Notes

Synthesis of [2,6-Bis(2-oxazolinyl)phenyl]palladium Complexes via the Ligand Introduction Route

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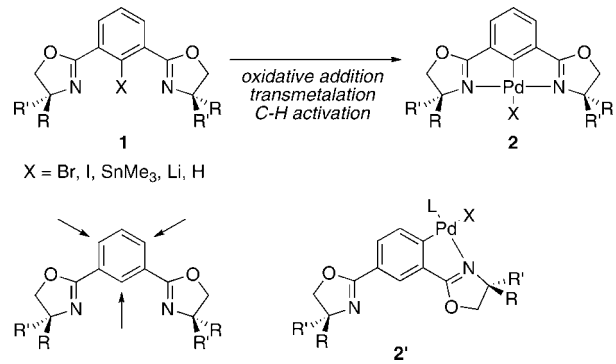
Received July 14, 2008

Summary: A series of [2,6-bis(2-oxazolinyl)phenyl]palladium (Phebox-Pd) complexes were synthesized via the ligand introduction route. trans-Bromo(2,6-dicarboxyphenyl)bis(triphenylphosphine)palladium was prepared by the reaction of 2-bromoisophthalic acid with $Pd(PPh_3)_4$ in 93% yield, and the carboxy groups of the palladium complex were converted into oxazolinyl groups to give the Phebox-Pd complexes in 44−57% yield.

Organometallic complexes containing monoanionic terdentate ligands, so-called pincer complexes, have received much attention not only as catalysts in synthetic organic chemistry but also as organometallic materials in the field of materials science.[1] In particular, the pincer palladium complexes having 2,6-bis(2-oxazolinyl)phenyl (abbreviated as Phebox) groups have been recognized as a useful class of catalysts for asymmetric transformations,[2,3] and considerable effort has been devoted toward their synthesis. In 1997, three independent groups reported the syntheses of the Phebox-Pd complexes **2** (Scheme 1). Denmark et al. described the synthesis of the Phebox-Pd complexes via the oxidative addition of 2-halo-1,3-bis(2-oxazolinyl)benzenes to $Pd_2(dba)_3 \cdot 2H_2O$.[4] Nishiyama et al. showed that the transmetalation of *i*-Pr-Phebox-$SnMe_3$ with $PdCl_2(PhCN)_2$ gave the *i*-Pr-Phebox-Pd complex.[5] Also, Richards et al. reported that the lithiation of 1,3-bis(2-oxazolinyl)-benzenes with LDA/TMEDA followed by transmetalation with $PdBr_2$(1,5-COD) gave the Phebox-Pd complexes.[6] Another method for the synthesis of Phebox-Pd complexes is the C−H bond activation of 1,3-bis(2-oxazolinyl)benzenes.[7]

Scheme 1. Synthesis of Phebox-Pd Complexes via Metal Introduction Routes



All of these methods use *the metal introduction route*, in which the palladium is introduced to the 1,3-bis(2-oxazolinyl)-arenes **1** in the final step. However, these methods suffer from several drawbacks: (1) diverse oxazolinyl groups are constructed at an early stage, (2) an extra metalation step is necessary for the synthesis via transmetalation,[5,6,8] (3) low regioselectivity of the direct cyclopalladation results in the formation of the undesirable 4-palladated complex **2′**,[3e] and (4) reactive oxazolines are troublesome in the metalation step.[3b,e,9]

Recently, we developed a new synthetic strategy, *the ligand introduction route*, in which the metal is introduced to the aromatic ring prior to the construction of the ligand units.[10] This strategy enabled us to prepare a novel class of pincer palladium complexes having sterically demanding and/or chemically unstable functional groups. If the ligand introduction route can be successfully applied to the synthesis of the Phebox-Pd complexes, the aforementioned inherent problems would be solved. We report here the synthesis of the Phebox-Pd complexes via the ligand introduction route and X-ray molecular structure analysis of the Phebox-Pd complexes.

