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Sterically Congested Molecules: Synthesis, Characterization, and Unique Spectral Characteristics of Hexa-*tert*-butyl-Substituted Biaryl Bis(1,3,2-oxazaphospholidines)

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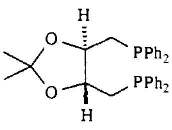
Abstract: The reaction of the alkanolamine **5** with phosphorus trichloride (**6**) gave the cyclic chloridite **7** in either the presence or absence of triethylamine. The reaction of **7** with the sterically hindered sodium phenolates **8a–c** gave the corresponding 2-aryloxy-substituted 1,3,2-oxazaphospholidines **9a–c**. The 2,4-di-*tert*-butyl- and unsubstituted-aryloxy derivatives **9d,e** were obtained by the reaction of **7** with the corresponding phenols **8h,i** using triethylamine as an acid acceptor. Increased shielding at phosphorus (upfield shifts) is observed in the ^{31}P NMR spectra of **9a–e** with a decrease in the steric bulk of the aryloxy groups bonded to phosphorus. The biaryl bis(1,3,2-oxazaphospholidines) **12a,b**, **14a,b**, **16**, and **18** were prepared by the reaction of 2 equiv of **7** with 1 equiv of the corresponding disodium bis(phenolates) **11b,c**, **13a**, **13c**, **15a**, and **17a**, respectively. In the case of the hexa-*tert*-butyl-substituted **12a** and **14b**, the formation of a single diastereomer was observed. In the ^{31}P NMR spectra of **12a** and **14b**, unprecedented long-range P–P ^7J and ^8J coupling of 30.3 and 30.6 Hz, respectively, was observed. Supporting ^{1}H, ^{13}C, and 2D COSY ^{31}P NMR spectra and crystallographic data are discussed. In the solid state, the crystallographic data show that the phosphorus atoms in **12a** and **14b** are chemically nonequivalent. This appears to be the case because of the steric interactions within the hexa-*tert*-butyl-substituted **12a** and **14b**. In **12a**, the aryl–aryl C–C single-bond length (1.511 Å) is significantly longer than that expected for a sp^2–sp^2 single bond (1.48 Å). Similarly, the aryl–ethylidine sp^2–sp^3 C–C single-bond lengths are unequal (1.550 and 1.518 Å, respectively), and one aryl–ethylidine C–C single-bond length is that expected for a sp^3–sp^3 C–C single bond (1.54 Å). The P–O–C$_{\mathrm{ARYL}}$ bond angles in **12a** (131.0 and 134.1°) and **14b** (122.9 and 126.2°) clearly show both the asymmetry and chemical nonequivalence of the phosphorus atoms within these molecules. Compound **12a** represents the first fully characterized example in the literature of a molecule containing both a chiral axis and two chiral P(III) centers. The observed diastereoselectivity and spectral data of **12a** and **14b** are explained on the basis of the severe geometric restraints and the resultant molecular asymmetry that is due to the extreme steric crowding within these molecules. This explanation is supported by the observed spectra and diastereoselectivity of **12b**, **14a**, **16**, and **18** in which long-range P–P coupling is absent. The biaryl bis(dioxaphosphorinane) **21**, which lacks asymmetry at phosphorus, was prepared by the reaction of **11b** with **20**. A single resonance was observed in the ^{31}P NMR spectrum of **21**.

Research efforts in phosphorus chemistry have expanded dramatically in the past 40 years.[1] Aside from the important role that phosphorus plays in biological systems, trivalent phosphorus compounds have achieved an important role as ligands in organometallic complexes.[2] In particular, organophosphorus ligands have played a dominant role in the development of synthetic methodology for the preparation of chiral molecules by asymmetric hydrogenation using transition-metal catalysts.[3] Chiral ligands such as DIOP (**1**), BINAP (**2**), CHIRAPHOS (**3**), and PROLOPHOS (**4**) have frequently been used as chiral auxiliaries in transition-metal catalyzed asymmetric reductions.[4-7]



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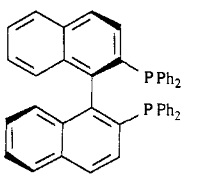

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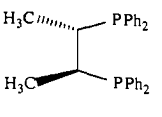

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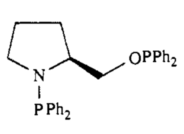

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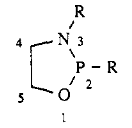

Figure 1. Oxazaphospholidine ring system.

Although the steric effects of ligands on the reactivity of transition-metal complexes are difficult to quantify, Tolman has used the cone angle of a phosphorus ligand to estimate their steric effect.[8] Sterically hindered trivalent phosphorus ligands should

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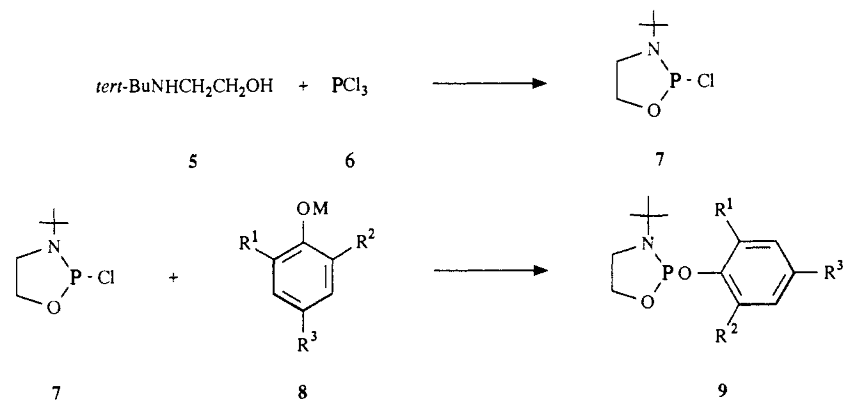
Scheme I



a. $R^1 = R^2 =$ *tert*-Butyl; $R^3 =$ Methyl; M = Na
b. $R^1 = R^2 = R^3 =$ *tert*-Butyl; M = Na
c. $R^1 = R^2 = R^3 =$ Methyl; M = Na
d. $R^1 =$ H; $R^2 = R^3 =$ *tert*-Butyl; M = Na
e. $R^1 = R^2 =$ *tert*-Butyl; $R^3 =$ Methyl; M = H
f. $R^1 = R^2 = R^3 =$ *tert*-Butyl; M = H
g. $R^1 = R^2 = R^3 =$ Methyl; M = H
h. $R^1 =$ H; $R^2 = R^3 =$ *tert*-Butyl; M = H
i. $R^1 = R^2 = R^3 =$ M = H

a. $R^1 = R^2 =$ *tert*-Butyl; $R^3 =$ Methyl
b. $R^1 = R^2 = R^3 =$ *tert*-Butyl
c. $R^1 = R^2 = R^3 =$ Methyl
d. $R^1 =$ H; $R^2 = R^3 =$ *tert*-Butyl
e. $R^1 = R^2 = R^3 =$ H

provide unique coordination spheres for transition-metal-mediated reactions. Indeed, sterically hindered dibenzo[*d,g*][1,3,2]dioxaphosphocins[9] and dibenzo[*d,f*][1,3,2]dioxaphosphepins[10] have recently been claimed to be superior ligands in transition-metal-catalyzed hydroformylation reactions.[11]

The kinetic stabilization of both reactive intermediates and strained molecules[12] by sterically bulky substituents is a well-known tool that we have recently employed to study the chemistry of hydroxyarenesulfenyl chlorides.[13,14] In principle, a similar kinetic stabilization of coordinatively unsaturated metal centers can be achieved by the use of sterically encumbered ligands.[15] The use of properly designed ligands should prevent the oligomerization of coordinatively unsaturated complexes that often occurs in solution.[16]

This paper reports the preparation and characterization of a class of highly sterically hindered bis(1,3,2-oxazaphospholidines). Aside from their potential applications in organometallic catalyses, these sterically congested biaryl bis(1,3,2-oxazaphospholidines) possess intriguing spectral and structural characteristics in their own right. In particular, the observed seven- and eight-bond phosphorus-phosphorus coupling in the ^{31}P NMR spectra of these compounds is the largest reported in the literature. In addition, the first example of a fully characterized molecule containing both a chiral axis and two chiral phosphorus(III) centers is reported.

Results and Discussion

The synthesis of the 1,3,2-oxazaphospholidine ring (Figure 1) by the reaction of an alkanolamine with phosphorus trichloride (**6**) was reported by Martynov et al.[17] Quite recently, the synthetic transformation of 1,3,2-oxazaphospholidine derivatives was used by McGuigan in an elegant synthesis of phospholipids.[18]

Table I. ^{31}P NMR Chemical Shifts of Monoaryloxy-Substituted Oxazaphospholidines

compd	aryl substitution	δ^a
9a	2,6-di-*tert*-butyl-4-methyl	153.0
9b	2,4,6-tri-*tert*-butyl	150.9
9c	2,4,6-trimethyl	135.4
9d	2,4-di-*tert*-butyl	130.0
9e	unsubstituted	134.0

^{a}In benzene-d_6.

The *tert*-butyl-substituted chloridite **7** was prepared by the reaction of 2-(*N*-*tert*-butylamino)ethanol (**5**) with **6** in the presence of triethylamine as an acid acceptor according to the method of Tumanskii et al. (67% distilled).[19] The chloridite **7** could also be prepared by heating a mixture of **5** and **6** in toluene at reflux in the absence of triethylamine, albeit in slightly lower yields (57% distilled). The MS and ^{1}H NMR and ^{31}P NMR spectra were entirely consistent with the structure illustrated.

