# Synthesis of *tert*-Leucine-Derived Cobalt Oxazoline Palladacycles. Reversal of Palladation Diastereoselectivity and Application to the Asymmetric Rearrangement of *N*-Aryl Trifluoroacetimidates

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Starting from ($\eta^5$-carboxycyclopentadienyl)($\eta^4$-tetraphenylcyclobutadiene)cobalt, ($\eta^5$-(*S*)-2-(4-*tert*-butyl)oxazolinylcyclopentadienyl)($\eta^4$-tetraphenylcyclobutadiene)cobalt and ($\eta^5$-(*S*)-2-(4-methyl)oxazolinylcyclopentadienyl)($\eta^4$-tetraphenylcyclobutadiene)cobalt were synthesized in 70 and 79% yield, respectively. On heating with palladium acetate, only the former oxazoline resulted in the formation of a palladacycle (79% yield) that was determined to have an (*S*)-($_p$*S*)-configuration. Following ligand exchange (acetate to chloride to trifluoroacetate), the *tert*-butyl palladacycle was applied as a catalyst for the rearrangement of *N*-(4-methoxyphenyl)trifluoroacetimidates.

## Introduction

Palladium complexes play a key role in modern organic synthesis, due largely to the efficiency and high stereoselectivity with which they achieve a broad range of carbon−carbon and carbon−heteroatom bond forming processes.[1] Of particular recent interest are C,N palladacycles in which the palladium is bound directly to an aromatic ring and also to a nitrogen-containing ring substituent, as such molecules often display good stability to air and moisture along with useful catalytic activity.[2] Previous investigations in one of our groups to introduce planar chirality in cobalt metallocene **1** resulted in the highly diastereoselective synthesis of cobalt oxazoline palladacycle **4a**.[3] Subsequently, complexes **4b**[4] and **4c**[5] were shown to be effective catalysts for enantioselective allylic imidate rearrangements, with complex **4b** (COP-Cl) proving to be the optimal catalyst reported to date. This complex gave markedly higher yields and enantioselectivities in the rearrangement of allylic *N*-aryl trifluoroacetimidates than ferrocene oxazoline palladacycles (FOP)[6] or related chromium arene structures.[4a] Previous studies of allylic rearrangements of *N*-arylbenzimidates with the FOP series of catalysts had revealed optimized enantioselectivities with tertiary (e.g., *tert*-butyl) substituents at position 4 of the oxazoline ring. We therefore reasoned that replacement of the isopropyl group of palladacycle **4** with a *tert*-butyl substituent might lead to a further improvement in enantioselectivity. In this Note we report on the surprising influence of the oxazoline 4-substituent on the diastereoselectivity of palladation and on the stereochemical features of this substituent that lead to high enantioselectivity in allylic imidate rearrangements.

## Results and Discussion

We first synthesized the oxazolines **2** and **3** to investigate the effect of both increasing and decreasing the size of the oxazoline 4-substituent relative to the isopropyl group of metallocene **1**. To prepare the former, treatment of **5** with oxalyl chloride was followed by addition of (*S*)-*tert*-leucinol to give $\beta$-hydroxy amide **6**. We previously used $PPh_3/CCl_4$ or methanesulfonyl chloride to cyclize the related $\beta$-hydroxy amide derived from (*S*)-valinol, but in this instance we found using DAST in the presence of potassium carbonate to be a more reliable procedure for the synthesis of **2**. Attempts to prepare $\beta$-hydroxyamide **7** using the oxalyl chloride procedure failed, so instead carboxylic acid **5** was coupled to (*S*)-alaninol by treatment with EDCI and DMAP; the product **7** was also cleanly cyclized using DAST to give oxazoline **3** in good overall yield.

Palladation reactions on complexes **2** and **3** were performed using the same procedure previously applied to palladate **1**. Thus, heating **2** with $Pd(OAc)_2$ in dry acetic acid resulted, within minutes, in the formation of an orange precipitate, which was isolated by filtration

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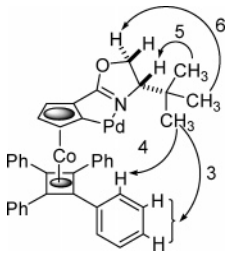
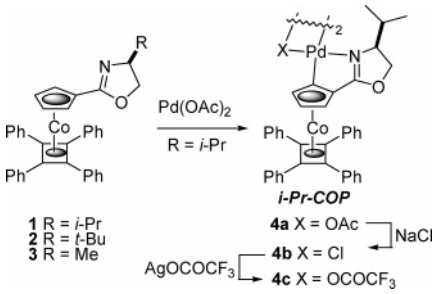
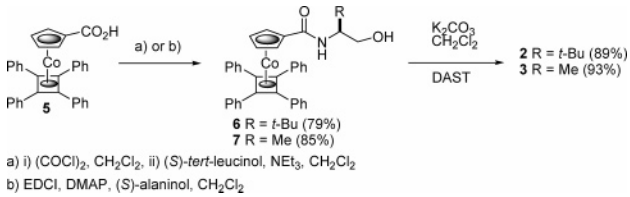