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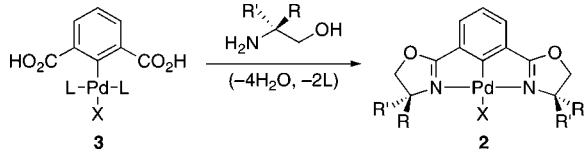
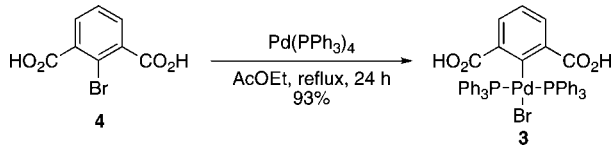
10.1021/om800666x CCC: $40.75
Publication on Web 09/11/2008

Scheme 2. Synthetic Strategy for Phebox-Pd Complexes via a Ligand Introduction Route



Scheme 3. Synthesis of Palladium Complex 3



As a key precursor, we designed *trans*-bromo(2,6-dicarboxyphenyl)bis(triphenylphosphine)palladium (**3**), in which two carboxy groups were attached to the 2,6-positions of the benzene ring (Scheme 2). The conversion of the carboxy groups into the oxazolinyl groups would give the Phebox-Pd complexes **2**.

The palladium complex **3** was prepared by the oxidative addition of 2-bromoisophthalic acid (**4**) to $Pd(PPh_3)_4$ in 93% yield (Scheme 3).[11] The structure of the palladium complex **3** was confirmed by X-ray molecular structure analysis (Figure 1). The square-planar palladium complex **3** bears two triphenylphosphines, the 2,6-dicarboxyphenyl group, and the bromide ligand, with the two triphenylphosphines located trans to each other. The 2,6-dicarboxyphenyl group is oriented almost perpendicular with respect to the square plane.

With the key precursor **3** in hand, we examined the synthesis of the Phebox-Pd complexes **2** (Scheme 4). Initially, the palladium complex having the 2,6-bis(chlorocarbonyl)phenyl group **5** was generated in situ from the reaction of the palladium complex **3** with oxalyl chloride. The palladium complex **5** was then treated with (*S*)-2-amino-1-propanol (**6a**) in the presence of Et_3N to give the (2,6-bis{*N*-[(*S*)-2-hydroxy-1-methylethyl]-carbamoyl}phenyl)palladium complex **7**. Finally, cyclization of the *N*-[(*S*)-2-hydroxy-1-methylethyl]carbamoyl groups with mesyl chloride in the presence of Et_3N under an oxygen atmosphere gave the desired Me-Phebox-Pd complex **2a** in 54% yield along with triphenylphosphine oxide. Similarly, the reaction of the palladium complex **3** with a variety of β-amino alcohols **6b**−**f** gave the Phebox-Pd complexes bearing benzyl (**2b**), isopropyl (**2c**), isobutyl (**2d**), (*S*)-*sec*-butyl (**2e**), and dimethyl groups (**2f**) at the 4-position of the oxazoline rings in 44−57% yield. The bromide ligand of the palladium complex **3** was replaced by the chloride ligand during the reaction, as revealed by elemental analysis and X-ray molecular structure analysis.

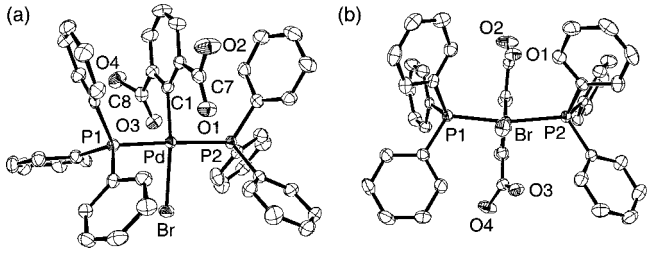
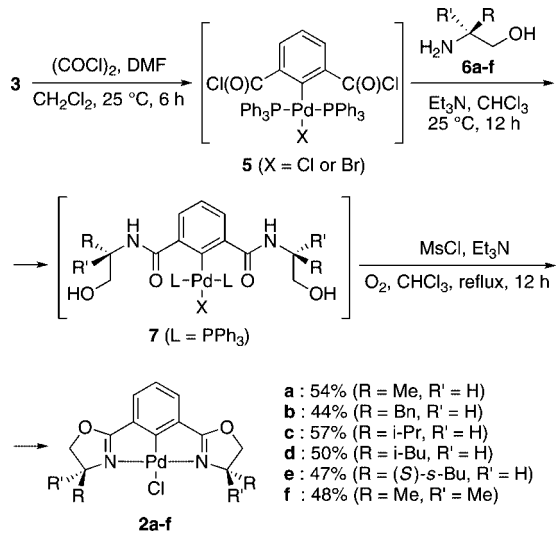