Monoaryl-Substituted Oxazaphospholidines: Synthesis and Spectral Data. The preparation of sterically hindered phosphorus,[20] silicon,[21] and transition-metal[22] aryloxy derivatives by the reaction of a phenolate anion with either an organometalloid or metal halide has been demonstrated in the literature. Indeed, the reaction of **7** with the phenolates **8a-c** gave the corresponding 2-aryloxy-substituted oxazaphospholidines **9a-c** in good yields (Scheme I). In the case of the less sterically hindered phenol **8h**, the use of the phenolate **8d** was not required.[20] The oxazaphospholidine **9d** was synthesized in satisfactory yield from **7**, prepared in situ, and **8h** with triethylamine as an acid acceptor (63% distilled). Interestingly, the same procedure using phenol **8i** gave a mixture of **9e** and the ring-opened compound **10a**.

The structure of **10a** was inferred from the NMR spectral data. In the ^{31}P NMR spectrum of **10a**, a resonance was observed at

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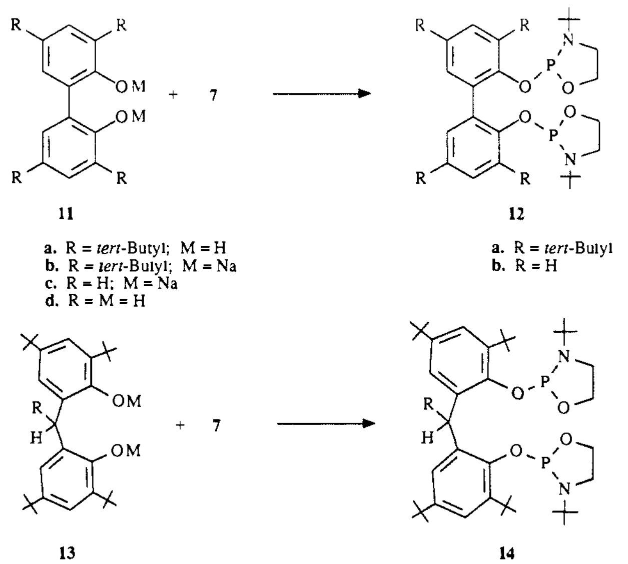
Scheme II



11

a. R = *tert*-Butyl; M = H
b. R = *tert*-Butyl; M = Na
c. R = H; M = Na
d. R = M = H

12

a. R = *tert*-Butyl
b. R = H

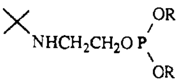
13

a. R = H; M = Na
b. R = H = M = H
c. R = Methyl; M = Na
d. R = Methyl; M = H

14

a. R = H
b. R = Methyl

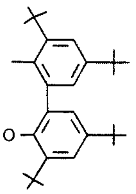
δ 136.6, which is in the region expected for a phosphite.[23,24] In the ^1H NMR spectrum, a triplet and a doublet of triplets resonance were observed at δ 2.80 and 2.91 that were assigned to the methylene protons adjacent to the nitrogen and phosphorus atoms, respectively. Added complexity in the ^1H NMR spectrum of **10a** due to either the presence of an oxazaphospholidine ring or asymmetry at phosphorus was absent. The spectral data were fully in accord with proposed structure **10a**.



10

a. R = Phenyl

b. R =



It is likely that **10a** was formed by the reaction of **8i** with the uncyclized adduct of **5** with **6** because this experiment involved the use of **7** prepared in situ, although a ring-opening reaction cannot be excluded. That this is the case is supported by the observation that the reaction of **7** with the sodium phenolate of **8i** gave only **9e** (73% distilled).

A general trend toward increased shielding at phosphorus (upfield shift) is observed in the ^{31}P NMR spectra of **9a–e** (Table I) with a decrease in the steric bulk of the aryloxy groups bonded to phosphorus, albeit the chemical shifts of **9d** and **9e** are not in the expected order. Although a downfield shift of the phosphorus resonance with increasing steric crowding at phosphorus has been previously reported for phosphines, which is due to changes in the hybridization of phosphorus,[8,25] this study is a particularly clear example for a structurally similar class of phosphoramidites.

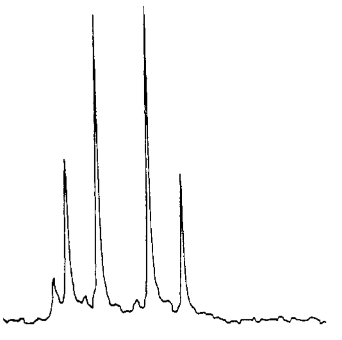


Figure 2. ^{31}P {^1H} NMR (benzene-d_6) spectrum of **12a**.

Biaryl Bis(oxazaphospholidine) Synthesis. The reaction of **11b** with 2 equiv of **7** in tetrahydrofuran (THF) gave a mixture of a single diastereomer of **12a** (vide infra) and **10b** (Scheme II). The diadduct **12a** could be obtained in pure form by trituration followed by recrystallization from hexane. From the recrystallization mother liquor, **10b** could be obtained as the major component contaminated by ~12% **12a**.

The structure of **10b** rests upon the following data. In the ^1H NMR spectrum of **10b**, a triplet and a doublet of triplets resonance were observed at δ 2.67 and 4.12 that were assigned to the methylene protons adjacent to the nitrogen and oxygen atoms, respectively. The observed multiplicity and chemical shift of the resonance at δ 4.12 strongly suggests that the oxygen atom is bonded to phosphorus. The coupling of these methylene protons to each other was confirmed by homonuclear proton decoupling experiments. Additional resonances were observed at δ 2.77, 3.09, 3.91, and 4.49 in the ^1H NMR spectrum that are consistent with an intact oxazaphospholidine ring. The integration of the ^1H NMR spectral resonances was consistent with the proposed structure.

Further support for the structure of **10b** was provided by the ^{31}P NMR spectrum. Two resonances were observed in the ^{31}P NMR spectrum at δ 137.6 and 138.1 that were assigned to the nonequivalent phosphorus atoms of the oxazaphospholidine ring and acyclic phosphorus atom, respectively. The integrated peak areas were in the approximate 2:1 ratio expected for the proposed structure. Caution, however, must be exercised in the interpretation of integrated ^{31}P NMR spectral resonances, because the relaxation time of nonequivalent phosphorus atoms are often significantly different.[26] The ^{13}C NMR spectrum of **10b** displayed the complexity expected for the structure illustrated.

Interestingly, the ^{31}P NMR spectrum of the crude reaction mixture showed that **12a** and **10b** were the major components. Other components assignable to diastereomers of **12a** were not observed in the ^{31}P NMR spectrum (vide infra).

The unsubstituted-bisaryl compound **12b** was prepared in a similar manner by the reaction of **11c** with 2 equiv of **7**. Analogously, the alkyl- and thio-bridged bis(aryloxyl)oxazaphospholidines **14a,b**, **16**, and **18** were prepared by the reaction of **7** with the corresponding bisphenolate anions **13a**, **13c**, **15a**, and **17a**, respectively (Schemes II and III).

The chloridite **20** was prepared by the method of Emondson.[27] The dioxaphosphorinane **21** was obtained by the reaction of **20** with **11b** (65% recrystallized) (Scheme IV).

Spectral Data and Structure. Surprisingly, in the ^{31}P NMR spectrum of **12a** (Figure 2), four resonances were observed with relative intensities and splittings consistent with an AB quartet. An obvious alternative that the four lines arose from a mixture of diastereomers pressed for an immediate examination.

A total of two asymmetric centers and one chiral axis is expected for compound **12a**. Both phosphorus atoms are chiral because inversion of the lone pair of electrons on phosphorus is known to have a high activation energy. Of particular relevance, Acher