**Figure 1.** GOSEY connectivity and percentage enhancements for **8a**.

**Scheme 1**



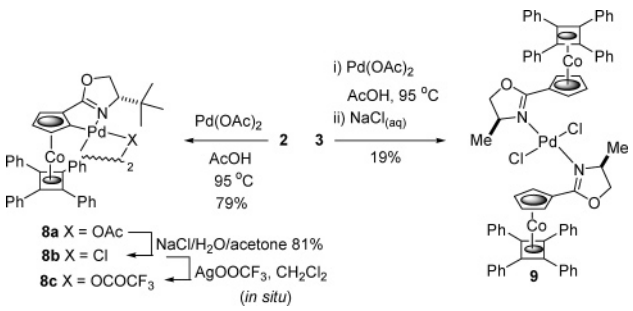

**Scheme 2**



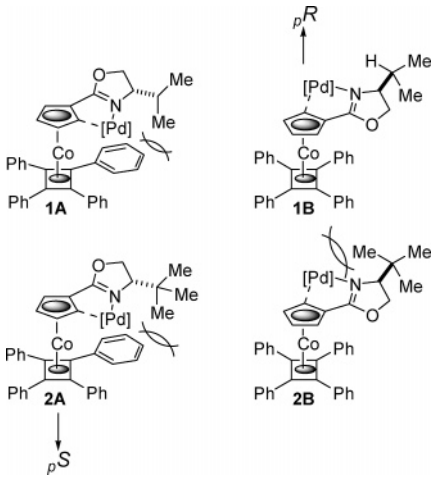

and shown to be a single diastereoisomer by $^1H/^{13}C$ NMR spectroscopy. A concentration of ca. 0.1 g of **2** in 1 mL of acetic acid is required for the successful precipitation of this product. Increasing the dilution 3-fold results in no precipitation and no evidence of product formation after evaporation of the solvent and examination of the residue by $^1H$ NMR. A clue to the stereochemical outcome of this reaction was noted by the large negative rotation ($[\alpha]_D = -903$) of the product compared to the large positive rotation ($[\alpha]_D = +942$) previously recorded for (*S*)-($_pR$)-**4a**, a difference that suggested a switching of the configuration of planar chirality. As we were unsuccessful in obtaining the X-ray crystal structure of the new palladacycle, the stereochemical identity of the product as (*S*)-($_pS$)-**8a** was confirmed by a subsequent gradient-enhanced nuclear Overhauser effect spectroscopy (GOESY) experiment (Figure 1).[7] Thus replacing an oxazoline 4-isopropyl substituent with a 4-*tert*-butyl substituent leads surprisingly to a complete reversal in the diastereoselectivity of palladation.

It has been proposed previously that the observed $_pR$-configuration of **4a** is a result of palladation occurring on a conformer **1B** in which the *i*-Pr group is directed away from the sterically demanding phenyl groups of the tetraphenylcyclobutadiene moiety (Scheme 4).[3] The opposite $_pS$-configuration of **8a** implies that electrophilic attack by palladium on the cyclopentadienyl ring occurs upon the opposite rotamer **2A**. Presumably for **1B** the methine hydrogen of the isopropyl group is directed

**Scheme 3**




**Scheme 4**




toward the palladium during electrophilic attack. For **2B** this hindrance-minimizing option is not available and palladation can occur only if the oxazoline adopts a conformation in which the *t*-Bu substituent is directed toward the phenyl groups and away from the bulk of the ligated palladium. This avoidance of a similar interaction between the metallating agent and the oxazoline 4-substituent has been used to explain the highly stereoselective lithiation of related ferrocenyl oxazolines.[8]

Heating **3** with $Pd(OAc)_2$ did not result in the formation of a precipitate, and a palladacycle was not observed in the resulting product mixture. The only compound identified, following ligand exchange using sodium chloride, isolation, and analysis by X-ray crystallography, was the *trans*-bis(oxazoline)palladium dichloride complex **9**. A relevant feature of this structure, in the context of the previous discussion, is the presence of both rotamers **A** and **B**, with the methyl substituent oriented both toward and away from the tetraphenylcyclobutadiene moiety. In this instance these different conformations arise to enable palladium to accommodate two bulky metallocene-containing ligands.

