Synthesis and Conformation of Chiral Eight-Membered 12*H*-Dibenzo[*d,g*][1,3,2]dioxaphosphocins[1]

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Introduction

The development of synthetic methodology for enantioselective bond formation is a topic of fundamental importance. A particularly attractive strategy involves the use of catalytic quantities of chiral transition-metal catalysts.[2] Chiral phosphine-based ligands have played an important role in the development of transition-metal-catalyzed asymmetric synthesis. The use of phosphite ligands derived from the chiral pool, e.g., carbohydrates,[3] provide an attractive alternative to phosphine-based ligands. Several recent publications report the successful application of chiral phosphite ligands in asymmetric synthesis.[4−7]

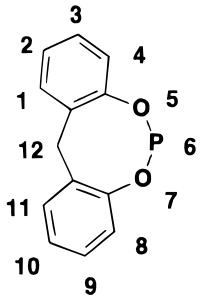
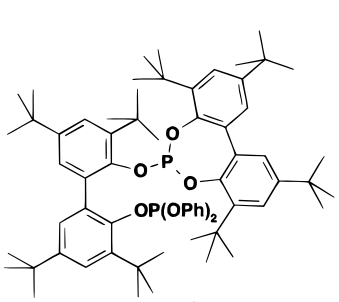


Figure 1. *Chemical Abstracts* numbering of the 12*H*-dibenzo[*d,g*]-[1,3,2]dioxaphosphocin ring system.

Bis(phosphite) ligands employing eight-membered 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin rings have appeared in the patent literature, which are reported as ligands for Rh(I)-catalyzed hydroformylation reactions.[8] Quite recently van Leeuwen and co-workers suggested that the large natural bite angle in ligands such as **1** increases the stereoselectivity of the Rh-(I)-catalyzed hydroformylation reaction.[9,10] Gladfelter *et al.*



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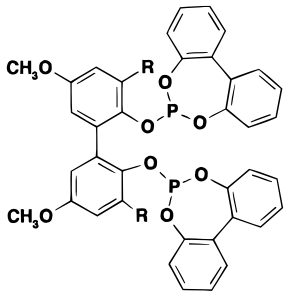

2
R = tert-butyl

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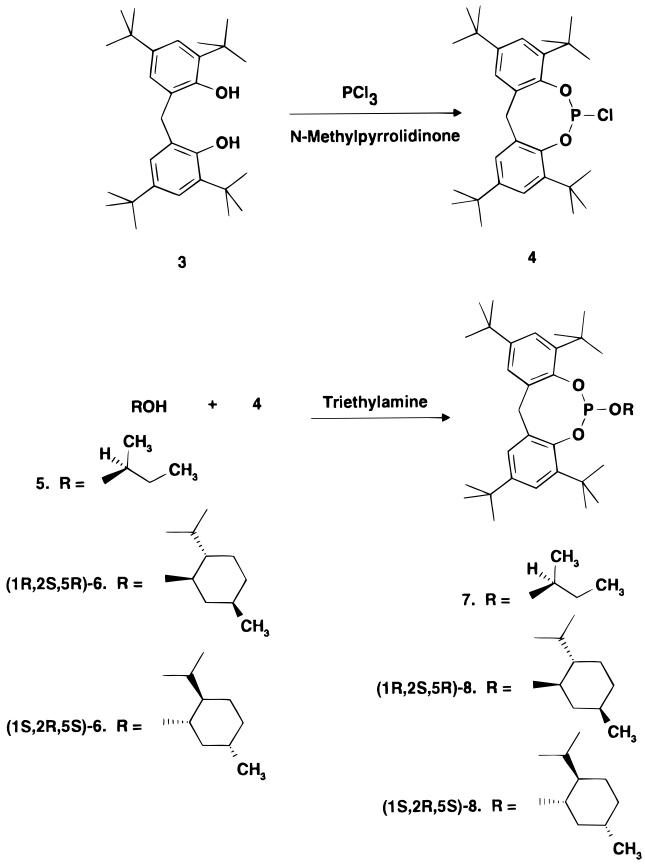
found that the geometric inclination of the ruthenium carbonyl complex of **2** is a result of steric rather than electronic effects.[11]