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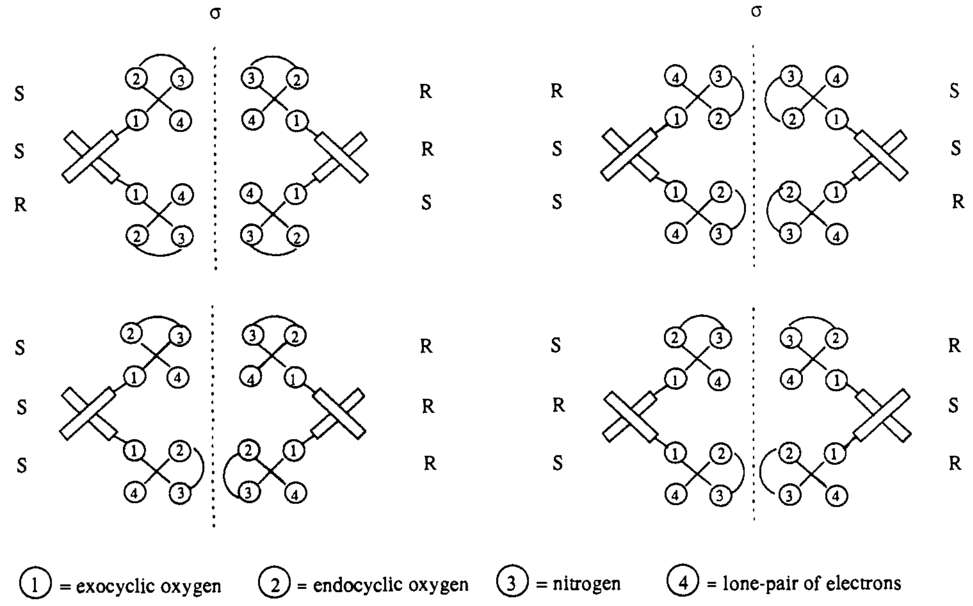
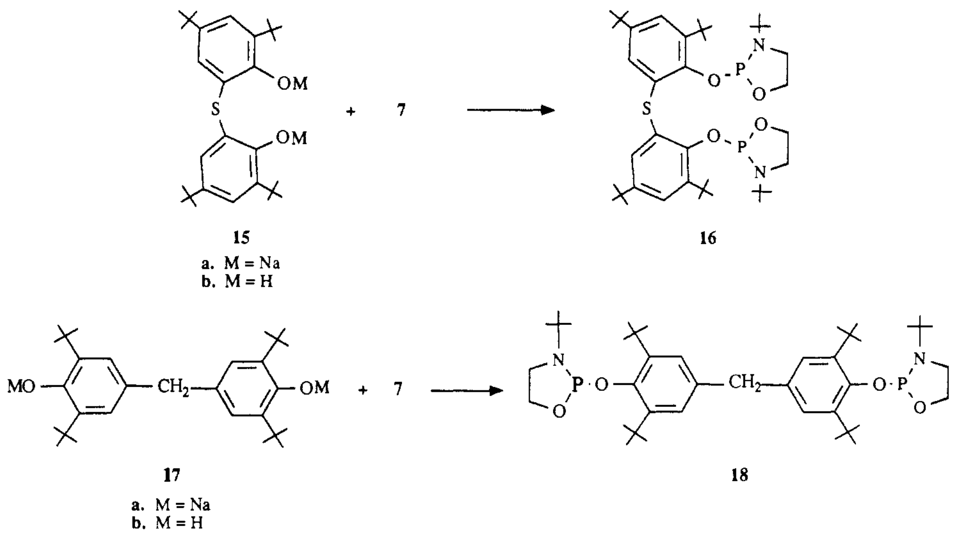
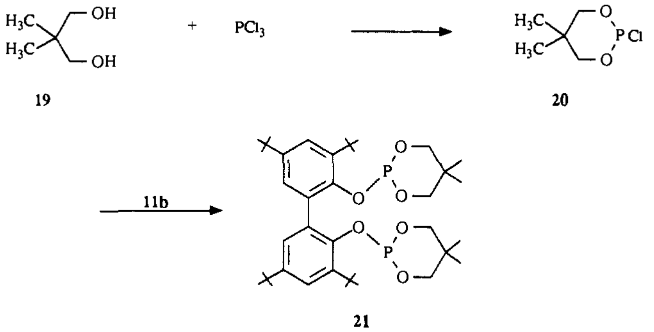


Figure 3. Stereoisomers of **12a**.

Scheme III



Scheme IV



et al. have reported the synthesis of optically active oxazaphospholidines.[28]

The examination of a molecular model of **12a** suggests that rotation about the aryl–aryl C–C single bond should be severely restricted due to the sterically bulky substituents on the aryl rings. Indeed, the resolution of molecules having a chiral axis[29] was demonstrated primarily by the pioneering work of Adams and co-workers.[30] The activation energy for rotation about the single bond in atropisomers can be considerable, as demonstrated, for example, by the work of Hall and Turner.[31]

An analysis[32] of the number of possible stereoisomers of **12a** shows that a maximum of four diastereomers is expected (Figure 3).[32] The observation of four resonances in the ^{31}P NMR spectrum of **12a** could therefore be simply due to a diastereomeric mixture. That this was *not* the case was shown by the fact that the line separations and intensities remained appropriate for an AB quartet ($^{7}J_{PP}$ = 30.3 Hz) at 32.20, 80.96, and 161.92 MHz. A *single* diastereomer was being observed *with two nonequivalent phosphorus atoms coupled to each other with* $^{7}J_{PP}$ = *30.3 Hz*. Seven-bond coupling of this magnitude is unprecedented in the literature. Quite recently, a six-bond coupling between trivalent phosphorus atoms with $^{6}J_{PP}$ = 12 Hz was reported by Szalontai et al.[33,34] Seven- to nine-bond P–P coupling (J = 1.4–7.8 Hz)

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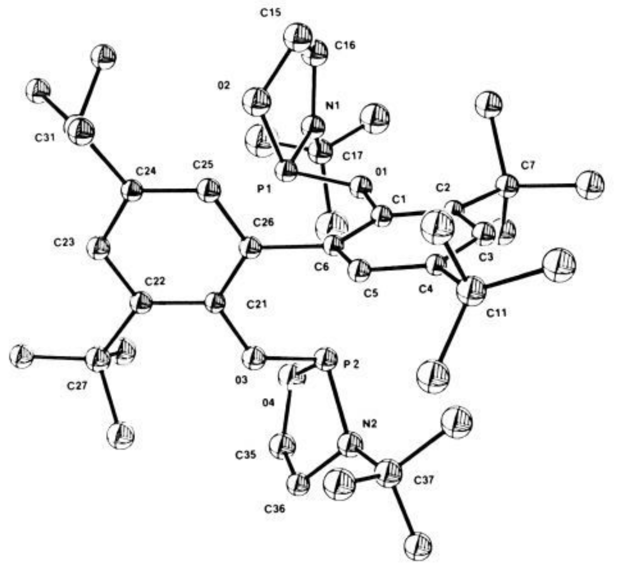

Figure 5. Molecular structure of **12a** (ORTEP diagram).

has only been reported for pentavalent phosphorus atoms.[35]

The coupling of the two phosphorus atoms was further demonstrated by a phosphorus homonuclear 2D COSY NMR experiment (Figure 4; supplementary material). The observation of cross peaks in the 2D COSY NMR spectrum[36] clearly demonstrates the existence of ^7J coupling between the phosphorus atoms.

Although the ^{1}H NMR and elemental analysis were in accord with the structure illustrated, the magnitude of the $^7J_{PP}$ coupling cast serious doubt upon the proposed structure. Indeed, Robert and Weichmann have reported that oxazaphospholidines can undergo acid-catalyzed dimerization to a ten-membered ring.[37] Fortunately, suitable crystals could be grown and an X-ray structure was obtained [Figures 5 and 6 (supplementary material), Table II (supplementary material)] that clearly confirms the oxazaphospholidine structure illustrated.

Caution must be exercised in the comparison of conformations obtained from X-ray structural data with the conformation in solution. Lattice energy and the resultant crystal-packing effects in the solid state can render the solid-state conformation different from that in solution. However, several aspects of the crystallographic data of **12a** suggest an explanation of the observed spectra in solution. The torsional angle defined by the planes of the aryl rings is −100.2°. The P(1)–P(2) interatomic distance is 3.704 Å. The C(6)–C(26) single-bond length is 1.511 (9) Å, compared to an average sp^2–sp^2 bond length of 1.48 Å.[38] For comparison, the central bond length in biphenyl is 1.492 Å.[39] The lengthening of the C(6)–C(26) single bond is presumably steric in nature, being near the average bond length of an sp^2–sp^3 single bond (1.50 Å).[38]

Furthermore, the examination of bonding angles in the crystal structure of **12a** indicates that the phosphorus atoms are clearly chemically nonequivalent. The P(2)–O(3)–C(21) and P(1)–O(1)–C(1) bond angles, for example, are 131.0 (4) and 134.1 (4)°, respectively. If these differences in the solid state, which make the entire molecule asymmetric (no C_2 axis of symmetry as in 1,3-dimethylallene), are obtained in solution, not only would both phosphorus atoms be expected to be nonequivalent, but each *tert*-butyl substituent would be expected to be nonequivalent. Indeed, in the 200-MHz ^{1}H NMR spectrum of **12a**, six resonances are observed for the protons of the six nonequivalent *tert*-butyl groups (Figure 7; supplementary material). The doublet resonances observed at δ 1.14 and 1.34 were assigned to the protons of the *tert*-butyl groups bonded to nitrogen with $^4J_{HCCNP} = 1.1$ Hz in both cases.

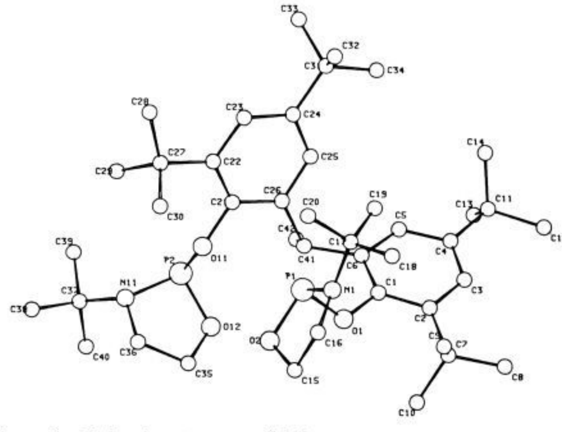

Figure 8. Molecular structure of **14b**.

In the ^{13}C NMR spectrum of **12a**, six different resonances were observed for both the methyl and methine carbon atoms of the six nonequivalent *tert*-butyl groups. Furthermore, distinct resonances were observed for the remaining carbon atoms of the nonequivalent aryl and oxazaphospholidine rings. A molecular ion in the MS of **12a** was observed at 700 mass units. The spectral and analytical data were fully in accord with the proposed structure.

