Inorg. Chem. **1996,** *35,* 949−958

Atomic Proximity Due to Molecular Congestion: Rational Design of Bis(phosphite) Ligands by Restriction of Molecular Motion[1]

Stephen D. Pastor,[*,†] Sai P. Shum,[†] Anthony D. DeBellis,[‡] Lilibeth P. Burke,[§] and Ronald K. Rodebaugh[§]

Research Department, Scientific Computing Department, and Analytical Research Services,
Ciba Additives Research Department, Ciba-Geigy Corporation, 444 Saw Mill River Road,
Ardsley, New York 10502

Frank H. Clarke

Therapeutic Area Support, Pharmaceutical Division, Ciba-Geigy Corporation,
Summit, New Jersey 07901

Grety Rihs

Central Function Research, Ciba-Geigy AG, Postfach, CH-4002 Basel, Switzerland

Received July 27, 1995[⊗]

The synthesis and conformational analysis of the sterically congested bis(phosphite) ligand $\{2\text{-}\{1\text{-}\{3,5\text{-}{}^t\mathrm{Bu}_2\text{-}2\text{-}[2,2'\text{-}\mathrm{CHCH_3}(4,6\text{-}{}^t\mathrm{Bu_2C_6H_2O})_2\mathrm{PO}]\mathrm{C_6H_2}\}\mathrm{Et}\}\text{-}4,6\text{-}{}^t\mathrm{Bu_2C_6H_2O}\}(\mathrm{PhO})_2\mathrm{P}$ (**5**) are reported. X-ray crystallographic, dynamic $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR, NOE, DNOE, CP-MAS ^{31}P NMR, and calculational studies of **5** as well as the structurally related bis(phosphites) **1** and **6** suggest that the conformational freedom of the molecule is severely restricted because of geometric restraints due to steric congestion. A through-space mechanism of coupling is suggested to explain the observed eight-bond P−P J coupling of 27.5 Hz in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of **5**, which is a result of the proximity of the two phosphorus atoms in **5**. The results of this study support the contention that the restriction of molecular motion by steric congestion can be used to rationally design a ligand favoring a particular disposition of phosphorus atoms.

Introduction

The development of synthetic methodology for enantioselective C−C bond formation is a topic of fundamental importance. Particularly desirable methodology involves the use of catalytic quantities of chiral transition-metal catalysts. Phosphine ligands have played a vital role in designing chiral coordination spheres for transition metals.[2] The use of chiral phosphite ligands derived from the chiral pool offers an attractive alternative to phosphine-based catalysts.[3] Although the successful application of chiral phosphite ligands for transition-metal-catalyzed reactions has been reported,[4−6] phosphite ligands are often not stable to the reaction conditions. Additionally, typical phosphite ligands require rigorous exclusion of atmospheric moisture during storage prior to use.

One potential solution to this problem involves the synthesis of sterically hindered phosphite ligands with both improved

---

[†] Research Department.

[‡] Scientific Computing Department.

[§] Ciba Additives Analytical Research Department.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

(1) Presented in part at the 207th National Meeting of the American Chemical Society, San Diego, CA, March 13−17, 1994; see Abstract INOR 342.

(2) For reviews, see: (a) Morrison, J. D. *Asymmetric Synthesis*; Academic Press: New York, 1983; Vol. 5. (b) Pignolet, L. H. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum: New York, 1983. (c) Chaloner, P. A. *Handbook of Coordination Catalysts in Organic Chemistry*; Butterworths: London, 1986. (d) Brunner, H. *Synthesis* **1988**, 645. (e) Brunner, H. *Top. Stereochem.* **1988**, *18*, 129. (f) Noyori, R.; Kitamura, M. *Mod. Synth. Methods* **1989**, *5*, 155. (g) Ojima, I.; Clos, N.; Bastos, C. *Tetrahedron* **1989**, *45*, 6901. (h) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (i) Sasaya, M.; Ito, Y. *Chem. Rev.* **1992**, *92*, 857. (j) Blaser, H.-U. *Chem. Rev.* **1992**, *92*, 935. (k) Dunina, V. V.; Beletskaya, I. P. *J. Org. Chem. USSR (Engl. Transl.)* **1992**, *28*, 1913. (l) Ojima, I. *Catalytic Asymmetric Synthesis*; VCH: Weinheim, Germany, 1993. (m) Noyori, R. *Asymmetric Catalysis in Organic Synthesis;* Wiley Interscience: New York, 1994.

