Synthesis and Characterization of Chiral Diphosphine Platinum(II) VANOL and VAPOL Complexes

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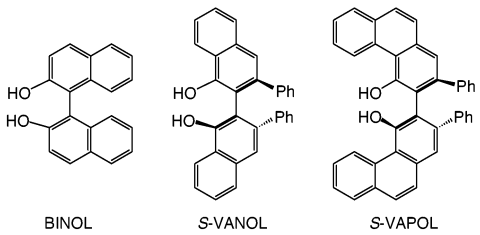
Reaction of (dppe)$PtCO_3$ with *S*-VANOL or *S*-VAPOL yielded (dppe)Pt(*S*-VANOL) and (dppe)Pt(*S*-VAPOL), respectively. NMR data indicate that the VANOL ligand in the former complex adopts a C_2-symmetric O,O′-bound form, while the VAPOL ligand binds to the metal in a C,O-binding mode that partially disrupts the ligand aromaticity. When matched complexes of *S*-VANOL and *S*-VAPOL were synthesized with (*S*,*S*-chiraphos)$PtCO_3$, both complexes adopt the symmetric O,O′-mode. Mismatched complexes with (*R*,*R*-chiraphos)-$PtCO_3$ have both ligands adopting the C,O-binding mode; however, the *S*-VANOL complex could not be isolated. Competition experiments between *S*-VANOL and *S*-VAPOL for the (*S*,*S*-chiraphos)Pt^{2+} fragment indicate that VANOL is the thermodynamically preferred ligand.

Introduction

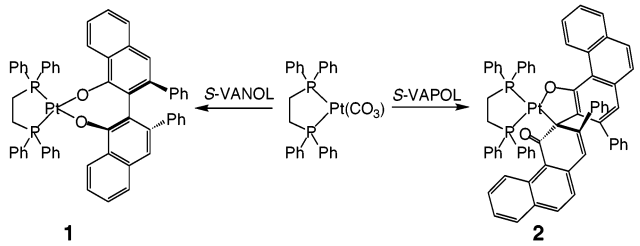
Enantiopure 1,1′-binaphth-2,2′-ol (BINOL) is a widely used ligand in asymmetric catalysis.[1] However since it does not always perform optimally, Wulff introduced the vaulted biaryl ligands, VANOL and VAPOL,[2] which were designed to project in an asymmetric fashion high-definition aromatic rings toward a chelated metal center. These design principles were validated in a number of highly enantioselective metal-VANOL and -VAPOL catalyzed reactions, including the Diels−Alder,[2a,3] aziridination,[4] and imino Aldol reactions,[5] with VAPOL generally producing the more selective catalysts. In all cases VANOL and VAPOL were used in combination with oxophilic early transition or main group metals. As a prelude to imprinting experiments with these topologically unique ligand structures, we wished to examine the coordination chemistry of these ligands with a more carbophilic late metal complex like the (dppe)Pt^{2+} fragment.



Results

(Dppe)Pt(*S*-VANOL) (**1**) and (dppe)Pt(*S*-VAPOL) (**2**) were synthesized from the versatile dppe$PtCO_3$ starting material by the method of Andrews in 70 and 81% yield, respectively (Scheme 1).[6] The reactions with VANOL and VAPOL required 2 and 4 days, respectively, in contrast to BINOL, which is typically converted in 4 h. The ^{31}P NMR spectrum of **1** displays the expected singlet at 24.7 ppm ($J_{P-Pt} = 3633$ Hz) for a C_2-symmetric structure. Suitable yellow crystals of **rac-1** were grown at room temperature from a saturated CH_2Cl_2 solution with slow diffusion of diethyl ether.[7] The ORTEP representation in Figure 1 of **rac-1** confirms the C_2-symmetric structure in the solid state and is the first reported structure of a VANOL-metal complex.[2b] The Pt−O and Pt−P bond lengths and P−Pt−P and O−Pt−O bond angles, reported in the caption, are similar to previously reported chelating Pt-biphenolate-type structures[8] and are otherwise unexceptional. The stereochemical projection of this ligand is directly linked to

Scheme 1



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(7) Enantiopure **1** proved too soluble for crystal growth. **rac-1** was prepared in an identical fashion to **1**, except with rac-VANOL.