The extreme steric congestion observed in the crystal structure of **12a** provides insight into the observation that only a single diastereomer of **12a** was formed in the reaction of **7** with **11b**. Other diastereomers of **12a**, which might correspond to trace peaks observed in the ^{31}P NMR spectrum of the crude reaction mixture, could be neither isolated nor identified. The steric congestion observed in **12a** suggests that the transition states leading to the formation of the various possible diastereomers of **12a** should have significant differences in energy ($\Delta G^\ddagger$) leading to the observed diastereoselectivity.

The use of steric arguments to rationalize diastereoselectivity in organic chemistry is well documented.[40] Denney et al., for example, reported significant diastereomeric selection in the formation of a relatively simple six-membered cyclic phosphite containing two chiral centers, one of which was at phosphorus.[41] In the present study, no information was obtained as to whether the observed diastereoselectivity was the result of kinetic or thermodynamic control.[40]

Quite interestingly, in the ^{31}P NMR spectrum of the corresponding ethylidine-bridged biaryl oxazaphospholidine **14b**, a similar AB quartet was observed. Again, the question arose as to whether a mixture of diastereomers or a single diastereomer with $^8J_{PP} = 30.6$ Hz was being observed. Eight-bond $^8J_{PP}$ coupling of this magnitude is unprecedented in the literature.

In the case of **14b**, the bridging ethylidine *quaternary* carbon atom provides a tool for probing the structure of the molecule. In particular, in the ^{13}C NMR of **14b**, the resonance for the methine carbon atom connecting both the aryl rings was observed as a doublet of doublets. A reasonable explanation of this observation is that the carbon atom is coupled to two nonequivalent phosphorus atoms with $^4J_{CP} = 17.1$ Hz and $^4J_{CP} = 13.5$ Hz, respectively. That this was indeed the case was demonstrated by

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[34] Szalontai, G.; Bakos, J.; Tôth, I.; Heil, B. *Magn. Reson. Chem.* **1987**, *25*, 761–765.

[35] (a) Ernst, L. *Org. Magn. Reson.* **1977**, *9*, 35–43. (b) Ernst, L. *J. Chem. Soc., Chem. Commun.* **1977**, 375–376. (c) a reviewer has suggested that oxidation of **12a** to the P oxide would provide information as to whether the lone pair of electrons were responsible for the observed large coupling.

[36] For a discussion, see: Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University: Oxford, 1978.

[37] Robert, J. B.; Weichmann, H. *J. Org. Chem.* **1978**, *43*, 3031–3035.

[38] March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley Interscience: New York, 1985; p 18.

[39] Almenningen, A.; Bastiansen, O. *Kgl. Norske Videnskab. Selskabs. Skrifter* **1985**, 1–16; *Chem. Abstr.* **1959**, *53*, 11917.

[40] For a recent discussion, see: Nógrádi, M. *Stereoselective Synthesis*; VCH: Weinheim, 1987.

[41] Denney, D. Z.; Denney, D. B. *J. Am. Chem. Soc.* **1966**, *88*, 1830–1831.

Table IV. Selected Bond Distances (Å) and Angles (deg) for **12a**

Distances			
P1–O1	1.651 (5)	N1–C16	1.468 (11)
P1–O2	1.609 (6)	N1–C17	1.448 (11)
P1–N1	1.674 (6)	N2–C36	1.475 (10)
P2–O3	1.680 (5)	N2–C37	1.468 (11)
P2–O4	1.617 (6)	C6–C26	1.511 (9)
P2–N2	1.685 (7)	C15–C16	1.509 (12)
O1–C1	1.369 (8)	C35–C36	1.498 (14)
O2–C15	1.426 (11)	C1–C6	1.394 (10)
O3–C21	1.401 (8)	C21–C26	1.388 (10)
O4–C35	1.463 (11)		

Angles			
O1–P1–O2	100.9 (3)	O3–P2–N2	99.3 (3)
O1–P1–N1	97.5 (3)	O3–P2–O4	99.7 (3)
O2–P1–N1	93.9 (3)	O4–P2–N2	93.0 (3)
P1–O1–C1	134.1 (4)	P2–O3–C21	131.0 (4)
P1–N1–C17	125.5 (6)	P2–N2–C37	124.2 (5)
P1–N1–C16	112.5 (5)	C36–N2–C37	118.7 (7)
C16–N1–C17	119.5 (6)	P2–N2–C36	110.2 (5)

^{13}C NMR spectra obtained at both 50.31 and 100.50 MHz showing identical coupling.

Upon attainment of suitable crystals, an X-ray structure of **14b** was obtained that confirmed the proposed structure [Figure 8, Table III (supplementary material)]. An examination of the crystallographic data shows that the C(41)–C(6) and C(41)–C(26) bond lengths of 1.550 (7) and 1.518 (8) Å, respectively, are unequal and, in one case, deviate markedly from the average sp^3–sp^2 bond distance of 1.50 Å.[38] The observed bond distance of 1.550 (7) Å of the C(41)–C(6) sp^2–sp^3 single bond is that expected for a sp^3–sp^3 single bond (1.54 Å). The intraatomic P(1)–P(2) distance is 4.502 Å.

The P(1)–O(1)–C(1) and P(2)–O(11)–C(21) bond angles are 122.9 (4) and 126.2 (4)°, respectively. As in the case of **12a**, the crystallographic data are consistent with the observed NMR spectral data in solution. The asymmetry of **14b** (as well as **12a**) explains the complex ^{1}H NMR spectrum observed for the oxazaphospholidine ring protons, because every proton in both oxazaphospholidine rings is nonequivalent. As in the case of **12a**, not only would both phosphorus atoms be expected to be nonequivalent, but each *tert*-butyl substituent would be expected to be nonequivalent. As expected, in the 200-MHz ^{1}H NMR spectrum of **14b**, six resonances are observed for the protons of the six nonequivalent *tert*-butyl groups. The doublet resonances observed at δ 1.03 and 1.31 were assigned to the protons of the *tert*-butyl groups bonded to nitrogen with $^4J_{\mathrm{HCCNP}}$ = 0.5 and 1.0 Hz, respectively.

It should be noted, however, that **14b** contains two asymmetric chiral phosphorus atoms and one pseudoasymmetric bridging ethylidine carbon atom. In such cases, four isomers are expected as in the case of 2,3,4-pentanetriol.[42] Restricted rotation of either aryl–ethylidine C–C single bond (or a requirement for coupled rotation) can, however, create additional asymmetry in the molecule.[43]

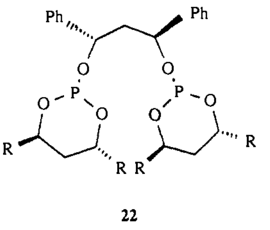
Table V. Selected Bond Distances (Å) and Angles (deg) for **14b**

Distances			
P1–O1	1.682 (4)	P2–O12	1.610 (6)
P1–O2	1.626 (6)	P2–N11	1.686 (8)
P1–N1	1.676 (5)	O11–C21	1.394 (8)
O1–C1	1.395 (9)	O12–C35	1.383 (15)
O2–C15	1.448 (9)	N11–C36	1.453 (11)
N1–C16	1.440 (11)	N11–C37	1.497 (9)
N1–C17	1.490 (11)	C21–C26	1.410 (9)
C1–C6	1.401 (9)	C26–C41	1.518 (8)
C6–C41	1.550 (7)	C35–C36	1.521 (13)
C15–C16	1.479 (13)	C41–C42	1.536 (7)
P2–O11	1.662 (4)		

Angles			
O1–P1–O2	95.3 (2)	O12–P2–N11	94.2 (3)
O1–P1–N1	104.3 (3)	O11–P2–N11	99.2 (2)
O2–P1–N1	92.5 (3)	O11–P2–O12	98.9 (3)
P1–O1–C1	122.9 (4)	P2–O11–C21	126.2 (4)
P1–N1–C16	113.2 (5)	P2–N11–C37	119.6 (4)
C16–N1–C17	119.6 (6)	C36–N11–C37	118.5 (6)
P1–N1–C17	121.3 (5)	P2–N11–C36	107.9 (5)

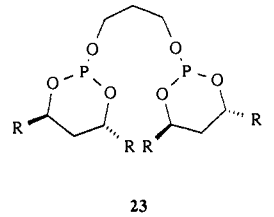
Although prior to this study only a single-crystal structure of an 1,3,2-oxazaphospholidine containing trivalent phosphorus had been reported,[44] the work of both Verkade and Zuckerman provide data for the closely related 1,3,2-diazaphospholidine in which a trigonal-planar geometry at nitrogen and a pyramidal geometry at phosphorus was found.[45,46] Given the posit that trigonal-planar geometry is achieved when the sum of the requisite bonds exceeds 355°,[45] the nitrogen atoms in both **12a** and **14b** approach planarity (Tables IV and V). The phosphorus atoms approach a pyramidal structure, and the sum of the appropriate bond angles for the phosphorus atoms in both **12a** and **14b** are very close to 292°. The sum of the angles about nitrogen vary significantly from 353.1 to 357.5° in **12a** and from 345.9 to 354.1° in **14b**. That these deviations are due to steric interactions in part due to the *tert*-butyl group on nitrogen is supported by the examination of the torsional angles.[47] In **14b**, for example, the C(35)–C(36)–N(11)–C(37) and C(15)–C(16)–N(1)–C(17) torsional angles are 112.7 (7) and 171.6 (7)°, respectively. These crystallographic data are of course consistent with the observed NMR spectral data in solution.