To investigate the use of the new palladacycle in catalysis, we first stirred a suspension of **8a** in an aqueous acetone solution of NaCl and isolated the chloride bridged dimer **8b** as an approximately 1:1 mixture of *cis*/*trans* isomers. The trifluoroacetate catalyst was prepared in situ by addition of excess silver trifluoroacetate to a solution of **8b** in dichloromethane.

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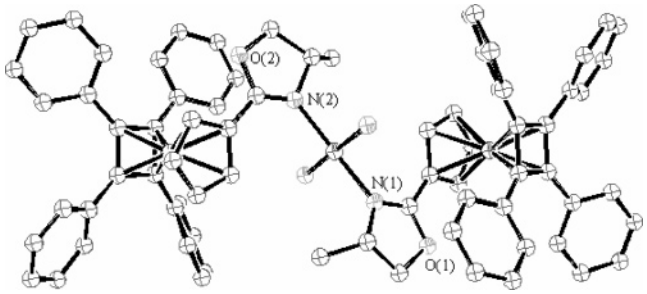



**Figure 2.** Representation of the crystal structure of **9**.

**Scheme 5**

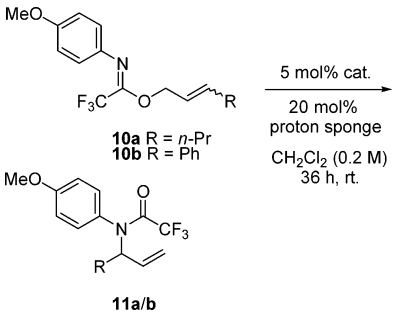


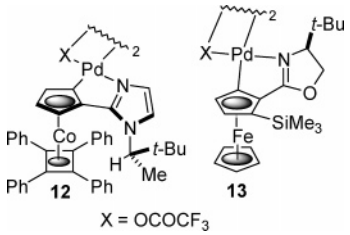

**Table 1. Rearrangement of Imidates 10a/b into Amides 11a/b with Catalysts 4c and 8c**

| entry | catalyst[a] | imidate | *E*/*Z* | yield[b] | % ee[c,d] (config) |
|---|---|---|---|---|---|
| 1 | **4c** | **10a** | *E* | 74 | 83/*S* |
| 2 | **8c** | **10a** | *E* | 64 | 41/*R* |
| 3 | **4c** | **10a** | *Z* | 78 | 95/*R* |
| 4 | **8c** | **10a** | *Z* | 24 | 58/*S* |
| 5 | **4c** | **10b** | *E* | 72 | 81[e]/*R* |
| 6 | **8c** | **10b** | *E* | 47 | 36[e]/*S* |

[a] Conditions: 5 mol % catalyst, 20 mol % Proton Sponge, 0.2 M in $CH_2Cl_2$, 23 °C, 36 h. [b] Mean values from duplicate experiments (±3%). [c] Determined by HPLC analysis after cleavage of the trifluoroacetate group (see Supporting Information for ref 4a). [d] Mean value of duplicate experiments (±2%). [e] Determined by HPLC analysis of amide.

Using conditions previously established for catalyst **4c**, allylic *N*-(4-methoxyphenyl)trifluoroacetimidate substrates **10a** (*E* and *Z*) and **10b** (*E*) were added to **8c** and the reaction mixtures were analyzed after a standard 36 h reaction time (Scheme 5, Table 1).

This study revealed **8c** to be an inferior catalyst compared to **4c** with respect to both yield and enantioselectivity, with **8c** giving a reversal in the configuration of the major product enantiomer. Thus the planar chirality of these bulky cobalt metallocenes is playing a major role in controlling the enantioselectivity of the allylic imidate rearrangement. This result is consistent with our previous observation that the cobalt imidazole palladacycle **12**, in which the element of central chirality is remote from palladium, catalyzes the rearrangement of allylic imidate **10a** to allylic amide **11a** with selectivities very similar to those obtained with **4c** (albeit with poorer yields).[9] In addition, previous studies with the related ferrocenyl oxazoline palladacycle (FOP) catalysts, exemplified by **13**, showed that for high enantioselectivity to be achieved in asymmetric allylic imidate rearrangements, the oxazoline side chain must project away from the CpFe fragment, placing steric influence (bulk) on both sides of the palladium(II) square plane.[6a,10] A similar explanation would rationalize the poor enantioselectivity realized with **8c** relative to COP-Cl (**4c**). Alternatively the detrimental role of the *endo*-oriented *tert*-butyl group in **8** might derive from a direct interaction between the two chiral elements. A consequence of the planar chirality in these cobalt metallocenes is projection of the phenyl groups over one of the two faces of the square planar palladium center. That the *tert*-butyl substituent of **8** must lie between two of these phenyl groups is anticipated to result in significant differences in the conformational preferences of the tetraphenylcyclobutadiene moieties of the two diastereoisomers, an outcome that may be at least in part responsible for the very different enantioselectivities observed.