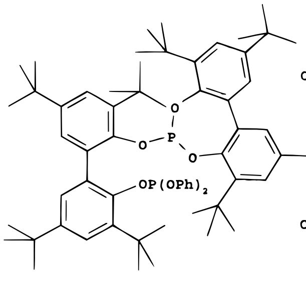
(3) For carbohydrate-derived phosphorus ligands, see: (a) Nifant'ev, E. E.; Tuseev, A. P.; Tarasov, V. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1966**, *36*, 1137; *Zh. Obshch. Khim*. **1966**, *36*, 1124. (b) Descotes, G.; Lafont, D.; Sinou, D. *J. Organomet. Chem.* **1978**, *150*, C14. (c) Lafont, D.; Sinou, D.; Descotes, G. *J. Organomet. Chem.* **1979**, *169*, 87. (d) Dzhemilev, U. M.; Fakhretdinov, R. N.; Telin, A. G.; Tolstikov, G. A. *Dokl. Chem. (Engl. Transl.)* **1980**, 1324; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 944. (e) Dzhemilev, U. M.; Fakhretdinov, R. N.; Telin, A. G.; Tolstikov, G. A.; Panasenko, A. A.; Vasil'eva, E. V. *Dokl. Chem. (Engl. Transl.)* **1980**, 1943; *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 2771. (f) Petit, M.; Mortreux, A.; Petit, F.; Buono, G.; Peiffer, G. *Nouv. J. Chim.* **1983**, *7*, 593. (g) Yamashita, M.; Kobayashi, M.; Sugiura, M.; Oshikawa, T.; Inokawa, S.; Yamamoto, H. *Carbohydr. Res.* **1984**, *131*, C6. (h) Saito, S.; Nakamura, Y.; Morita, Y. *Chem. Pharm. Bull.* **1985**, *33*, 5284. (i) Massonneau, V.; Le Maux, P.; Simonneaux, G. *J. Organomet. Chem.* **1985**, *288*, C59. (j) Le Maux, P.; Massonneau, V.; Simonneaux, G. *J. Organomet. Chem.* **1985**, *284*, 101. (k) Iida A.; Yamashita, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2365. (l) Felföldi, K.; Kapocsi, I.; Bartók, M. *J. Organomet. Chem.* **1989**, *362*, 411. (m) Yamashita, M.; Naoi, M.; Imoto, H.; Oshikawa, T. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 942. (n) Pastor, S. D. *Sulfur Lett.* **1989**, *9*, 39. (o) Babiarz, J. E.; Pastor, S. D. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *91*, 263.

(4) (a) RajanBabu, T. V.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6265. (b) Bendayan, A.; Masotti, H.; Peiffer, G.; Siv, C.; Archavlis, A. *J. Organomet. Chem.* **1993**, *444*, 41. (c) Casalnuovo, A. L.; RajanBabu, T. V.; Ayers, T. A.; Warren, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 9869.

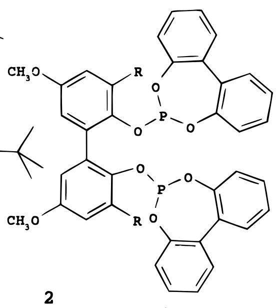
(5) (a) Higashizima, T.; Sakai, N.; Nozaki, K.; Takaya, H. *Tetrahedron Lett.* **1994**, *35*, 2023. (b) Sakai, N.; Nozaki, K.; Mashima, K.; Takaya, H. *Tetrahedron: Asymmetry* **1994**, *3*, 583.

