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Sterically Congested Tripodal Phosphites: Conformational Analysis, Solid-State Polymorphism, Metal Complexation, and Application to the Asymmetric Hydrosilation of Ketones[1]

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The synthesis as well as isolation and crystallographic analysis of two solid-state polymorphs of the tripodal ligand tri{2,2′,2′′-tris[(2,4,8,10-tetrakis(1,1-dimethylethyl)dibenzo[*d*,*f*][1,3,2]dioxaphosphepin-6-yl)oxy]ethyl}amine (**3**) is described. Form I crystallized from ethyl acetate in the space group $P2_1/n$ with the unit-cell parameters $a = 20.070(10)$ Å, $b = 17.477(2)$ Å, $c = 27.620(3)$ Å, and $\beta = 93.050(10)°$, $V = 9674.5(14)$ Å^3, and $Z = 4$. Form II crystallized from a mixture of acetone and toluene in the space group $P\bar{1}$ with the unit-cell parameters $a = 12.493(1)$ Å, $b = 19.701(2)$ Å, $c = 21.027(2)$ Å, $\alpha = 116.23(1)°$, $\beta = 100.15(1)°$, and $\gamma = 91.07(1)°$, $V = 4542$ Å^3, and $Z = 2$. Differences in the relative absolute stereochemistry of the stereoaxes in the seven-membered dibenzo[*d*,*f*][1,3,2]dioxaphosphepin ring are discussed. The synthesis and X-ray characterization of enantiomerically pure (*S*,*S*,*S*)-tri{2,2′,2′′-tris[(2,4,8,10-tetrakis(1,1-dimethylethyl)dibenzo[*d*,*f*][1,3,2]dioxaphosphepin-6-yl)oxy]propyl}amine [(*S*,*S*,*S*)-**7**] are reported. Two crystallographically independent molecules exist in the unit cell that cannot be superimposed with each other by either a translation or a symmetry operation. The two solid-state conformers in the unit cell differed predominately by the absolute stereochemistry of the stereoaxes in the seven-membered dibenzo[*d*,*f*][1,3,2]dioxaphosphepin ring. The Rh(I)-catalyzed hydrosilation of acetophenone with the chiral ligands (*R*,*R*,*S*)-**7** and (*S*,*S*,*S*)-**7** showed significant differences in chiral induction. Chiral cooperativity between the stereoaxes and stereocenters in (*S*,*S*,*S*)-**7** is observed. The mechanism of the communication between the stereocenters and stereoaxes leading to chiral cooperativity in the stereoselective transition state is suggested to be primarily steric in nature.

Introduction

Phosphine ligands have played a ubiquitous role in designing coordination spheres for transition-metal catalysts. Recently, both achiral and chiral phosphite ligands have been reported as viable alternatives to phosphine ligands.[2−8] Rationally designed sterically hindered phosphite ligands provide a tool in the synthetic chemist's arsenal for achieving high stereoselectivity in transition-metal-catalyzed reactions.[9] Relatively little attention, however, has been paid to the synthesis of tripodal ligands with phosphite functionality.[10,11]

Recently, we communicated the synthesis and utility of a chiral tripodal ligand, (*S*,*S*,*S*)-TRISPHOS, an acronym for (*S*,*S*,*S*)-tri{2,2′,2′′-tris[(2,4,8,10-tetrakis(1,1-dimethylethyl)-dibenzo[*d*,*f*][1,3,2]dioxaphosphepin-6-yl)oxy]propyl}-amine [(*S*,*S*,*S*)-**7**], in the Rh(I)-catalyzed asymmetric hydrosilation of ketones.[12] (*S*,*S*,*S*)-**7** is a sterically congested tripodal phosphite in which the phosphorus atom is bound

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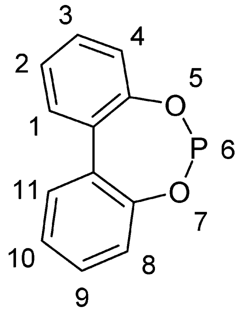

Figure 1. Chemical Abstracts numbering system for the dibenzo[*d*,*f*][1,3,2]-dioxaphosphepin ring system.

in a seven-membered dibenzo[*d*,*f*][1,3,2]dioxaphosphepin ring (Figure 1). The presence of both a stereocenter and stereoaxis in **7** provides an interesting model to investigate the concept of internal cooperativity of chirality, or simply *chiral cooperativity*. The concept of chiral cooperativity as originally proposed by Pastor and Togni[13] is defined as cooperativity between the individual chirotopic elements within a ligand that promotes the appropriate steric and electronic interactions necessary to obtain high diastereo- or enantioselectivity for a particular reaction.[14,15] Additionally, the presence of multiple stereocenters and stereoaxes in the TRISPHOS ligand class suggests the existence of polymorphism in the solid state. We report herein a detailed investigation of the (1) synthesis, (2) solution and solid-state conformational analysis, (3) solid-state polymorphism, and (4) formation of rhodium complexes of the tripodal phosphite ligands. The result of Rh(I)-catalyzed asymmetric hydrosilations demonstrated chiral cooperativity between the stereocenters and stereoaxes in the chiral ligand (*S*,*S*,*S*)-**7** as well as the lack thereof in the newly synthesized (*R*,*R*,*S*)-**7**. In the case of (*S*,*S*,*S*)-**7**, the conformational analysis suggests that the communication between the stereocenters and stereoaxes leading to chiral cooperativity is primarily steric in nature.

Results and Discussion

Synthesis. The biphenyl-2,2′-diol **1** was prepared by the oxidative coupling of 2,4-di-*tert*-butylphenol with hydrogen peroxide under alkaline conditions as previously described by Shum et al.[16] The phosphorochloridite **2** was prepared in situ by the reaction of **1** with phosphorus(III) chloride in the presence of triethylamine as an acid acceptor (Scheme 1).[17,18] The reaction of 3 equiv of **2** with 1 equiv of triethanolamine in the presence of triethylamine gave the tripodal phosphite **3**.[17a]

The enantiomerically pure tri-2-propanol (*S*,*S*,*S*)-**6** was prepared by the reaction of the chiral epoxide (*S*)-**5** with a methanolic solution of **4a** as reported by Nugent and Harlow.[19] The reaction of 3 equiv of **2** with (*S*,*S*,*S*)-**6** gave the chiral tripodal ligand (*S*,*S*,*S*)-**7**, where the absolute stereochemical descriptors refer to the three stereocenters at carbon. In the $^{31}P\{^1H\}$ NMR spectrum of (*S*,*S*,*S*)-**7**, a singlet is observed at δ 145.2, which is consistent with the presence of a C_3 proper axis of symmetry within the molecule that renders the three phosphorus atoms homotopic and isochronous. Three stereoaxes (the sp^2−sp^2 C−C single bond connecting the aryl groups in each dioxaphosphepin ring) are also present in (*S*,*S*,*S*)-**7**, which in principle should lead to observable atropisomers. However, the energy barrier to ring inversion of the seven-membered dibenzo[*d*,*f*][1,3,2]-dioxaphosphepin ring (rapid rotation about the stereoaxis)