In conclusion, we have established that changing the C-4 oxazoline substituent from isopropyl to *tert*-butyl completely reverses the planar chirality of the palladacycle obtained from the reaction of cobalt oxazoline metallocenes with palladium acetate. Application of the *tert*-butyl (*S*)-($_p$*S*)-palladacycle to the rearrangement of *N*-4-methoxyphenyl trifluoroacetimidates gave lower conversions and lower reversed enantioselectivities compared to those achieved with the isopropyl (*S*)-($_p$*R*)-palladacycle.

## Experimental Section

Dichloromethane was distilled from calcium hydride, and acetic acid (>99% purity) was distilled from phosphorus pentoxide, both under a nitrogen atmosphere. Petroleum ether refers to that fraction boiling in the range 40−60 °C. Column chromatography was performed on Matrix silica 60 (35−70 m).

**($\eta^5$-(*S*)-*N*-2-(1-Hydroxy-3,3-dimethyl)butylcyclopentadienylcarboxamide)($\eta^4$-tetraphenylcyclobutadiene)cobalt, 6.** To a solution of **5** (0.923 g, 1.76 mmol) in $CH_2Cl_2$ (10 mL) under nitrogen were added oxalyl chloride (0.700 g, 0.48 mL, 5.51 mmol) and 2 drops of DMF, and the resulting solution stirred at room temperature for 20 min. Volatiles were removed in vacuo, the crude acid chloride was redissolved in anhydrous $CH_2Cl_2$ (15 mL) and added to a solution of (*S*)-*tert*-leucinol (0.232 g, 1.98 mmol) and triethylamine (0.5 mL) in $CH_2Cl_2$ (5 mL), and the mixture was stirred at room temperature for 18 h, before the addition of water (10 mL). The reaction mixture was partitioned, and the organic layer washed with 10% aqueous citric acid (10 mL), dried ($Na_2SO_4$), and evaporated in vacuo. The residue was purified by column chromatography (EtOAc) to give an orange gum, which was triturated with petroleum ether to give the title compound **6** as an orange crystalline solid (0.87 g, 79%): mp 209−212 °C. Anal. Found: C, 76.70; H, 6.26; N, 2.18. Calcd for $C_{40}H_{38}CoNO_2$: C, 77.03; H, 6.14; N, 2.25. $[\alpha]^{23}_D$ +5.7 (*c* 0.46, $CHCl_3$); IR (film) $\nu_{max}$ 3363 (O−H), 1635 (C=O) $cm^{-1}$; $^1H$ NMR ($\delta$, 270 MHz, $CDCl_3$) 0.79 (9H, s, C($CH_3$)$_3$), 2.52 (1H, dd, *J* 7.2, 4.1,

(9) Rearrangement with **12**: *E*-**10a** gave (*S*)-**11a** in 86% ee (43% yield), *Z*-**10a** gave (*R*)-**11a** in 88% ee (19% yield); see ref 4a.

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O*H*), 3.08−3.16 (1H, m, C*H*N), 3.48−3.60 (2H, m, C$H_2$OH), 4.66 (1H, brs, Cp*H*), 4.75 (1H, brs, Cp*H*), 4.87 (1H, brs, Cp*H*), 5.19 (1H, brs, Cp*H*), 5.36 (2H, brd, *J* 8.7, N*H*), 7.10−7.30 (12H, m, *m*+*p*-Ph*H*), 7.41−7.50 (8H, m, *o*-Ph*H*); $^{13}C\{^1H\}$ NMR ($\delta$, 67 MHz, $CDCl_3$) 27.1 (C($CH_3$)$_3$), 33.5 (*C*($CH_3$)$_3$), 60.7 (*C*HN), 63.5 (*C*$H_2$OH), 76.4 (*C*$_4$Ph$_4$), 81.8 (Cp*C*), 82.4 (Cp*C*), 86.7 (Cp*C*), 87.1 (Cp*C*), 90.3 (*ipso*-Cp*C*), 127.0 (*p*-Ph*C*), 128.3 (Ph*C*), 128.9 (Ph*C*), 135.3 (*ipso*-Ph*C*), 167.5 (*C*═O); MS (*m*/*z*, ES$^+$) 624 (MH$^+$, 60%), 415 (100%); high-resolution MS (*m*/*z*, ES$^+$) found MH$^+$ 624.2314; $C_{40}H_{39}CoNO_2$ requires 624.2307.