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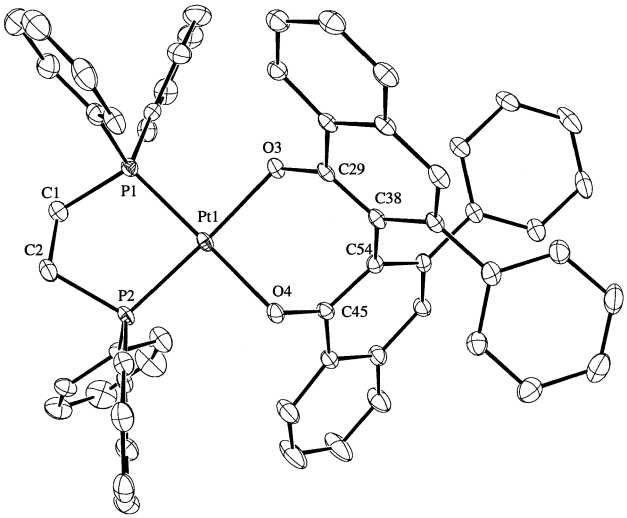

Figure 1. ORTEP representation of **rac-1**. Selected bond distances (Å) and bond angles (deg): Pt1−P1 = 2.2299(12), Pt1−P2 = 2.2191(10), Pt1−O3 = 2.067(3), Pt1−O4 = 2.063(3), P1−Pt1−P2 = 86.40(4), O3−Pt1−O4 = 90.37(11), C29−C38−C54−C45 = 66.0.

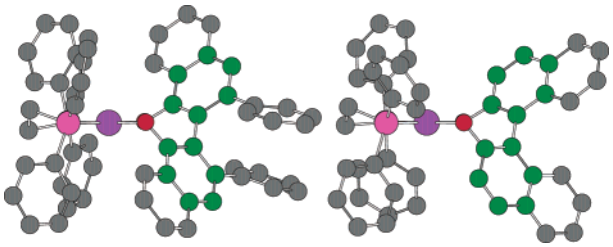

Figure 2. Chem3D representations of (dppe)Pt(VANOL) (left) and (dppe)Pt(BINOL)[8a] (right); the common biphenyl portions on the ligands are colored green.

the naphthyl−naphthyl dihedral angle of 66.0°, which is reinforced by a slipped π-stack between the 3,3′-Ph_2 substituents (3.35 Å from plane to plane).[9]

The coordination geometries of the VANOL and BINOL ligands on the (dppe)Pt^{2+} fragment are compared in Figure 2. Both have a similar dihedral angle relating the naphthyl planes (66° and 63°, respectively), which skews the rings into a chiral environment capable of distinguishing the chiral reactive quandrants on the metal. One obvious difference between the two structures is the enhanced directionality of VANOL, which more effectively projects its chirality toward the metal, consistent with its enhanced performance in several asymmetric catalysis reactions.[2−5]

In contrast to the symmetric structure of **1**, the −24 °C ^{31}P NMR spectrum of the VAPOL product **2** contains two doublets with significantly different couplings to ^{195}Pt (δ 33.9, J_{P-Pt} = 3603 Hz; 40.0 ppm, J_{P-Pt} = 2620 Hz; J_{P-P} = 10.4 Hz), consistent with a compound with inequivalent phosphorus nuclei. The smaller Pt−P coupling for the downfield resonance suggests a ligand with a trans influence that is stronger than oxygen across the square plane of platinum. On the basis of spectroscopic similarities (two doublets, J_{P-Pt} = 3560 and 2510 Hz) with a previously structurally characterized (dppe)Pt(3,3′-Me_2BINOL) complex,[8b] we propose a similar C,O-binding mode for **2** (Scheme 1).[10−12] The relief of steric strain and the carbophilic nature of Pt are largely responsible for this platinum "keto−enol" tautomerism. Also consistent with this formulation of one C2 carbon as a carbonyl is its downfield shift (194.1 ppm) in the ^{13}C NMR, a shift that was also observed in (dppe)Pt(3,3′-Me_2BINOL) (195.5 ppm). Structurally, the spirocyclic carbon center will project the phenanthrene ligands orthogonal to one another (90° dihedral), one in and one out of the Pt-square plane.[13]

In addition to the doublets, a singlet at 27.2 ppm (J_{Pt-P} = 3740 Hz) is also observed, which integrates for 8% of the total at −24 °C, and is assigned to the O,O′-bound form. The C,O-/O,O′- ratio is temperature dependent and is described by the parameters $\Delta H = +1.6 \pm 0.1$ kcal mol^{-1} and $\Delta S = +1.4 \pm 0.4$ eu for C,O- ↔ O,O′- over a temperature range of −61 (95.5:4.5) to +19 °C (87.5:12.5) in CD_2Cl_2.[14] Above 20 °C the signal ascribed to the O,O′-form disappears into the baseline as the doublets similarly broaden, in both CD_2Cl_2 and chlorobenzene.[15] Although the O,O′-form presumably acts to interconvert the inequivalent phosphorus nuclei in the C,O-form, a fast exchange limit is never reached in chlorobenzene (up to 90 °C).