The study of cyclic pentaoxyphosphoranes provides mechanistic information concerning nucleophilic displacement reactions at tetracoordinate phosphorus.[12,13] Typically, in cyclic pentaoxyphosphoranes with trigonal bipyramidal geometry, the ring assumes an axial−equatorial placement.[14] Extensive studies by Holmes and co-workers on pentaoxyphosphoranes incorporating certain tetra-*tert*-butyl-substituted 12*H*-dibenzo[*d*,*g*][1,3,2]-dioxaphosphocin rings pointed to diequatorial ring placement in both the solid state and solution.[15−24] These studies have important ramifications for literature proposals describing activated states of cyclic adenosine monophosphites where trigonal bipyramidal geometries are invoked.[25]

The conformational analysis of medium-sized organophosphorus ring systems has only recently become the focus of a number of studies.[26] As part of our continuing interest in the stereochemistry of the medium-sized metallocycles,[27,28] we report herein the synthesis and conformational analysis in both the solid state and solution of several chiral derivatives of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring system, as well as a solution ^{31}P NMR spectral study of a Pt(II) complex.

Results and Discussion

Synthesis. The phosphorochloridite **4**[29] was prepared by the reaction of the bisphenol **3** with phosphorus(III) chloride using



1-methyl-2-pyrrolidinone as a catalyst. In the ^{31}P{^{1}H} NMR spectrum of **4**, a singlet was observed at δ 160.1 (lit.[3o] δ 160.0), which is in the region expected for a trivalent phosphorochloridite.[30,31]

The chiral phosphite **7** was prepared by the reaction of **4** with (*S*)-(+)-butanol (**5**) using triethylamine as an acid acceptor (69% recrystallized). In the ^{31}P{^{1}H} NMR spectrum of **7**, a singlet is observed at δ 131.9, which is in the region expected for a trivalent P(III) ester.[30a,32] In the proton-coupled ^{31}P NMR spectrum of **7**, a doublet is observed with three-bond P−H *J* coupling of 7.5 Hz. In the ^{1}H NMR spectrum of **7** in benzene-d_6, singlets are observed for the protons of four nonequivalent *tert*-butyl substituents, which is consistent with the presence of a stereocenter in the molecule. In chloroform-*d*, two of the *tert*-butyl groups are observed to be accidentally isochronous in the ^{1}H NMR spectrum.[2n] The spectral data were fully in accord the structure **7**, illustrated.

The menthol derivative (1*R*,2*S*,5*R*)-**8** was prepared in an analogous manner by the reaction of (1*R*,2*S*,5*R*)-**6** with **4**. In the ^{31}P{^{1}H} NMR of (1*R*,2*S*,5*R*)-**8**, a singlet resonance is observed at δ 134.6. The bridging methylene C(12) protons are observed to be nonequivalent in the ^{1}H NMR spectrum and appear as two doublets with $^{2}J_{HCH} = -12.6$ Hz.[33] The downfield signal is further split by five-bond *J* coupling to phosphorus ($^{5}J_{HP} = 2.2$ Hz). The magnitude of the observed

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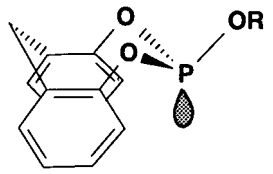

Figure 2. Boat−chair conformer without *tert*-butyl substituents.

geminal coupling constant and the observation of five-bond coupling of the downfield proton signal to phosphorus are consistent with a boat−chair conformation in solution, *vide ante* (Figure 1).[27,34−37]

In an analogous manner, (1*S*,2*R*,5*S*)-**8** was prepared by the reaction of (1*S*,2*R*,5*S*)-**6** with **4**. The observed optical rotation of (1*S*,2*R*,5*S*)-**8** is equal and opposite to that observed for the enantiomeric menthol derivative (1*R*,2*S*,5*R*)-**8**.