0020-1669/96/1335-0949$12.00/0

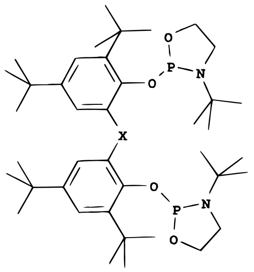
stability to the reaction conditions and handling characteristics. Indeed, sterically hindered bis(phosphite) ligands incorporating either the seven-membered dibenzo-[*d,f*][1,3,2]dioxaphosphepin or eight-membered 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin ring systems are reported to be highly efficient ligands for rhodium-catalyzed hydroformylation reactions.[7] van Leeuwen *et al.* suggested that the large natural bite angle in ligands such as **1** increases the stereoselectivity of the rhodium(I)-catalyzed hydroformylation reaction.[8] A relationship between the ratio of normal to iso olefin hydroformylation as a function of ligand bite angle has been established.[9] Gladfelter *et al.* made the important observation that the geometric inclination of the bis(phosphite) ruthenium carbonyl complex (P−Ru−P bond angle of 118.98°) prepared from **2** is due to steric rather than electronic factors.[10]



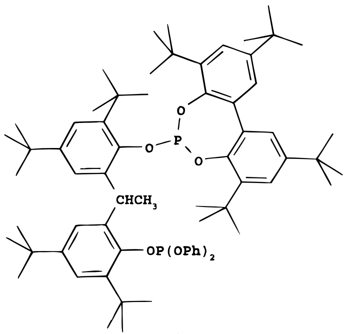
1



2
R = *tert*-butyl



3
a. R = direct bond
b. R = CHCH$_3$
c. R = CH$_2$



4

Our investigations have revealed that the geometric constraints in sterically congested bis(phosphite) ligands can lead to unique spectral properties.[11] In the $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectra of the sterically congested bis(oxazaphospholidines) **3a**,**b**, seven- and eight-bond P−P couplings of 30.3 and 30.6 Hz, respectively, are observed.[12,13] In $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectra of **4**, an unprecedented $^{8}J_{\mathrm{P-P}}$ coupling of 72.8 Hz is observed.[14] The observed solid-state intramolecular P−P distance in **4** (3.67 Å) suggested that a through-space-coupling mechanism was operative. The calculated geometry of **4** (PM3 method) suggested that the solid-state structure is near a true energy minimum and that the proximity of the P atoms in **4** is due to restricted conformational freedom resulting from steric congestion within the molecule.[14] Chiral homologues of **3a** derived from norephedrine were used as ligands for the Rh(I)-catalyzed enantioselective hydrosilylation of ketones.[15]

The study of cyclic pentaoxyphosphoranes provides mechanistic information concerning nucleophilic displacement reactions at tetracoordinate phosphorus.[16,17] Typically in cyclic pentaoxyphosphoranes with trigonal bipyramidal geometries, the ring occupies axial−equatorial positions.[18] A variable-temperature (VT) NMR study by Denney *et al.* on a pentaoxyphosphorane incorporating a tetra-*tert*-butyl-substituted 12*H*-dibenzo-[*d,g*][1,3,2]dioxaphosphocin ring suggested diequatoral ring placement.[19] Extensive systematic studies by Holmes and coworkers provided clear evidence of conformational preferences in both the solid state and solution.[20−28] The axial−equatorial or diequatorial placement of eight-membered rings in pentaoxyphosphoranes was found to be dependent upon the ring substitution. These studies have important ramifications for literature proposals describing activated states for cyclic adenosine monophosphites where trigonal bipyramidal geometries are invoked.[29]

The restriction of molecular motion by steric congestion is a potentially powerful tool in designing a molecule that favors a

---

(6) (a) Cuny, G. D.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2066. (b) Moasser, B.; Gladfelter, W. L. Presented at the 208th National Meeting of the American Chemical Society, Washington, DC, Aug 21−25, 1994; see Abstract INOR 22.