Although the mechanism for the observed magnitude of the $^7J_{\mathrm{PP}}$ and $^8J_{\mathrm{PP}}$ was not investigated, the structural features of the molecule suggest an explanation. From the crystallographic data, the interatomic P(1)–P(2) distances *in the solid state*, 3.704 and 4.502 Å, respectively, are larger than both the sum of the phosphorus covalent radii (covalent radius of P = 1.10 Å) and, in the case of **14b**, the van der Waals radii (van der Waals radius of P = 1.90 Å).[48] Although these distances, especially in the case of **14b**, argue against a through-space contribution to the observed long-range coupling,[49] the average intraatomic distances in solution may be different. The translational and vibrational energy of either **12a** or **14b** in solution may lead to a shortened time-averaged P–P bond distance with a possible through-space contribution to the observed coupling. Such arguments were used by Szalontai and co-workers[34] to explain the large $^6J_{\mathrm{PP}}$ coupling observed in **22** and appear to be a reasonable explanation in the present study.



22

R = Methyl



23

R = Methyl

However, without further study, this explanation for the observation of long-range coupling must be regarded as tenuous

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because a restricted geometry can favor other mechanisms for the long-range transmission of coupling. For example, geometries that favor transmittal of coupling through the π system or the lone pairs of electrons are possible.[35] Of course, more than one mechanism may be operative. The similar magnitude of P-P coupling observed for **12a** and **14b**, which contains a sp^3 bridging-carbon atom separating the π systems, strongly suggests that the observed coupling must be related to the effective solution P-P intraatomic distance regardless of the exact mechanism or mechanisms of coupling. This interpretation is strongly supported in the case of **12a** by the ^{13}C NMR spectrum, where only the *tert*-butyl group carbon atoms of *one* oxazaphospholidine ring are coupled *to both phosphorus atoms* ($^3J_{CP}$ = 10.6 Hz and $^{10}J_{CP'}$ = 0.7 Hz, respectively). The observation of ^{10}J coupling for the methyl carbon atoms of only one of the oxazaphospholidine *tert*-butyl groups strongly suggests that a specific conformation in solution favors a through-space mechanism of coupling.

In the ^{31}P NMR spectrum of **14a**, two singlet resonances were observed at δ 136.6 and 137.1 and $^8J_{PP}$ coupling was absent. The question as to whether either a single diastereomer, with nonequivalent noncoupling phosphorus atoms, or two distinct diastereomers, each with equivalent (or accidentally equivalent) phosphorus atoms, were being observed could be answered by the examination of the proton-decoupled ^{13}C NMR spectrum. In particular, two triplets were observed at δ 37.4 and 37.5 in benzene-d_6 that could be assigned to the briding methylene carbon atoms of the two distinctly different diastereomers. The methylene carbon atom of each diastereomer was coupled to two equivalent oxazaphospholidine phosphorus atoms with $^4J_{CP}$ = $^4J_{CP'}$ = 21.1 Hz. A single diastereomer with two chemically nonequivalent phosphorus atoms would show only one resonance for the bridging methylene carbon atom. That the two triplet patterns at δ 37.4 and 37.5 did indeed represent two, and only two resonances, rather than some anomalous, fortuitously spaced sequence of resonances was reinforced by the spectrum in deuteriochloroform in which the separation between the centers of the triplets increased (δ 37.1 and 37.3, respectively) while the splitting remained constant.

The observed ^{1}H NMR spectrum is consistent with this explanation. In particular, a discrete resonance was observed for the bridging methylene protons of each diastereomer. One resonance was observed at δ 5.24 as an AB quartet with $^2J_{HCH}$ = 16.2 Hz, whereas the other resonance was a singlet at δ 5.22. This explanation is consistent with the observation of two diastereomers, one of which is a *d,l* pair (singlet resonance) and the other a meso form (AB quartet).

The examination of a molecular model of **14a** and **14b** suggests that the removal of the methyl group from the bridging carbon atom in **14b** to give **14a** allows for increased internal rotational modes. The consequences of this increased rotational freedom is a smaller $\Delta\Delta G^*$ between various diastereomeric transition states leading to the formation of two major diastereomers in a 1:1 ratio. A further consequence of the increased conformational freedom is the observed equivalence of the phosphorus atoms in the ^{31}P NMR spectrum of each diastereomer.

Significantly, Szalontai and co-workers[34] reported that $^6J_{PP}$ coupling in **23** in which the substituents on the propane bridge were removed was not observed. The lack of observable coupling in **23** was attributed to the removal of steric interactions favoring rotomers that bring the phosphorus atoms in close proximity to each other. A similar explanation is advanced for the observed spectra of **14a** and **14b**.

Similarly, in the ^{31}P NMR spectrum of **16**, two singlet resonances were observed at δ 135.7 and 136.2. In analogy with the observed spectrum of **14a**, a 1:1 ratio (obtained by integration of the ^{31}P NMR peak areas) of diastereomers of **16** appears to be present. The complex ^{1}H NMR spectrum of **16** is consistent with this interpretation. Several structural modifications of the bis(oxazaphospholidine) structure were made to test the preceding interpretations. The linear bis(phenol) derivative **18** was prepared in order to study the effect of removing the chiral axis of symmetry. Furthermore, the asymmetric phosphorus atoms are separated by 12 bonds, and at that distance neither the J coupling of the phosphorus atoms nor the observation of discrete diastereoisomers is expected. The observation of a singlet resonance in the ^{31}P NMR spectrum of **18** at δ 144.2 was consistent with these expectations. The bridging methylene protons and carbon atoms were observed as a singlet in the ^{1}H and ^{13}C NMR spectra, respectively.

The unsubstituted-aryl derivative **12b** was prepared in which the steric constraints imposed by the *tert*-butyl substituents in the corresponding derivative **12a** are absent. With increased conformational freedom in the molecule, both the loss of $^7J_{PP}$ coupling and the formation of more than one diastereomer are expected. Consistent with this analysis, two singlet resonances were observed in the ^{31}P NMR spectrum of **12b** at δ 130.5 and 130.9. The ^{1}H NMR spectrum of **12b** is also consistent with the observation of two distinct resonances at δ 1.15 and 1.17 that were assigned to the *tert*-butyl protons of each diastereomer.

Although the observed spectrum of **12b** is totally consistent with the interpretation that the lack of P-P $^7J_{PP}$ coupling is due to increased conformational freedom, the observation of a single diastereomer with nonequivalent, uncoupled phosphorus atoms cannot be excluded. However, the degree of nonequivalence of the observed *tert*-butyl resonances in **12b** ($\Delta\delta$ = 0.02) is similar to that observed for the diastereomeric **14a** ($\Delta\delta$ = 0.08) and quite different from that observed for **12a** ($\Delta\delta$ = 0.20) and for **14b** ($\Delta\delta$ = 0.28), which supports the suggestion that **12b** is a diastereomeric mixture. The complexity of the ^{1}H NMR spectrum provides further support for a diastereomeric mixture. In either case, however, the important observation to be made is that the increased conformational mobility leads to a loss of $^7J_{PP}$ coupling between phosphorus atoms *within a diastereomer*.

The absolute configurations of **12a** and **14b** are unknown, but their relative configurations can be obtained from the X-ray structure. The configuration of **12a** is (R^*,R^*S^*)[50,51] and that of **14b** is (R^*,R^*).

The structure of **12a** deserves further comment. Well-defined studies of molecules containing both two chiral centers and a chiral axis are rare. The best examples are provided by the work of Prelog and co-workers.[52] To our knowledge, **12a** is the first example in the literature of a fully characterized molecule containing both a chiral axis and two chiral phosphorus(III) centers. The axial chirality of **12a** is *independent* of the asymmetry at the two phosphorus atoms, unlike the case of the pseudoasymmetric ethylidene carbon atom in **14b**. Only when both chiral phosphorus atoms are either *R* or *S* is the pseudoasymmetric ethylidine carbon atom in **14b** not asymmetric.[42] Both **12a** and **14b** are a *d,l* pair.

It was clearly of interest to remove the chirality at phosphorus. Toward this end, the bis(aryl)dioxophosphorinane **21** was prepared and the ^{31}P NMR spectrum obtained. A single resonance is observed at δ 114.6, which is consistent with the fact that only a chiral axis of symmetry is present and that only a *d,l* pair is obtained. The removal of the oxazaphospholidine rings containing a sterically demanding *tert*-butyl group and replacement by the less sterically demanding dioxaphosphorinane ring precludes any nonequivalence of the phosphorus atoms due to restricted conformational mobility as observed for **12a** and **14b**.[53]

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[50] For **12a** (R^*,R^*,S^*) refers to P(1), chiral axis, P(2), respectively. The configuration of P(1) is assigned R^* following the customary convention when the absolute configuration of a molecule is unknown. The nomenclature adopted here is based upon recent Chemical Abstract Service practice. See: (a) Cross, L. C.; Klyne, W. *Pure Appl. Chem.* **1976**, *45*, 11-30. (b) *Chemical Abstracts, Ninth Collective Index, Index Guide* to Vol. 76-85 Chemical Abstracts Service: Columbus, OH, 1977.

[51] For the sequencing of molecules having axial chirality, see: (a) Reference 42b, pp 33-35. (b) Krow, G. *Top. Stereochem.* **1970**, *5*, 62-63.

[52] (a) von Helmchen, G.; Prelog, V. *Helv. Chim. Acta* **1972**, *55*, 2599-2611. (b) Helmchen, G.; Haas, G.; Prelog, V. *Helv. Chim. Acta* **1973**, *56*, 2255-2270.

