Synthesis and Characterization of Chiral Palladium(II) Complexes Containing a Pd–C*(sp^3) σ-Bond

Akio Yoneda* and Tadao Hakushi

Department of Applied Chemistry, Faculty of Engineering, Himeji Institute of Technology, 2167 Shosha, Himeji, Hyogo, Japan

George R. Newkome

Department of Chemistry, University of South Florida, Tampa, Florida 33620

Frank R. Fronczek

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804

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A series of cyclometalated palladium(II) complexes containing a Pd–C*(sp^3) σ-bond has been prepared. 2-Substituted 8-quinolinol derivatives possessing two- or three-carbon side chains were synthesized. The terminal ethyl acetoactate moiety was shown to exist predominantly in the keto form. When these ligands were treated with potassium tetrachloropalladate(II) in the presence of pyridine, the corresponding complexes were formed. Single-crystal X-ray structure analyses on both the hemibenzene and chloroform solvates revealed that these molecules were racemic. When the pyridine ligand was exchanged with L-(−)-1-phenylethylamine, an *SS* or *RS* diastereomeric mixture resulted. Separation of the diastereomers was accomplished by column chromatography, and the structure of one isomer was characterized by X-ray crystallography. Ligand exchange with pyridine of each diastereomer generated the chiral Pd(II) complexes possessing a Pd–C(sp^3) σ-bond. $C_{24}H_{26}N_2O_4Pd$: $a = 9.9763(7)$ Å, $b = 18.0736(14)$ Å, $c = 12.4876(8)$ Å, $\beta = 100.877(6)°$, monoclinic, $P2_1$, $Z = 4$. $C_{22}H_{21}N_2O_4Cl_3Pd$: $a = 8.4858(9)$ Å, $b = 11.1272(7)$ Å, $c = 13.6216(8)$ Å, $\alpha = 71.736(5)°$, $\beta = 76.393(7)°$, $\gamma = 80.612(7)°$, triclinic, $P\bar{1}$, $Z = 2$. $C_{24}H_{23}N_2O_4Pd$: $a = 8.4205(7)$ Å, $b = 11.2537(13)$ Å, $c = 12.599(2)$ Å, $\alpha = 69.539(10)°$, $\beta = 82.987(9)°$, $\gamma = 81.956(9)°$, triclinic, $P\bar{1}$, $Z = 2$.

Introduction

Recently, we reported[1] a series of 2-substituted 8-quinolinol derivatives, possessing different *C*(sp^3),*N*,*O*-donor atoms, which formed a stable class of Pd complexes encompassing a Pd(II)–C(sp^3) σ-bond and a fused 5,5- or 5,6-chelate ring system. Although several Pd–C(sp^3) organometallic compounds have been documented,[2,3] as catalysts and in organic syntheses, reports of chiral Pd complex formation are albeit known[4,5] but very limited. We herein describe improved ligand syntheses as well as the resolution of the resultant cyclometalated Pd complexes due to a terminal chiral carbon center (Scheme 1).

Experimental Section

General Comments. Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were determined on a JEOL JNM-EX270 FT NMR spectrometer with $CDCl_3$ as solvent and $CHCl_3$ (7.26 ppm) as the internal standard. IR spectra were recorded on a JASCO FT/IR-5M spectrophotometer. For preparative thick-layer chromatography (TLC), 2 mm silica gel Kieselgel 60 $PF_{254-366}$ plates were used. Elemental analyses were performed on a Yanaco MT2 CHN recorder. Optical rotations were measured on a Perkin-Elmer 243B polarimeter.

X-ray. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Cu Kα ($\lambda = 1.54184$ Å) or