**($\eta^5$-(*S*)-*N*-2-(1-Hydroxy)propylcyclopentadienylcarboxamide)($\eta^4$-tetraphenylcyclobutadiene)cobalt, 7.** To a solution of **5** (2.00 g, 3.81 mmol) in $CH_2Cl_2$ (30 mL) under a nitrogen atmosphere were added EDCI (0.880 g, 4.59 mmol), DMAP (0. 558 mg, 4.57 mmol), and a solution of (*S*)-alaninol (0. 343 g, 4.57 mmol) in $CH_2Cl_2$ (20 mL), and the resulting mixture stirred for 48 h at room temperature. The reaction was quenched by the addition of 10% aqueous citric acid (20 mL), followed by stirring for 5 min. The mixture was then partitioned and the orange organic fraction dried ($Na_2SO_4$) and evaporated in vacuo to afford a solid, which was purified by column chromatography (EtOAc) to give the title compound **7** as an orange crystalline solid (1.88 g, 85%): mp 226 °C. Anal. Found: C, 75.14; H, 5.65; N, 2.18. Calcd for $C_{37}H_{32}CoNO_2\cdot 1/2H_2O$: C, 75.25; H, 5.63; N, 2.37. $[\alpha]_D^{23}$ +19.4 (*c* 0.54, $CHCl_3$); IR (film) $\nu_{max}$ 3352 (O−H), 1632 (C═O) cm$^{-1}$; $^1$H NMR ($\delta$, 270 MHz, $CDCl_3$) 0.85 (3H, d, *J* 6.9, C$H_3$), 3.22 (1H, dd, *J* 11.0, 6.5, C*H*HOH), 3.37 (1H, dd, *J* 11.0, 3.0, CH*H*OH), 3.60−3.73 (1H, m, C*H*N), 4.67 (2H, brs, Cp*H*), 4.99 (1H, brs, Cp*H*), 5.03 (1H, brs, Cp*H*), 5.21 (2H, brd, *J* 6.2, N*H*), 7.20−7.29 (12H, m, *m*+*p*-Ph*H*), 7.41−7.50 (8H, m, *o*-Ph*H*); $^{13}C\{^1H\}$ NMR ($\delta$, 67 MHz, $CDCl_3$) 16.8 (*C*$H_3$), 48.9 (*C*HN), 67.7 (*C*$H_2$OH), 76.3 (*C*$_4$Ph$_4$), 81.9 (Cp*C*), 82.5 (Cp*C*), 86.7 (Cp*C*), 87.0 (Cp*C*), 89.9 (*ipso*-Cp*C*), 126.9 (*p*-Ph*C*), 128.3 (Ph*C*), 128.8 (Ph*C*), 135.3 (*ipso*-Ph*C*), 167.2 (*C*═O); MS (*m*/*z*, ES$^+$) 582 (MH$^+$, 28%); high-resolution MS (*m*/*z*, ES$^+$) found MH$^+$ 582.1842; $C_{37}H_{33}CoNO_2$ requires 582.1838.