[53] No evidence was observed for the slowing of inversion of the nitrogen lone pair of electrons (see discussion on crystal structure in text). If this was the case, diastereomers would be observed in the monoaryl oxazaphospholidines **9a-e**. For a spectral study on the conformation of 1,3,2-oxazaphospholidines, see: Samitov, Yu. Yu.; Pudovik, M. A.; Khayarov, A. I.; Kibardina, L. K. *Zh. Obshch. Khim.* **1973**, *43*, 42-46.

[54] Loev, B.; Goodman, M. M. *Chem. Ind.* (*London*) **1967**, 2026-2032.

Experimental Section

3-*tert*-Butyl-2-chloro-1,3,2-oxazaphospholidine (7). Method A. To a solution of 8.7 mL (100 mmol) of **6** in 200 mL of toluene was added dropwise a solution of 11.72 g (100 mmol) of **5** in 50 mL of toluene. After the addition was complete, the reaction mixture was heated at reflux for 16 h. The reaction mixture was cooled, and the suspension of orange solids was removed by filtration. The filtrate was concentrated in vacuo, and the residue was distilled to give 10.3 g (57%) of a colorless liquid: bp 82 °C (1.0 mm) [lit.[19] bp 75–76 °C (3 mm)]; ^{31}P NMR (benzene-d_6) δ 164; ^{1}H NMR (200 MHz) (benzene-d_6) δ 1.26 (s, $(CH_3)_3C$, 9 H), 2.74 (m, 2 H), 4.14 (m, 2 H); MS m/z 181, 183 ($M^{\bullet +}$).

Method B. To a solution of 68.8 mL (0.5 mol) of **6** in 1.0 L of dichloromethane cooled with an acetone/dry ice bath was added dropwise over a period of 10 min a solution of 58.6 g (0.5 mol) of **5** and 101.2 g (1.0 mol) of triethylamine in 250 mL of dichloromethane. The reaction mixture was warmed to room temperature, and then it was heated at reflux for 2 h. The reaction mixture was stirred overnight at room temperature, and the solids were removed by filtration. The solvent was removed in vacuo, and the residue was dissolved in 250 mL of toluene. The mixture was filtered through a bed of Celite, and the solvent was removed in vacuo. The residue was distilled to give 60.5 g (67%) of **7** in every respect identical with that prepared by method A above.

3-*tert*-Butyl-2-(2,6-di-*tert*-butyl-4-methylphenoxy)-1,3,2-oxazaphospholidine (9a). To a suspension of 4.40 g (110 mmol) of a 60% dispersion of sodium hydride in mineral oil, which was washed with two 20-mL aliquots of hexane, in 45 mL of THF was added dropwise a solution of 22.04 g (100 mmol) of **8e** in 150 mL of THF at a rate that maintained the reaction temperature between 20 and 30 °C. The reaction mixture was heated at 40 °C for 1 h and then cooled with an ice bath. To the cooled reaction mixture was added dropwise a solution of 18.16 g (100 mmol) of **7** in 150 mL of THF. The reaction mixture was sitrred for 16 h at room temperature, and then the turbid reaction mixture was filtered. The solvent was removed in vacuo, and the residue was dissolved in 200 mL of toluene. The solution was filtered, and the solvent was removed in vacuo. The residue was triturated with methyl alcohol to give 24.50 g (67%) of a white solid: mp 105–107 °C; ^{31}P NMR (benzene-d_6) δ 153; ^{1}H NMR (80 MHz) ($CDCl_3$) δ 1.13 (s, 9 H), 1.48 (s, 18 H), 2.28 (s, 3 H), 3.20 (complex m, 2 H), 4.45 (complex m, 2 H), 6.98 (s, 2 H); ^{13}C NMR (benzene-d_6) δ 21.2, 30.0 (d), [33.1, 33.2],[56] 36.0, 44.4 (d), 52.4 (d), 68.8 (d), 127.6, 130.4 (d), 142.8 (d), 148.8 (d). Anal. Calcd for $C_{21}H_{36}NO_2P$: C, 69.0; H, 9.9; N, 3.9. Found: C, 69.3; H, 10.0; N, 3.9.

3-*tert*-Butyl-2-(2,4,6-tri-*tert*-butylphenoxy)-1,3,2-oxazaphospholidine (9b). By the procedure used to prepare compound **9a**, compound **9b** was prepared from 2.30 g (55 mmol) of a 60% dispersion of sodium hydride in mineral oil, 13.12 g (50 mmol) of **8f**, and 9.08 g (50 mmol) of **7**. The residue was triturated with methanol to give 9.00 g (44%) of a white solid: mp 72.5–73.5 °C; ^{31}P NMR (benzene-d_6) δ 150.9; ^{1}H NMR (200 MHz) (benzene-d_6) δ 1.07 (s, $NC(CH_3)_3$, $^4J_{HCCNP}$ = 0.8 Hz, 9 H), 1.48 (s, 9 H), 1.76 (s, 18 H), 2.82 (m, 1 H), 2.95 (m, 1 H), 4.07 (m, 1 H), 4.42 (m, 1 H), 7.55 (s, 2 H). Anal. Calcd for $C_{24}H_{42}NO_2P$: C, 70.7; H, 10.4; N, 3.4. Found: C, 70.7; H, 10.5; N, 3.5.

3-*tert*-Butyl-2-(2,4,6-trimethylphenoxy)-1,3,2-oxazaphospholidine (9c). By the procedure used to prepare compound **9a**, compound **9c** was prepared from 4.40 g (110 mmol) of a 60% dispersion of sodium hydride in mineral oil, 13.62 g (100 mmol) of **8g**, and 18.16 g (100 mmol) of **7**. The residue was distilled to give 21.27 g (76%) of a colorless liquid: bp 99–103 °C (0.01 mm); ^{31}P NMR (benzene-d_6) δ 135.4; ^{1}H NMR (80 MHz) (benzene-d_6) δ 1.21 (s, 9 H), 1.38 (s, 3 H), 1.48 (s, 6 H), 3.01 (m, 2 H), 4.22 (m, 2 H), 6.61 (s, 2 H). Anal. Calcd for $C_{15}H_{24}NO_2P$: C, 64.0; H, 8.6; N, 5.0. Found: C, 64.4; H, 8.4; N, 4.6.

3-*tert*-Butyl-2-(2,4-di-*tert*-butylphenoxy)-1,3,2-oxazaphospholidine (9d). To a solution of 8.70 mL (100 mmol) of **6** in 200 mL of diethyl ether at 5 °C was added dropwise a solution of 11.72 g (100 mmol) of **5** and 20.24 g (200 mmol) of triethylamine in 50 mL of diethyl ether. The reaction mixture was stirred for 1 h at room temperature, and then a solution of 20.63 g (100 mmol) of **8h** and 11.13 g (110 mmol) of triethylamine in 50 mL of diethyl ether was added dropwise. The reaction mixture was stirred for 16 h at room temperature, and the suspension of triethylamine hydrochloride was removed by filtration. The solvent was removed in vacuo, the residue was dissolved in 200 mL of toluene, and the insolubles were removed by filtration. The solvent was removed in vacuo, and the residue was distilled to give 22.25 g (63%) of a colorless liquid: bp 118–123 °C (0.01 mm); ^{31}P NMR (benzene-d_6) δ 130.0; ^{1}H NMR (80 MHz) ($CDCl_3$) δ 1.10 (s, 9 H), 1.22 (s, 18 H), 3.06 (m, 2 H), 4.11 (m, 2 H), 7.04 (s, 3 H). Anal. Calcd for $C_{20}H_{34}NO_2P$: C, 68.4; H, 9.8; N, 4.0. Found: C, 68.0; H, 9.7; N, 4.1.

Reaction of 7 with 8i. Method A: Isolation of a Mixture of 9e and 10a. By the procedure used to prepare compound **9d**, compound **9e** was prepared from 21.1 g (180 mmol) of **5**, 15.7 mL (180 mmol) of **6**, 20.2 g (200 mmol) of triethylamine, and 43.1 g (180 mmol) of **8g**. The residue was bulb-to-bulb distilled (Kugelrohr) to give a mixture of **9e** and **10a**, bp 90–95 °C (0.03 mm). The spectral assignments were made on the resonances observed for the mixture. The integration of the observed resonances were internally consistent with a **10a**:**9e** ratio of 2:1.

Compound **9e**: ^{31}P NMR (benzene-d_6) δ 134.0; ^{1}H NMR (80 MHz) ($CDCl_3$) δ 1.17 (s, 9 H), 2.98 (m, 2 H), 3.91 (m, 2 H), 6.61 (m, 5 H).

Compound **10a**: IR (neat) ν 3260 (NH) cm^{-1}; ^{31}P NMR (benzene-d_6) δ 136.6; ^{1}H NMR (80 MHz) ($CDCl_3$) δ 1.22 (s, 9 H), 2.80 (t, 2 H), 3.91 (dt, 2 H), 6.61 (m, 10 H).

Method B: Reaction of the Phenolate of 8i with 7. By the procedure used to prepare compound **9a**, compound **9e** was prepared from 4.00 g (100 mmol) of a 60% dispersion of sodium hydride in mineral oil, 9.40 g (100 mmol) of **8i**, and 18.20 g (100 mmol) of **7**. The residue was distilled to give 17.40 g (73%) of a colorless liquid in every respect identical with that obtained by method A above.