Solid-State and Solution Conformation. Studies on the conformation of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring have appeared only within the past 10 years. Quite recently, several reviews have appeared on the subject.[26,34−37] The commonly accepted nomenclature to describe the conformation of eight-membered rings is used herein; namely the boat−chair (C_s symmetry), boat−boat (C_s symmetry), twist-boat (C_1 symmetry), and twist (C_2 symmetry), which are abbreviated BC, BB, TB, and T, respectively.[38−40] Arshinova has noted that the boat conformer (C_1 symmetry; abbreviated B) should also be considered as it is commonly found in the solid state.[34−37] The B conformation represents a highly distorted TB geometry about halfway between the symmetric C_2 T and BB geometries.[38] The B conformation is characterized by a $C_{aromatic}$−O−P−O torsion angle of 0°.[34]

The originally observed dependence of the magnitude of the couplings of the C(12) geminal protons in substituted 5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctenes upon ring conformation[41−44] was extended to probe the conformation of 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocins in solution.[34−37] The observation of a geminal coupling constant of −12 to −13 Hz with observable $^5J_{HP}$ coupling of 2−4 Hz in 12*H*-dibenzo[*d*,*g*]-[1,3,2]dioxaphosphocins is consistent with a BC conformation with the exocyclic substituent on phosphorus assuming a pseudoequatorial placement.[34] Both the magnitude of the observed coupling constants and the observation of $^5J_{HP}$ suggest that **7** and **8** assume a biased BC conformation in solution with a pseudoequatorial substituent on phosphorus.

Very few X-ray crystal structures of 2*H*-dibenzo[*d*,*g*][1,3,2]-dioxaphosphocins containing tricoordinate P(III) are known. BC conformations have been found in the solid state with a pseudoequatorial substituent on phosphorus,[45,46] although caution must be exercised in comparing solid-state and solution conformations. Lattice energy and the resultant crystal-packing effects in the solid state can render the solid-state conformation different from that in solution.

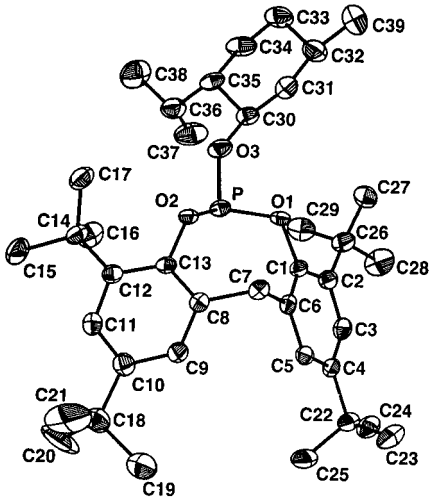

Figure 3. ORTEP view of (1*R*,2*S*,5*R*)-**8** showing the crystallographic numbering scheme (arbitrary).

Upon growing suitable crystals of (1*R*,2*S*,5*R*)-**8**, we obtained an X-ray crystal structure (Figure 2).[47] A BC conformation is found for the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring in (1*R*,2*S*,5*R*)-**8**. The C(1)−O(1)−P−O(2) and C(13)−O(2)−P−O(1) torsion angles are 90.1 and −91.3°, values expected for a BC conformation (Figure 3). The exocyclic oxygen atom bonded to phosphorus assumes a pseudoequatorial placement on the ring. The pseudoequatorial placement of the ring substituent on phosphorus provides an example of the difference between conformational energies of substituents in six- and eight-membered rings.[48] The sum of the O−P−O bond angles about phosphorus is 292.7°, which is nearly midway between pyramiddal (270° for "pure" p character) and tetrahedral (328.5° for sp^3 hybridization) geometries.