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Scheme 1

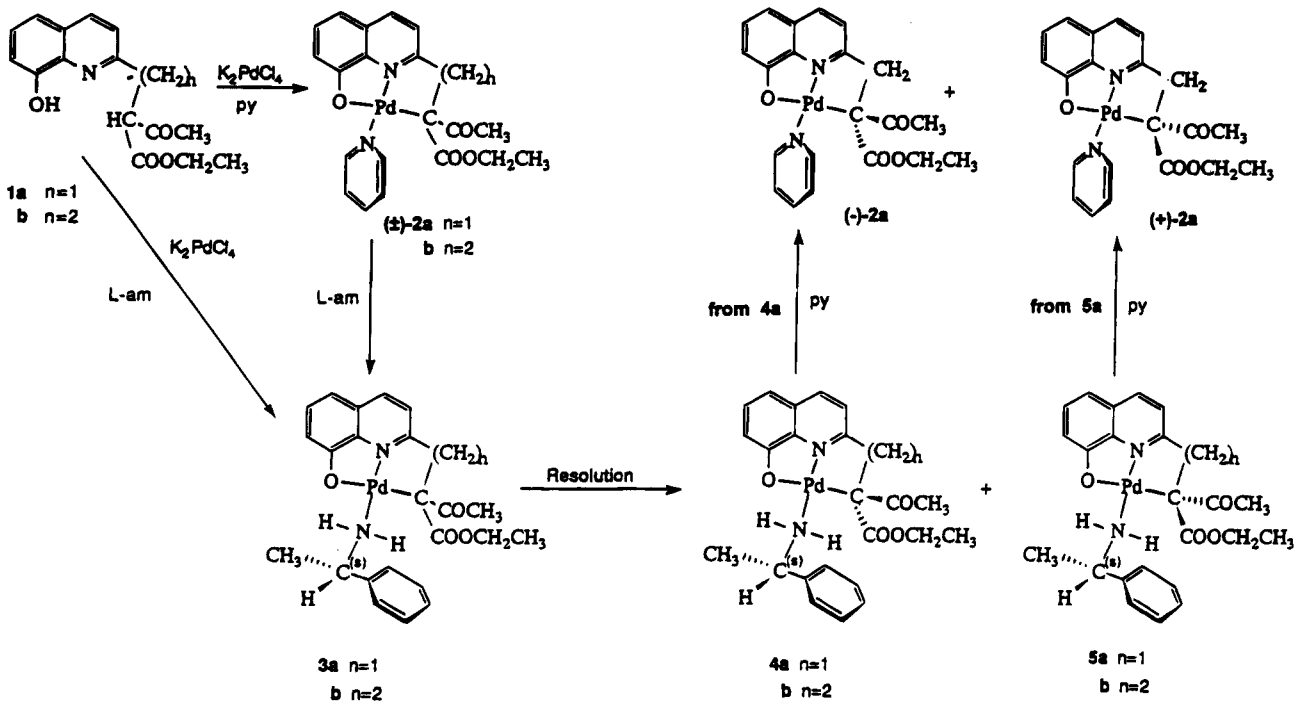

Table 1. Crystal Data and Data Collection Parameters for 2a and 5a

	2a (chloroform solvate)	*hemi*-**2a** (benzene solvate)	**5a**
formula	$C_{22}H_{21}N_2O_4Cl_3Pd$	$C_{24}H_{23}N_2O_4Pd$	$C_{24}H_{26}N_2O_4Pd$
fw	590.2	509.9	512.9
cryst system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1$
a, Å	8.4858(9)	8.4205(7)	9.9763(7)
b, Å	11.1272(7)	11.2537(13)	18.0736(14)
c, Å	13.6216(8)	12.599(2)	12.4876(8)
α, deg	71.736(5)	69.539(10)	
β, deg	76.393(7)	82.987(9)	100.877(6)
γ, deg	80.612(7)	81.956(9)	
V, Å^3	1181.5(2)	1104.1(3)	2211.1(5)
d, g cm^{-3}	1.659	1.534	1.537
Z	2	2	4
T, °C	21	21	20
radiation	Mo Kα	Cu Kα	Mo Kα
μ, cm^{-1}	11.47	72.00	8.6
cryst size, mm	0.42 × 0.35 × 0.12	0.20 × 0.27 × 0.42	0.30 × 0.38 × 0.55
color	yellow-orange	yellow-orange	orange
min rel trans, %	82.40	79.32	84.83
2*θ* limits, deg	$2 < 2\theta < 60$	$4 < 2\theta < 150$	$2 < 2\theta < 62$
data collected	sphere $1° < \theta < 22.5°$, hemisphere 22.5–30°	hemisphere	hemisphere $1° < \theta < 25°$, quadrant 25–31°
scan rates, deg min^{-1}	0.5–3.3	0.8–3.3	1.0–3.3
max scan time, s	60	60	30
collected data	10137	4369	11428
unique data	6876	4369	10842
obs data	5776	4160	9869
criterion	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
variables	371	281	575
R	0.034	0.027	0.023
R_w	0.042	0.039	0.027
GOF	1.940	2.403	1.452
extinction		$1.71(11) \times 10^{-6}$	$2.0(9) \times 10^{-8}$
max residual, e Å^{-3}	0.69	0.61	0.87
H atoms	refined iso	calculated positions	NH_2 hydrogens refined iso, others in calculated positions
comments		racemic, solvent lies on inversion center	2 independent molecules. refinement of mirror-image structure yields $R = 0.027$, $R_w = 0.034$

Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator, by $\omega-2\theta$ scans of variable speed designed to yield equal relative precision for all significant data. A maximum was placed on the time allowed for scanning a single reflection. Crystal data and experimental details are listed in Table 1. Data reduction included corrections for background, Lorentz, polarization, and absorption by ψ scans.

Structures were solved by heavy-atom methods and refined by full-matrix least-squares, treating non-hydrogen atoms anisotropically. Hydrogen atoms were located by difference

Table 2. Non-Hydrogen Coordinates and Isotropic Thermal Parameters for 2a(chloroform solvate)

atom	*x*	*y*	*z*	B_{eq} (Å^2)[a]
Pd	0.54662(2)	0.63674(2)	0.62396(2)	3.263(3)
O1	0.6015(2)	0.7325(2)	0.4629(2)	4.20(4)
O2	0.1811(2)	0.5219(2)	0.7761(2)	6.34(6)
O3	0.5910(3)	0.4182(2)	0.8933(2)	5.87(6)
O4	0.6419(2)	0.6189(2)	0.8500(2)	4.65(4)
N1	0.3829(2)	0.7796(2)	0.6235(2)	3.59(4)
N2	0.7280(2)	0.4925(2)	0.6167(2)	3.61(4)
C1	0.4979(3)	0.8352(2)	0.4426(2)	3.91(5)
C2	0.4950(4)	0.9220(3)	0.3444(2)	4.93(7)
C3	0.3783(4)	1.0274(3)	0.3319(2)	5.54(7)
C4	0.2619(4)	1.0509(3)	0.4125(3)	5.42(7)
C5	0.2575(3)	0.9679(2)	0.5158(2)	4.48(6)
C6	0.3767(3)	0.8632(2)	0.5267(2)	3.78(5)
C7	0.1487(3)	0.9789(3)	0.6094(3)	5.12(7)
C8	0.1622(3)	0.8958(3)	0.7042(3)	4.88(7)
C9	0.2853(3)	0.7937(2)	0.7112(2)	3.91(5)
C10	0.3276(3)	0.6989(3)	0.8080(2)	4.40(6)
C11	0.4311(3)	0.5792(2)	0.7839(2)	3.70(5)
C12	0.3238(3)	0.4874(3)	0.7799(2)	4.41(6)
C13	0.3889(4)	0.3559(3)	0.7734(3)	5.50(7)
C14	0.5592(3)	0.5271(2)	0.8483(2)	3.85(5)
C15	0.7662(4)	0.5796(3)	0.9140(2)	5.54(8)
C16	0.8300(5)	0.6943(4)	0.9129(3)	8.8(2)
C17	0.8599(3)	0.4847(3)	0.6577(2)	4.41(6)
C18	0.9931(3)	0.3999(3)	0.6426(3)	5.23(7)
C19	0.9962(3)	0.3221(3)	0.5832(3)	5.47(8)
C20	0.8615(4)	0.3274(3)	0.5419(3)	5.97(7)
C21	0.7294(3)	0.4140(3)	0.5600(2)	4.83(6)
C1S	0.2384(5)	0.8511(3)	0.0660(3)	6.74(9)
CL1S	0.3265(2)	0.9523(2)	−0.0520(2)	11.63(5)
CL2S	0.0528(2)	0.8161(2)	0.0599(2)	12.11(4)
CL3S	0.2280(2)	0.9125(2)	0.16963(9)	9.63(4)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

Table 3. Non-Hydrogen Coordinates and Isotropic Thermal Parameters for *hemi*-2a(benzene solvate)

atom	*x*	*y*	*z*	B_{eq} (Å^2)[a]
Pd	0.58288(2)	0.64978(2)	0.61536(2)	3.606(4)
O1	0.6068(2)	0.7308(2)	0.4367(2)	4.56(4)
O2	0.2378(2)	0.5538(2)	0.7730(2)	5.66(5)
O3	0.6685(3)	0.4440(2)	0.9133(2)	6.74(6)
O4	0.7162(2)	0.6461(2)	0.8595(2)	4.93(4)
N1	0.4244(3)	0.7968(2)	0.5982(2)	3.91(4)
N2	0.7554(2)	0.5007(2)	0.6240(2)	3.81(4)
C1	0.4984(3)	0.8301(2)	0.4050(2)	4.21(6)
C2	0.4711(4)	0.9021(3)	0.2931(3)	5.13(7)
C3	0.3508(4)	1.0055(3)	0.2675(3)	5.66(8)
C4	0.2569(4)	1.0424(3)	0.3491(3)	5.65(7)
C5	0.2792(3)	0.9730(2)	0.4650(3)	4.63(6)
C6	0.3980(3)	0.8696(2)	0.4886(2)	4.04(5)
C7	0.1909(4)	0.9957(2)	0.5600(3)	5.30(7)
C8	0.2216(4)	0.9216(3)	0.6685(3)	5.17(7)
C9	0.3435(3)	0.8187(2)	0.6871(2)	4.15(5)
C10	0.4027(3)	0.7313(3)	0.7986(2)	4.44(6)
C11	0.4933(3)	0.6060(2)	0.7869(2)	3.96(5)
C12	0.3790(3)	0.5154(3)	0.7887(2)	4.60(6)
C13	0.4352(4)	0.3776(3)	0.8052(3)	6.31(9)
C14	0.6308(3)	0.5539(3)	0.8605(2)	4.36(6)
C15	0.8557(4)	0.6042(3)	0.9256(2)	5.20(7)
C16	0.9263(4)	0.7158(4)	0.9246(4)	8.1(2)
C17	0.8961(3)	0.4955(3)	0.6649(2)	4.49(6)
C18	1.0237(4)	0.4063(3)	0.6587(3)	5.10(7)
C19	1.0069(4)	0.3184(3)	0.6105(3)	5.41(7)
C20	0.8603(4)	0.3219(3)	0.5703(3)	6.18(8)
C21	0.7390(3)	0.4133(3)	0.5781(3)	5.17(6)
C1S	0.9127(8)	1.1017(5)	0.9266(5)	11.6(2)
C2S	1.1607(8)	0.9716(5)	0.9761(5)	11.2(2)
C3S	1.0691(9)	1.0718(5)	0.9023(4)	11.9(2)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