The stereochemical consequences of the diphosphine-VANOL/VAPOL interaction were further probed by replacing dppe with the chiral diphosphine, chiraphos. Incorporation of two chiral, C_2-symmetric ligands into the platinum complex leads to either an efficient gearing of the ligands (matched) or a steric clashing (mismatched). On the basis of previous experiments between chiraphos and 3,3′-Me_2BINOL[8b] we hoped to overturn the C,O- propensity of the VAPOL ligand in **2** by making a matched complex, and the O,O′- propensity of VANOL in **1** by making a mismatched complex.

Treatment of (*S*,*S*-chiraphos)$PtCO_3$ with *S*-VANOL and *S*-VAPOL produced the corresponding (*S*,*S*-chiraphos)Pt(*S*-VANOL) (**3**) and (*S*,*S*-chiraphos)Pt(*S*-VAPOL) (**4**) complexes in 77 and 72% yield, respectively (Scheme 2). As in the case of dppe, the reaction with VANOL reached completion in half the time of the VAPOL reaction. The ^{31}P NMR data for these complexes indicate a C_2-symmetric O,O′-binding mode for both the VANOL and VAPOL ligands (singlets at 29.1 (J_{P-Pt} = 3536 Hz) and 30.7 ppm (J_{P-Pt} = 3626 Hz), respectively). The combinations of *S*,*S*-chiraphos and *S*-VANOL or *S*-VAPOL are conformationally and configurationally *matched*, and no traces of any asymmetric products are observed in the ^{31}P NMR.

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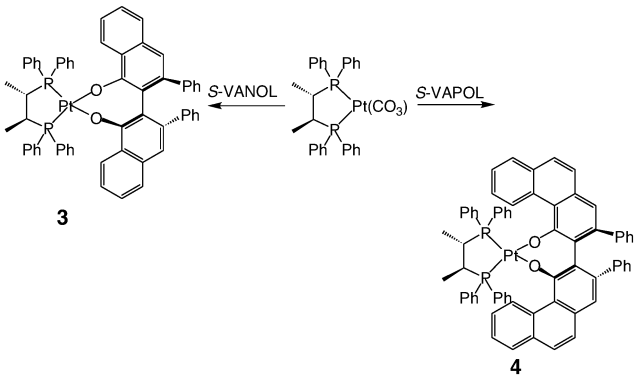
(13) Unfortunately, all attempts to obtain X-ray quality crystals of either racemic or enantiomerically pure **2** were unsuccessful.

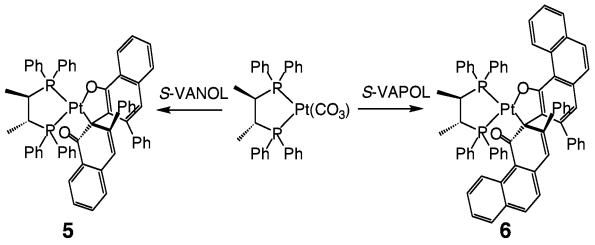
(14) Errors were calculated by a nonlinear least-squares method; computer program kindly provided by Prof. Barry Carpenter of Cornell University.

(15) A slight solvent dependence is observed. At −24 °C in CD_2Cl_2 and chlorobenzene the C,O/O,O′ ratio is 92.1:7.9 and 89.8:10.2, respectively (by ^{31}P NMR).

Scheme 2



Scheme 3



Treatment of (*R*,*R*-chiraphos)$PtCO_3$ with *S*-VAPOL produced a C,O-bound complex (**6**) in 69% yield (Scheme 3), the ^{31}P NMR signatures being nearly identical to the dppe analogue **2** (two doublets at 47.7, $J_{P-Pt} = 2594$ Hz, $J_{P-P} = 23.2$ Hz, trans to C and 35.6 ppm, $J_{P-Pt} = 3558$ Hz, $J_{P-P} = 23.2$ Hz, trans to O). Similar reaction of (*R*,*R*-chiraphos)$PtCO_3$ with *S*-VANOL produced what appeared to be a clean C,O-bound complex (**5**) by in situ ^{31}P NMR (δ 45.3, $J_{P-Pt} = 2554$ Hz, and 33.7, $J_{P-Pt} = 3543$ Hz); however attempts to isolate this complex led to extensive decomposition. The combination of *R*,*R*-chiraphos and *S*-VANOL or *S*-VAPOL is stereochemically *mismatched*.