(7) (a) Billig, E.; Abatjoglou, A. G.; Bryant, D. R. U.S. Patent 4,748,-261, 1988; *Chem. Abstr.* **1987**, *107*, 7392. (b) See also: Babin, J. E.; Whiteker, G. T. U.S. Patent 5,360, 938, 1994; *Chem. Abstr.* **1995**, *122*, 186609.

(8) (a) Buisman, G. J. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1993**, *4*, 1625. (b) van Leeuwen, P. W. N. M.; Buisman, G. J. H.; van Rooy, A.; Kamer, P. C. J. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 61. (c) See also: Jongsma, T.; Fossen, M.; Challa, G.; van Leeuwen, P. W. N. M. *J. Mol. Catal.* **1993**, *83*, 17. (d) van Rooy, A.; Orij, E. N.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1995**, *14*, 34. (e) Buisman, G. J. H.; Martin, M. E.; Vos, E. J.; Klootwijk, A.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Tetrahedron: Asymmetry* **1995**, *6*, 719.

(9) (a) Casey, C. P.; Whiteker, G. T. *Isr. J. Chem.* **1990**, *3*, 299. (b) Casey, C. P.; Whiteker, G. T. *J. Org. Chem.* **1990**, *55*, 1394. (c) Casey, C. P.; Whiteker, G. T.; Campana, C. F.; Powell, D. R. *Inorg. Chem.* **1990**, *29*, 3376. (d) Casey, C. P.; Whiteker, G. T.; Melville, M. G.; Petrovich, L. M.; Gavney, J. A., Jr.; Powell, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 5535.

(10) Moasser, B.; Gross, C.; Gladfelter, W. L. *J. Organomet. Chem.* **1994**, *471*, 201.

(11) Holmes, R. R.; Prakasha, T. K.; Pastor, S. D. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; Quin, L. D., Verkade, J. G., Eds.; VCH: New York, 1994; pp 27−39.

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

(13) For metal complexes, see: Pastor, S. D.; Togni, A. *Inorg. Chim. Acta* **1989**, *159*, 3.

(14) Pastor, S. D.; Shum, S. P.; Rodebaugh, R. K.; Debellis, A. D.; Clarke, F. H. *Helv. Chim. Acta* **1993**, *76*, 900.

(15) Pastor, S. D.; Rodebaugh, R. K.; Odorisio, P. A.; Pugin, B.; Rihs, G.; Togni, A. *Helv. Chim. Acta* **1991**, *74*, 1175.

(16) Holmes, R. R. *Pentacoordinated Phosphorus: Reaction Mechansisms, Vol. II*; ACS Monograph 176; American Chemical Society: Washington, DC, 1980.

(17) For related work with pentacoordinated siloxanes, see: Day, R. O.; Prakasha, T. K.; Holmes, R. R. *Organometallics* **1994**, *13*, 1285.

(18) For reviews, see: (a) Luckenbach, R. *Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements*; G. Thieme: Stuttgart, Germany, 1973. (b) Holmes, R. R. *Pentacoordinated Phosphorus: Reaction Mechansisms, Vol. I*; ACS Monograph 176; American Chemical Society: Washington, DC, 1980.

(19) Abdou, W. M.; Denney, D. B.; Denney, D. Z.; Pastor, S. D. *Phosphorus Sulfur* **1985**, *22*, 99.

(20) Swamy, K. C. K.; Sreelatha, C.; Day, R. O.; Holmes, J.; Holmes, R. R. *Inorg. Chem.* **1991**, *30*, 3126.

(21) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 725.

(22) Hans, J.; Day, R. O.; Howe, L.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 1279.

(23) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 1913.

(24) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 3391.

(25) Prakasha, T. K.; Burton, S. D.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 5494.