maps and treated as specified in Table 1. Final *R* factors and residual electron densities are given in Table 1; coordinates are listed in Tables 2–4.

Preparation of 2-[2-Acetyl-2-(ethoxycarbonyl)ethyl]-8-quinolinol (1a). A mixture of 2-(chloromethyl)-8-quinolinol[1] (232.6 mg, 1.2 mmol), ethyl acetoacetate (500 mg, 3.8 mmol), and anhydrous K_2CO_3 (566.7 mg, 4.1 mmol) in dry DMF (10 mL) was stirred at 25 °C. After 24 h, the mixture was filtered; the residue was thoroughly washed with $CHCl_3$. The combined extract was concentrated in vacuo to afford a brown oil, which was chromatographed (SiO_2), eluting with EtOAc–C_6H_{14} (1:4), to give (61.5%) **1a** as colorless needle crystals: mp 68–69 °C; 212.2 mg; ^{1}H NMR δ 1.26 (t, OCH_2CH_3, J = 7.3 Hz, 3H), 2.37 (s, $COCH_3$, 3H), 3.58 (d, β-CH_2, J = 6.6 Hz, 1H), 3.59 (d, β-CH_2, J = 7.9 Hz, 1H), 4.22 (q, OCH_2CH_3, J = 6.9 Hz, 1H), 4.23 (q, OCH_2CH_3, J = 7.2 Hz, 1H), 4.39 (t, α-CH, J = 7.9 Hz, 1H); ^{13}C NMR δ 13.96 (CH_3), 29.29 (β-CH_2),

Table 4. Non-Hydrogen Coordinates and Isotropic Thermal Parameters for 5a

atom	*x*	*y*	*z*	B_{eq} (Å^2)[a]
Pd1A	0.56061(2)	0	0.28456(2)	2.942(3)
O1A	0.6576(2)	−0.1030(2)	0.3177(2)	3.88(4)
O2A	0.3946(3)	0.0930(2)	0.0452(2)	6.02(5)
O3A	0.5097(2)	0.1784(2)	0.3603(2)	4.45(4)
O4A	0.3418(2)	0.1069(2)	0.3990(2)	4.60(4)
N1A	0.4110(2)	−0.0633(2)	0.2170(2)	3.40(4)
N2A	0.7199(2)	0.0670(2)	0.3609(2)	3.50(4)
C1A	0.5760(3)	−0.1556(2)	0.2670(2)	3.74(5)
C2A	0.6099(3)	−0.2298(2)	0.2664(2)	4.69(6)
C3A	0.5164(4)	−0.2813(2)	0.2115(3)	5.55(7)
C4A	0.3886(4)	−0.2620(2)	0.1595(3)	5.65(7)
C5A	0.3461(3)	−0.1875(2)	0.1587(2)	4.47(6)
C6A	0.4444(2)	−0.1361(2)	0.2120(2)	3.56(5)
C7A	0.2180(3)	−0.1588(2)	0.1128(3)	5.27(7)
C8A	0.1873(3)	−0.0859(2)	0.1226(2)	4.90(6)
C9A	0.2884(2)	−0.0364(2)	0.1773(2)	3.78(5)
C10A	0.2719(3)	0.0425(2)	0.2017(2)	4.29(5)
C11A	0.4114(2)	0.0824(2)	0.2338(2)	3.52(5)
C12A	0.4524(3)	0.1142(2)	0.1341(2)	4.06(5)
C13A	0.5641(3)	0.1693(2)	0.1394(3)	5.02(7)
C14A	0.4274(3)	0.1291(2)	0.3349(2)	3.61(5)
C15A	0.3579(3)	0.1409(2)	0.5051(2)	5.11(7)
C16A	0.2489(4)	0.1072(2)	0.5588(3)	6.67(8)
C17A	0.8653(3)	0.0610(2)	0.3441(2)	4.14(5)
C18A	0.9300(3)	−0.0093(2)	0.3936(2)	5.44(7)
C19A	0.8725(3)	0.0702(2)	0.2246(2)	4.25(6)
C20A	0.9254(3)	0.1347(2)	0.1897(3)	6.32(8)
C21A	0.9273(4)	0.1442(3)	0.0784(3)	8.25(9)
C22A	0.8787(4)	0.0902(3)	0.0057(3)	8.5(2)
C23A	0.8297(3)	0.0257(3)	0.0401(2)	6.91(9)
C24A	0.8259(3)	0.0160(2)	0.1495(2)	5.12(7)
Pd1B	0.79975(2)	−0.04406(2)	0.64877(2)	3.072(3)
O1B	0.7154(2)	0.0578(2)	0.5878(2)	3.64(3)
O2B	1.1046(2)	−0.1149(2)	0.6157(2)	8.91(8)
O3B	0.7801(2)	−0.2287(2)	0.7096(2)	6.04(6)
O4B	0.8530(2)	−0.1762(2)	0.8702(2)	5.02(4)
N1B	0.9415(2)	0.0210(2)	0.7255(2)	3.46(4)
N2B	0.6413(2)	−0.1082(2)	0.5679(2)	3.44(4)
C1B	0.7987(2)	0.1123(2)	0.6305(2)	3.61(5)
C2B	0.7744(3)	0.1866(2)	0.6079(2)	4.40(6)
C3B	0.8693(3)	0.2400(2)	0.6576(2)	4.91(6)
C4B	0.9865(3)	0.2218(2)	0.7278(2)	4.88(6)
C5B	1.0155(3)	0.1474(2)	0.7541(2)	4.00(5)
C6B	0.9210(2)	0.0942(2)	0.7041(2)	3.37(4)
C7B	1.1315(3)	0.1183(2)	0.8267(2)	4.65(6)
C8B	1.1467(3)	0.0452(2)	0.8464(2)	4.65(6)
C9B	1.0476(2)	−0.0052(2)	0.7934(2)	3.86(5)
C10B	1.0434(3)	−0.0863(2)	0.8110(2)	4.94(6)
C11B	0.9365(2)	−0.1264(2)	0.7221(2)	3.87(5)
C12B	0.9981(3)	−0.1460(2)	0.6262(3)	5.86(7)
C13B	0.9316(4)	−0.1999(3)	0.5399(3)	7.90(9)
C14B	0.8509(3)	−0.1827(2)	0.7635(2)	4.19(6)
C15B	0.7594(3)	−0.2234(2)	0.9141(3)	6.53(8)
C16B	0.7500(5)	−0.1948(3)	1.0228(3)	8.7(2)
C17B	0.5028(2)	−0.0792(2)	0.5744(2)	3.43(5)
C18B	0.3931(3)	−0.1260(2)	0.5057(2)	5.04(7)
C19B	0.4885(2)	−0.0727(2)	0.6926(2)	3.37(4)
C20B	0.5202(3)	−0.0065(2)	0.7481(2)	4.28(5)
C21B	0.5084(3)	−0.0003(2)	0.8559(2)	5.07(6)
C22B	0.4666(3)	−0.0579(2)	0.9104(2)	5.40(6)
C23B	0.4328(3)	−0.1236(2)	0.8564(2)	5.55(7)
C24B	0.4432(3)	−0.1314(2)	0.7479(2)	4.56(6)

