz, COD-CH), 74.8 (NCH_2), 71.6 (d, $^1J(^{103}Rh^{13}C)$ = 11 Hz, COD-CH), 64.8 (=NCH), 48.5 (OCH_2), 41.3 (CH) 37.3 (NCH_3), 32.9, 29.2, 28.7, 26.8 (COD-CH_2). MS (FAB): *m*/*z* 466 ([M^+ − PF_6], 100). Anal. Calcd for $C_{23}H_{29}N_3ORhPF_6$ (611.37): C, 45.16; H, 4.78; N, 6.87. Found: C, 44.86; H, 4.79; N, 6.83.

(η^4-1,5-Cyclooctadiene)(1-[(2*S*)-(4-isopropyl-4,5-dihydrooxazolyl)methyl]-3-methylimidazolin-2-ylidene)rhodium(I) Hexafluorophosphate 6a. Compound **6a** was prepared using the same procedure as for **5a** from imidazolium salt **6** (200 mg, 0.82 mmol) and $(RhCODCl)_2$ (200 mg, 0.41 mmol). After purification, the product was crystallized from CH_2Cl_2/ether, yielding **6a** (261 mg, 58%) as yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, ^3J(HH) = 2 Hz, 1H, NCH), 6.89 (d, ^3J(HH) = 2 Hz, 1H, NCH), 5.33 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 4.80 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 4.70 (m, 1H, =NCH), 4.57 ("t", J(HH) = 9 Hz, 1H, OCH_2), 4.41 (m, 1H, OCH_2), 4.23 (m, 2H, COD-CH), 3.76 (s, 3H, NCH_3), 3.64 (m, 2H, COD-CH), 2.45 (m,1H, CH), 2.21 (m, 4H, COD-CH_2), 1.69 (m, 4H, COD-CH_2), 0.78 (d, ^3J(HH) = 7 Hz, 3H, CH_3), 0.72 (d, ^3J(HH) = 7 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 175.8 (d, $^1J(^{103}Rh^{13}C)$ = 51 Hz, CN_2), 166.0 (CNO), 123.3 (NCH), 122.5 (NCH), 98.0 (d, $^1J(^{103}Rh^{13}C)$ = 8 Hz, COD-CH), 93.9 (d, $^1J(^{103}Rh^{13}C)$ = 8 Hz, COD-CH), 78.6 (d, $^1J(^{103}Rh^{13}C)$ = 12 Hz, COD-CH), 72.3 (d, $^1J(^{103}Rh^{13}C)$ = 11 Hz, COD-CH), 72.6 (NCH_2), 68.9 (=NCH), 47.1 (OCH_2), 38.0 (NCH_3), 33.6 (CH), 31.8, 30.2, 30.0, 27.4 (COD-CH_2), 17.8 (CH_3), 16.8 (CH_3). MS (FAB): *m*/*z* 418 ([M^+ − PF_6], 100), 307 (36), 208 (53).

(η^4-1,5-Cyclooctadiene)(1-[(2*S*)-(4-benzyl-4,5-dihydrooxazolyl)methyl]-3-*tert*-butylimidazolin-2-ylidene)rhodium-(I) Hexafluorophosphate (7a). Compound **7a** was prepared using the same procedure as for **5a** from imidazolium salt **7** (289 mg, 0.90 mmol) and $(RhCODCl)_2$ (200 mg, 0.41 mmol). After purification, the product was crystallized from CH_2Cl_2/ether, yielding **7a** (337 mg, 58%) as yellow crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.2−6.8 (m, 7H, phenyl-CH, NCH), 5.45 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 4.72 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 4.68 (m, 1H, =NCH), 4.41 (m, 2H, COD-CH), 4.32 (m, 2H, COD-CH), 4.32 (m, 1H, OCH_2), 4.12 (m, 1H, OCH_2), 2.70 (m, 1H, CH_2), 2.54 (m, 1H, CH_2), 2.21 (m, 4H, COD-CH_2), 2.10 (m, 4H, COD-CH_2) 1.85 (s, 9H, $NC(CH_3)_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 175.9 (d, $^1J(^{103}Rh^{13}C)$ = 50 Hz, CN_2), 166.4 (CNO), 137.7, 129.8, 128.7, 125.9 (phenyl-C), 122.9 (NCH), 119.6 (NCH), 95.9 (d, $^1J(^{103}Rh^{13}C)$ = 9 Hz, COD-CH), 92.1 (d, $^1J(^{103}Rh^{13}C)$ = 8 Hz, COD-CH), 79.6 (d, $^1J(^{103}Rh^{13}C)$ = 13 Hz, COD-CH), 74.8 (NCH_2), 71.1 (d, $^1J(^{103}Rh^{13}C)$ = 11 Hz, COD-CH), 64.6 (=NCH), 58.4 ($C(CH_3)_3$), 48.2 (OCH_2), 40.5 (CH) 37.3 (NCH_3), 34.7, 31.7, 28.5, 26.3 (COD-CH_2), 32.3 ($C(CH_3)_3$). MS (FAB): *m*/*z* 508 ([M^+ − PF_6], 100). Anal. Calcd for $C_{26}H_{35}N_3ORhPF_6$ (653.14): C, 47.77; H, 5.40; N, 6.43. Found: C, 47.78; H, 5.27; N, 6.31.