The relative binding affinities of VANOL and VAPOL to platinum were also determined through a variety of pairwise ligand exchange reactions. Only the (*S*,*S*-chiraphos)Pt fragment was used in this study, as it promotes an O,O′-binding mode for both ligands. Monitoring the ratio of products by ^{31}P NMR to equilibrium afforded information about the relative binding strengths of *S*-VANOL and *S*-VAPOL to the (*S*,*S*-chiraphos)Pt fragment. When (*S*,*S*-chiraphos)Pt(*S*-VAPOL) and 1.01 equiv of *S*-VANOL were allowed to equilibrate, the VANOL complex was the major product (74%) after 55 h (Scheme 4) and was accompanied by an unknown asymmetric byproduct; the VAPOL complex was no longer detected.[16] Consistent with (*S*,*S*-chiraphos)Pt(*S*-VANOL) being favored, reaction of (*S*,*S*-chiraphos)Pt(*S*-VANOL) and 1.08 equiv of *S*-VAPOL showed no detectable amounts of the VAPOL complex, though the same byproduct was observed (days). This byproduct was observed in all reactions where *both* VANOL and VAPOL were present; however attempts to isolate and identify this species were unsuccessful.[17]

Scheme 4

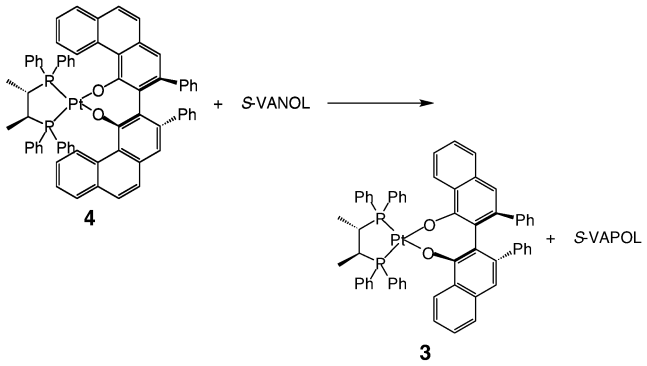
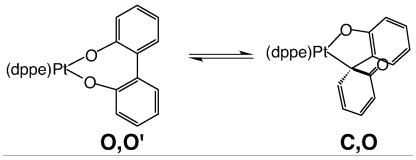


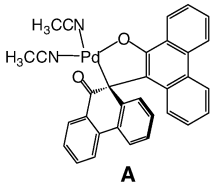
Table 1. Equilibrium Ratio of C,O- and O,O′-Bound Structures at Room Temperature in CD_2Cl_2



	(dppe)Pt(O,O′)	(dppe)Pt(C,O)
BINOL	>98	<2
3,3′-Me_2BINOL	24	76
VANOL	>98	<2
VAPOL	12	88

Discussion

To date we have synthesized a number of (dppe)Pt^{2+} coordinated biphenol-type complexes. The BINOL[18] and VANOL compounds appear to be exclusively of the O,O′-type, while the seemingly more bulky ligands 3,3′-Me_2BINOL and VAPOL prefer the C,O-form (Table 1). In both of the C,O-forms the symmetric O,O′-isomer is present and a dynamic process equilibrates the tautomers. Related to these observations is 10,10′-dihydroxy-9,9′-biphenanthol, which was the first crystallographically characterized biphenol-type ligand to adopt a C,O-binding mode (**A**).[10] The propensity of this ligand



to adopt the C,O-mode only may be related to the diminished cost of dearomatizing the central ring of the phenanthrene, at least when compared to an end ring, as in VAPOL.

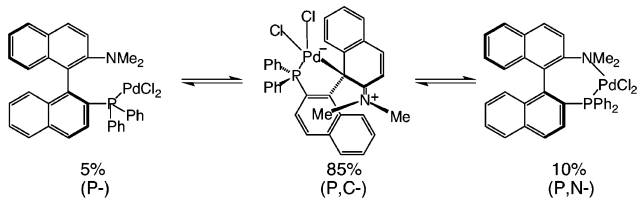
Dearomatizing nonsymmetric bonding modes are also observed in nonbiphenol-type ligands, especially when the ligand is a natural seven-membered chelator. The significant ring strain (and subsequent skew conformations) in these chelates can often be attenuated by tautomerization to the five-membered chelate. Several cases have been documented with the MAP and MOP

(16) After 25 h, the ratio of compounds was (*S*,*S*-chiraphos)Pt(VANOL) 54%; (*S*,*S*-chiraphos)Pt(VAPOL) 21%, and asymmetric byproduct 25%.