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$.

35.31 (α-*C*H), 57.97 (COCH$_3$), 61.73 (O*C*H$_2$), 169.86 (*C*OCH$_3$), 202.35 (*C*O$_2$CH$_2$); IR (KBr) 1733, 1712 (C=O), 1608, 1578 (C=C) cm^{-1}. Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96; N, 4.88. Found: C, 66.69; H, 5.77; N, 4.78.

2-[3-Acetyl-3-(ethoxycarbonyl)propyl]-8-quinolinol (1b). To a stirred solution of ethyl acetoacetate (500 mg, 3.8 mmol) and EtONa (50 mg, 730 μmol) in dry EtOH (30 mL) was added 2-vinyl-8-quinolinol[6] (190 mg, 1.1 mmol) in EtOH (20 mL) under reflux. After 24 h, the solution was concentrated in vacuo to give a crude oil, which was extracted with $CHCl_3$ (30 mL). The organic extract was washed with 1 N HCl and then 1 N NaOH, dried (Na_2SO_4), and concentrated in vacuo to afford an oil, which was chromatographed (SiO_2), eluting with EtOAc–C_6H_{14} (1:4), to give (78.6%) ligand **1b** as an oil: 263 mg; ^{1}H NMR δ 1.26 (t, OCH$_2$C*H*$_3$, J = 6.9 Hz, 3H), 2.23 (s, COC*H*$_3$, 3H), 2.40 (dt, β-C*H*$_2$, J = 7.3, 7.3 Hz, 2H), 2.97 (t, γ-C*H*$_2$, J = 7.3 Hz, 2H), 3.57 (t, α-C*H*, J = 7.3 Hz, 1H), 4.19 (q, OC*H*$_2$CH$_3$, J = 7.3 Hz, 2H); ^{13}C NMR δ 13.95 (*C*H$_3$), 26.74 (γ-*C*H$_2$), 28.92 (β-*C*H$_2$), 35.31 (α-*C*H), 58.64 (CO*C*H$_3$), 61.40 (O*C*H$_2$), 169.67 (*C*OCH$_3$), 202.80 (*C*O$_2$CH$_2$); IR (neat) 1734, 1708 (C=O), 1600, 1570 (C=C) cm^{-1}. Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.54; H, 6.52; N, 4.59.

Preparation of *C*-Metalated Pd(II) Complexes. Pyridine[2-[2-acetyl-2-(ethoxycarbonyl)ethyl]-8-quinolinol-*C,N,O*]palladium(II) (2a). To a stirred solution of **1a** (94.8 mg, 330 μmol) in EtOH (10 mL) was added a solution of K_2PdCl_4 (108 mg, 330 μmol) in water (20 mL), followed by the addition of KOH (70 mg, 1.2 mmol). After 20 min at 25 °C, pyridine (1 mL) was added and the mixture was stirred for an additional 19 h. The mixture was concentrated in vacuo to give the Pd complex, which was dissolved in $CHCl_3$ and dried (Na_2SO_4). Upon concentration, the residue was chromatographed (SiO_2), eluting with EtOAc, to give two major components. **Fraction A** gave (5%) the *N,O*-chelated 2:1 complex (ligand-to-metal ratio) as brick crystals: mp 150–155 °C. **Fraction B** afforded (57%) the desired complex **2a**, as yellow crystals (4×; C_6H_6): mp 151 °C; 88.3 mg; ^{1}H NMR δ 1.17 (t, OCH$_2$C*H*$_3$, J = 7.3 Hz, 3H), 1.94 (s, COC*H*$_3$, 3H), 3.86 (d, β-C*H*$_A$H$_B$, J = 18.2 Hz, 1H), 4.16 (q, OC*H*$_2$CH$_3$, J = 5.3 Hz, 2H), 4.17 (d, β-CH$_A$*H*$_B$, J = 17.8 Hz, 1H); ^{13}C NMR δ 14.25 (*C*H$_3$), 29.54 (β-*C*H$_2$), 44.48 (*C*Pd), 57.74 (CO*C*H$_3$), 60.22 (O*C*H$_2$), 173.23 (*C*OCH$_3$), 202.51 (*C*O$_2$CH$_2$); IR (KBr) 1693 (C=O), 1640 (C=O), 1572 (C=C) cm^{-1}. Anal. Calcd for $C_{21}H_{20}N_2O_4Pd \cdot {}^1/_2H_2O$: C, 52.57; H, 4.41; N, 5.84. Found: C, 52.35; H, 4.30; N, 5.86.

Pyridine[2-[3-acetyl-3-(ethoxycarbonyl)propyl]-8-quinolinol-*C,N,O*]palladium(II) (2b) was similarly prepared. **Fraction A** gave (3.3%) the 2:1 complex as brick crystals: mp 120–123 °C. **Fraction B** afforded (60.6%) the desired complex **2b** as yellow crystals ($CHCl_3$–C_6H_{14}): mp 127–129 °C; 97.0 mg; ^{1}H NMR δ 1.28 (t, OCH$_2$C*H*$_3$, J = 7.3 Hz, 3H), 1.81 (dt, β-C*H*$_A$H$_B$, J = 4.3, 14.7 Hz, 1H), 1.97 (s, COC*H*$_3$, 3H), 2.17 (dt, β-CH$_A$*H*$_B$, J = 6.6, 15.5 Hz, 1H), 3.34 (t, γ-C*H*$_2$, J = 6.1 Hz, 2H), 4.06–4.15 (m, OC*H*$_A$H$_B$, 1H), 4.17–4.26 (m, OCH$_A$*H*$_B$, 1H); ^{13}C NMR δ 14.29 (*C*H$_3$), 28.18 (γ-*C*H$_2$), 29.13 (β-*C*H$_2$), 37.36 (*C*Pd), 50.14 (CO*C*H$_3$), 60.38 (O*C*H$_2$), 175.63 (*C*OCH$_3$), 208.73 (*C*O$_2$CH$_2$); IR (KBr) 1700, 1654 (C=O), 1574 (C=C) cm^{-1}. Anal. Calcd for $C_{22}H_{22}N_2O_4Pd \cdot H_2O$: C, 52.55; H, 4.81; N, 5.57. Found: C, 52.06; H, 4.74; N, 5.18.