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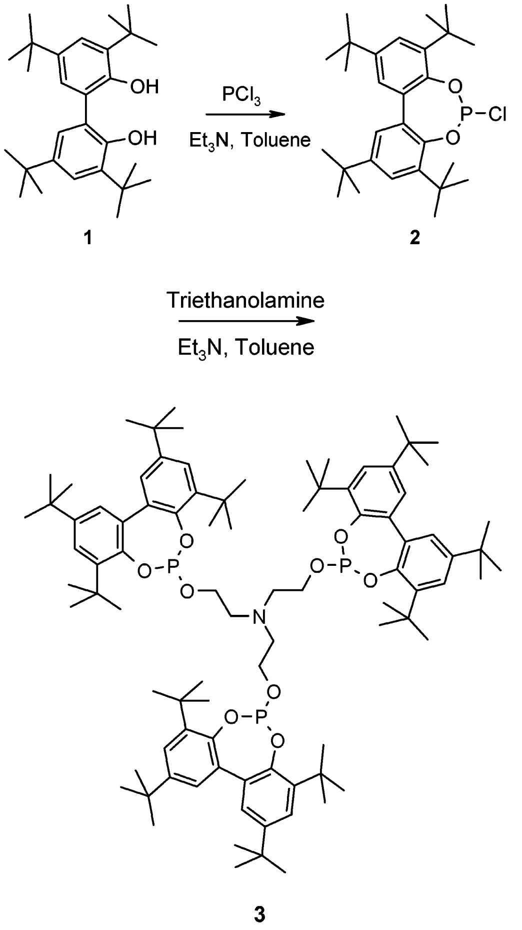
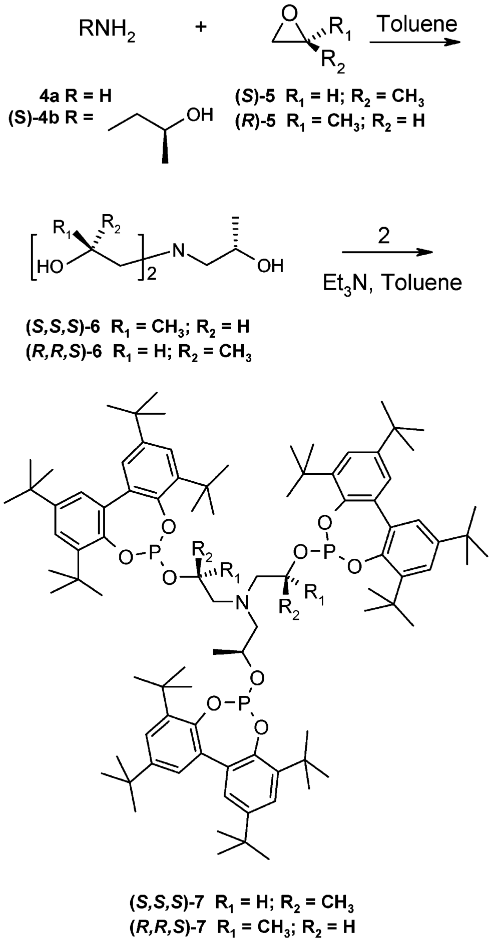
Scheme 1



Scheme 2



is known to be low,[18] and additional atropisomerism is not observed at room temperature.[20]

The tri-2-propanolamine (*R*,*R*,*S*)-**6** was prepared by the reaction of the 2-propanolamine (*S*)-**4b** with 2 equiv of (*R*)-**5**. The tripodal phosphite (*R*,*R*,*S*)-**7** was prepared by the reaction of (*R*,*R*,*S*)-**6** with 3 equiv of the phosphorochloridite **2** using triethylamine as an acid acceptor. In the $^{31}P\{^{1}H\}$ NMR spectrum of (*R*,*R*,*S*)-**7**, two singlets are observed at δ 145.2 and 144.9 in a 2:1 ratio, respectively, by integration of the peak areas.[21]

Solid-State Conformation. The presence of three stereoaxes in **3** suggested that several crystal forms could exist in the solid state. In accord with this expectation, two polymorphs of **3** were isolatable.[22] Form I crystallized from ethyl acetate in the space group $P2_1/n$ with the unit-cell parameters $a = 20.070(10)$ Å, $b = 17.477(2)$ Å, $c = 27.620(3)$ Å, and $\beta = 93.050(10)°$, $V = 9674.5(14)$ Å^3, and $Z = 4$ (Figure 2). Form II crystallized from a mixture of acetone and toluene in the space group $P\bar{1}$ with the unit-cell parameters $a = 12.493(1)$ Å, $b = 19.701(2)$ Å, $c = 21.027(2)$ Å; $\alpha = 116.23(1)°$, $\beta = 100.15(1)°$, and $\gamma = 91.07(1)°$, $V = 4542$ Å^3, and $Z = 2$ (Figure 3).

In the solid state of **3** (form I), the relative absolute configurations of all three stereoaxes are the same [relative absolute configuration (*aR**,*aR**,*aR**) using the Cahn−Ingold−Prelog system or (*M**,*M**,*M**) if the stereoaxes are alternately viewed as a helix].[23] The dihedral angles about the stereoaxes (the sp^2−sp^2 σ bond connecting the two aryl rings) in the three dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings [C(16)−C(17)−C(30)−C(31), C(46)−C(47)−C(60)−C(61), and C(76)−C(77)−C(90)−C(91)] are essentially the same [49.0°, 49.6°, and 51.8°, respectively] (Table 1). The

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(20) For a discussion of averaged symmetry, residual stereoisomers, and the NMR of conformationally mobile systems, see: Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; pp 54−58.

(21) Although the three phosphorus atoms in (*R*,*R*,*S*)-**4** are inherently nonequivalent, two of the phosphorus atoms are interchanged by a pseudo-C_2 axis of rotation and are accidently equivalent. For a discussion on topicity and NMR spectra, see: Eliel. E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; pp 465−508.

(22) Two other crystal forms were also observed. Form III was obtained by recrystallization from a mixture of toluene and acetonitrile, mp 128−138 °C, in the space group $P2_1/n$ with the unit-cell parameters $a = 20.308(2)$ Å, $b = 17.615(3)$ Å, $c = 27.918(5)$ Å, and $\beta = 93.730(10)°$, $V = 9966$ (3) Å^3, and $Z = 4$. Form III contained half a molecule of toluene in the crystal cell (see the Supporting Information). Form IV was obtained by recrystallization from 1-butanol, mp 182 °C. Crystals suitable for X-ray crystallography could not be obtained. The X-ray diffraction pattern obtained using Cu Kα (2θ) is different from those of forms I−III. An amorphous form V was obtained by heating **3** at 210 °C until a clear melt was obtained followed by rapid cooling to ambient temperature, $T_g = 105−110$ °C. The X-ray diffraction pattern obtained using Cu Kα (2θ) is featureless.

(23) For a discussion on the assignment of stereochemical descriptors to molecules containing a stereoaxis, see: Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; pp 1119−1155.

Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for Form I of **3**

		Bond Lengths			
P(1)−O(4)	1.599(5)	P(2)−O(7)	1.604(4)	P(3)−O(10)	1.597(5)
P(1)−O(5)	1.619(5)	P(2)−O(8)	1.620(4)	P(3)−O(11)	1.625(4)
P(1)−O(6)	1.642(5)	P(2)−O(9)	1.646(4)	P(3)−O(12)	1.652(5)
		Bond Angles			
O(4)−P(1)−O (5)	101.1(3)	O(7)−P(2)−O(8)	100.5(2)	O(10)−P(3)−O(11)	101.2(2)
O(4)−P(1)−O (6)	96.0(3)	O(7)−P(2)−O(9)	96.2(2)	O(10)−P(3)−O(12)	96.5(2)
O(5)−P(1)−O (6)	101.4(3)	O(8)−P(2)−O(9)	101.6(2)	O(11)−P(3)−O(12)	101.3(2)
		Dihedral Angles			
C(16)−C(17)−C(30)−C(31)	+49.0	N(13)−C(14)−C(15)−O(4)	−59.6	P(1)−O(4)−C(15)−C(14)	−103.6
C(46)−C(47)−C(60)−C(61)	+49.6	N(13)−C(44)−C(45)−O(7)	−59.3	P(2)−O(7)−C(45)−C(44)	−103.3
C(76)−C(77)−C(90)−C(91)	+51.8	N(13)−C(74)−C(75)−O(10)	−59.5	P(3)−O(10)−C(75)−C(74)	−104.0

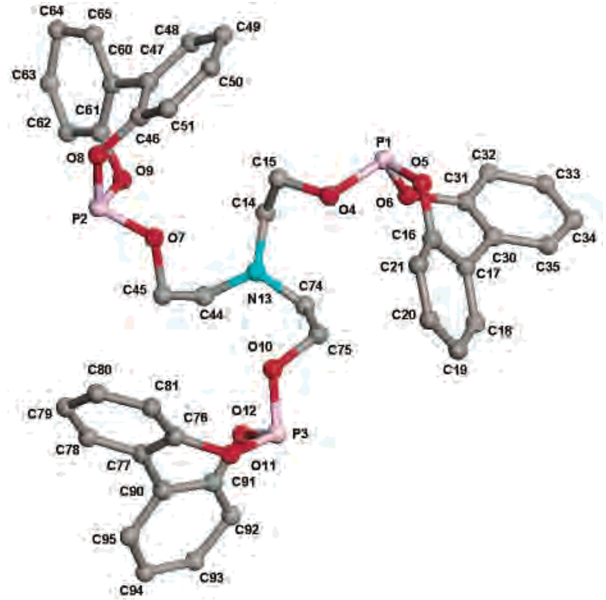

Figure 2. Molecular structure of crystal form I of **3** with *tert*-butyl substituents omitted for clarity (numbering of atoms arbitrary).