(17) The asymmetric byproduct was characterized by two doublets in the ^{31}P NMR at 41.3 ($J_{Pt-P} = 1704$ Hz, $J_{P-P} = 12.3$ Hz) and 36.8 ppm ($J_{Pt-P} = 4129$ Hz, $J_{P-P} = 12.3$ Hz).

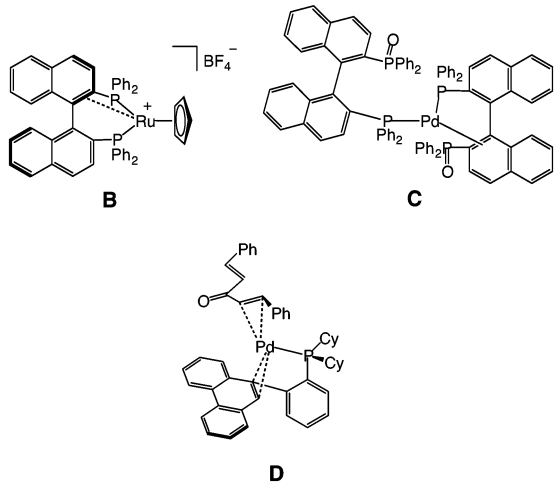
(18) We have synthesized numerous P_2M(BINOL) compounds (M = Pd, Pt; P_2 = BINAP, MeObiphep, Biphep, dppe; BINOL = 6,6′,4,4′-substituted), and each of these remotely substituted cases adopts the O,O′-binding mode (ref 8 and unpublished results).

Scheme 5



ligands (MAP, Scheme 5). For example, (MAP)$PdCl_2$ exists as an equilibrium mixture of P-, P,N-, and P,C-modes,[19] the P,C-form being implicated in unique cross-coupling reactivity.[19b]

Diphosphine ligands are also well known to participate in binding modes that permit secondary interactions with backbone unsaturation. Pregosin has extensively characterized[20] this η^2-olefin binding interaction[21] by NMR and noted the significant upfield shifts of the affected H's and C's (e.g., in CpRu(BINAP)$^+$) (**B**). The diminished ligating effectiveness of the oxidized phosphorus in BINAPO also promotes a partial dearomatizing P,C-binding mode (**C**).[22] Similarly, Buchwald has noted a Pd$-\eta^2$-olefin binding interaction in the ground state structure of complexes used for Suzuki couplings (**D**).[23] These examples capture the spirit of the argument



that carbophilic late metals can satisfy steric or electronic discomfort by tautomerizing (N→C or O→C) or simply employing secondary chelation interactions to backbone unsaturation, often at the expense of partial aromaticity.

Summary

We report herein the synthesis of several diphosphine Pt(II) VANOL and VAPOL complexes. For dppe, the less sterically encumbered VANOL complex exists in the more traditional O,O′-form, but the bulkier VAPOL prefers the C,O-isomer, despite the partial dearomatization of one ring. The binding preference of each ligand can be overturned by a suitable matching or mismatching with chiraphos. For VANOL, the C,O-isomer is accessible (but unstable) by synthesizing the mismatched diastereomer, while the O,O′-bound form of VAPOL is accessible via the matched diastereomer. Competition experiments between *S*-VAPOL and *S*-VANOL for the (*S*,*S*-chiraphos)Pt^{2+} fragment indicate that the *S*-VANOL ligand is thermodynamically preferred, presumably for steric reasons.

Experimental Details

General Methods. Starting materials (dppe)$PtCO_3$, (*S*,*S*-chiraphos)$PtCO_3$, and (*R*,*R*-chiraphos)$PtCO_3$[8a,b] were prepared according to literature procedures. VANOL and VAPOL ligands were generously donated by Prof. William Wulff. NMR spectra were recorded on a Bruker Avance400 or Bruker AMX300 spectrometer. Chemical shifts are reported in ppm and referenced to residual solvent peaks (^{1}H and ^{13}C NMR) or to an external standard (85% H_3PO_4, ^{31}P NMR). Elemental microanalyses were performed by Complete Analysis Laboratories, Parsippany, NJ.