**($\eta^5$-(*S*)-2-(4-*tert*-Butyl)oxazolinylcyclopentadienyl)($\eta^4$-tetraphenylcyclobutadiene)cobalt, 2.** To a solution of **6** (0.630 g, 1.01 mmol) in $CH_2Cl_2$ (20 mL) at 0 °C under a nitrogen atmosphere were added DAST (0.193 g, 0.158 mL, 1.20 mmol) and $K_2CO_3$ (0.150 g, 1.09 mmol). The mixture was stirred overnight at room temperature before the addition of saturated aqueous sodium bicarbonate (20 mL). The mixture was then partitioned, the aqueous layer was extracted with $CH_2Cl_2$ (20 mL), and the combined organic fractions were dried ($MgSO_4$) and evaporated in vacuo. Purification of the residue by column chromatography (ethyl acetate/petroleum ether, 1:9) gave the title compound **2** as an orange crystalline solid (0.546 g, 89%): mp 187−189 °C; $[\alpha]^{23}_D$ −45.7 (*c* 0.39, $CHCl_3$); IR (film) $\nu_{max}$ 1651 (C═N) cm$^{-1}$; $^1$H NMR ($\delta$, 270 MHz, $CDCl_3$) 0.81 (9H, s, C(C$H_3$)$_3$), 3.25 (1H, dd, *J* 9.9, 7.7, C*H*HO), 3.37 (1H, dd, *J* 9.9, 7.2, CH*H*O), 3.71 (1H, t, *J* 7.4, C*H*N), 4.73 (1H, brs, Cp*H*), 4.78 (1H, brs, Cp*H*), 5.02 (1H, brs, Cp*H*), 5.23 (1H, brs, Cp*H*), 7.20−7.25 (12H, m, *m*+*p*-Ph*H*), 7.30−7.45 (8H, m, *o*-Ph*H*); $^{13}C\{^1H\}$ NMR ($\delta$, 67 MHz, $CDCl_3$) 26.0 (C(*C*$H_3$)$_3$), 33.6 (*C*(CH$_3$)$_3$), 67.8 (*C*HN), 76.0 (*C*$H_2$O), 76.2 (*C*$_4$Ph$_4$), 82.3 (Cp*C*), 84.4 (Cp*C*), 84.9 (Cp*C*), 85.8 (*ipso*-Cp*C*), 86.0 (Cp*C*), 126.5 (*p*-Ph*C*), 128.0 (Ph*C*), 129.0 (Ph*C*), 135.5 (*ipso*-Ph*C*), 160.1 (*C*═N); MS (*m*/*z*, ES$^+$) 606 (MH$^+$, 100%); high-resolution MS (*m*/*z*, ES$^+$) found MH$^+$ 606.2208; $C_{40}H_{37}CoNO$ requires 606.2202.

**($\eta^5$-(*S*)-2-(4-Methyl)oxazolinylcyclopentadienyl)($\eta^4$-tetraphenylcyclobutadiene)cobalt, 3.** To a solution of **7** (0.100 g, 0.17 mmol) in $CH_2Cl_2$ (30 mL) at 0 °C under a nitrogen atmosphere were added DAST (0.036 g, 0.030 mL, 0.22 mmol) and $K_2CO_3$ (0.035 g, 0.25 mmol). The mixture was stirred overnight at room temperature before the dropwise addition of saturated aqueous sodium bicarbonate (20 mL). The mixture was then partitioned, the aqueous layer was extracted with $CH_2Cl_2$ (20 mL), and the combined organic fractions were dried ($MgSO_4$) and evaporated in vacuo. Purification of the residue by column chromatography (ethyl acetate/petroleum ether, 1:9) gave the title compound **3** as an orange crystalline solid (0.092 g, 93%): mp 179−182 °C. Anal. Found: C, 77.54; H, 5.45; N, 2.40. Calcd for $C_{37}H_{30}CoNO\cdot 1/2H_2O$: C, 77.61; H, 5.46; N, 2.45. $[\alpha]_D^{23}$ −58.1 (*c* 0.19, $CHCl_3$); IR (film) $\nu_{max}$ 1651 (C═N) cm$^{-1}$; $^1$H NMR ($\delta$, 270 MHz, $CDCl_3$) 1.07 (3H, d, *J* 6.9, C$H_3$), 3.32 (1H, t, *J* 7.4, C*H*HO), 3.65 (1H, t, *J* 7.9, CH*H*O), 3.69−3.80 (1H, m, C*H*N), 4.70 (1H, brs, Cp*H*), 4.76 (1H, brs, Cp*H*), 5.07 (1H, brs, Cp*H*), 5.15 (1H, brs, Cp*H*), 7.10−7.30 (12H, m, *m*+*p*-Ph*H*), 7.30−7.60 (8H, m, *o*-Ph*H*); $^{13}C\{^1H\}$ NMR ($\delta$, 67 MHz, $CDCl_3$) 21.4 (*C*$H_3$), 61.7 (*C*HN), 73.2 (*C*$H_2$O), 76.1 (*C*$_4$Ph$_4$), 82.4 (Cp*C*), 84.6 (Cp*C*), 84.8 (Cp*C*), 85.1 (Cp*C*), 86.2 (*ipso*-Cp*C*), 126.6 (*p*-Ph*C*), 128.1 (Ph*C*), 129.0 (Ph*C*), 135.4 (*ipso*-Ph*C*), 167.2 (*C*═N); MS (*m*/*z*, FAB) 563 (M$^+$, 100%); high-resolution MS (*m*/*z*, ES$^+$) found M$^+$ 563.1651; $C_{37}H_{30}CoNO$ requires 563.1654.