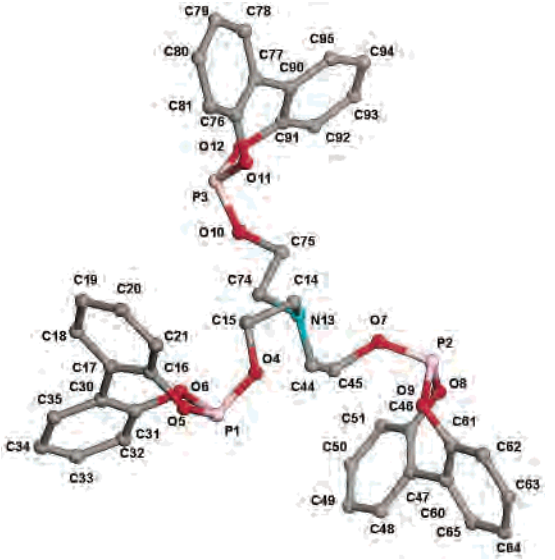

Figure 3. Molecular structure of crystal form II of **3** with *tert*-butyl substituents omitted for clarity (numbering of atoms arbitrary).

magnitude of these dihedral angles is in the range previously observed for substituted dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings.[18,24,25] Similarly, the three N−C−C−O and P−O−C−C dihedral angles are nearly the same. Given the posit that pyramidal geometry is achieved when the sum of the appropriate bond angles about phosphorus is near 270°, the three phosphorus atoms in form I of **3** are midway between pyramidal (270° for "pure" p character) and tetrahedral (328.5° for sp^3 hybridization) geometry.

Interestingly, the three exocyclic P−O bond lengths in form I [P(1)−O(4), P(2)−O(7), and P(3)−O(10)] are shorter than the endocyclic P−O bond lengths. Furthermore, the longest endocyclic P−O bond forms with the exocyclic P−O the smallest O_{endo}−P−O_{exo} bond angle in every case [O(4)−P(1)−O(6) = 96.0°, O(7)−P(2)−O(9) = 96.2°, O(10)−P(3)−O(12) = 96.5°]. The other O−P−O bond angles about phosphorus all range between 100.5° and 101.6°. This difference has been observed before in substituted dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings.[18,24] A reasonable explanation for this observation is that steric interactions between the substituted oxygen on the exocyclic bond to phosphorus and the adjacent *tert*-butyl substituent on the dioxaphosphepin ring cause the observed reduction of the O−P−O bond angle and endocyclic bond length variation.[26]

In the solid state of form II of compound **3**, the relative absolute configuration of one of the three stereoaxes is different [relative absolute configuration (*aR**,*aR**,*aS**) using the Cahn−Ingold−Prelog system or (*M**,*M**,*P**) if the stereoaxes are alternately viewed as a helix].[23] The dihedral angles about the stereoaxes (the sp^2−sp^2 σ bond connecting the two aryl rings) in the three dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings [C(16)−C(17)−C(30)−C(31), C(46)−C(47)−C(60)−C(61), and C(76)−C(77)−C(90)−C(91)] are −50.7°, 51.4°, and 49.4°, respectively (Table 2). The three phosphorus atoms in form II of **3** are midway between pyramidal and tetrahedral geometry. A relationship similar to that observed in form I of **3** in regard to the bond lengths and bond angles about phosphorus is seen in form II, vide infra. One O−P−O bond angle in form II is found, however, to be greater than the corresponding angle in form I; e.g., O(4)−P(1)−(5) is 107.4° in form II and 101.1° in form I. Unlike form I, the three N−C−C−O and P−O−C−C dihedral angles in form II of **3** show significant differences.

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(26) Suggested by examination of a Dreiding molecular model.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for Form II of **3**

		Bond Lengths			
P(1)−O(4)	1.597	P(2)−O(7)	1.582	P(3)−O(10)	1.575
P(1)−O(5)	1.628	P(2)−O(8)	1.638	P(3)−O(11)	1.667
P(1)−O(6)	1.657	P(2)−O(9)	1.654	P(3)−O(12)	1.618
		Bond Angles			
O(4)−P(1)−O(5)	107.4(6)	O(7)−P(2)−O(8)	107.1(8)	O(10)−P(3)−O(11)	97.7(0)
O(4)−P(1)−O(6)	96.9(0)	O(7)−P(2)−O(9)	96.8(5)	O(10)−P(3)−O(12)	105.6(1)
O(5)−P(1)−O(6)	101.6(2)	O(8)−P(2)−O(9)	100.6(6)	O(11)−P(3)−O(12)	100.6(2)
		Dihedral Angles			
C(16)−C(17)−C(30)−C(31)	−50.7	C(76)−C(77)−C(90)−C(91)	+49.4	P(1)−O(4)−C(15)−C(14)	−150.4
C(46)−C(47)−C(60)−C(61)	+51.4	N(13)−C(14)−C(15)−O(4)	+77.6	P(2)−O(7)−C(45)−C(44)	+105.3
C(76)−C(77)−C(90)−C(91)	+49.4	N(13)−C(44)−C(45)−O(7)	+63.1	P(3)−O(10)−C(75)−C(74)	+116.9

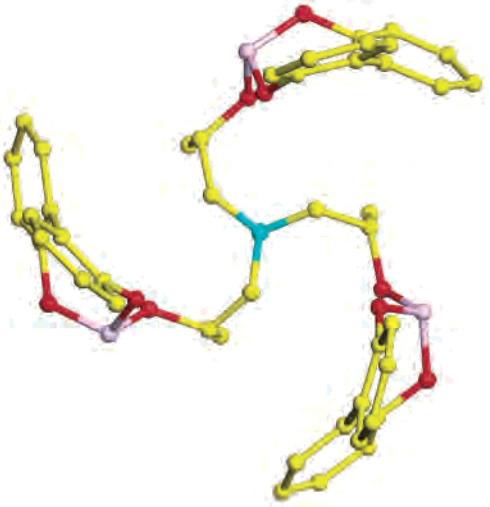

Figure 4. Molecular structure of crystal (*S*,*S*,*S*)-**7** viewed down the C_3 axis with *tert*-butyl substituents omitted for clarity.

(*S*,*S*,*S*)-**7** crystallized from a mixture of acetonitrile and tetrahydrofuran in the space group $R\bar{3}$ (hexagonal axis) with the unit-cell parameters $a = b = 25.991(3)$ Å, $c = 24.649(3)$ Å, and $\gamma = 120°$, $V = 14420(3)$ Å^3, and $Z = 6$. In the solid state of (*S*,*S*,*S*)-**7**, two crystallographically independent molecules exist in the unit cell that cannot be superimposed with each other by either a translation or a symmetry operation. All the molecules in the unit cell lie on a 3-fold axis and therefore have C_3 symmetry (Figure 4). Both molecules of (*S*,*S*,*S*)-**7** adopt a different conformation, designated conformers A and B, respectively (Figures 5 and 6). As found in forms I and II of compound **3**, the exocyclic P−O bond lengths in both conformers A and B of (*S*,*S*,*S*)-**7** are shorter than the endocyclic P−O bond lengths. The observed bond lengths (Table 3) agree within the limits of accuracy with the expected values. The magnitude of the final *R* factor values that range from 0.08 to 0.10 for the molecules of this study is due to disorder in the *tert*-butyl substituents.