(η^4-1,5-Cyclooctadiene)(3-*tert*-butyl-1-[(2*S*)-(4-isopropyl-4,5-dihydrooxazolyl)methyl]imidazolin-2-ylidene)rhodium(I) Hexafluorophosphate (8a). Compound **8a** was prepared using the same procedure as for **5a** from imidazolium salt **8** (254 mg, 0.90 mmol) and $(RhCODCl)_2$ (200 mg, 0.41 mmol). After removal of the solvents, the product was obtained as a yellow powder (304 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, ^3J(HH) = 2 Hz, 1H, NCH), 7.10 (d, ^3J(HH) = 2 Hz, 1H, NCH), 5.65 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 4.87 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 4.77 (m, 1H, =NCH), 4.67 ("t", J(HH) = 9 Hz, 1H, OCH_2), 4.53 (m, 1H, OCH_2), 4.36 (m, 2H, COD-CH), 3.93 (m, 1H, COD-CH), 3.82 (m, 1H, COD-CH), 2.39 (m, 1H, CH), 2.21 (m, 4H, COD-CH_2), 1.78 (s, 9H, $NC(CH_3)_3$), 1.69 (m, 4H, COD-CH_2), 0.69 (d, ^3J(HH) = 7 Hz, 3H, CH_3), 0.68 (d, ^3J(HH) = 7 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 176.7 (d, $^1J(^{103}Rh^{13}C)$ = 50 Hz, CN_2), 166.2 (CNO), 122.7 (NCH), 119.4 (NCH), 96.3 (d, $^1J(^{103}Rh^{13}C)$ = 9 Hz, COD-CH), 91.8 (d, $^1J(^{103}Rh^{13}C)$ = 8 Hz, COD-CH), 79.7 (d, $^1J(^{103}Rh^{13}C)$ = 13 Hz, COD-CH), 72.6 (NCH_2), 71.6 (d, $^1J(^{103}Rh^{13}C)$ = 11 Hz, COD-CH), 68.6 (=NCH), 58.3 (NCR_3), 48.5 (OCH_2), 34.6 (CH), 32.2 ($C(CH_3)_3$), 31.7, 31.6, 28.5, 26.4 (COD-CH_2), 17.2 (CH_3), 17.0 (CH_3). MS (FAB): *m*/*z* 460 ([M^+ − PF_6], 100).

Tetraiodobis{1-[(2*S*)-(4-isopropyl-4,5-dihydrooxazolyl)methyl]-3-methylimidazolin-2-ylidene}dipalladium-(II) (6b). $Pd(OAc)_2$ (200 mg, 0.89 mmol), LiOtBu (200 mg, 2.50 mmol), NaI (450 mg, 3.00 mmol), and imidazolium salt **6** (219 mg, 0.90 mmol) were mixed in a Schlenk tube. THF (20 mL) was syringed in, and the reaction vessel was placed in