The phosphocin ring as defined by the plane passing through atoms O(1), O(2), C(6), and C(8) is twisted 80° relative to the plane of the cyclohexane ring as defined by atoms C(30), C(31), C(33), and C(34). The torsion angle defined by C(31)−C(30)−O(2)−C(8) is −71.0° (Figure 4). This conformational preference no doubt minimizes the interaction of the substituted cyclohexane ring with the ortho *tert*-butyl substituents bonded to C(2) and C(12) of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring. The cyclohexane ring is in a chair conformation with all substituents situated equatorially.

Platinum(II) Complexation. The complexation of (1*S*,2*R*,5*S*)-**8** with Pt(II) was studied by ^{31}P NMR spectroscopy.[49] In the ^{31}P{^{1}H} NMR spectrum of the complex formed from 2 equiv of (1*S*,2*R*,5*S*)-**8** with 1 equiv of (1,5-cyclooctadiene)-platinum(II) chloride in $CDCl_3$, two doublets are observed at δ 20.3 and 24.1 with corresponding ^{195}Pt satellites ($^1J_{PPt}$ = 6497 and $^1J_{PPt}$ = 6273 Hz, repectively), which were assigned to two nonequivalent phosphorus atoms ($^2J_{PP}$ = 43 Hz) (Figure 5). At 50 °C the signals are near coalescence. At 110 °C in $C_2D_2Cl_4$, a singlet with ^{195}Pt satellites is observed at δ 21.2, which was assigned to two equivalent phosphorus atoms ($^1J_{PPt}$ = 6372

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(49) Coalescence of the ^{31}P signals was near 50 °C in $CDCl_3$.

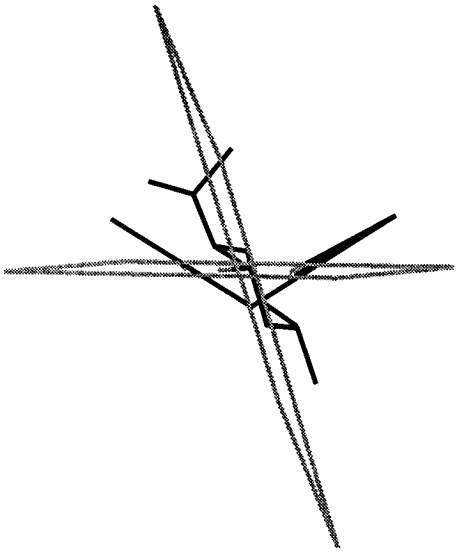
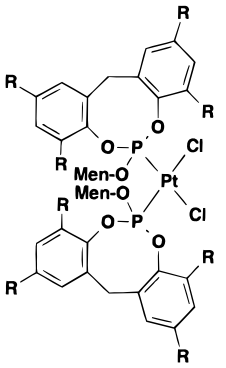
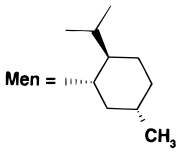


Figure 4. Plane of the 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin ring relative to the plane of the exocyclic cyclohexane ring as defined in the text.

Hz).[50] The ^{31}P NMR spectral data are consistent with the formation of the phosphite complex **9**. No evidence of $^{3}J_{PPt}$



9
R = tert-Bu



was seen in the ^{31}P{^{1}H} NMR spectrum of the complex, supporting the monomer structure **9** illustrated rather than a dimeric platinum species.[51]