Preparation of the Diastereomeric Pd(II) Complexes by External Ligand Exchange. (L-(−)-1-Phenylethylamine)[2-[2-acetyl-2-(ethoxycarbonyl)ethyl]-8-quinolinol-*C,N,O*]palladium(II) (3a). To a stirred solution of **2a** (85 mg, 180 μmol) in benzene (30 mL) was added L-(−)-1-phenylethylamine (1.0 g, 8.3 mmol). After 24 h, the mixture was concentrated in vacuo to give a residue, which was extracted with CH_2Cl_2 and subsequently chromatographed (SiO_2), eluting with EtOAc–C_6H_{14} (1:1), to give (87%) diastereomeric **3a**, as orange crystals: 80.3 mg; mp 161–164 °C; $[\alpha]^{25}_D$ = −84.3° (*c* 1.036, $CHCl_3$); ^{1}H NMR δ 1.16 (t, OCH$_2$C*H*$_3$, J = 7.3 Hz, 1.5H), 1.33 (t, OCH$_2$C*H*$_3$, J = 7.3 Hz, 1.5H), 1.72 (d, CHC*H*$_3$, J = 6.9 Hz, 1.5H), 1.82 (d, CHC*H*$_3$, J = 6.9 Hz, 1.5H), 2.29 (s, COC*H*$_3$, 1.5H), 2.46 (s, COC*H*$_3$, 1.5H); ^{13}C NMR δ 44.46 (*C*Pd), 44.53 (*C*Pd), 173.23 (*C*OCH$_3$), 202.51 (*C*O$_2$CH$_2$); IR (KBr) 1662, 1644 (C=O), 1578 (C=C) cm^{-1}. Anal. Calcd for $C_{24}H_{26}N_2O_4Pd$: C, 56.20; H, 5.11; N, 5.46. Found: C, 56.04; H, 5.19; N, 5.37.

(L-(−)-1-Phenylethylamine)[2-[3-acetyl-3-(ethoxycarbonyl)propyl]-8-quinolinol-*C,N,O*]palladium(II) (3b) was similarly prepared (91%) from **2b** and L-(−)-1-phenylethylamine as yellow diastereomeric crystals ($CHCl_3$–C_6H_{14}): mp 186–188 °C; 93.1 mg; $[\alpha]^{25}_D$ = −106.9° (*c* 0.732, $CHCl_3$); ^{1}H NMR δ 1.15 (t, OCH$_2$C*H*$_3$, J = 7.3 Hz, 1.5H), 1.32 (t, OCH$_2$C*H*$_3$, J = 7.3 Hz, 1.5H), 1.67 (d, CHC*H*$_3$, J = 6.9 Hz, 1.5H), 1.76 (d, CHC*H*$_3$, J = 6.6 Hz, 1.5H), 2.21 (s, COC*H*$_3$, 1.5H), 2.53 (s, COC*H*$_3$, 1.5H); ^{13}C NMR δ 38.33 (*C*Pd), 38.64 (*C*Pd), 173.46 (*C*OCH$_3$), 205.23 (*C*O$_2$CH$_2$); IR (KBr) 1701, 1638 (C=O), 1575 (C=C) cm^{-1}. Anal. Calcd for $C_{25}H_{28}N_2O_4Pd$: C, 56.99; H, 5.36; N, 5.32. Found: C, 56.86; H, 5.32; N, 5.29.

Preparation of the Diastereomeric Pd(II) Complexes by Reaction of 1 and L-(−)-1-Phenylethylamine. 3a and **3b** were prepared from **1a** and **1b**, respectively, and L-(−)-1-phenylethylamine via the direct treatment in the presence of K_2PdCl_4: **3a** (from **1a**) 21.5%, yellow crystals; **3b** (from **1b**) 41.0%, yellow crystals.

Preparation of the Chiral Pd(II) Complexes (4 and 5) by Optical Resolution of the Diastereomer 3. Diastereomeric **3a** was resolved by column chromatograph (SiO_2, 150 cm length, 2.7 cm i.d glass tube), eluting with a mixture of EtOAc–C_6H_{14} (1:1). **Fraction A** gave **4a** as yellow crystals: mp 193–198 °C; $[\alpha]^{25}_D$ +57.9° (*c* 1.036, $CHCl_3$); ^{1}H NMR δ 1.33 (t, OCH$_2$C*H*$_3$, J = 7.3 Hz, 3H), 1.82 (d, CHC*H*$_3$, J = 6.6 Hz, 3H), 2.25 (s, COC*H*$_3$, 3H), 3.06 (N*H*$_A$H$_B$, 1H), 3.65 (d, β-C*H*$_A$H$_B$, J = 18.5 Hz, 1H), 3.87 (NH$_A$*H*$_B$, 1H), 4.19–4.28 (m, OC*H*$_2$H$_3$, C*H*CH$_3$, 3H), 4.34 (d, β-CH$_A$*H*$_B$, J = 18.5 Hz, 1H); ^{13}C NMR δ 14.38 (OCH$_2$*C*H$_3$), 23.58 (CH*C*H$_3$), 29.20 (β-*C*H$_2$), 44.46 (*C*Pd), 54.59 (*C*HCH$_3$), 57.27 (O*C*H$_2$), 60.81 (CO*C*H$_3$), 173.26 (*C*OCH$_3$), 199.14 (*C*O$_2$C$_2$H$_5$); IR (KBr) 1669 (C=O), 1635 (C=O), 1572 (C=C) cm^{-1}. Anal. Calcd for $C_{24}H_{26}N_2O_4Pd$: C, 56.20; H, 5.11; N, 5.46. Found: C, 56.15; H, 5.17; N, 5.49.

Fraction B gave **5a** as yellow crystals: mp 176–178 °C; $[\alpha]^{25}_D$ −244.3° (*c* 0.991, $CHCl_3$); ^{1}H NMR δ 1.16 (t, OCH$_2$C*H*$_3$, J = 7.3 Hz, 3H), 1.76 (d, CHC*H*$_3$, J = 6.9 Hz, 3H), 2.44 (s, COC*H*$_3$, 3H), 3.23 (N*H*$_A$H$_B$, 1H), 3.35 (NH$_A$*H*$_B$, 1H), 3.67 (d, β-C*H*$_A$H$_B$, J = 19.1 Hz, 1H), 3.90–4.12 (m, OC*H*$_2$CH$_3$, 2H), 4.22–4.30 (m, C*H*CH$_3$, 1H), 4.31 (d, β-CH$_A$*H*$_B$, J = 19.1 Hz, 1H); ^{13}C NMR δ 14.20 (OCH$_2$*C*H$_3$), 23.51 (C*C*H$_3$), 29.63 (β-*C*H$_2$), 44.53 (*C*Pd), 54.41 (*C*HCH$_3$), 56.75 (O*C*H$_2$), 60.67 (CO*C*H$_3$), 172.42 (*C*OCH$_3$), 199.37 (*C*O$_2$C$_2$H$_5$); IR (KBr) 1670 (C=O), 1643 (C=O), 1578 (C=C) cm^{-1}. Anal. Calcd for $C_{24}H_{26}N_2O_4Pd$: C, 56.20; H, 5.11; N, 5.46. Found: C, 56.11; H, 5.18; N, 5.44.