Table 1. Crystallographic Data for 6b and 7a

	6b	**7a**
	Crystal Data	
formula	$C_{22}H_{34}I_4N_6O_2Pd_2$	$C_{26}H_{35}F_6N_3OPRh$
cryst color, habit	orange, plate	yellow, fragment
cryst size	0.22 × 0.13 × 0.05	0.38 × 0.28 × 0.13
space group	$P2_1$	$P2_12_12_1$
unit cell dimens		
a (Å)	15.4317(7)	14.0706(8)
b (Å)	12.0243(4)	14.3340(7)
c (Å)	8.9869(7)	13.3676(8)
α (deg)	90	90
β (deg)	97.41(5)	90
γ (deg)	90	90
V (Å^3)	1653.6(2)	2696.1(3)
no. of peaks to determine cell	25	25
temp (K)	193	193
wavelength (Å)	0.710 73	1.540 51
Z	2	4
fw	1135.01	653.45
D (calcd, g/cm^3)	2.280	1.610
abs coeff (mm^{-1})	48.5	62.8
F(000)	1056	1336
	Data Collection	
diffractometer	MACH 3	CAD4
θ range for data collection (deg)	1.0−26.0	1.0−68.0
index ranges	$-18 \le h \le 0$	$0 \le h \le 16$
	$-14 \le k \le 14$	$0 \le k \le 17$
	$-10 \le l \le 11$	$-16 \le l \le 16$
scan type	ω	$\omega-2\theta$
abs corr	empirical	
max/min transmission	99.91/73.91	99.78/41.63
no. of reflns collcd	10 663	5277
no. of indept reflns	6444 (R_{int} = 0.0377)	4883 (R_{int} = 0.0427)
no. of obsd reflns [$I > 2\sigma(I)$]	5400	4506
	Solution and Refinement	
solution	direct methods	
refinement method	full-matrix least squares on F^2	
H atoms	calculated	refined
weighting scheme a, b[a]	0.0439, 2.2394	0.0553, 2.2416
data/restraints/params	6444/0/326	4883/0/483
goodness-of-fit on F^2	1.020	1.055
final R[b] indices [$I > 2\sigma(I)$]	$R_1(F)$ = 0.0302	$R_1(F)$ = 0.0342
final R[b] indices [all data]	$R_1(F)$ = 0.0559	$R_1(F)$ = 0.0422
	$wR_2(F^2)$ = 0.0755	$wR_2(F^2)$ = 0.0889
χ	0.00(2)	−0.028(9)
largest diff peak and hole (e Å^{-3})	0.71/−0.57	1.21/−0.35
largest Δ/esd	<0.001	<0.001

[a] $w = 1/[\sigma^2(F_o2) + (aP)^2 + bP]$; $P = [F_o^2 + 2F_c^2]/3$. [b] $R_1(F) = (F_o - F_c)/F_o$; $wR_2(F^2) = [[w_i(F_o^2 - F_c^2)^2/[w_i(F_o^2)^2]]^{1/2}$.

an ultrasonic bath until all the solids had dissolved. The reaction mixture was stirred at room temperature for 4 h and was then heated to 60 °C for another 2 h. The progress of the reaction was monitored by TLC. The solvent was removed in vacuo, and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/pentane). Crystallization from CH_2Cl_2/pentane afforded **6b** as orange crystals (161 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 7.03 (s, 1H, NCH), 6.92 (s, 1H, NCH), 4.94 (m, 1H, =NCH), 4.67 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 4.32 ("t", J(HH) = 9 Hz, 1H, OCH_2), 4.19 ("t", J(HH) = 7 Hz, 1H, OCH_2), 3.84 (s, 3H, NCH_3), 2.37 (m, 1H, =NCH), 1.12 (d, ^3J(HH) = 7 Hz, 3H, CH_3), 1.00 (d, ^3J(HH) = 7 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.1 (CNO), 148.8 (CN_2), 123.6 (NCH), 123.3 (NCH), 72.2 (NCH_2), 70.7 (=NCH), 52.2 (OCH_2), 38.7 (NCH_3), 30.6 (CH), 18.3 (CH_3), 16.7 (CH_3). MS (FAB): m/z 1008 ([M$^+$ − I], 10). Anal. Calcd for $C_{22}H_{34}N_6O_2Pd_2I_4$ (1135.01): C, 23.28; H, 3.02; N, 7.40. Found C, 23.66; H, 3.32; N, 7.19.

Tetraiodobis{1-[(2*S*)-(4-benzyl-4,5-dihydrooxazolyl)-methyl]-3-methylimidazoline-2-ylidene}dipalladium-(II) (5b). Compound **5b** was prepared using the same procedure as for **6b** from palladium acetate (200 mg, 0.89 mmol) and imidazolium salt **6** (262 mg, 0.90 mmol). After crystallization from CH_2Cl_2/ether, the product was obtained as orange crystals (230 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.22 (m, 5H, phenyl-CH), 7.28 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 7.03 (d, ^3J(HH) = 2 Hz, 1H, NCH), 6.91 (d, ^3J(HH) = 2 Hz, 1H, NCH), 5.32 (m, 1H, =NCH), 4.68 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 4.27 ("t", J(HH) = 9 Hz, 1H, OCH_2), 4.13 ("t", J(HH) = 9 Hz, 1H, OCH_2), 3.84 (s, 3H, NCH_3), 3.83 (dd, ^2J(HH) = 14 Hz, ^3J(HH) = 6 Hz, 1H, CH_2), 2.69 (dd, ^2J(HH) = 14 Hz, ^3J(HH) = 6 Hz, 1H, CH_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.7 (CNO), 148.9 (CN_2), 136.4 (phenyl-C), 129.5, 128.7 (phenyl-CHs), 126.9 (*p*-phenyl-CH), 123.7 (NCH), 123.3 (NCH), 73.3 (NCH_2), 68.7 (=NCH), 52.1 (OCH_2), 40.5 (CH), 38.8 (NCH_3). MS (FAB): m/z 1104 ([M$^+$ − I], 10).