The cis geometry of the phosphite ligands in **9** is supported by the magnitude of the observed P−P and P−^{195}Pt coupling constants.[52−57] The magnitude of the $^{1}J_{PPt}$ coupling is quite large, although several other examples are known in the literature with coupling of this magnitude.[58−61] The nonequivalence of the phosphorus atoms in the ^{31}P{^{1}H} NMR spectrum of **9** at room temperature is unexpected. This is the case because, in principle, the two phosphorus atoms are interchanged in **9** by a proper axis of rotation (C_2) and are therefore homotopic and isochronous.[2n] A reasonable explanation for the observed variable-temperature ^{31}P{^{1}H} NMR spectra is that at room temperature rotation about the P−Pt bonds is restricted because of the steric hindrance within the molecule. At 110 °C rapid single-bond rotation occurs and the P atoms are rendered equivalent. Similar observations of hindered rotation in platinum−aryl complexes was reported by Brown *et al.*[62] A dissociative process is ruled out because rapid reversible dissociation of the phosphorus ligands would result in the loss of P−^{195}Pt coupling.[63]

The observation of restricted rotation about the P−Pt bond in the P(II) complex **9** supports the contention that the *tert*-butyl-substituted 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin ligand provides a sterically congested environment about the metal. Although the 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin ring adopts a BC conformation in the free ligand, further studies are required to determine the effect of metal complexation upon the conformation of the ring.

Experimental Section

All melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. ^{1}H NMR (499.84 and 300.08 MHz, respectively) spectra were taken on a Varian Model Gemini-300 or Unity-500 spectrometer. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. ^{31}P NMR (80.98, 202.33, and 121.47 MHz, respectively) spectra were obtained on a Varian Model XL-200, Gemini-300, or Unity-500 spectrometer. All ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. Significant ^{1}H NMR data are tabulated in the following order: multiplicity (m, multiplet; s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dq, doublet of quartets; dt, doublet of triplets; ds, doublet of septets), atom assignments, coupling constant in hertz, and number of protons. Merck precoated (0.25 mm) silica gel F-254 plates were used for TLC. Reagents were purchased from commercial laboratory supply houses. Solvents were dried prior to use when necessary with appropriate drying agents. Reactions were carried out in flame-dried apparatus under a dry inert atmosphere of either nitrogen or argon. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. MOLYROO Version 1.0 from the Quantum Chemical Exchange Program (Program No. QCMP094), Indiana University, Department of Chemistry, was used for inputing atomic coordinates and subseqent data manipulation.

(2*S*)-2-[(2,4,8,10-Tetrakis(1,1-dimethylethyl)-12*H*-dibenzo[*d,g*]-[1,3,2]dioxaphosphocin-6-yl)-6-oxy]butane, 7. To a solution of 12.74 g (30 mmol) of **3** and 0.3 mL (3 mmol) of 1-methyl-2-pyrrolidone in 50 mL of toluene was added dropwise over a 10 min duration a solution of 8.24 g (60 mmol) of phosphorus(III) chloride in 5 mL of toluene. The reaction mixture was stirred at 90 °C for 1 h and then overnight at ambient temperature. The volatiles were removed *in vacuo*, and the residue was recrystallized from a mixture of 20 mL of toluene and