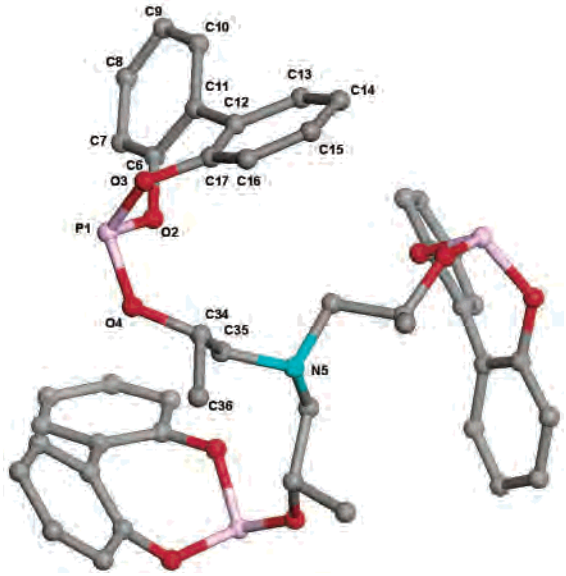

Figure 5. Molecular structure of conformer A of (*S*,*S*,*S*)-**7** with *tert*-butyl substituents omitted for clarity (numbering of atoms arbitrary).

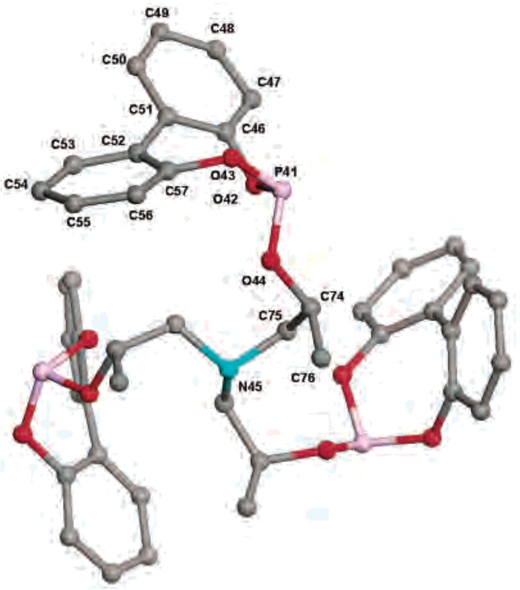

Figure 6. Molecular structure of conformer B of (*S*,*S*,*S*)-**7** with *tert*-butyl substituents omitted for clarity (numbering of atoms arbitrary).

In the solid state, conformer A of **7** corresponds to the (*aS*,*aS*,*aS*,*S*,*S*,*S*)-**7** [or (*P*,*P*,*P*,*S*,*S*,*S*)-**7**] diastereoisomer, whereas conformer B corresponds to the (*aR*,*aR*,*aR*,*S*,*S*,*S*)-**7** [or (*M*,*M*,*M*,*S*,*S*,*S*)-**7**] diastereoisomer. The dihedral angles about the stereoaxes (the sp^2−sp^2 σ bond connecting the two aryl rings) in the three dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings of conformer A [C(6)−C(11)−C(12)−C(17)] and conformer B [C(46)−C(51)−C(52)−C(57)] are −48.5° and 48.0°, respectively (Table 3). The P−O−C−C and particularly the N−C−C−O dihedral angles in conformers A and B of **7** show significant differences (see Table 3). Although the geometry about phosphorus is midway between pyramidal

Table 3. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for the Independent Conformers A and B in the Unit Cell of (*S*,*S*,*S*)-**7**

bond lengths		bond angles		dihedral angles	
		Conformer A			
P(1)−O(4)	1.586(5)	O(4)−P(1)−O(2)	97.9(3)	C(6)−C(11)−C(12)−C(17)	−48.5
P(1)−O(3)	1.641(5)	O(4)−P(1)−O(3)	108.9(4)	P(1)−O(4)−C(34)−C(35)	−82.9
P(1)−O(2)	1.650(5)	O(2)−P(1)−O(3)	99.4(1)	O(4)−C(34)−C(35)−N(5)	+169.2
		Conformer B			
P(41)−O(44)	1.556(5)	O(44)−P(41)− O(43)	103.4(2)	C(46)−C(51)−C(52)−C(57)	+48.0
P(41)−O(42)	1.592(5)	O(44)−P(41)−O(42)	99.9(2)	P(41)−O(44)−C(74)−C(75)	−92.9
P(41)−O(43)	1.573(5)	O(43)−P(41)−O(42)	104.9(7)	O(44)−C(74)−C(75)−N(45)	−79.5

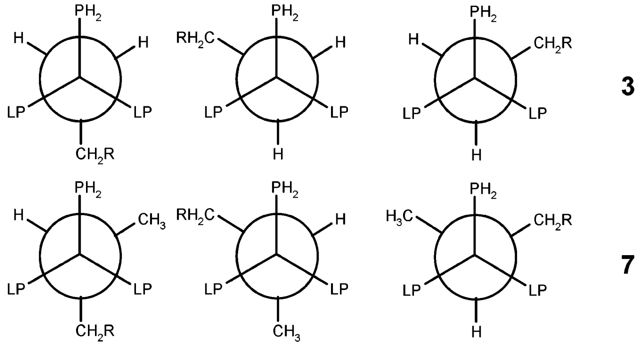

Figure 7. Newman projections looking down the O−C bond in compounds **3** and **7**.

and tetrahedral in conformers A and B, the sums of the O−P−O bond angles about phosphorus, 306.2° and 308.2°, respectively, are somewhat larger than those found for either form I (298.3−299.0°) or form II (303.9−305.9°).

Caution must be exercised in the comparison of conformations obtained from X-ray structural data with those in solution. Anet and Yavari warned that the lattice energy and the resultant crystal-packing effects in the solid state can render the solid-state conformation different from that in solution.[27] Cognizant of the fact that solid-state and solution conformations can be different, the effect of the stereocenter at carbon on the geometry about the phosphorus atom provides insight into the nature of chiral cooperativity in transition-metal-catalyzed reactions with a chiral ligand. Although the bonding for the observed diastereomeric conformers A and B in the solid state may not directly relate to the conformation in solution, it does provide insight into the effect of the stereocenter and stereoaxis upon the geometry at phosphorus. In conformer A, (*aS*,*aS*,*aS*,*S*,*S*,*S*)-**7**, and conformer B, (*aR*,*aR*,*aR*,*S*,*S*,*S*)-**7**, significant differences are observed for the O−P−O bond angles about phosphorus (Table 3). These observed differences in the geometry about phosphorus suggest that the chiral environment about the metal would be necessarily different if ligand (*S*,*S*,*S*)-**7** with the geometry found in either conformer A or conformer B was coordinated to a metal in the enantioselective transition state, vide infra. The examination of Newman projections about the P−O−C−C and O−C−C−N dihedral angles suggests the effect of the stereocenter is predominantly steric in nature (see Figure 7). At least one gauche (or eclipsed) interaction exists for each conformation upon rotation about the P−O−C−C and O−C−C−N dihedral angles in (*S*,*S*,*S*)-**7**. This is not the case for **3**, which is devoid of a stereocenter. The absolute value of the P−O−C−C dihedral angles for conformers A and B of (*S*,*S*,*S*)-**7**, −82.9° and −92.9°, respectively, are smaller than those found in form I (103.6−104.0°) and form II (105.3−150.4°) of **3**. Smaller differences are found for the absolute values of the O−C−C−N dihedral angles in the compounds of this study. This would be the case on the basis of steric arguments (smaller covalent radii of oxygen and nitrogen). Significantly larger steric effects are expected for the phosphorus atom constrained within the seven-membered dibenzo[*d*,*f*][1,3,2]-dioxaphosphepin ring with the methyl substituent bonded to the stereocenter.

In the solid state of either conformer A or conformer B of (*S*,*S*,*S*)-**7**, the molecule adopts a C_3 symmetric structure with nitrogen at the apex. All of the methyl substituents bonded to a stereocenter are pointing down (away from the apex) and in the same direction (see Figures 4−6). A similar structure was observed by Nugent and Harlow for early-transition-metal complexes bearing homochiral 2-propanolamine ligands.[19] In the solid state of either conformer A or conformer B of (*S*,*S*,*S*)-**7**, the methyl substituents bonded to the C(34) stereocenter point away from the phosphorus atom. The P(1)−O(4)−C(34)−C(36) and P(41)−O(44)−C(74)−C(76) dihedral angles are 157° and 140°, respectively, for conformers A and B of **7**.