Tetraiodobis{1-[(2*S*)-(4-benzyl-4,5-dihydrooxazolyl)-methyl]-3-*tert*-butylimidazoline-2-ylidene}dipalladium-(II) (7b). Compound **7b** was prepared using the same procedure as for **6b** from palladium acetate (200 mg, 0.89 mmol) and imidazolium salt **7** (289 mg, 0.90 mmol). After crystallization from CH_2Cl_2/ether the product was obtained as orange crystals (337 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 7.32−7.23 (m, 5H, phenyl-CH), 7.13 (d, ^3J(HH) = 2 Hz, 1H, NCH), 7.09 (d, ^3J(HH) = 2 Hz, 1H, NCH), 5.26 (m, 1H, =NCH), 4.87 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 4.27 ("t", J(HH) = 9 Hz, 1H, OCH_2), 4.12 ("t", J(HH) = 9 Hz, 1H, OCH_2), 3.81 (dd, ^2J(HH) = 14 Hz, ^3J(HH) = 4 Hz, 1H, CH_2), 2.67 (dd, ^2J(HH) = 14 Hz, ^3J(HH) = 10 Hz, 1H, CH_2), 1.97 (s, 9H, $N(CH_3)_3$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.0 (CNO), 144.2 (CN_2), 136.7 (phenyl-C), 129.4, 128.8 (phenyl-CHs), 126.9 (*p*-phenyl-CH), 123.7 (NCH), 121.1 (NCH), 73.0 (NCH_2), 68.8 (=NCH), 59.5 (OCH_2), 54.7 (NCR_3), 40.0 (CH), 31.8 ($C(CH_3)_3$). MS (FAB): m/z 1188 ([M$^+$ − I], 55).

Tetraiodobis{1-[(2*S*)-(4-isopropyl-4,5-dihydrooxazol-yl)methyl]-3-*tert*-butylimidazoline-2-ylidene}dipalladium-(II) (8b). Compound **8b** was prepared using the same procedure as for **6b** from palladium acetate (200 mg, 0.89 mmol) and imidazolium salt **8** (257 mg, 0.90 mmol). The product was obtained as an orange oil (276 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 7.12 (d, ^3J(HH) = 2 Hz, 1H, NCH), 7.08 (d, ^3J(HH) = 2 Hz, 1H, NCH), 4.90 (m, 1H, =NCH), 4.85 (d, ^2J(HH) = 17 Hz, 1H, NCH_2), 4.31 ("t", J(HH) = 9 Hz, 1H, OCH_2), 4.17 ("t", ^3J(HH) = 7 Hz, 1H, OCH_2), 2.62 (m, 1H, =NCH), 1.94 (s, 9H, $C(CH_3)_3$), 1.01 (d, ^3J(HH) = 7 Hz, 3H, CH_3), 0.92 (d, ^3J(HH) = 7 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.4 CNO), 144.1 (CN_2), 123.7 (NCH), 121.1 (NCH), 72.3 (NCH_2), 69.3 (=NCH), 59.3 (NCR_3), 54.7 (OCH_2), 31.8 ($C(CH_3)_3$), 29.3 (CH), 18.9 (CH_3), 15.3 (CH_3). MS (FAB): m/z 1092 ([M$^+$ − I], 56).

X-ray Crystallographic Determinations and Refinements. Each crystal was mounted inside a Lindemann glass capillary. Intensity data were obtained at 193 K, in the case of **6b** with graphite-monochromated Mo Kα radiation on a Nonius MACH 3 diffractometer and in the case of **7a** with graphite-monochromated Cu Kα radition on a Nonius CAD4 diffractometer.

The intensities of three standard reflections showed no significant variations during the entire collection of data.

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Empirical absorption corrections based upon ψ-scan measurements at different azimuthal angles were applied to each data set.

The preliminary positions of heavy atoms were found by direct methods,[17] while the positions of the other non-hydrogen atoms were determined from successive Fourier difference maps coupled with initial isotropic least-squares refinement.[18]

The absolute configurations were confirmed by refinement of the enantimorphic models and by refinement of the Flack parameter χ.[19] In both cases, the refinement of the enantiomorphic model resulted in higher R values and a Flack parameter near 1. Crystal data, data collection and refinement parameters are presented in Table 1.

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Supporting Information Available: Tables giving crystal data and structure determination details, atomic and thermal parameters, and bond distances and angles for **6b** and **7a** (14 pages). Ordering information is given on any current masthead page.

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