(50) Minor peaking observed in the baseline corresponding to unidentified complexes at 110 °C. Upon cooling, the original spectrum is observed.
(51) For a compilation of $^{3}J_{PPt}$ coupling constants in dimeric Pt complexes, see: Pregosin, P. S. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis;* Verkade, J. G., Quin, L. D., Eds.; VCH: Weinheim, Germany, 1987; pp 465−530 and references therein.
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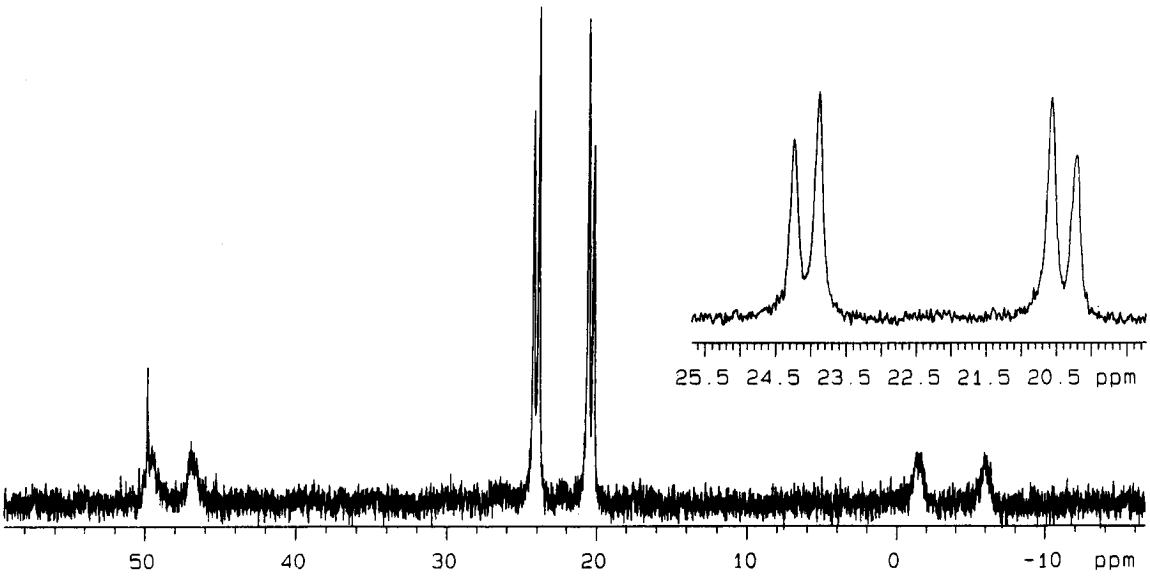

Figure 5. $^{31}P\{^{1}H\}$ NMR spectrum of the Pt(II) complex **9**.

25 mL of acetonitrile to give 8.34 g (57%) of **4** as white solid, which was used immediately for the next step without further purification: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) (121.47 MHz) δ 160.1 (lit.[30] δ 160.0); ^{1}H NMR ($CDCl_3$) (300.08 MHz) δ 1.35 (s, 18 H), 1.46 (s, 18 H), 3.71 (d, C(12)H, $^{2}J_{HCH}$ = 12.8 Hz, 1 H), 4.25 (d, C(12)H, $^{2}J_{HCH}$ = 12.8 Hz, $^{5}J_{HP}$ = 2.7 Hz, 1 H), 7.33 (d, 2 H), 7.35 (d, 2 H).

To a solution of 3.38 g (7 mmol) of **4** in 30 mL of toluene maintained at 3−4 °C was added dropwise over a 10 min duration a solution of 0.52 g (7 mmol) of **5** and 0.71 g (7 mmol) of triethylamine in 10 mL of toluene. After warming to room temperature, the reaction mixture was stirred for 10 days, and the resultant suspension of triethylamine hydrochloride was removed by filtration. The volatiles were removed *in vacuo*, and the residue was triturated with 25 mL of acetonitrile followed by recrystallization from a mixture of 1.4 mL of toluene and 25 mL of acetonitrile to give 2.54 g (69%) of a white solid: mp 170−174 °C. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) (121.47 MHz) δ 131.9; ^{31}P NMR ($CDCl_3$) (121.47 MHz) δ 131.9 (d, $^{3}J_{POCH}$ = 7.2 Hz); ^{1}H NMR ($CDCl_3$) (300.08 MHz) δ 0.94 (t, $^{3}J_{HCCH}$ = 7.5 Hz, 3 H), 1.32 (s, 18 H), 1.44 (s, 9 H), 1.45 (s, 9 H), 1.53 (d, $^{3}J_{HCCH}$ = 6.5 Hz, 3 H), 1.88 (m, 2 H), 3.44 (d, C(12)H, 1 H), 4.42 (dd, C(12)H, 1 H), 5.16 (m, 1 H), 7.28 (m, 2 H), 7.32 (m, 2 H); ^{1}H NMR (benzene-d_6) (300.08 MHz) δ 0.93 (t, $^{3}J_{HCCH}$ = 7.5 Hz, 3 H), 1.243 (s, 9 H), 1.248 (s, 9 H), 1.46 (d, $^{3}J_{HCCH}$ = 6.5 Hz, 3 H), 1.48 (s, 9 H), 1.50 (s, 9 H), 1.80 (m, 2 H), 3.34 (d, C(12)H, $^{2}J_{HCH}$ = 12.6 Hz; 1 H), 4.48 (dd, C(12)H, $^{2}J_{HCH}$ = 12.6 Hz, $^{5}J_{HP}$ = 2.8 Hz, 1 H), 5.36 (m, 1 H), 7.34 (m, 2 H), 7.37 (m, 2 H). Anal. Calcd for $C_{33}H_{51}O_3P$: C, 75.24; H, 9.75. Found: C, 75.43; H, 10.01.