Optical resolution of 3b was conducted by an identical manner to that of **3a**. **Fraction A** gave **4b** as yellow crystals: mp 178–182 °C; $[\alpha]^{25}_D$ −331.0° (*c* 0.052, $CHCl_3$); ^{1}H NMR δ 1.15 (t, OCH$_2$C*H*$_3$, J = 6.9 Hz, 3H), 1.67 (d, CHC*H*$_3$, J = 6.6 Hz, 3H), 2.01 (t, β-C*H*$_2$, J = 6.6 Hz, 2H), 2.53 (s, COC*H*$_3$, 3H), 3.28 (t, γ-C*H*$_2$, J = 5.9 Hz, 2H), 3.70 (N*H*$_A$H$_B$, 1H), 3.99–4.14 (m, OC*H*$_2$CH$_3$, C*H*CH$_3$, 3H), 4.48 (NH$_A$*H*$_B$, 1H); ^{13}C NMR δ 14.22 (OCH$_2$*C*H$_3$), 23.54 (CH*C*H$_3$), 27.64 (γ-*C*H$_2$), 31.02 (β-*C*H$_2$), 38.33 (*C*Pd), 50.37 (*C*HCH$_3$), 53.43 (CO*C*H$_3$), 60.36 (O*C*H$_2$CH$_3$), 173.08 (*C*OCH$_3$), 206.72 (*C*O$_2$C$_2$H$_5$); IR (KBr) 1700, 1638 (C=O), 1568 (C=C) cm^{-1}.

Fraction B gave **5b** as yellow crystals: mp 169–172 °C; $[\alpha]^{25}_D$ +115.4° (*c* 0.062, $CHCl_3$); ^{1}H NMR δ 1.32 (t, OCH$_2$C*H*$_3$, J = 7.3 Hz, 3H), 1.76 (d, CHC*H*$_3$, J = 6.9 Hz, 3H), 1.91 (t, β-C*H*$_2$, J = 5.6 Hz, 2H), 2.20 (s, COC*H*$_3$, 3H), 2.74 (N*H*$_A$H$_B$, 1H), 3.23–3.49 (m, γ-C*H*$_2$, 2H), 4.03–4.33 (m, OC*H*$_2$CH$_3$, C*H*CH$_3$, 3H), 4.50 (NH$_A$*H*$_B$, 1H); ^{13}C NMR δ 14.22 (OCH$_2$*C*H$_3$), 23.54 (CH*C*H$_3$), 27.64 (γ-*C*H$_2$), 31.02 (β-*C*H$_2$), 38.33 (*C*Pd), 50.37 (*C*HCH$_3$), 53.43 (CO*C*H$_3$), 60.36 (O*C*H$_2$CH$_3$), 173.46 (*C*OCH$_3$), 205.23 (*C*O$_2$C$_2$H$_5$); IR (KBr) 1701, 1639 (C=O), 1571 (C=C) cm^{-1}.

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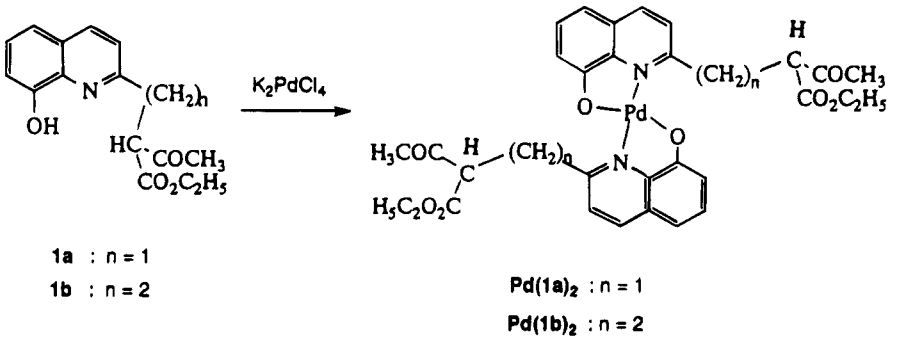
Scheme 2



1a : n = 1
1b : n = 2

Pd(1a)$_2$: n = 1
Pd(1b)$_2$: n = 2

Preparation of the Chiral Pd(II) Complexes (−)-2a and (+)-2a by Ligand Exchange. To a stirred solution of **4a** (310 mg, 600 μmol) in benzene (30 mL) was added pyridine (1 mL). After 24 h, the solution was concentrated in vacuo and the residue was chromatographed (SiO_2), eluting with EtOAc, to give (7%) (−)-**2a** as yellow crystals: $[\alpha]^{25}_D$ −10.4° (*c* 0.241, $CHCl_3$). (+)-**2a** was prepared (19%) from **5a** by this procedure, as yellow crystals: $[\alpha]^{25}_D$ +4.6° (*c* 0.194, $CHCl_3$).

Results and Discussion

Ligands. Treatment of 2-(chloromethyl)-8-quinolinol[1] with ethyl acetoacetate using the K_2CO_3–DMF procedure[5] gave (61%) **1a** as white crystals. The ^{1}H NMR spectrum of **1a** in $CDCl_3$ showed that the ethyl acetoacetate moiety is exclusively the keto tautomer as evidenced by the lack of enolic signals and the integration ratio due to the acidic C*H* signal of the substituted ethyl acetoacetate moiety.[8] The two doublets at δ 3.58 and 3.59 for the quinolinol β-CH_2 groups suggest the juxtaposition of an adjacent enantiotopic center.[5] Comparison of the ^{1}H NMR spectra of **1a** and analogous ligands possessing the acetylacetonyl or diethyl malonate moiety for terminal carbon in the previous report[1] showed similar chemical shifts.

Ligand **1b** was synthesized (79%) by treatment of ethyl acetoacetate with 2-vinyl-8-quinolinol[6] in ethanol under reflux for 24 h. Analysis of the ^{1}H NMR spectrum for **1b** indicated that the β-methylene hydrogens at δ 2.40 were shifted slightly upfield compared to ligands possessing the acetylacetonyl (δ 2.51) or diethyl malonato moieties (δ 2.48).[1]

Cyclometalation. Treatment of **1a** or **1b** with K_2PdCl_4 in the presence of pyridine afforded the 2:1 complexes **Pd(1a)$_2$** (5%) and **Pd(1b)$_2$** (3%), respectively, as yellow brick-shaped crystals (Scheme 2).