(dppe)Pt(*S*-VANOL), 1. To a solution of (dppe)$PtCO_3$ (103.0 mg, 0.158 mmol) in 20 mL of CH_2Cl_2 was added 69.0 mg (0.158 mmol) of *S*-VANOL. The reaction was stirred at room temperature, open to the atmosphere to allow CO_2 escape. By ^{31}P NMR, the reaction was complete after 48 h. The solvent was evaporated in vacuo and the yellow solid recrystallized from CH_2Cl_2/Et_2O to yield 113.0 mg of (dppe)Pt(*S*-VANOL) (70%). ^{31}P NMR (121.0 MHz, CD_2Cl_2): δ 24.7 (J_{P-Pt} = 3633 Hz). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.49 (m, 4 H), 7.76 (m, 4 H), 7.62 (m, 6 H), 7.49 (m, 6 H), 7.28 (t, J = 6.9 Hz, 4 H), 7.07 (t, J = 7.3 Hz, 2 H), 6.96 (m, 4 H), 6.83 (t, J = 7.6 Hz, 4 H), 6.55 (d, J = 7.3 Hz, 4 H), 6.35 (t, J = 7.4 Hz, 2 H), 2.43 (m, 2 H), 2.05 (br. s, 2 H). ^{13}C{^{31}P, ^{1}H} (75.5 MHz, CD_2Cl_2): δ 160.9, 143.1, 142.8, 134.6, 134.3, 133.6, 132.4, 132.3, 130.1, 129.7, 129.4, 128.9, 128.7, 127.36, 127.1, 126.9, 125.6, 125.2, 124.9, 122.3, 118.5, 28.4.[24] Anal. Calcd for $C_{58}H_{44}P_2PtO_2$: C, 67.63; H, 4.31. Found: C, 67.84; H, 4.11.

(dppe)Pt(*S*-VAPOL), 2. To a solution of (dppe)$PtCO_3$ (99.1 mg, 0.152 mmol) in 20 mL of CH_2Cl_2 was added 99.0 mg (0.184 mmol) of *S*-VAPOL. The reaction was stirred at room temperature, open to the atmosphere to allow CO_2 escape. By ^{31}P NMR, the reaction was complete after 96 h. The solvent was evaporated in vacuo and the orange solid recrystallized from CH_2Cl_2/pentane, to yield 136.3 mg of (dppe)Pt(*S*-VAPOL) (81%). At room temperature, the NMR spectra were broad and uninterpretable, and characterization was carried out at −24 °C, which results in sharp spectra. At −24 °C, the O,O′-bound structure is observed in 8%.[25] ^{31}P NMR (121.0 MHz, CD_2Cl_2): δ 40.0 (J_{P-Pt} = 2620 Hz, J_{P-P} = 10.4 Hz, trans to C, **2$_{C,O}$**), 33.9 (J_{P-Pt} = 3603 Hz, J_{P-P} = 10.4 Hz, trans to O, **2$_{C,O}$**), 27.2 (J_{P-Pt} = 3746 Hz, **2$_{O,O'}$**). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 10.47 (d, J = 8.7 Hz, 1 H, **2$_{C,O}$** only), 9.64 (d, J = 8.7 Hz, 1 H), 8.33 (m, 2 H), 7.82 (m, 4 H), 7.69 (m, 5 H), 7.51 (m, 10 H), 7.29 (m, 1 H), 7.19 (m, 1 H), 7.01 (m, 5 H), 6.68 (m, 2 H), 6.52 (d, J = 8.4 Hz, 1 H), 6.43 (d, J = 7.2 Hz, 2 H), 6.31 (dd, J = 7.5, 11.7 Hz, 2 H), 5.94 (m, **2$_{O,O'}$** only), 4.46 (s, 1 H, **2$_{C,O}$** only), 2.42 (m, 2 H), 1.89 (br s, 1 H), 1.68 (m, 1 H). ^{13}C{^{31}P,^{1}H} (75.5 MHz, CD_2Cl_2): δ 194.1 (**2$_{C,O}$**), 176.4 (**2$_{C,O}$**), 152.6 (**2$_{C,O}$**), 142.2, 141.5, 140.6, 139.4, 135.1, 133.5, 133.4, 133.2, 132.9, 132.6, 132.1,

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(24) Not all aromatic ^{13}C NMR resonances were observed.

(25) Most ^{1}H and ^{13}C resonances for **2$_{C,O}$** and **2$_{O,O}$** overlap and are indistinguishable. Those that could be assigned to a single isomer are noted.