(1*R*,2*S*,5*R*)-5-Methyl-2-(1-methylethyl)-1-[(2,4,8,10-tetrakis(1,1-dimethylethyl)-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin-6-yl)-6-oxy]-cyclohexane, (1*R*,2*S*,5*R*)-8. To a solution of 3.43 g (7 mmol) of **4** in 30 mL of toluene was added dropwise over a 20 min duration a solution of 1.09 g (7 mmol) of **(1*R*,2*S*,5*R*)-6** and 0.71 g (7 mmol) of triethylamine in 20 mL of toluene. After the addition was complete, the reaction mixture was heated to 90 °C for 1 h. The reaction mixture was stirred for 5 days at ambient temperature, and the resultant suspension of triethylamine hydrochloride was removed by filtration. The volatiles were removed *in vacuo*, and the residue was triturated with acetonitrile, followed by recrystallization from a mixture of 4.2 mL of toluene and 25 mL of acetonitrile to give 2.44 g (57 %) of a white crystalline solid: mp 172−173 °C. $[\alpha]^{22}_{D} = -44.9$ [c = 4.004, toluene]; $^{31}P\{^{1}H\}$ NMR (benzene-d_6) (202.37 MHz) δ 134.6; ^{1}H NMR (benzene-d_6) (499.87 MHz) (60 °C) δ 0.82 (m, 1 H), 0.91 (d, 3 H), 0.98 (overlapping d, 6 H), 1.00 (partially obscured m, 1 H), 1.275 (s, 9 H), 1.285 (s, 9 H), 1.35 (m, 1 H), 1.55 (s, 18 H), 1.58 (partially obscured m, 4 H), 2.66 (ds, 1 H), 2.84 (m, 1 H), 3.49 (d, C(12)H, 1 H), 4.62 (dd, C(12)H, $^{2}J_{HCH}$ = 12.6 Hz, $^{5}J_{HP}$ = 2.2 Hz, 1 H), 4.66 (m, 1 H), 7.34 (d, 1 H), 7.35 (d, 1H), 7.38 (overlapping d, 2 H).

Crystals suitable for crystallographic analysis (colorless plates) were prepared by slow diffusion on acetonitrile into a solution of **(1*R*,2*S*,5*R*)-8** in toluene. Crystal data and experimental details: $PO_3C_{39}H_{61}$; fw = 608.89; crystal size (mm) 0.5 × 0.3 × 0.5; crystal system orthorhombic; space group $P2_12_12_1$; cell parameters a = 9.979 (5) Å, b = 13.498 (6) Å, c = 28.298 (15) Å, V = 3811 (5) Å^3, Z = 4; d_{calcd} = 1.061 g·cm^{-3}; F_{000} = 2368 electrons; μ(Mo Kα) = 0.997 cm^{-1}; Enraf-Nonius CAD4 diffractometer; monochromated Mo Kα radiation; temperature = 100-(2) K; scan type $\omega-2\theta$; detector aperture (mm) = 4.0 × 4.0; $2\theta_{max}$ = 50°; number of reflections measured 4069; number of observed reflections ($I > 3\sigma_I$) 3026; number of variables 617; R = 0.044; R_w = 0.059; convergence (Δ/σ) 0.02; GOF = 2.27.