VT NMR Spectra. In the ^{31}P{^{1}H} NMR (CD_2Cl_2) spectrum of **3** at 26 °C, a single signal is observed at δ 140.6 due to conformational averaging, vide ante. In the VT ^{31}P{^{1}H} NMR spectrum of **3** below −55 °C, the coalescence temperature, two broad singlets are observed in an approximate 2.5:1 ratio by integration of the appropriate peak areas. We previously suggested that the observed VT ^{31}P{^{1}H} NMR spectrum is consistent with the observation of a mixture of the (*aR**,*aR**,*aS**) and (*aR**,*aR**,*aR**) atropisomers of **3**. A reasonable explanation of this observation is that below T_C rotation about the three stereoaxes of **3** is slow on the NMR time scale.[18] Although additional lines would be expected in the ^{31}P{^{1}H} NMR spectrum of **3** if both the (*aR**,*aR**,*aS**) and (*aR**,*aR**,*aR**) atropisomers were present below the coalescence temperature, accidental equivalence could not be ruled out because the signals were broad. An alternate explanation that the (*aR**,*aR**,*aS**) atropisomer is selectively formed, which was found in the solid state of form II of compound **3**, cannot be completely ruled out, although the integration of the appropriate peak areas is not that expected for a single atropisomer. High diastereoselec-

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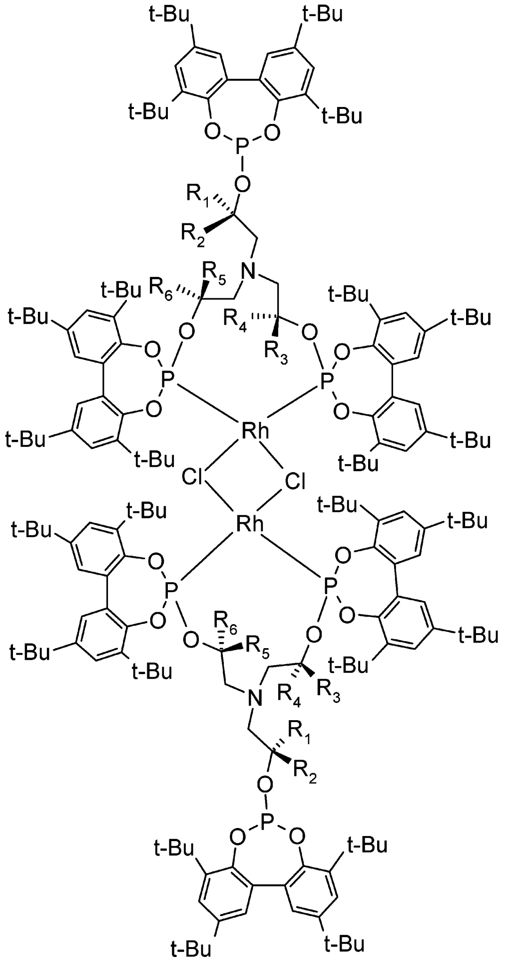
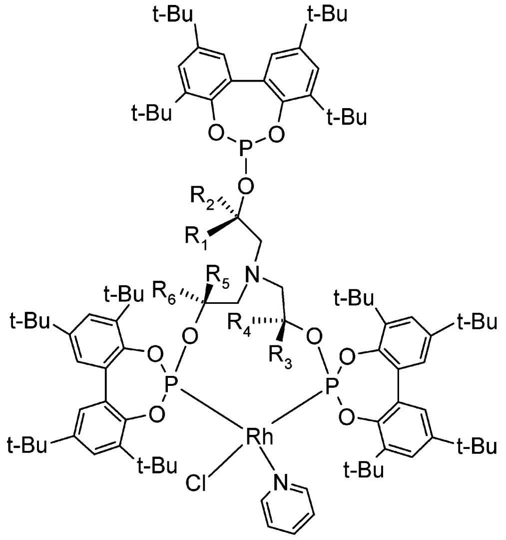
(27) Anet, F. A. L.; Yavari, I. *J. Am. Chem. Soc.* **1977**, *99*, 6986.

tivity has been observed in the synthesis of similar sterically congested molecules.[28] In the (*aR**,*aR**,*aS**) atropisomer of **3**, as in (*R*,*R*,*S*)-**7**, the phosphorus atoms are not interchanged by either a C_n or an S_n operation and are diastereotopic. Caution must be exercised in the interpretation of the accuracy of ratios determined by integrating peak areas of ^{31}P resonances, however, because the relaxation times of nonequivalent P atoms are often significantly different.[29]

Metal Complexation. Previously we reported Rh(I) complexes of both **3** and (*S*,*S*,*S*)-**7**, and their use as ligands for the hydrosilation of ketones.[12] For both **3** and (*S*,*S*,*S*)-**7**, the NMR spectral data are consistent with a metal complex in which two phosphorus atoms are bonded to Rh(I) and one phosphorus atom is noncoordinated.[12] The metal complexes **8a**,**b** with the suggested dimeric structures illustrated were obtained by the reaction of chloro(1,5-cyclooctadiene)rhodium(I) dimer with either **3** or (*S*,*S*,*S*)-**7**, respectively. For example, in the ^{31}P{^{1}H} NMR (C_6D_6) spectrum of complex **8b** formed by the reaction of (*S*,*S*,*S*)-**7** with chloro(1,5-cyclooctadiene)rhodium(I) dimer, a singlet and a doublet are observed at δ 146.6 and 125.5 ($^1J_{PRh}$ = 323 Hz), whose peak areas integrated in a 1:2 ratio, respectively. The observation of $^1J_{PRh}$ coupling in the ^{31}P{^{1}H} NMR spectrum of complexes **8a**,**b** precludes rapid exchange of phosphorus at rhodium on the NMR time scale. This must be the case because rapid exchange would result in a loss of the observed coupling. Specifically, coupling is lost in an exchanging system when $T_e^{-1} > J$, where T_e is the lifetime at a particular site and J is the coupling constant in hertz.[30] The assignment of a dimeric structure for these complexes was further supported by the formation of the monomeric complexes **9a**,**b** by the reaction of **8a**,**b** with pyridine, respectively.[12] If the structure of the complexes **8a**,**b** is that illustrated, further addition of chloro(1,5-cyclooctadiene)rhodium(I) dimer to complexes **8a**,**b** would be expected to lead to the disappearance of the signal for the uncomplexed phosphorus atom in the ^{31}P{^{1}H} NMR spectra. This was found to be the case. For example, addition of chloro(1,5-cyclooctadiene)rhodium(I) dimer to **8a** [^{31}P{^{1}H} NMR(C_6D_6): δ 138.5 (s), 123.4 (d, $^1J_{PRh}$ = 324 Hz)] led to the disappearance of the signal at δ 138.5 with the formation of a new complex with all phosphorus atoms coupled to Rh(I) [δ 122.9 (d, $^1J_{PRh}$ = 328 Hz), 125.8 (d, $^1J_{PRh}$ = 268 Hz)].



8a R_1 = H; R_2 = H; R_3 = H; R_4 = H; R_5 = H; R_6 = H
8b R_1 = CH_3; R_2 = H; R_3 = CH_3; R_4 = H; R_5 = CH_3; R_6 = H
8c R_1 = CH_3; R_2 = H; R_3 = H; R_4 = CH_3; R_5 = H; R_6 = CH_3



9a R_1 = H; R_2 = H; R_3 = H; R_4 = H; R_5 = H; R_6 = H
9b R_1 = CH_3; R_2 = H; R_3 = CH_3; R_4 = H; R_5 = CH_3; R_6 = H
9c R_1 = CH_3; R_2 = H; R_3 = H; R_4 = CH_3; R_5 = H; R_6 = CH_3

However, if the same structure is obtained in the case of the reaction of (*R*,*R*,*S*)-**7** with chloro(1,5-cyclooctadiene)rhodium(I) dimer, at least two different complexes would be anticipated. This would be the case because Rh(I) could be bonded to two phosphorus atoms wherein the absolute configurations of the stereocenters in the 2-propyloxy substituents bonded to phosphorus could be either the same (both *R*) or different (*R* and *S*). In the ^{31}P{^{1}H} NMR (C_6D_6)

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(28) Pastor, S. D.; Hyun, J. L.; Odorisio, P. A.; Rodebaugh, R. K. *J. Am. Chem. Soc.* **1988**, *110*, 6547.

(29) Shortt, A. B.; Burham, L. J.; Mosher, H. S. *J. Org. Chem.* **1983**, *48*, 3125.