The desired Pd complex (±)-**2a** containing a Pd–C(sp^3) σ-bond and pyridine was isolated (57%) as yellow crystals. In the ^{1}H NMR spectrum for (±)-**2a**, the singlet at δ 1.94 (3H) for the acetyl methyl hydrogens indicated the presence of a single methyl group. For complex (±)-**2b**, the ^{1}H NMR signal of the acetyl methyl hydrogens also appears as one singlet at δ 1.97. In the NMR spectrum of **2b**, the ester methylene hydrogens [H_A (δ ca. 4.10) and H_B (δ ca. 4.20)] are diastereotopic and shifted slightly downfield as compared to the related *C*-metalated complex,[1] derived from the diethyl malonato moiety, which appeared similar to that[7] of **2a**. The IR spectrum of **2a** showed very strong carbonyl absorptions (ca. 1693 and 1640 cm^{-1}); a 40–70 cm^{-1} shift (1733 and 1712 cm^{-1} for **1a**) for the carbonyl stretching vibration upon complexation confirmed Pd–C bond formation.[8] Similar carbonyl shifts for **1b** (1734 and 1708 cm^{-1} upon cyclometalation to generate **2b** were experienced. To prove the existence of the Pd–C bond as well as to ascertain the absolute configuration at the Pd–C* center, an X-ray structure determination was undertaken.

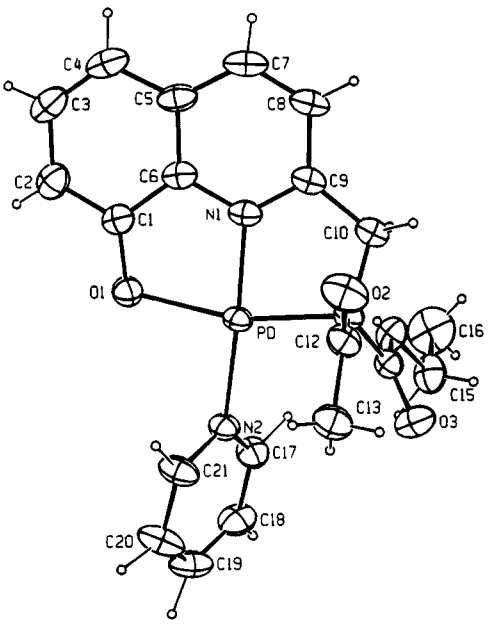


Figure 1. ORTEP drawing of **2a** (chloroform solvate).

Figure 1 illustrates the molecular structure of **2a**. This structure is described by the relative orientations of three district planes: (1) the quinolinol portion of the tridentate ligand; (2) the four atoms coordinated to the Pd center; and (3) the pyridine ligand. The Pd atom nearly lies on the line defined by nitrogen atoms [N1–Pd–N2 = 176.6(7)°]; thus, there is little steric constrant placed on the pyridine ligand, which possesses a more perpendicular orientation (110.92°) to the coordination plane. Important bond distances and angles for **2a** are presented in Table 5. The Pd–C bond distance of 2.108(2) Å is typical of a Pd–C(sp^3) bond length.[9,10] The Pd–C bond is bent 11.6(8)° from perpendicular. The Pd–N2(pyridine) bond distance of 2.044(2) Å is comparable to those found in similar Pd(II)–pyridine complexes.[5,8,10] The Pd–N1(quinoline) bond distance 1.933-

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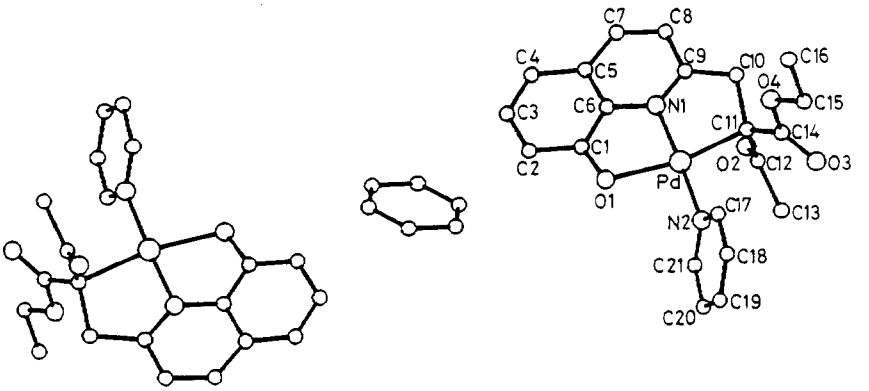

Figure 2. PLUTO drawing for the (±)-**2a**(benzene solvate).

Table 5. Important Bond Lengths (Å) and Bond Angles (deg) for 2a and 5a

	2a (chloroform solvate)	**2a** (benzene solvate)	**5a** molecule A	**5a** molecule B
		Distances		
Pd–N1	1.933(2)	1.941(2)	1.943(2)	1.947(2)
Pd–N2	2.044(2)	2.041(2)	2.081(2)	2.065(2)
Pd–C11	2.108(2)	2.109(3)	2.116(2)	2.108(3)
Pd–O1	2.093(2)	2.108(2)	2.103(2)	2.106(2)
C9–C10	1.487(4)	1.503(3)	1.475(4)	1.484(5)
		Angles		
N1–Pd–N2	176.59(7)	176.63(8)	178.52(8)	176.68(8)
N1–Pd–C11	81.54(8)	81.61(9)	81.08(9)	82.07(9)
N1–Pd–O1	82.04(7)	81.68(8)	81.43(7)	81.56(7)
N2–Pd–C11	101.58(8)	101.64(8)	99.26(9)	100.90(9)
N2–Pd–O1	94.91(7)	95.16(8)	98.18(7)	95.61(7)
O1–Pd–C11	163.25(8)	162.54(8)	162.41(8)	162.90(8)
Pd–C11–C10	106.3(1)	106.5(1)	107.3(2)	106.3(2)
Pd–C11–C12	100.0(2)	97.7(2)	103.4(2)	98.7(2)
Pd–C11–C14	108.2(1)	108.9(2)	100.7(1)	105.6(2)
C12–C11–C14	117.1(2)	117.4(2)	118.7(2)	118.0(3)
C10–C11–C12	110.6(2)	111.3(2)	109.7(2)	110.6(2)
C10–C11–C14	113.2(3)	113.4(3)	115.2(2)	115.5(2)

(2) Å is considerably shorter in this tridentate ligand, apparently as a result of geometrical constraints imposed by chelation. From the best plane generated by the fused five-membered ring, the important deviations are Pd (−0.04 Å), O1 (−0.09 Å), C10 (−0.19 Å), and C11 (0.15 Å). No unusual bond distances or angles are noted within the remainder of the structure, and no unusually short intermolecular contacts exist.

After repeated recrystallization of **2a** from benzene, a new benzene solvate of **2a** was prepared. X-ray analysis of this solvate shows that the unit cell possesses both enantiomers equal distant from the center of the benzene solvate. The bond lengths and angles are nearly identical to the above chloroform solvated crystals of **2a**. The non-hydrogen coordinates for (±)-**2a** (benzene solvate) are given in Table 3, and its PLUTO structure with numbering scheme is shown in Figure 2.