Figure 1. (a) ORTEP drawing of the palladium complex **3**·2DMSO with thermal ellipsoids drawn at the 50% probability level. (b) ORTEP drawing of **3**·2DMSO along the Br−Pd bond. Hydrogen atoms and DMSO are omitted for clarity. Selected bond lengths (Å) and angles (deg): Br−Pd = 2.5282(4), Pd−P1 = 2.3040(7), Pd−P2 = 2.3507(8), Pd−C1 = 2.026(3), C7−O1 = 1.208(4), C7−O2 = 1.327(4), C8−O3 = 1.208(4), C8−O4 = 1.336(4), Pd···O1 = 2.953, Pd···O2 = 2.871; P1−Pd−P2 = 168.80 (3), Br−Pd−C1 = 172.04(8).

Scheme 4. Synthesis of Phebox-Pd Complexes 2



The substituents at the 4-position of the oxazoline rings in the C_2-symmetric Phebox ligands play an important role in the asymmetric induction, and the oxazolines can supply sufficient substituent diversity by using β-aminoalcohols. The formation of the oxazoline rings in the final step is preferred when the Phebox ligands are screened in the asymmetric reactions.

The structures of the Phebox-Pd complexes **2c**,**d**,**f** were determined by X-ray molecular structure analyses (Figure 2, Table 1).[12] The structural features of the Phebox-Pd complexes **2** are similar to those of the Phebox-Ni[13] and Phebox-Pt complexes.[3c−e,14] The Phebox-Pd complexes **2c**,**d**,**f** adopt distorted-square-planar geometries at the palladium atom with the two nitrogen atoms of the oxazolinyl groups, the chlorine atom, and the carbon atom of the benzene ring. Isopropyl and isobutyl groups attached to the oxazoline rings in the Phebox-Pd complexes **2c**,**d** provide the stereochemical environment around the palladium center. The palladium−carbon bond lengths of the pincer complexes **2** (1.934−1.940 Å) are slightly shorter than that of the palladium complex **3** (2.026 Å) by 0.086−0.092 Å. The Cl−Pd−C1 angles of the Phebox-Pd complexes **2** (177.3−179.1°) are almost linear, whereas the N1−Pd−N2 angles (157.1−158.0°) are bent.

In summary, we have developed a new synthetic route for the Phebox-Pd complexes. A variety of Phebox-Pd complexes were successfully synthesized via the ligand introduction route, in which the palladium−carbon bond was formed prior to the construction of the oxazoline rings. This synthetic method is attractive from the standpoint of a diversity-based approach, and the yields of the complexes[15] are comparable to or higher

(11) The oxidative addition of 2-bromobenzoic acid to $Pd(PPh_3)_4$ has been reported; see: Fernández-Rivas, C.; Cárdenas, D. J.; Martín-Matute, B.; Monge, Á.; Gutiérrez-Puebla, E.; Echavarren, A. M. *Organometallics* **2001**, *20*, 2998.

(12) X-ray structural analyses of analogous pincer type Phebox-palladium complexes have been reported.[3b,c,4,5]

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(15) Total chemical yields of **2a**−**f** are 41−53% from the dicarboxylic acid **4**.