2,2′-[[3,3′,5,5′-Tetrakis(1,1-dimethylethyl)[1,1′-biphenyl]-2,2′-diyl]bis(oxy)]bis[3-(1,1-dimethylethyl)-1,3,2-oxazaphospholidine] (12a). By the procedure used to prepare compound **9a**, compound **12a** was prepared from 4.40 g (110 mmol) of a 60% dispersion of sodium hydride in mineral oil, 20.53 g (50 mmol) of **11a**,[57] and 19.98 g (110 mmol) of **7**. The residue was triturated with methyl alcohol to give 12.20 g (35%) of a white solid, mp 169–172 °C. Recrystallization from hexane increased the melting point to 179–184 °C: ^{31}P NMR (benzene-d_6) δ 133.5 (d, upfield half of AB q, $^7J_{PP}$ = 30.3 Hz), 135.7 (d, downfield half of AB q,); ^{1}H NMR (200 MHz) (benzene-d_6) δ 1.14 (d, $NC(CH_3)_3$, $^4J_{HCCNP}$ = 1.1 Hz, 9 H), 1.34 (d, $NC(CH_3)_3$, $^4J_{HCCNP}$ = 1.1 Hz, 9 H), 1.45 (s, $C(CH_3)_3$, 9 H), 1.51 (s, $C(CH_3)_3$, 9 H), 1.77 (s, $C(CH_3)_3$, 9 H), 1.79 (s, $C(CH_3)_3$, 9 H), 2.76 (complex m, 2 H), 3.00 (complex m, 2 H), 3.90 (complex m, 2 H), 4.30 (complex m, 2 H), 7.37–7.73 (complex m, 4 H). ^{13}C NMR obtained at both 50.3 and 100.6 MHz. Carbon atom assignments are derived from APT and DEPT experiments. ^{13}C NMR ($CDCl_3$) δ 29.7 (d, $NC(\mathit{C}H_3)_3$, $^3J_{CCNP}$ = 10.5 Hz), 29.9 (dd, $NC(\mathit{C}H_3)_3$, $^3J_{CCNP'}$ = 10.6 Hz, $^{10}J_{CP}$ = 0.7 Hz), 30.6 (s, $C(\mathit{C}H_3)_3$), 30.7 (s, $C(\mathit{C}H_3)_3$), 31.4 (s, $C(\mathit{C}H_3)_3$), 31.5 (s, $C(\mathit{C}H_3)_3$), 34.1 (s, $\mathit{C}(CH_3)_3$), 34.2 (s, $\mathit{C}(CH_3)_3$), 35.2 (s, $\mathit{C}(CH_3)_3$), 35.4 (s, $\mathit{C}(CH_3)_3$), 42.0 (d, $PNCH_2$, $^2J_{CNP}$ = 6.0 Hz), 42.2 (d, $PNCH_2$, $^2J_{CNP'}$ = 6.6 Hz), 51.6 (d, $PN\mathit{C}(CH_3)_3$, $^2J_{CNP}$ = 13.5 Hz), 51.7 (d, $PN\mathit{C}(CH_3)_3$, $^2J_{CNP'}$ = 13.2 Hz), 67.6 (d, $POCH_2$, $^2J_{COP}$ = 8.4 Hz), 67.9 (d, $POCH_2$, $^2J_{COP'}$ = 8.1 Hz), 123.3 (d, $^4J_{CP}$ = 0.6 Hz), 123.7 (d, $^4J_{CP'}$ = 0.8 Hz), 129.0 (d, $^4J_{CP}$ = 5.0 Hz), 130.0 (d, $^4J_{CP'}$ = 4.7 Hz), 130.8 (dd, $C_{Ar}-\mathit{C}_{Ar'}$, $^3J_{CP}$ = 4.9 Hz, $^4J_{CP'}$ = 3.8 Hz), 131.5 (dd, $C_{Ar}-\mathit{C}_{Ar'}$, $^3J_{CP'}$ = 4.7 Hz, $^4J_{CP}$ = 3.5 Hz), 138.2 (s), 139.1 (s), 141.2 (s), 141.8 (s), 150.40 (dd, POC_{Ar}, $^2J_{COP}$ = 5.2 Hz, $^5J_{CP'}$ = 1.8 Hz), 150.42 (dd, POC_{Ar}, $^2J_{COP'}$ = 5.1 Hz, $^5J_{CP}$ = 3.9 Hz); MS m/z 700 ($M^{\bullet +}$). Anal. Calcd for $C_{40}H_{66}N_2O_4P_2$: C, 68.5; H, 9.5; N, 4.0. Found: C, 68.9; H, 9.7; N, 4.0.

From the mother liquor of the above was isolated a sample enriched in **10b**: IR ν 3500 (NH) cm^{-1}; ^{1}H NMR (benzene-d_6) δ 1.05 (s, 9 H), 1.38 (s, 18 H), 1.42 (s, 18 H), 1.72 (s, 18 H), 1.75 (s, 18 H), 1.82 (d, 18 H), 2.62 (t, NCH_2, 2 H), 2.77 (m, 2 H), 3.09 (m, 2 H), 3.91 (m, 2 H), 4.12 (dt, OCH_2, 2 H), 4.49 (m, 2 H), 7.35–7.74 (m, 8 H). Due to resonance overlap in the aliphatic region, multiplicity was not assigned in the ^{13}C NMR spectrum. ^{13}C NMR (benzene-d_6) δ 29.0, 30.0, 31.4, 31.6, 31.7, 34.4, 35.5, 35.55, 42.5, 43.2, 49.98, 51.8, 67.6, 68.0, 123.5, 124.4, 125.1, 126.0, 127.0, 133.3, 137.1, 139.3, 140.2, 143.3, 146.5, 150.4; ^{31}P NMR (benzene-d_6) δ 1.37, 1.38.

2,2′-[(1,1′-Biphenyl-2,2′-diyl)bis(oxy)]bis[3-(1,1-dimethylethyl)-1,3,2-oxazaphospholidine] (12b). By the procedure used to prepare compound **9a**, compound **12b** was prepared from 0.88 g (22 mmol) of a 60% dispersion of sodium hydride in mineral oil, 1.86 g (10 mmol) of **11d**, and 3.63 g (20 mmol) of **7**. The solvent was removed in vacuo to give 4.0 g (84%) of a light-amber liquid. The spectral data were obtained immediately without attempted purification: ^{31}P NMR (benzene-d_6) δ 130.5, 130.9. The ^{1}H NMR spectrum was consistent with a mixture of diastereomers. Integration of the singlet resonances at δ 1.15 and 1.17 that were assigned to the *tert*-butyl resonance of each diastereomer indicated a 1:1 mixture of diastereomers. The following assignments are from the spectrum of the diastereomeric mixture. The integration of the resonances of the diastereomeric mixture is internally consistent: ^{1}H NMR (200 MHz) (benzene-d_6) δ 1.15 and 1.17 (two s, $NC(CH_3)_3$, 18 H each), 2.67 (overlapping m, 1 H each), 2.91 (overlapping m, 1 H each), 3.97

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(overlapping m, 1 H each), 4.24 (overlapping m, 1 H each), 7.07–7.59 (overlapping m, 8 H each).

2,2′-[Methylenebis[[4,6-bis(1,1-dimethylethyl)-2,1-phenylene]oxy]]bis[3-(1,1-dimethylethyl)-1,3,2-oxazaphospholidine] (14a). By the procedure used to prepare compound **9a**, compound **14a** was prepared from 2.20 g (55 mmol) of a 60% dispersion of sodium hydride in mineral oil, 10.62 g (25 mmol) of **13b**,[58] and 9.08 g (50 mmol) of **7**. The solvent was removed in vacuo to give 6.5 g (85%) of a white solid. Attempts to separate the diastereomeric mixture were unsuccessful. The diastereomeric mixture was purified by flash chromatography (94:4:2 hexane/ethyl acetate/triethylamine): mp 59–63 °C; ^{31}P NMR (benzene-d_6) δ 136.6, 137.1. Integration of singlet resonances at δ 136.6 and 137.1 that were assigned to the phosphorus resonance of each diastereomer indicated a 1:1 mixture of diastereomers.[59] The resonances in the ^{1}H NMR spectrum were not assigned to a particular diastereomer; however, the spectrum was consistent with a mixture of diastereomers. The following assignments are from the spectrum of the diastereomeric mixture. The integration of the resonances of the diastereomeric mixture is internally consistent: ^{1}H NMR (200 MHz) (benzene-d_6) δ 1.28 and 1.36 (s, NC(CH$_3$)$_3$, 9 H each), 1.40 and 1.45 (s, C(CH$_3$)$_3$, 9 H each), 1.71 and 1.82 (s, C(CH$_3$)$_3$, 9 H each), 2.88–4.79 (overlapping m, 16 H), 5.22 (br s, ArCH$_2$Ar, 2 H), 5.24 (AB q, ArCH$_2$Ar, $^2J_{\mathrm{HCH}}$ = 16.2 Hz, 2 H)8 7.14–7.63 (complex m, 8 H); ^{13}C NMR (50.3 MHz) (benzene-d_6)[60] δ 25.2, 30.0, 30.2, 31.8, 34.6, 35.8, 37.4 (t, $^4J_{\mathrm{CP}} = {}^4J_{\mathrm{CP'}}$ = 21.1 Hz), 37.5 (t, $^4J_{\mathrm{CP}} = {}^4J_{\mathrm{CP'}}$ = 21.1 Hz), 42.5 (d), 69.2 (d), 124.3, 124.6, 125.4, 127.2, 132.8 (d), 140.3, 144.3, 149.3, 150.5. Anal. Calcd for $C_{41}H_{68}N_2O_4P_2$: C, 68.9; H, 9.6; N, 3.9. Found: C, 68.8; H, 9.8; N, 3.7.