(30) Abragam, A. *The Principles of Nuclear Magnetism*; Clarendon Press: London, 1961; p 308.

spectrum of the reaction of (*R*,*R*,*S*)-**7** with chloro(1,5-cyclooctadiene)rhodium(I) dimer, a major component is observed exhibiting a singlet and a doublet at δ 148.8 and 126.0 ($^1J_{PRh} = 322$ Hz), respectively. Additional signals are apparent in the $^{31}P\{^1H\}$ NMR spectrum including starting (*R*,*R*,*S*)-**7** along with several other minor components.

The major component observed in the $^{31}P\{^1H\}$ NMR (C_6D_6) spectrum of the reaction of (*R*,*R*,*S*)-**7** with chloro(1,5-cyclooctadiene)rhodium(I) dimer is assigned to complex **8c** illustrated. The observation of isochronous phosphorus atoms bonded to Rh(I) in the $^{31}P\{^1H\}$ NMR spectrum of **8c** suggests that a single diastereomeric complex is dominant in solution in which Rh(I) is bonded to two phosphorus atoms wherein the absolute configurations of the stereocenters in the 2-propyloxy substituents bonded to phosphorus are both *R*. This suggestion is supported by the observation of isochronous phosphorus atoms bonded to Rh(I) in the $^{31}P\{^1H\}$ NMR spectrum of complex **8b**, where in all cases the absolute configuration of the 2-propyloxy substitutents bonded to phosphorus must be *S*. In the $^{31}P\{^1H\}$ NMR spectrum of one minor species, a doublet of doublets is observed at δ 116.3 ($^1J_{PRh} = 275$ Hz; $^2J_{PP'} = 45$ Hz). Additional broad signals are observed at δ 134.0, 126.2, 125.6, 124.0, and 122.9, which suggests additional exchanging components are present. This suggestion is further supported by the fact that integration of the signals due to these minor components changes upon standing. The variation of the molar ratio of (*R*,*R*,*S*)-**7** to chloro(1,5-cyclooctadiene)rhodium(I) dimer from 3:1 to 1:1 shows the appearance and disappearance of both signals due to uncoordinated phosphorus atoms as well as other minor components present.

In the $^{31}P\{^1H\}$ NMR (C_6D_6) spectrum of the complex formed by addition of pyridine to **8c**, a major species exhibiting a singlet and two AB quartets at δ 147.0 and 125.1 ($^1J_{PRh} = 331$ Hz; $^2J_{PP'} = 72$ Hz) and δ 134.6 ($^1J_{PRh} = 285$ Hz; $^2J_{PP'} = 72$ Hz), respectively, whose peak areas integrated in a 1:1:1 ratio, is observed. The $^{31}P\{^1H\}$ NMR spectrum of the major component obtained was consistent with structure **9c** illustrated. In addition, signals due to minor components are observed with coupling of phosphorus to rhodium, and in several cases P−P coupling of nonequivalent phosphorus atoms.

Asymmetric Hydrosilations. The availability of both (*S*,*S*,*S*)-**7** and (*R*,*R*,*S*)-**7** that possess both a stereocenter and stereoaxes afforded the opportunity to assess the concept of cooperativity in asymmetric hydrosilation reactions.[31] Previously we communicated that the hydrosilation of acetophenone with diphenylsilane using the catalyst formed from (*S*,*S*,*S*)-**7** with chloro(1,5-cyclooctadiene)rhodium(I) dimer gave (*R*)-*sec*-phenethyl alcohol in 81% ee. As noted previously by van Leeuwen[6f] for hydroformylation reactions using chiral seven-membered phosphite ligands, the high reaction stereoselectivity observed suggests that there is a cooperative effect in the stereoselective transition state between the stereocenters and stereoaxes in the coordinated ligand, a manifestation of the concept of chiral cooperativity.[13] The high enantioselectivity obtained using (*S*,*S*,*S*)-**7** as a chiral ligand suggests that the absolute configuration of the stereocenter and stereoaxis in the stereoselective transition state is that required to achieve high stereoselectivity.

Although the elegant work of Halpern[32] has shown that the predominant species observed in solution is not necessarily that involved in the stereoselective transition state, both the solid-state and NMR spectral data obtained in this study suggest that a significant difference in reaction stereoselectivity would be expected using (*R*,*R*,*S*)-**7** as a chiral ligand. Consistent with these expectations, the hydrosilation of acetophenone using a catalyst prepared from (*R*,*R*,*S*)-**7** with chloro(1,5-cyclooctadiene)rhodium(I) dimer gave (*R*)-*sec*-phenethyl alcohol in only 5% ee. The absolute stereochemistries of the stereocenter and stereoaxis in the enantioselective transition state using (*R*,*R*,*S*)-**7** as a ligand are clearly noncooperative (mismatched).

Conclusions

The achiral and chiral tripodal phosphorus ligands **3** and **7** were fully characterized by X-ray crystallography. Both ligands were shown to exhibit solid-state polymorphism, which differed both in the conformation of the exocyclic linking groups and in atropisomerism in the seven-membered dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings. Two solid-state conformers were observed for the chiral ligand (*S*,*S*,*S*)-**7**. In conformer A, (*aS*,*aS*,*aS*,*S*,*S*,*S*)-**7**, and conformer B, (*aR*,*aR*,*aR*,*S*,*S*,*S*)-**7**, significant differences are observed for the O−P−O bond angles about phosphorus, which are suggested to be the result of steric interactions with the stereogenic and chirotopic carbon atom two bonds removed. These observed differences in the geometry about phosphorus suggest that the chiral environment about the metal would be necessarily different if ligand (*S*,*S*,*S*)-**7** with the geometry found in either conformer A or conformer B was coordinated to a metal in the enantioselective transition state. Furthermore, the imposed geometries about phosphorus due to the stereocenter would interact in either a cooperative or a noncooperative manner with the influence of the stereoaxis in the dibenzo[*d*,*f*][1,3,2]dioxaphosphepin ring. These suggestions are supported by the stereoselectivity observed using the chiral ligands (*R*,*R*,*S*)-**7** and (*S*,*S*,*S*)-**7** in asymmetric hydrosilation reactions. In the case of (*S*,*S*,*S*)-**7**, the confor-

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(31) For an example of an asymmetric hydrosilation reaction using a chiral phosphite ligand, see: (a) Babin, J. E.; Whiteker, G. T. U.S. Patent 5,360,938; *Chem. Abstr.* **1995**, *122*, 186609. For recent work on catalytic hydrosilation reactions, see: (b) Dinh, L. V.; Gladysz, J. A. *Tetrahedron Lett.* **1999**, *40*, 8995. (c) Heldmann, D. K.; Seebach, D. *Helv. Chim. Acta* **1999**, *82*, 1096. (d) Moreau, C.; Frost, C. G.; Murrer, B. *Tetrahedron Lett.* **1999**, *40*, 5617. (e) Bideau, F. L.; Henique, J.; Samuel, E.; Elschenbroich, C. *Chem. Commun. (Cambridge)* **1999**, 1397. (f) Yun, J.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 5640. (g) Tsuruta, H.; Imamoto, T. *Tetrahedron: Asymmetry* **1999**, *10*, 877. (h) Kuwano, R.; Uemura, T.; Saitoh, M.; Ito, Y. *Tetrahedron Lett.* **1999**, *40*, 1327. (i) Nagashima, H.; Suzuki, A.; Iura, T.; Ryu, K.; Matsubara, K. *Organometallics* **2000**, *19*, 3579. (j) Son, S. U.; Paik, S. J.; Chung, Y. K. *J. Mol. Catal. A* **2000**, *151*, 87. (k) Kuwano, R.; Sawamura, M.; Shirai, J.; Takahashi, M.; Ito, Y. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 485. (l) Smith, A. R.; Bruno, J. W.; Pastor, S. D. *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, *177*, 479. (m) Castanet, A.-S.; Colobert, F.; Broutin, P.-E.; Obringer, M. *Tetrahedron: Asymmetry* **2002**, *13*, 659. (n) Jensen, J. F.; Sørensen, H. O.; Johannsen, M. *J. Org. Chem.* **2003**, *68*, 1258.