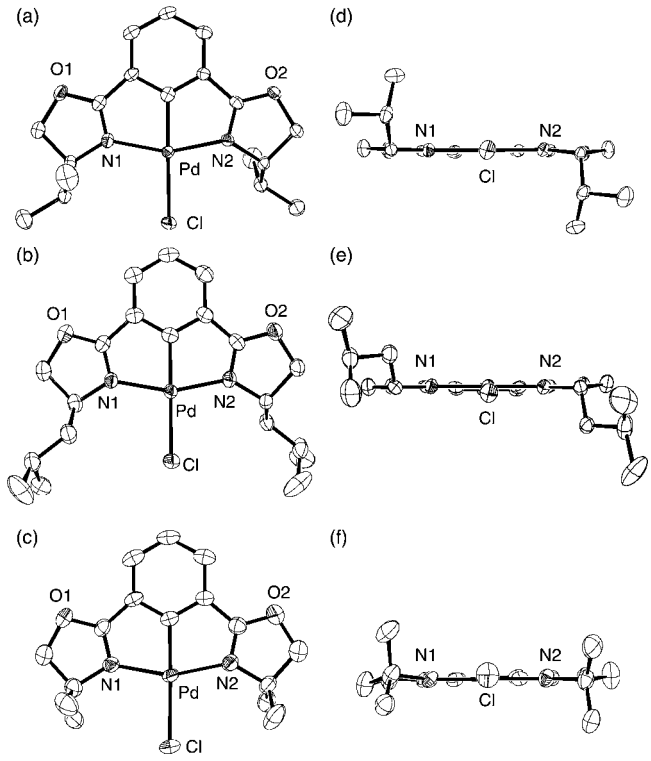

Figure 2. ORTEP drawings of the Phebox-Pd complexes **2c**,**d**,**f** drawn with thermal ellipsoids at the 50% probability level: (a) *i*-Pr-Phebox-PdCl (**2c**); (b) *i*-Bu-Phebox-PdCl (**2d**); (c) Me_2-Phebox-PdCl (**2d**); (d−f) side views of **2c**,**d**,**f** along the Cl−Pd bond. Hydrogen atoms have been omitted for clarity. Three and two independent molecules were present in the asymmetric units of **2d**,**f**, respectively. One is shown.

than those employing conventional methods. Further applications of the ligand introduction route to the synthesis of other types of pincer complexes are underway and will be reported in due course.

Experimental Section

General Procedures. All manipulations were performed under a nitrogen atmosphere. Nitrogen gas was dried by passage through P_2O_5. NMR spectra were recorded on a JEOL JNM-AL500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C, 202 MHz for ^{31}P). ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 at 25 °C. Chemical shifts are reported in δ (ppm) referenced to an internal Me_4Si standard for ^{1}H NMR. Chemical shifts of ^{13}C NMR are given relative to $CDCl_3$ (δ 77.0) or DMSO-d_6 (δ 39.7) as an internal standard. The ^{31}P NMR data are reported relative to external 85% H_3PO_4. ESI mass spectra were recorded on a JEOL JMS-T100LC spectrometer. Melting points were determined using a Yanaco MP-J3 micro melting point apparatus and are uncorrected. The IR spectra were obtained using a JASCO FT/IR-460plus spectrophotometer in the ATR mode. Optical rotations were recorded on a JASCO P-1020 polarimeter. Commercially available reagents were used without purification. 2-Bromoisophthalic acid (**4**)[16] and $Pd(PPh_3)_4$[17] were prepared according to the procedures in the literature. The β-amino alcohols **6** were prepared by the reduction of the corresponding amino acids with $LiAlH_4$.

Synthesis of *trans*-Bromo(2,6-dicarboxyphenyl)bis(triphenylphosphine)palladium (3). To a suspension of $Pd(PPh_3)_4$ (5.780 g, 5.00 mmol) in AcOEt (100 mL) was added 2-bromoisophthalic acid (**4**; 1.344 g, 5.49 mmol), and the mixture was stirred under reflux for 24 h. The resulting colorless solid was collected by filtration and washed with AcOEt (20 mL × 3) to give *trans*-bromo(2,6-dicarboxyphenyl)bis(triphenylphosphine)palladium (**3**; 4.060 g, 4.635 mmol, 93%) as a colorless solid. Mp: 213−215 °C dec. MS (ESI): *m*/*z* 874 (M^+). ^{1}H NMR (DMSO-d_6): δ 6.47 (t, J = 7.3 Hz, 1H, Ar H), 7.10 (d, J = 7.3 Hz, 2H, Ar H), 7.20−7.60 (m, 30H, Ar H), 12.21 (s, 2H, CO_2H). ^{13}C NMR (DMSO-d_6): δ 122.0 (Ar), 127.4 (Ar), 129.4 (Ar), 131.8 (virtual t, J = 21.7 Hz, Ar), 133.5 (Ar), 134.5 (Ar), 135.9 (Ar), 169.3 (Ar), 170.9 (C=O). ^{31}P NMR (DMSO-d_6): δ 13.6. Anal. Calcd for $C_{44}H_{35}BrO_4P_2Pd$ (876.02): C, 60.33; H, 4.03. Found: C, 60.34; H, 4.09. IR (ATR mode): ν 1685 cm^{-1} (C=O).