The exchange reaction[5] of the pyridine ligand in **2** with L-(−)-1-phenylethylamine ($[\alpha]^{25}_D$ −30 ± 2.0°) readily afforded **3a** and **3b** in 87 and 91% yield, respectively. Both Pd complexes exist as an *SS* or an *RS* diastereoisomeric mixture[5] as shown by the two distinctive singlets for the acetyl methyl groups and two triplets for the ester methyl groups. A direct one-step conversion of **1** with an aqueous solution of K_2PdCl_4 and KOH in the presence of L-(−)-1-phenylethylamine gave the same diastereomeric Pd complexes **3a** ($[\alpha]^{25}_D = -84.3°$) and **3b** ($[\alpha]^{25}_D = -106.9°$) but in lower, 21 and 41%, yield, respectively.

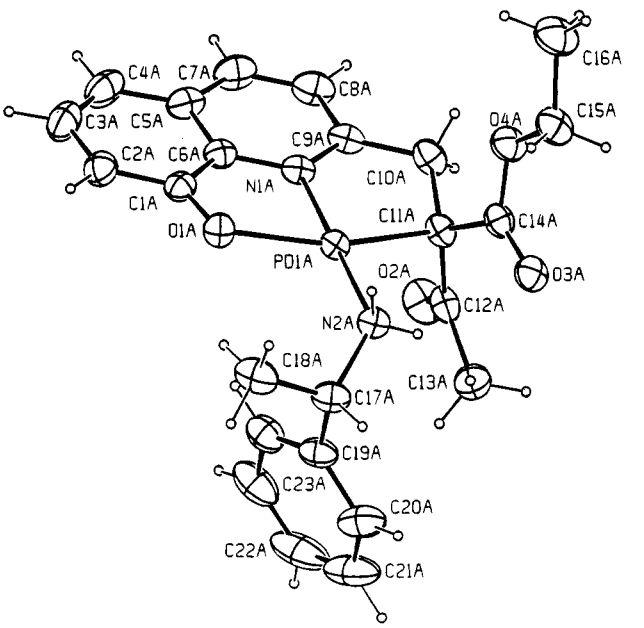

Figure 3. ORTEP drawing for two independent molecules of **5a**.

Separation of the diastereomer **3a** was accomplished by column chromatography [with a 150 cm length and 2.7 cm i.d. packed by a Wakogel C-200] over SiO_2, eluting with a mixture of ethyl acetate–hexane (1:1) to give (*S**,*S**)-**4a** [fraction A] and (*R**,*S**)-**5a** [fraction B]. The NMR spectrum of fraction A, the initial eluent {$[\alpha]^{25}_D$ + 57.9° in $CHCl_3$}, showed a singlet at δ 2.25 for the acetyl methyl hydrogen and a triplet at δ 1.33 for the ester methyl group. Fraction B possessed an $[\alpha]^{25}_D$ −244.3° in $CHCl_3$ and the same protons are shifted slightly downfield (δ 2.44) for $COCH_3$ and upfield (δ 1.16) for OCH_2CH_3. Comparison (IR) between fractions A and B shows slightly different absorptions (ca. 1650 cm^{-1}) for the very strong carbonyl groups. The IR absorption for fraction A of 1669 cm^{-1} is faintly stronger than that of 1635 cm^{-1}, whereas, the relationship on the absorptions of 1670 cm^{-1} against 1643 cm^{-1} of fraction B is reverse.

In order to ascertain the relative configurations of the chiral centers, an X-ray analysis of **5a** was conducted. Figure 3 illustrates its crystal structure, which confirms the *RS* diastereomeric relationship, in which C11 possesses an *R* configuration. Table 5 presents the important bond lengths and angles for both molecules found in the unit cell. The Pd–C bond lengths [2.116(2) and 2.108(3) Å] are within the typical range for Pd(II)–C(sp^3) bond distances.[9,10] The two five-membered che-

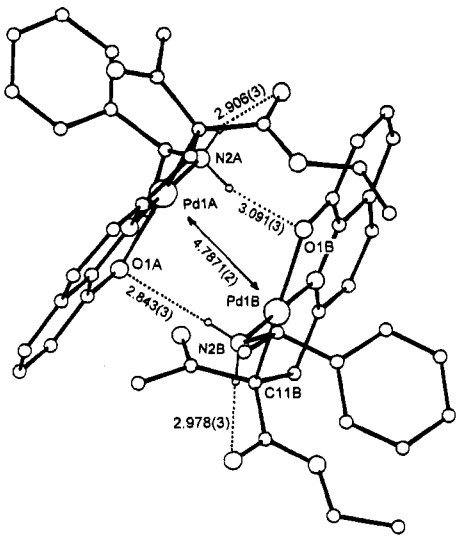

Figure 4. PLUTO drawing for **5a** showing the critical hydrogen bonding interactions.

late rings are notably nonplanar as suggested by the O1A–PdA–C11A bond angle [162.41(8)°] which is analogous to the value found in **2a**. The two independent molecules are similar in most respects but possess minor differences as in the Pd–N bond distances [A = 2.081(2) Å; B = 2.065(2) Å], which is caused by the orientation of the ester moieties as shown in Figure 4. The face-to-face orientation for **5a** (A and B) results from two intermolecular hydrogen bonds between the NH and the quinolinol oxygen [2.843(3) and 3.091(3) Å]. The two intramolecular hydrogen bonds between the NH and ester carbonyl [2.906(3) and 2.978(3) Å] help stabilize this orientation. A Pd–Pd distance of 4.7871(2) Å is similar to that of related complexes.[11,12]

The crystal structure of **5a** establishes the absolute configuration at C11 as R, thus **4a** must possess the S configurations at C11. Ligand exchange of (S*,S*)-**4a** and (S*,R*)-**5a** with pyridine in benzene generated in low yield the desired enantiomeric (−)-**2a** ($[\alpha]^{25}_D$ −10.4°) possessing the S configuration at C11 and (+)-**2a** ($[\alpha]^{25}_D$ +4.6°) possessing the R configuration at C11, respectively. The ^{1}H NMR spectra of both (−)- and (+)-**2a** afforded similar signals for each hydrogen when compared to that of (±)-**2a**. No attempts were made to maximize the exchange process.

This transformation of **4a** to (−)-**2a** or **5a** to (+)-**2a** confirms the stability of the Pd–C bond throughout the exchange process. If the Pd–C bond were broken during the ligand exchange, the molecular chirality would be lost. The actual exchange process can be envisioned to occur by a limited number of routes, but more importantly this resolution technique should be applicable to other related organometallic systems.

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Supplementary Material Available: Tables of atomic coordinates, crystal and intensity collection data, anisotropic thermal parameters, torsion angles, least-squares planes, and bond lengths and angles for **2a** (chloroform solvate), **2a** (benzene solvate), and **5a** (41 pages). Ordering information is given on any current masthead page.

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