(32) For an excellent review of this work, see: Halpern, J. *Asymmetric Synthesis*; Academic Press: New York, 1985; Vol. 5, Chapter 2.

mational analysis of the solid-state conformations observed, (a*S*,*aS*,*aS*,*S*,*S*,*S*)-**7** and (a*R*,*aR*,*aR*,*S*,*S*,*S*)-**7**, respectively, supports the suggestion that the communication between the stereocenters and stereoaxes leading to chiral cooperativity in the stereoselective transition state is primarily steric in nature.

Experimental Section

All melting points were determined in open capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR (300.08 and 499.84 MHz) spectra were obtained on a Varian model Gemini-300, Unity-500, or Unity-INOVA 500 spectrometer. ^{13}C NMR (125.70 MHz) spectra were obtained on a Varian model Unity-INOVA 500. ^{31}P NMR (202.33 and 121.47 MHz) spectra were obtained on a Varian model Unity-500, Unity-INOVA 500, or Gemini-300 spectrometer. All ^{31}P and ^{31}P{^{1}H} chemical shift values (proton coupled and decoupled, respectively) are reported in parts per million relative to that of 85% phosphoric acid (external), where a positive sign is downfield from the standard. Significant ^{1}H NMR spectral 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; ddt, doublet of doublets of triplets), atom assignments, coupling constant in hertz, and number of protons. IR spectra were obtained on a Bruker model Vector 22. Merck silica gel 60 (200−400 mesh) was used for column chromatography. MS spectra were obtained on a Perspective Biosystems Voyager DE-STR matrix-assisted laser desorption ionization mass spectrometer (MALDI TOF) equipped with a 337 nm N_2 laser and a time-of-flight analyzer. The instrument was operated in the positive ion reflector mode with an accelerating voltage of 24 900 V. The samples were prepared by depositing a methylene chloride solution of the substrate onto a gold-metal-coated sample plate. 2-Benzotriazol-2-yl-4-methylphenol was deposited as a matrix, and silver trifluoroacetate (11 mg·mL^{-1} acetonitrile) was used as a catonization agent. Merck precoated (0.25 mm) silica gel F-254 plates were used for TLC. Reagents were purchased from commercial laboratory supply houses. Toluene and triethanolamine were dried over 4 Å molecular sieves prior to use. Reactions were carried out in a flame-dried apparatus under a dry inert atmosphere of nitrogen. Elemental analyses were performed by the Analytical Research Department, Ciba Specialty Chemicals. Calculations were performed using MacroModel version 7.0 and Spartan version 5.1 on an SGI Octane or DEC Alphaserver 4000 workstation.

Tri{2,2′,2″-Tris[(2,4,8,10-tetrakis(1,1-dimethylethyl)dibenzo-[*d*,*f*][1,3,2]dioxaphosphepin-6-yl)oxy]ethyl}amine (3). To a solution of phosphorus(III) chloride (6.87 g, 50 mmol) and triethylamine (15.18 g, 150 mmol) in 100 mL of toluene maintained at 5 °C was added dropwise over 20 min a solution of **1** (20.53 g, 50 mmol) in 80 mL of toluene (warmed to effect solution). The reaction mixture was allowed to warm to room temperature, and the resultant mixture was stirred overnight at room temperature. The reaction mixture was heated to 45 °C for 4 h, and then to the resultant reaction mixture cooled to 5 °C was added triethanolamine (2.49 g, 17 mmol). The reaction mixture was stirred overnight at room temperature, and then the resultant suspension of triethylamine hydrochloride was removed by filtration. The volatiles were removed in vacuo, and the residue was recrystallized from a mixture of acetonitrile (800 mL) and toluene (50 mL) to give 9.04 g (37%) of a white solid. Form I was obtained by recrystallization from ethyl acetate, and form II was obtained by recrystallization from a mixture of acetone and toluene in a ratio of 8:2: mp 160−163 °C (form I), 202−203 °C (form II); ^{31}P{^{1}H} NMR ($CDCl_3$) (202.36 MHz) δ 134.9; ^{1}H NMR ($CDCl_3$) (499.85 MHz) δ 1.32 (s, 54 H), 1.42 (s, 54 H), 2.62 (t, $^{3}J_{HCCH} = 6.4$ Hz, 6H), 3.71 (dt, $^{3}J_{HCCH} = 6.4$ Hz, $^{3}J_{POCH} = 6.9$ Hz, 6 H), 7.14 (d, $^{4}J_{HCCCH} = 2.5$ Hz, 3 H), 7.40 (d, $^{4}J_{HCCCH} = 2.5$ Hz, 3 H); ^{13}C{^{1}H} NMR ($CDCL_3$) (125.69 MHz) δ 31.1 (d, C*C*H_3, $^{5}J_{PC} = 2.7$ Hz), 31.5 (s, C*C*H_3), 34.6 (s, *C*CH_3), 35.3 (s, *C*CH_3), 54.8 (d, $^{3}J_{PC} = 2.9$ Hz, NCH_2), 62.4 (s, $POCH_2$), 124.1 (s), 126.5 (s), 132.6 (d, $^{3}J_{PC} = 3.6$ Hz), 139.8 (s), 146.1 (d, $^{2}J_{PC} = 5.8$ Hz), 146.3 (s); MS (MALDI TOF) *m*/*z* 1570.80 (calcd 1570.82) (M + Ag). Anal. Calcd for $C_{90}H_{132}NO_9P$: C, 73.79; H, 9.08; N, 0.96. Found: C, 73.89; H, 8.78; N, 1.06.

Form I Crystallographic Data. Suitable crystals for X-ray analysis were grown from ethyl acetate. Crystal data: $C_{90}H_{132}NO_9P_3$; fw = 1464.96; crystal size (mm) 0.3 × 0.3 × 0.6; crystal system monoclinic; cell parameters $a = 20.070(10)$ Å, $b = 17.477(2)$ Å, $c = 27.620(3)$ Å, and $\beta = 93.050(10)°$; $V = 9674.5(14)$ Å^3; space group $P2_1/n$; $d_{calcd} = 1.006$ Mg·m^{-3}; $Z = 4$; data collection on a Siemens R3m/V diffractometer; Cu Kα ($\lambda = 1.54178$ Å) radiation; highly oriented graphite crystal monochromator; scan type $2\theta-\theta$; 2θ range 3.15−115.0°; number of observed reflections 9094 ($I > 3.0\sigma(I)$); number of parameters 878; $R = 0.115$, $R_w = 0.169$; refinement method full-matrix least-squares; hydrogen atoms riding model, fixed isotropic *U*; maximum density in final difference map (e Å^{-3}) 1.02; Siemens SHELXTL PLUS (VMS).

Form II Crystallographic Data. Suitable crystals for X-ray analysis were grown from acetone/toluene. Crystal data: $C_{90}H_{132}NO_9P_3$; fw = 1464.96; crystal size (mm) 0.5 × 0.3 × 0.2; crystal system triclinic; cell parameters $a = 12.493(1)$ Å, $b = 19.701(2)$ Å, $c = 21.027(2)$ Å, $\alpha = 116.23(1)°$; $\beta = 100.15(1)°$, and $\gamma = 91.07(1)°$; $V = 4542$ Å^3; space group $P\bar{1}$; $d_{calcd} = 1.072$ Mg·m^{-3}; $Z = 2$; data collection on a NONIUS CAD4 automatic diffractometer; Cu Kα ($\lambda = 1.5418$ Å) radiation; graphite monochromator; scan type $2\theta-\theta$; 2θ range 3−50°; number of observed reflections 9672 ($I > 3.0\sigma(I)$); number of parameters 928; $R = 0.083$, $R_w = 0.090$; refinement method full-matrix least-squares with anisotropic displacement parameters; hydrogen atom positions were calculated assuming normal geometry and not refined; maximum density in final difference map (e Å^{-3}) 0.91; Siemens SHELXS.