Synthesis of {2,6-Bis[(4*S*)-4-methyl-2-oxazolinyl]phenyl}chloropalladium (2a). To a suspension of *trans*-bromo(2,6-dicarboxyphenyl)bis(triphenylphosphine)palladium (**3**; 219.0 mg, 0.25 mmol) in CH_2Cl_2 (20 mL) was added $(COCl)_2$ (69.7 mg, 0.55 mmol) and DMF (3.8 mg, 0.05 mmol) at 0 °C, and the mixture was stirred at 25 °C for 6 h. After the solvent was removed, $CHCl_3$ (10 mL) was added to the residue. To the resulting solution was added Et_3N (55.6 mg, 0.55 mmol) and (*S*)-2-amino-1-propanol (**6a**; 41.4 mg, 0.55 mmol) at 0 °C, and the mixture was stirred at 25 °C for 12 h. The reaction mixture was poured into water (10 mL), and the organic layer was washed with water (10 mL × 2), dried over Na_2SO_4, and concentrated in vacuo. The residue was dissolved in $CHCl_3$ (10 mL), and to the resulting solution was added Et_3N (111.2 mg, 1.10 mmol) and MsCl (126.0 mg, 1.10 mmol) at 0 °C. The mixture was stirred under reflux under an oxygen atmosphere for 12 h. The reaction mixture was poured into water (10 mL), and the organic layer was washed with water (10 mL × 2), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using $CHCl_3$ as the eluent to give {2,6-bis[(4*S*)-4-methyl-2-oxazolinyl]phenyl}chloropalladium (**2a**; 51.8 mg, 0.13 mmol, 54%) as a colorless solid. Mp: 185−187 °C. MS (ESI): *m*/*z* 384 [M^+]. $[\alpha]_D^{20}$ = 320° (*c* 0.1, EtOH). ^{1}H NMR ($CDCl_3$): δ 1.55 (d, J = 6.7 Hz, 6H, CH_3), 4.37 (dd, J = 6.7, 8.5 Hz, 2H, OCH_2), 4.40−4.47 (m, 2H, NCH), 4.86 (t, J = 8.5 Hz, 2H, OCH_2), 7.12 (t, J = 7.9 Hz, 1H, Ar H), 7.27 (d, J = 7.9 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$): δ 21.4 (CH_3), 58.3 (NCH), 77.7 (OCH_2), 123.9 (Ar), 126.8 (Ar), 129.8 (Ar), 168.0 (Ar), 173.8 (C=N). IR (ATR mode): ν 1615 cm^{-1} (C=N).

{2,6-Bis[(4*S*)-4-(phenylmethyl)-2-oxazolinyl]phenyl}chloropalladium (2b). Yield: 44% (59.2 mg, 0.11 mmol), colorless solid. Mp: 278−280 °C dec. MS (ESI): *m*/*z* 501 [(M − Cl)$^+$]. $[\alpha]_D^{20}$ = 604° (*c* 0.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 3.08 (dd, J = 7.3, 13.9 Hz, 2H, $PhCH_2$), 3.72 (dd, J = 2.1, 13.9 Hz, 2H, $PhCH_2$), 4.63−4.76 (m, 6H, NCH, OCH_2), 7.17 (t, J = 7.3 Hz, 1H, Ar H), 7.26 (d, J = 7.3 Hz, 2H, Ar H), 7.29−7.34 (m, 6H, Ar H), 7.41 (d, J = 7.3 Hz, 4H, Ar H). ^{13}C NMR ($CDCl_3$): δ 40.0 (CH_2), 63.3 (NCH), 75.0 (OCH_2), 124.0 (Ar), 126.8 (Ar), 127.0 (Ar), 128.6 (Ar), 129.6 (Ar), 129.8 (Ar), 136.4 (Ar), 168.4 (Ar), 174.5 (C=N). Anal. Calcd for $C_{26}H_{23}ClN_2O_2Pd$ (537.35): C, 58.11; H, 4.31; N, 5.21. Found: C, 57.96; H, 4.56; N, 5.11. IR (ATR mode): ν 1611 cm^{-1} (C=N).