**Di-$\mu$−acetatobis[($\eta^5$-(*S*)-($_p$*S*)-2-(2′-(4′-tert-butyl)oxazolinyl)cyclopentadienyl-*C*$^1$,*N*$^{3'}$)($\eta^4$-tetraphenylcyclobutadiene)cobalt]dipalladium(II), 8a.** Palladium acetate (0.043 g, 0.19 mmol) was added to a solution of **2** (0.110 g, 0.18 mmol) in acetic acid (1.0 mL) and the mixture stirred at 95 °C for 30 min. The orange precipitate that appeared was isolated by suction filtration and washed with cold acetic acid (4 × 5 mL), followed by petroleum ether (5 mL), and dried in vacuo to give **8a** as an orange powder (0.110 g, 79%). A small portion was recrystallized ($CH_2Cl_2$/petroleum ether) to give the product as red cubes: mp >250 °C (dec). Anal. Found: C, 64.97; H, 5.00; N, 1.76. Calcd for $C_{84}H_{76}Co_2N_2O_6Pd_2$: C, 65.50; H, 4.97; N, 1.82. $[\alpha]_D^{23}$ −903 (*c* 0.13, $CHCl_3$); IR (film) $\nu_{max}$ 1582 (C═N), 1500, 1411 (acetate bridge) cm$^{-1}$; $^1$H NMR ($\delta$, 270 MHz, $CDCl_3$) 0.37 (18H, s, C(C$H_3$)$_3$), 2.01 (6H, s, C$H_3$CO$_2$), 2.56 (2H, dd, *J* 9.6, 3.7, C*H*N), 3.72 (2H, t, *J* 9.3, C*H*HO), 3.86 (2H, t, *J* 2.2, Cp*H*), 4.10 (2H, dd, *J* 7.4, 4.0 CH*H*O), 4.39 (2H, brs, Cp*H*), 4.56 (2H, d, *J* 2.5, Cp*H*), 7.10−7.20 (24H, m, *m*+*p*-Ph*H*), 7.60−7.70 (16H, m, *o*-Ph*H*); $^{13}C\{^1H\}$ NMR ($\delta$, 67 MHz, $CDCl_3$) 24.3 (*C*$H_3$CO$_2$), 25.5 (C(*C*$H_3$)$_3$), 33.6 (*C*(CH$_3$)$_3$), 70.0 (*C*HN), 73.6 (*C*$H_2$O), 75.1 (Cp*C*) 85.8 (Cp*C*), 86.9 (*ipso*-Cp*C*), 88.7 (Cp*C*), 96.3 (*ipso*-Cp*C*), 126.4 (*p*-Ph*C*), 128.1 (Ph*C*), 129.5 (Ph*C*), 135.4 (*ipso*-Ph*C*), 175.0 (*C*═N), 180.8 (*C*O$_2$); MS (*m*/*z*, MALDI) 769 (1/2M$^+$ 75%), 710 (1/2M − OAc, 100%); high-resolution MS (*m*/*z*, FAB) found 1/2M$^+$ 769.1210; $C_{42}H_{38}CoNO_3Pd$ requires 769.1213.

**Di-$\mu$-chloro[($\eta^5$-(*S*)-($_p$*S*)-2-(2′-(4′-*tert*-butyl)oxazolinyl)-cyclopentadienyl-*C*$^1$,N$^{3'}$)($\eta^4$-tetraphenylcyclobutadiene)-cobalt]dipalladium(II), 8b.** To a suspension of **8a** (0.085 g, 0.055 mmol) in acetone (1 mL) was added aqueous sodium chloride (2 M, 0.5 mL) and the heterogeneous mixture stirred at room temperature overnight. The resulting yellow solid was collected by filtration of the reaction mixture, washed with water (10 mL), followed by acetone (5 mL), and finally dried in vacuo to provide **8b** as a yellow powder (0.069 mg, 81%): mp >250 °C (dec). Anal. Found: C, 62.19; H, 4.61; N, 1.65. Calcd for $C_{80}H_{70}Cl_2Co_2N_2O_2Pd_2\cdot 3H_2O$: C, 62.11; H, 4.95; N, 1.81. $[\alpha]_D^{23}$ −1354 (*c* 0.19, $CHCl_3$); IR (film) $\nu_{max}$ 1587 (C═N) cm$^{-1}$; $^1$H NMR ($\delta$, 270 MHz, $CDCl_3$) ratio of *cis*/*trans* isomers ~1:1: 0.57 (18H, s, C(C$H_3$)$_3$), 3.40−3.52 (2H, m), 4.13 (1H, brs, Cp*H*), 4.28−4.43 (3H, m), 4.49−4.58 (3H, m), 4.70 (1H, brs, Cp*H*), 4.77 (2H, brs, Cp*H*), 7.10−7.30 (24H, m, *m*+*p*-Ph*H*), 7.52−7.62 (8H, m, *o*-Ph*H*), 7.62−7.74 (8H, m, *o*-Ph*H*); $^{13}C\{^1H\}$ ($\delta$, 67 MHz, $CDCl_3$) 26.2 (C(*C*$H_3$)$_3$), 34.1 (*C*(CH$_3$)$_3$), 126.6 (*p*-Ph*C*), 128.1 (Ph*C*), 129.4, 129.5 (Ph*C*), 135.6 (*ipso*-Ph*C*), other peaks not observed; MS (*m*/*z*, MALDI) 1492 (M$^+$, 40%), 710 (1/2M$^+$ − Cl, 100%); high-resolution MS (*m*/*z*, FAB) found 1/2M$^+$ 745.0769; $C_{40}H_{35}ClCoNOPd$ requires 745.0769.