Table 2. Crystallographic Data and Collection Parameters for rac-1

	(dppe)Pt(*rac*-VANOL)·CH_2Cl_2
formula	$PtP_2C_{58}H_{46}O_2 \cdot CH_2Cl_2$
fw	1114.94
space group	$P2_1/c$
a, Å	18.6328(6)
b, Å	12.1003(4)
c, Å	22.1229(7)
β, deg	104.802(1)
V, Å^3	4822.4(3)
Z	4
T, °C	−100
D_c, g/cm^3	1.536
λ,Å	1.5418
μ, mm^{-1}	7.22
R indices (all data)	$R_f{}^a = 0.042$ $R_w{}^b = 0.034$
R indices (sig. reflns)	$R_f{}^a = 0.031$ $R_w{}^b = 0.034$
GoF^c	1.5362

^{a} $R_f = \sum(F_o - F_c)/\sum F_o$. ^{b} $R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$. ^{c} GoF = $[\sum w(F_o - F_c)^2/(n - p)]^{1/2}$, where n = number of reflections and p = number of parameters.

131.9, 131.84, 131.81, 131.7, 131.1, 130.9, 130.4, 130.1, 129.4, 129.3, 129.2, 128.8, 128.2, 127.9, 127.4, 127.2, 127.1, 126.7, 126.4, 126.2, 125.7, 125.0, 124.9, 123.9, 123.7, 122.2, 120.4, 118.2, 115.6, 88.3 (**2$_{C,O}$**), 35.6, 22.3.[24] Anal. Calcd for $C_{58}H_{44}P_2PtO_2$: C, 70.14; H, 4.28. Found: C, 70.05; H, 4.34.

(*S,S*-chiraphos)Pt(*S*-VANOL), 3. To a solution of (*S,S*-chiraphos)$PtCO_3$ (103.1 mg, 0.151 mmol) in 20 mL of CH_2Cl_2 was added 68.5 mg (0.156 mmol) of *S*-VANOL. The reaction was stirred at room temperature, open to the atmosphere to allow CO_2 escape. By ^{31}P NMR, the reaction was complete after 38 h. The solvent was evaporated in vacuo and the yellow solid recrystallized from CH_2Cl_2/pentane, to yield 123.2 mg of (*S,S*-chiraphos)Pt(*S*-VANOL) (77%). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 29.1 (J_{P-Pt} = 3536 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.28 (m, 4 H), 7.80 (dd, J = 8.0, 10.4 Hz, 4 H), 7.65 (m, 8 H), 7.52 (d, J = 8.0 Hz, 2 H), 7.43 (m, 6 H), 7.10 (m, 2 H), 6.93 (m, 4 H), 6.80 (m, 4 H), 6.47 (m, 4 H), 6.38 (m, 2 H), 2.37 (m, 2 H), 0.99 (m, 6 H). ^{13}C{^{31}P,^{1}H} (75.5 MHz, CD_2Cl_2): δ 161.4, 142.9, 142.7, 136.4, 134.2, 133.1, 132.7, 132.2, 130.1, 129.9, 129.3, 128.8, 127.1, 127.0, 126.7, 125.5, 125.4, 125.2, 125.1, 124.7, 122.2, 118.2, 36.5, 13.9. Anal. Calcd. for $C_{60}H_{48}P_2PtO_2$: C, 68.11; H, 4.57. Found: C, 67.98; H, 4.47.

(*S,S*-chiraphos)Pt(*S*-VAPOL), 4. To a solution of (*S,S*-chiraphos)$PtCO_3$ (113.1 mg, 0.166 mmol) in 20 mL of CH_2Cl_2 was added 104.5 mg (0.194 mmol) of *S*-VAPOL. The reaction was stirred at room temperature, open to the atmosphere to allow CO_2 escape. By ^{31}P NMR, the reaction was complete after 132 h. The solvent was evaporated in vacuo and the orange solid recrystallized from CH_2Cl_2/pentane, to yield 139.2 mg of (*S,S*-chiraphos)Pt(*S*-VAPOL) (72%). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 30.7 (J_{P-Pt} = 3626 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.93 (d, J = 8.4 Hz, 2 H), 8.28 (dd, J = 8.4, 11.2 Hz, 4 H), 7.61 (m, 2 H), 7.54 (t, J = 6.8 Hz, 4 H), 7.49 (m, 2 H), 7.43 (m, 4 H), 7.33 (m, 6 H), 7.10 (m, 6 H), 6.85 (m, 2 H), 6.74 (br. s, 2 H), 6.67 (t, J = 4.8 Hz, 4 H), 6.42 (d, J = 7.6 Hz, 4 H), 6.17 (t, J = 7.6 Hz. 2 H), 1.96 (m, 2 H), 0.74 (m, 6 H). ^{13}C{^{31}P,^{1}H} (75.5 MHz, CD_2Cl_2): δ 143.0, 134.5, 134.2, 133.8, 132.5, 132.2, 132.1, 132.0, 130.0, 129.9, 129.2, 128.4, 127.7, 127.4, 126.7, 126.6, 126.5, 125.4, 124.4, 124.1, 123.1, 121.8, 118.0, 39.5, 14.0.[24] Anal. Calcd for $C_{68}H_{52}P_2PtO_2$: C, 70.52; H, 4.53. Found: C, 70.37; H, 4.52.