{2,6-Bis[(4*S*)-4-(1-methylethyl)-2-oxazolinyl]phenyl}chloropalladium (2c). Yield: 57% (62.9 mg, 0.14 mmol), colorless solid. Mp: 261−263 °C dec. MS (ESI): *m*/*z* 405 [(M − Cl)$^+$]. $[\alpha]_D^{20}$ = 493° (*c* 0.1, EtOH). ^{1}H NMR ($CDCl_3$): δ 0.80 (d, J = 6.7 Hz, 6H, CH_3), 0.91 (d, J = 6.7 Hz, 6H, CH_3), 2.80 (dh, J = 3.4, 6.7 Hz, 2H, C*H*CH_3), 4.33 (ddd, J = 3.4, 6.7, 9.5 Hz, 2H, NCH), 4.612 (d, J = 6.7 Hz, 2H, OCH_2), 4.615 (d, J = 9.5 Hz, 2H, OCH_2), 7.13 (t, J = 7.9 Hz, 1H, Ar H), 7.27 (d, J = 7.9 Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$): δ 14.2 (CH_3), 18.9 (CH_3), 28.9 (CH), 66.9 (NCH), 71.1 (OCH_2), 123.9 (Ar), 126.9 (Ar), 129.5 (Ar), 167.9 (Ar), 173.8 (C=N). Anal. Calcd for $C_{18}H_{23}ClN_2O_2Pd$ (441.26): C, 48.99; H, 5.25; N, 6.35. Found: C, 48.72; H, 5.17; N, 6.38. IR (ATR mode): ν 1612 cm^{-1} (C=N).

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Palladium Complexes 2c,d,f and 3

	bond lengths				bond angles	
compd	Pd−X[a]	Pd−L1[a]	Pd−L2[a]	Pd−C1	L1−Pd−L2[a]	X−Pd−C1[a]
3	2.5282(4)	2.3040(7)	2.3507(8)	2.026(3)	168.80(3)	172.04(8)
2c	2.385(1)	2.070(3)	2.040(3)	1.934(3)	158.0(1)	179.1(2)
2d	2.410(1)	2.060(6)	2.076(6)	1.940(5)	157.1(2)	177.4(2)
2f	2.4109(9)	2.059(3)	2.076(3)	1.936(3)	157.7(1)	177.3(1)

[a] Legend: for **3**, X = Br, L1 = L2 = P; for **2c**,**d**,**f**, X = Cl, L1 = L2 = N.

{2,6-Bis[(4*S*)-4-(2-methylpropyl)-2-oxazolinyl]phenyl}chloropalladium (2d). Yield: 50% (58.8 mg, 0.13 mmol), colorless solid. Mp: 262−264 °C dec. MS (ESI): *m*/*z* 433 [(M − Cl)$^+$]. $[\alpha]_D^{20} = 484°$ (*c* 0.1, EtOH). ^{1}H NMR ($CDCl_3$): δ 0.95 (d, $J = 6.7$ Hz, 6H, CH_3), 0.97 (d, $J = 6.1$ Hz, 6H, CH_3), 1.38 (ddd, $J = 4.9$, 10.4, 13.1 Hz, 2H, CH_2), 1.61−1.68 (m, 2H, CH), 2.42−2.47 (ddd, $J = 2.4$, 9.2, 13.1 Hz, 2H, CH_2), 4.30−4.35 (m, 2H, NCH), 4.47 (t, $J = 8.1$ Hz, 2H, OCH_2), 4.82 (t, $J = 8.1$ Hz, 2H, OCH_2), 7.10 (t, $J = 7.3$ Hz, 1H, Ar H), 7.24 (d, $J = 7.3$ Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$): δ 21.6 (CH_3), 23.7 (CH_3), 25.5 (CH), 43.8 (CH_2), 61.3 (NCH), 76.5 (OCH_2), 123.8 (Ar), 126.6 (Ar), 129.8 (Ar), 168.2 (Ar), 173.6 (C═N). Anal. Calcd for $C_{20}H_{27}ClN_2O_2Pd$ (469.31): C, 51.18; H, 5.80; N, 5.97. Found: C, 50.93; H, 5.72; N, 5.99. IR (ATR mode): ν 1616 cm^{-1} (C═N).