(1*S*,2*R*,5*S*)-5-Methyl-2-(1-methylethyl)-1-[(2,4,8,10-tetrakis(1,1-dimethylethyl)-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin-6-yl)-6-oxy]-cyclohexane, (1*S*,2*R*,5*S*)-8. By the procedure used to prepare **(1*R*,2*S*,5*R*)-8**, compound **(1*S*,2*R*,5*S*)-8** was prepared from 2.94 g (6 mmol) of **4**, 0.94 g (6 mmol) of **(1*S*,2*R*,5*S*)-6**, and 0.61 g (6 mmol) of triethylamine in 40 mL of toluene (ambient temperature, 4 days). The residue was triturated with acetonitrile followed by recrystallization from a mixture of 4.5 mL of toluene and 30 mL of acetonitrile to give 2.02 g (55%) of a white solid: mp 172−173 °C; $[\alpha]^{22}_{D} = +42.7$ [c = 4.004, toluene]; NMR spectral data in benzene-d_6 were identical to those obtained for **(1*R*,2*S*,5*R*)-8**; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) (121.47 MHz) δ 134.5; ^{1}H NMR ($CDCl_3$) (300.08 MHz) δ 0.82−1.78 (complex overlapping m, 7 H), 0.87 (d, $^{3}J_{HCCH}$ = 7.0 Hz, 3 H), 0.94 (d, $^{3}J_{HCCH}$ = 6.2 Hz, 3 H), 0.98 (d, $^{3}J_{HCCH}$ = 7.0 Hz, 3 H), 1.31 (s, 18 H), 1.44 (s, 9 H), 1.45 (s, 9 H), 2.50 (ds, 1 H), 2.72 (m, 1 H), 3.47 (d, C(12)H, 1 H), 4.43 (dd, C(12)H, $^{2}J_{HCH}$ = 12.6 Hz, $^{5}J_{HP}$ = 2.8 Hz, 1 H), 4.58 (m, 1 H), 7.26 (m, 2 H), 7.31 (m, 2 H). Anal. Calcd for $C_{39}H_{61}O_3P$: C, 76.93; H, 10.09. Found: C, 77.24; H, 10.40.

Dichlorobis{(1*S*,2*R*,5*S*)-5-methyl-2-(1-methylethyl)-1-[(2,4,8,10-tetrakis(1,1-dimethylethyl)-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin-6-yl)-6-oxy]cyclohexane}platinum(II), 9. A mixture of 0.610 g (1 mmol) of (1*S*,2*R*,5*S*)-**8** and 0.1.87 g (0.5 mmol) of (1,5-cyclooctadiene)-platinum(II) chloride in 20 mL of toluene was stirred overnight. The volatiles were removed *in vacuo*, and the resultant complex was analyzed spectroscopically without further purification. $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) (121.47 MHz) (24 °C)[49] δ 20.3 (d, $^{1}J_{PPt}$ = 6497 Hz, $^{2}J_{PP}$ = 43 Hz), 24.1 (d, $^{1}J_{PPt}$ = 6273 Hz, $^{2}J_{PP}$ = 43 Hz), ^{195}Pt satellites observed at δ −1.8, −6.4, 47.1, and 49.9; $^{31}P\{^{1}H\}$ NMR ($C_2D_2Cl_4$) (121.47 MHz) (110 °C) δ 21.2 ($^{1}J_{PPt}$ = 6372 Hz), ^{195}Pt satellites observed at δ −5.0 and 47.4.

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Supporting Information Available: From the X-ray crystallographic analysis of the phosphite (1*R*,2*S*,5*R*)-**8**, tables of bond angles, bond lengths, torsion angles, thermal parameters, and positional parameters (16 pages). This material is contained in many libraries on microfiche, which immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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