(*S*,*S*,*S*)-Tri{2,2′,2″-tris[(2,4,8,10-tetrakis(1,1-dimethylethyl)-dibenzo[*d*,*f*][1,3,2]dioxaphosphepin-6-yl)oxy]propyl}amine [(*S*,*S*,*S*)-7]. To a solution of (*S*,*S*,*S*)-tri-2-propanolamine (1.5 g, 9.1 mmol) and triethylamine (2.7 g, 27 mmol) in 20 mL of toluene was added dropwise a solution of **2** (13.0 g, 27 mmol) in 50 mL of toluene. The reaction mixture was stirred for 16 h at room temperature and then the resultant precipitate removed by filtration. The volatiles were removed in vacuo, and the residue was purified by trituration with acetonitrile (100 mL) followed by crystallization from an 8:2 mixture of acetonitrile/toluene to give 7.0 g (51%) as a white crystalline solid: mp 187−188 °C; $[\alpha]^{25}$ −72.49 (*c* 1.0, $CHCl_3$); ^{31}P{^{1}H} NMR ($CDCl_3$) (202.36 MHz) δ 145.2; ^{1}H NMR ($CDCl_3$) (499.85 MHz) δ 1.16 (d, 9 H), 1.33 (s, 27 H), 1.34 (s, 27 H), 1.45 (s, 27 H), 1.46 (s, 27 H), 2.30 (dd, $^{2}J_{HCH} = 12.8$ Hz, 3 H), 2.64 (dd, $^{2}J_{HCH} = 12.8$ Hz, 3 H), 4.28 (dd, $^{3}J = 10.1$ Hz, $^{3}J = 3.8$ Hz, 3 H), 7.14 (d, 3 H), 7.15 (d, 3 H), 7.41 (d, 6 H). Anal. Calcd for $C_{93}H_{138}NO_9P_3$: C, 74.12; H, 9.23; N, 0.93. Found: C, 73.90; H, 9.29; N, 0.86.

Suitable crystals for X-ray analysis were grown from THF/acetonitrile. Crystal data: $C_{93}H_{138}NO_9P_3$; fw = 1506.96; crystal size (mm) 0.62 × 0.32 × 0.03; crystal system rhombohedral; cell parameters $a = b = 25.991(3)$ Å, $c = 24.649(3)$ Å, and $\gamma = 120°$; $V = 14420(3)$ Å^3; space group $R\bar{3}$ (hexagonal axes); $d_{calcd} = 1.041$ g·m^{-3}; $Z = 6$; data collection on a NONIUS CAD4 automatic diffractometer; Cu Kα ($\lambda = 1.54178$ Å) radiation; graphite monochromator; scan type $2\theta-\theta$; 2θ range 3−70°; number of observed reflections 9871 ($I > 3.0\sigma(I)$); number of parameters 637; $R = 0.091$; refinement method full-matrix least-squares (SHELXL); hydrogen atom positions calculated assuming normal geometry and not refined; Siemens SHELXS.

(*R*,*R*,*S*)-Tri{2,2′,2″-tris[(2,4,8,10-tetrakis(1,1-dimethylethyl)dibenzo[d,f][1,3,2]dioxaphosphpin-6-yl)oxy]propyl}amine [(*R*,*R*,*S*)-7]. Synthesis of the Alkanolamine Intermediate (*R*,*R*,*S*)-Tri-2-propanolamine [(*R*,*R*,*S*)-6]. To a solution of 1.41 g (24 mmol) of (*R*)-(+)-propylene oxide in 4 mL of toluene was added 0.83 g (12 mmol) of (*S*)-(−)-2-propanolamine at ambient temperature. After 16 h, the toluene was removed in vacuo to give 1.9 g (82.6% yield) of a white solid: mp 184−186 °C; $[\alpha]^{25}$ +3.68 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) (499.85 MHz) δ 1.12 (d, $^3J_{HCCH} = 6.19$ Hz, 3 H), 1.13 (d, $^3J_{HCCH} = 6.2$ Hz, 6 H), 2.46 (dd, $^2J_{HCH} = 13.6$ Hz, $^3J_{HCCH} = 10.3$ Hz, 2 H), 2.53 (dd, $^2J_{HCH} = 13.7$ Hz, $^3J_{HCCH} = 9.2$ Hz, 1 H), 2.61 (dd, $^2J_{HCH} = 13.7$ Hz, $^3J_{HCCH} = 3.8$ Hz, 1 H), 2.62 (dd, $^2J_{HCH} = 13.6$ Hz, $^3J_{HCCH} = 2.7$ Hz, 2 H), 3.69 (br s, 3 H), 3.83 (m, 3 H).

Synthesis of (*R*,*R*,*S*)-7. By the procedure used to prepare (*S*,*S*,*S*)-**7**, (*R*,*R*,*S*)-**7** was prepared from 1.85 g (9.7 mmol) of (*R*,*R*,*S*)-**6**, 4 mL (29.1 mmol) of triethylamine, and 13.8 g (29.1 mmol) of **2** in 60 mL of toluene (24 h at ambient temperature). The product was purified by trituration with 150 mL of acetonitrile followed by crystallization from a 9:1 mixture of acetonitrile/toluene to give 11.0 g (75.2%) as a white crystalline solid: mp 184−186 °C; $^{31}P\{^1H\}$ NMR (C_6D_6) (202.36 MHz) δ 145.2 (s), 144.9 (s); ^1H NMR ($CDCl_3$) (499.85 MHz) δ 1.08 (d, $^3J_{HCCH} = 6.2$ Hz, 3 H), 1.27 (s, 18 H), 1.28 (s, 36 H), 1.29 (d, $^3J_{HCCH} = 6.3$ Hz, 6 H); 1.58 (s, 18 H), 1.60 (s, 36 H), 2.51 (dd, $^3J_{HCCH} = 4.2$ Hz, $^2J_{HCH} = 14.0$ Hz, 1 H), 2.58 (dd, $^3J_{HCCH} = 7.9$ Hz, $^2J_{HCH} = 13.4$ Hz, 2 H), 2.67 (dd, $^3J_{HCCH} = 6.4$ Hz, $^2J_{HCH} = 14.0$ Hz, 1 H), 2.81 (dd, $^3J_{HCCH} = 4.7$ Hz, $^2J_{HCH} = 13.2$ Hz, 2 H), 4.62 (m, 1 H), 4.56 (m, 2 H), 7.34 (dd, $^4J_{HCCCH} = 2.0$ Hz, $^5J_{PH} = 2.0$ Hz, 2 H), 7.36 (dd, $^4J_{HCCCH} = 2.5$ Hz, $^5J_{PH} = 4.2$ Hz, 4 H), 7.58 (d, $^4J_{HCCCH} = 2.5$ Hz, 2 H), 7.59 (dd, $^4J_{HCCCH} = 2.3$ Hz, $^5J_{PH} = 0.9$ Hz, 4 H). Anal. Calcd for $C_{93}H_{138}NO_9P_3$: C, 74.12; H, 9.23; N, 0.93. Found: C, 73.91; H, 9.29; N, 0.72

General Procedure for Hydrosilation with Catalyst Prepared from a Rhodium Dimer and TRISPHOS. A solution of (*S*,*S*,*S*)-**7** (602 mg, 0.40 mmol) and chloro(1,5-cyclooctadiene)rhodium(I) dimer (49 mg, 0.20 mmol) in 10 mL of toluene was added to a solution of acetophenone (1.2 mL, 10 mmol) and diphenylsilane (1.9 mL,10 mmol) in 11 mL of toluene. After the reaction mixture was stirred for 6 h at room temperature (complete disappearance of acetophenone), a mixture of 5 mL of 2.5 N aqueous sodium hydroxide and 7 mL of methanol was added. After being stirred for 10 min, the reaction mixture was extracted with diethyl ether (3 × 3 mL), and the combined organic extracts were dried over anhydrous sodium sulfate. The volatiles were removed in vacuo, and the ee of the resultant *sec*-phenethyl alcohol was determined both by ^1H NMR spectroscopy using the chiral solvating agent (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol and by GLC using a Chiraldex B-PM chiral column (30 m × 0.25 mm). The crude alcohol was purified by dissolution in 3 mL of hexane and filtration of any precipitate formed followed by flash chromatography (silica gel, hexane eluent) to give 0.46 g (38%) of (*R*)-*sec*-phenethyl alcohol (81% ee).

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Supporting Information Available: X-ray crystallographic files, in PDB format (**3**, form I) and CIF format [**3**, form II; (*S*,*S*,*S*)-**7**], of the crystal forms of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepins **3** and (*S*,*S*,*S*)-**7** including crystal data, bond angles, bond lengths, and atomic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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