2,2′-[Ethylidinebis[[4,6-bis(1,1-dimethylethyl)-2,1-phenylene]oxy]]bis[3-(1,1-dimethylethyl)-1,3,2-oxazaphospholidine] (14b). By the procedure used to prepare compound **9a**, compound **14b** was prepared from 4.40 g (110 mmol) of a 60% dispersion of sodium hydride in mineral oil, 21.94 g (50 mmol) of **13d**,[58] and 18.16 g (100 mmol) of **7**. The residue was triturated from methyl alcohol to give 20.20 g (55%) of a white solid, mp 142–148 °C. Recrystallization from 2-propyl alcohol increased the melting point to 145–148 °C: ^{31}P NMR (benzene-d_6) δ 144.2 (d, upfield half of AB q, $^8J_{\mathrm{PP}}$ = 30.6 Hz), 147.4 (d, downfield half of AB q); ^{1}H NMR (200 MHz) (benzene-d_6) δ 1.03 (d, NC(CH$_3$)$_3$, $^4J_{\mathrm{HCCNP}}$ = 0.5 Hz, 9 H), 1.31 (d, NC(CH$_3$)$_3$, $^4J_{\mathrm{HCCNP}}$ = 1.0 Hz, 9 H), 1.46 (s, C(CH$_3$)$_3$, 9 H), 1.50 (s, C(CH$_3$)$_3$, 9 H), 1.72 (s, C(CH$_3$)$_3$, 9 H), 1.77 (s, C(CH$_3$)$_3$, 9 H), 2.19 (d, ethylidene CH$_3$, 3 H), 2.77–4.47 (overlapping m, 8 H), 5.91 (dq, methine H, 1 H), 7.55 (meta d, 1 H), 7.59 (meta d, 1 H), 7.63 (meta d, 1 H), 7.64 (meta d, 1 H); ^{13}C NMR (50.51 MHz) (benzene-d_6) δ 24.9 (d, Ar$_2$CH*C*H$_3$, $^5J_{\mathrm{CP}}$ = 7.3 Hz), 29.7 (d, NC(*C*H$_3$)$_3$, $^3J_{\mathrm{CP}}$ = 9.8 Hz), 30.0 (d, NC(*C*H$_3$)$_3$, $^3J_{\mathrm{CP'}}$ = 9.8 Hz), 31.4 (s, ArC(*C*H$_3$)$_3$), 31.5 (s, ArC(*C*H$_3$)$_3$), 31.6 (s, ArC(*C*H$_3$)$_3$), 34.3 (s, Ar*C*(CH$_3$)$_3$), 34.4 (s, Ar*C*(CH$_3$)$_3$), 35.3 (s, Ar*C*(CH$_3$)$_3$), 35.6 (s, Ar*C*(CH$_3$)$_3$), 37.1 (dd, Ar*C*Ar, $^4J_{\mathrm{CP}}$ = 17.1 Hz, $^4J_{\mathrm{CP'}}$ = 13.5 Hz), 42.9 (d, PNCH$_2$, $^2J_{\mathrm{CNP}}$ = 4.9 Hz), 43.6 (d, PNCH$_2$, $^2J_{\mathrm{CNP'}}$ = 4.9 Hz), 56.0 (d, N*C*(CH$_3$)$_3$, $^2J_{\mathrm{CNP}}$ = 19.5 Hz), 57.2 (d, N*C*(CH$_3$)$_3$, $^2J_{\mathrm{CNP'}}$ = 17.1 Hz), 73.0 (d, POCH$_2$, $^2J_{\mathrm{COP}}$ = 7.3 Hz), 73.2 (d, POCH$_2$, $^2J_{\mathrm{COP}}$ = 8.6 Hz), 122.0 (=CH), 122.2 (=CH), 124.5 (=CH), 125.8 (=CH), 137.0 (unresolved m), 138.7 (unresolved m), 140.2, 140.8, 143.1, 143.6, 149.0, 149.5. Anal. Calcd for $C_{42}H_{70}N_2O_4P_2$: C, 69.2; H, 9.7; N, 3.8. Found: C, 69.6; H, 9.6; N, 3.6.

2,2′-[Thiobis[[4,6-bis(1,1-dimethylethyl)-2,1-phenylene]oxy]]bis[3-(1,1-dimethylethyl)-1,3,2-oxazaphospholidine] (16). By the procedure used to prepare compound **9a**, compound **16** was prepared from 0.88 g (22 mmol) of a 60% dispersion of sodium hydride in mineral oil, 4.43 g (10 mmol) of **15b**,[61] and 3.63 g (20 mmol) of **7**. The solvent was removed in vacuo to give 6.50 g (85%) of a light-amber liquid. The spectral data were obtained immediately without attempted purification: ^{31}P NMR (benzene-d_6) δ 135.7, 136.2. Integration of singlet resonances at δ 135.7 and 136.2 that where assigned to the phosphorus resonance of each diastereomer indicated a 1:1 mixture of diastereomers. The resonances in the ^{1}H NMR spectrum were not assigned; however, the spectrum was consistent with a mixture of diastereomers. The following assignments are from the spectrum of the diasteromeric mixture. The integration of the resonances of the diastereomeric mixture are internally consistent: ^{1}H NMR (200 MHz) (benzene-d_6) δ 1.25–1.70 (complex, NC(CH$_3$)$_3$ and C(CH$_3$)$_3$, 54 H), 2.87 (overlapping m, 2 H), 3.21 (overlapping m, 2 H), 3.95 (overlapping m, 2 H), 4.39 (overlapping m, 2 H), 7.14–7.53 (overlapping m, 4 H).

4,4′-[Methylenebis[[4,6-bis(1,1-dimethylethyl)-2,1-phenylene]oxy]]bis[3-(1,1-dimethylethyl)-1,3,2-oxazaphospholidine] (18). By the procedure used to prepare compound **9a**, compound **18** was prepared from 1.76 g (44 mmol) of a 60% dispersion of sodium hydride in mineral oil, 8.49 g (20 mmol) of **17b**, and 7.26 g (40 mmol) of **7**. The residue was triturated and washed with methyl alcohol to give 5.00 g (35%) of a white solid: mp 156–159 °C; ^{31}P NMR (benzene-d_6) δ 144.2 (s); ^{1}H NMR (200 MHz) (benzene-d_6) δ 1.08 (s, NC(CH$_3$)$_3$, 18 H), 1.54 (s, C(CH$_3$)$_3$, 36 H), 2.16 (overlapping m, 4 H), 3.83 (s, ArCH$_2$Ar, 2 H), 4.39 (m, 2 H), 4.46 (m, 2 H), 7.01 (s, 4 H); ^{13}C NMR (50.51 MHz) (benzene-d_6) δ 29.9 (d, NC(*C*H$_3$)$_3$), [32.2, 32.3],[56] 35.6 (Ar*C*(CH$_3$)$_3$), 40.4 (Ar*C*Ar), 43.8 (d, PNCH$_2$), 52.4 (d, N*C*(CH$_3$)$_3$, 68.9 (d, POCH$_2$), 126.8 (=CH), 133.3, 141.9, 147.7 (d). Anal. Calcd for $C_{41}H_{68}N_2O_4P_2$: C, 68.9; H, 9.6; N, 3.9. Found: C, 68.7; H, 9.4; N, 3.9.

2,2′-[[3,3′,5,5′-Tetrakis(1,1-dimethylethyl)[1,1′-biphenyl]-2,2′-diyl]bis(oxy)]bis[5,5-dimethyl-1,3,2-dioxaphosphorinane] (21). By the procedure used to prepare compound **9a**, compound **21** was prepared from 3.52 g (88 mmol) of a 60% dispersion of sodium hydride in mineral oil, 16.43 g (40 mmol) of **11a**, and 13.47 g (80 mmol) of **20**.[27] The residue was triturated with 2-propyl alcohol to give 17.60 g (65%) of a white solid: mp 176–180 °C; ^{31}P NMR (benzene-d_6) δ 114.6; ^{1}H NMR (200 MHz) (benzene-d_6) δ 0.31 (s, 6 H), 0.97 (s, 6 H), 1.30 (s, C(CH$_3$)$_3$, 18 H), 1.69 (s, C(CH$_3$)$_3$, 18 H), 2.99 (complex m, 4 H), 4.07 (complex m, 4 H), 7.37 (meta d, 2 H), 7.59 (meta d, 2 H). Anal. Calcd for $C_{38}H_{60}O_6P_2$: C, 67.7; H, 9.0. Found: C, 67.2; H, 8.8.

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Supplementary Material Available: Tables of positional and thermal parameters, bond distances, bond angles, and crystal and refinement data for **12a** and **14b**, Table II (crystal data and structural analysis results of **12a**), Table III (crystal data and structural analysis results of **14b**), Figure 4 (^{31}P homonuclear COSY NMR of **12a**), Figure 6 (computer-generated stereorepresentation of **12a**), Figure 7 (aliphatic region of the ^{1}H NMR spectrum of **12a**), and the general experimental section (36 pages); table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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(59) Integration of the singlet resonances at δ 1.71 and 1.82 in the ^{1}H NMR spectrum of **14a** also suggests a 1:1 mixture of diastereomers.

(60) The apparent simplicity of the aliphatic region of the spectrum due to accidental equivalence is removed upon running the spectrum in CDCl$_3$.

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