***trans*-Dichlorobis[($\eta^5$-(*S*)-2-(4-methyl)oxazolinylcyclopentadienyl)($\eta^4$-tetraphenylcyclobutadiene)cobalt-*N*,*N*′)-palladium(II), 9.** Palladium acetate (0.062 g, 0.28 mmol) was added to a solution of oxazoline **3** (0.160 g, 0.28 mmol) in acetic acid (1 mL) and the mixture stirred at 95 °C for 30 min. The reaction mixture was evaporated in vacuo, redissolved in $CH_2Cl_2$ (50 mL), and filtered. Petroleum ether was added to the

filtrate and the cloudy solution evaporated in vacuo to afford a yellow solid (ca. 0.2 g). This crude material was suspended in acetone (10 mL), aqueous sodium chloride (5 mL) and $CH_2Cl_2$ (5 mL) were added, and the mixture was stirred overnight. The reaction mixture was then partitioned between water (20 mL) and $CH_2Cl_2$ (50 mL). The organic extract was dried ($MgSO_4$) and evaporated in vacuo to give the crude product, which was separated by column chromatography into two components. The first component was unidentifiable. The second component was crystallized ($CH_2Cl_2$/petroleum ether) to give **9** (0.035 g, 19%), whose structure was confirmed by X-ray crystallography, with the following spectroscopic data: mp 170 °C (dec); $[\alpha]_D^{23}$ +116 (*c* 0.18, $CHCl_3$); IR (film) $\nu_{max}$ 1633 (C=N) $cm^{-1}$; $^1H$ NMR ($\delta$, 270 MHz, $CDCl_3$) 1.67 (6H, d, *J* 6.4, C*H*$_3$), 3.20−3.30 (2H, m, C*H*HO), 3.65 (2H, t, *J* 9, CH*H*O), 3.90−4.08 (2H, m, C*H*N), 4.49 (2H, brs, Cp*H*), 4.70 (2H, brs, Cp*H*), 5.86 (2H, brs, Cp*H*), 5.98 (2H, brs, Cp*H*), 7.10−7.30 (24H, m, *m*+*p*-Ph*H*), 7.37−7.55 (16H, m, *o*-Ph*H*); $^{13}C\{^1H\}$ NMR ($\delta$, 67 MHz, $CDCl_3$) 126.7 (*p*-Ph*C*), 128.3 (Ph*C*), 129.1 (Ph*C*), 135.3 (*ipso*-Ph*C*), other peaks not observed; MS (*m*/*z*, $ES^+$) 1269 ($[M - Cl]^+$, 50%), 1233 (M − 2Cl, 100%).

**General Procedure for Allylic Imidate Rearrangement.** Palladium chloride catalysts **4b** or **8b** (0.036 mmol) and $AgOCOCF_3$ (0.032 g, 0.15 mmol) were dissolved with stirring in $CH_2Cl_2$ (0.6 mL) under an argon atmosphere and protected from light. After 3 h the resulting mixture, containing the COP catalyst, was filtered through Celite while under Ar and rinsed with $CH_2Cl_2$ to a final volume of 1.2 mL (0.03 M). A portion of this catalyst solution (0.26 mL, 0.03 M, 0.008 mmol) and Proton Sponge (0.007 g, 0.03 mmol) in $CH_2Cl_2$ (0.3 mL) were added successively at room temperature by syringe to a solution of imidate **10a** or **10b** (0.16 mmol) and $CH_2Cl_2$ (0.24 mL). The reaction flask then was sealed under argon, wrapped with aluminum foil, and maintained at room temperature. After 36 h the reaction was concentrated and purification of the residue by chromatography ($SiO_2$, 95:5 hexanes/EtOAc) afforded **11a/b**, identified as previously described.[4a]

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**Supporting Information Available:** Details of the X-ray structure determination of **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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