(*R,R*-chiraphos)Pt(*S*-VAPOL), 6. To a solution of (*R,R*-chiraphos)$PtCO_3$ (116.5 mg, 0.171 mmol) in 20 mL of CH_2Cl_2 was added 103.5 mg (0.192 mmol) of *S*-VAPOL. The reaction was stirred at room temperature, open to the atmosphere to allow CO_2 escape. By ^{31}P NMR, the reaction was complete after 96 h. The solvent was evaporated in vacuo and the orange solid recrystallized from CH_2Cl_2/pentane, to yield 135.9 mg of (*R,R*-chiraphos)Pt(*S*-VAPOL) (69%). ^{31}P NMR (121.0 MHz, CD_2Cl_2): δ 47.7 (J_{P-Pt} = 2594 Hz, J_{P-P} = 23.2 Hz, trans to C), 35.6 (J_{P-Pt} = 3558 Hz, J_{P-P} = 23.2 Hz, trans to O). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 10.12 (d, J = 8.7 Hz, 1 H), 9.55 (d, J = 8.7 Hz, 1 H), 8.36 (m, 2 H), 7.99 (m, 2 H), 7.67 (m, 8 H), 7.46 (m, 10 H), 7.32 (d, J = 7.8 Hz, 1 H), 7.25 (t, J = 7.2 Hz, 2 H), 7.10 (m, 2 H), 6.86 (m, 6 H), 6.66 (m, 6 H), 6.52 (br. s, 2 H), 4.66 (d, J = 2.1 Hz, 1 H), 2.23 (m, 1 H), 1.47 (m, 1 H), 0.89 (m, 3 H), 0.60 (m, 3 H). ^{13}C{^{31}P,^{1}H} (75.5 MHz, CD_2Cl_2): δ 193.9 (C=O), 177.4, 151.9, 143.0, 142.4, 141.2, 139.2, 136.4, 135.0, 134.4, 133.9, 133.3, 133.2, 132.5, 132.2, 132.1, 131.0, 130.9, 130.8, 129.6, 129.5, 129.3, 128.5, 127.8, 127.6, 127.5, 127.4, 127.2, 127.1, 126.7, 126.4, 126.2, 125.8, 125.4, 125.0, 124.8, 124.0, 120.9, 120.8, 118.2, 115.5, 88.3, 49.6, 31.7, 14.8, 13.6.[24] Anal. Calcd for $C_{68}H_{52}P_2PtO_2$: C, 70.52; H, 4.53. Found: C, 70.26; H, 4.32.

Typical Equilibration Experiment. To a solution of **4** (28.4 mg, 24.5 μmol) in 0.5 mL of CD_2Cl_2 was added *S*-VANOL (10.8 mg, 24.7 μmol). The NMR tube was sealed and was allowed to equilibrate at ambient temperature. Monitoring by ^{31}P NMR after 55 h indicated that 74% of **3** and 26% of an asymmetric byproduct (^{31}P NMR: δ 41.3, J_{Pt-P} = 1707 Hz, and 36.9, J_{Pt-P} = 4128 Hz, J_{P-P} = 12.4 Hz) was present.

Crystallography. Crystals of (dppe)Pt(rac-VANOL) suitable for X-ray crystallography were grown at room temperature from a saturated CH_2Cl_2 solution with slow diffusion of Et_2O. Single crystals were mounted in oil on the end of a fiber. Intensity data were collected on a Bruker SMART diffractometer using the omega scan mode. The structure was solved by direct methods and refined by a least-squares technique on *F* using structure solution programs from the NRCVAX System.[26] All non-hydrogen atoms were refined anisotropically. Absorption corrections were performed using SADABS; hydrogen atoms were included using a riding model. Crystal data, data collection, and refinement parameters are listed in Table 2.

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Supporting Information Available: van't Hoff plot for **2** and X-ray crystallographic files for (dppe)Pt(rac-VANOL) are available free of charge via the Internet at http://pubs.acs.org.

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