(2,6-Bis{(4*S*)-4-[(1*S*)-1-methylpropyl]-2-oxazolinyl}phenyl)chloropalladium (2e). Yield: 47% (52.4 mg, 0.12 mmol), colorless solid. Mp: 283−285 °C dec. MS (ESI): *m*/*z* 433 [(M − Cl)$^+$]. $[\alpha]_D^{20} = 478°$ (*c* 0.1, EtOH). ^{1}H NMR ($CDCl_3$): δ 0.78 (d, $J = 6.7$ Hz, 6H, CH_3), 0.96 (t, $J = 7.3$ Hz, 6H, CH_3), 1.14−1.23 (m, 2H, CH_2), 1.25−1.33 (m, 2H, CH_2), 2.64 (d of sextets, $J = 3.2$, 6.7 Hz, 2H, CH), 4.43 (ddd, $J = 3.2$, 6.4, 9.8 Hz, 2H, NCH), 4.57−4.64 (m, 4H, OCH_2), 7.13 (t, $J = 7.3$ Hz, 1H, Ar H), 7.27 (d, $J = 7.3$ Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$): δ 11.77 (CH_3), 11.83 (CH_3), 26.4 (CH_2), 35.6 (CH), 65.6 (NCH), 71.2 (OCH_2), 123.9 (Ar), 126.8 (Ar), 129.6 (Ar), 168.1 (Ar), 173.8 (C═N). Anal. Calcd for $C_{20}H_{27}ClN_2O_2Pd$ (469.31): C, 51.18; H, 5.80; N, 5.97. Found: C, 50.97; H, 5.92; N, 5.73. IR (ATR mode): ν 1613 cm^{-1} (C═N).

[2,6-Bis(4,4-dimethyl-2-oxazolinyl)phenyl]chloropalladium (2f). Yield: 48% (49.2 mg, 0.12 mmol), pale yellow solid. Mp: 261−263 °C dec. MS (ESI): *m*/*z* 377 [(M − Cl)$^+$]. ^{1}H NMR ($CDCl_3$): δ 1.63 (s, 12H, CH_3), 4.44 (s, 4H, CH_2), 7.13 (t, $J = 7.9$ Hz, 1H, Ar H), 7.26 (d, $J = 7.9$ Hz, 2H, Ar H). ^{13}C NMR ($CDCl_3$): δ 27.9 (CH_3), 65.8 (CCH_3), 82.9 (OCH_2), 123.8 (Ar), 126.7 (Ar), 130.1 (Ar), 167.2 (Ar), 172.4 (C═N). Anal. Calcd for $C_{16}H_{19}ClN_2O_2Pd$ (413.21): C, 46.51; H, 4.63; N, 6.78. Found: C, 46.43; H, 4.57; N, 6.80. IR (ATR mode): ν 1617 cm^{-1} (C═N).

X-ray Structure Determination. Single crystals of **3** suitable for an X-ray diffraction study were grown by slow diffusion of Et_2O into the DMSO solution. Single crystals of **2c**,**d**,**f** were obtained by their crystallization from hot AcOEt. X-ray data for single crystals were collected on a Rigaku Saturn CCD area detector at −100 °C using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The structures were solved by direct methods (SIR 92) and expanded using Fourier techniques (DIRDIF99). All non-hydrogen atoms except for C30, C31, and C32 in **2d** and C29 in **2f** were refined anisotropically, and the hydrogen atoms were refined using the riding model. All calculations were performed using the CrystalStructure crystallographic software package. Crystallographic data and details of structure refinement are summarized in Table S1 (see the Supporting Information).

Acknowledgment. This work was supported by the CREST program, sponsored by the JST. We also thank the JSPS (GRANT-in-AID for Scientific Research, No. 15205015) and the MEXT (Scientific Research on Priority Areas, No. 420) for partial financial support of this work.

Supporting Information Available: Selected crystallographic data (Table S1) and CIF files giving crystallographic data for **2c**,**d**,**f** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM800666X