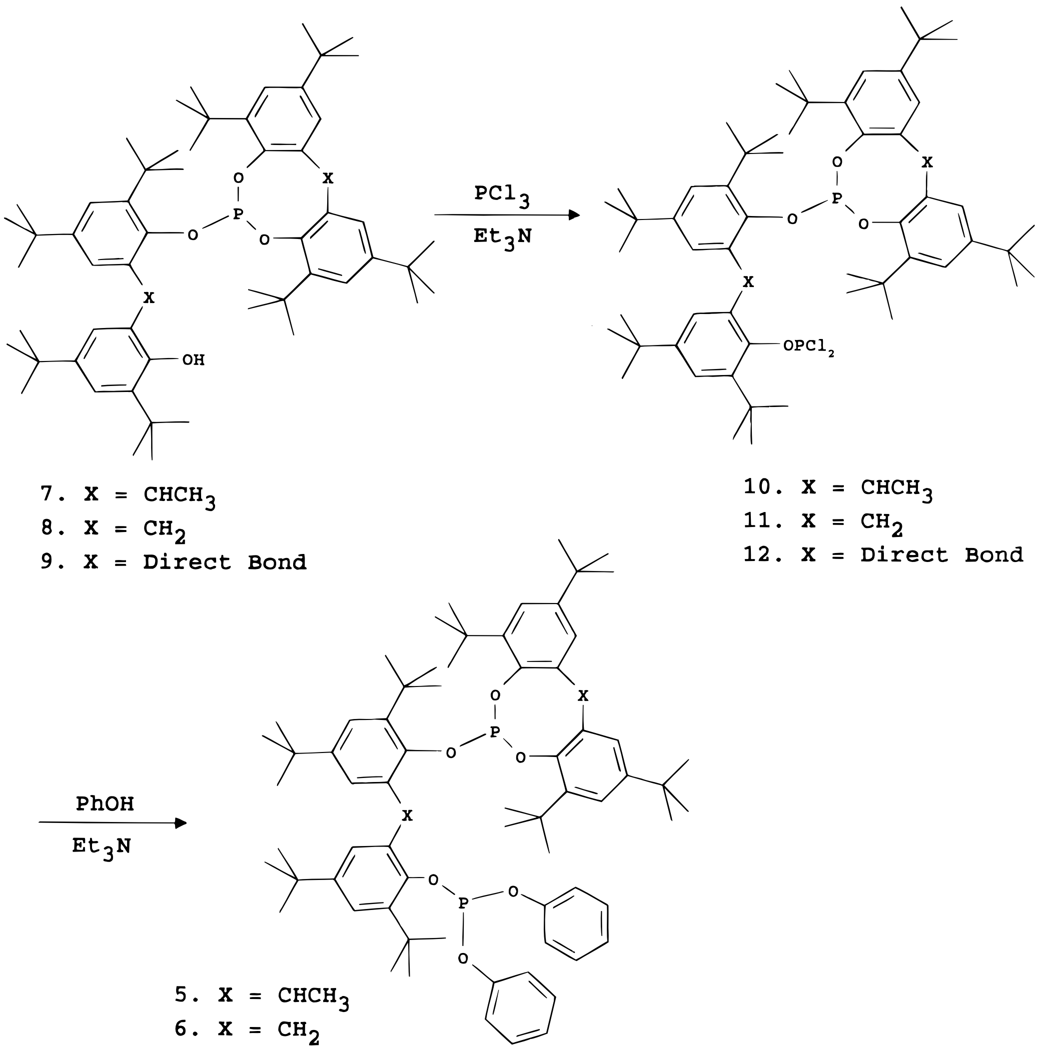
(26) Holmes, R. R.; Prakasha, T. K.; Day, R. O. *Inorg. Chem.* **1993**, *32*, 4360.

(27) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 2690.

(28) Prakasha, T. K.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1994**, *33*, 93.

(29) Holmes, R. R.; Dieters, J. A. *Inorg. Chem.* **1994**, *33*, 3235.

Scheme 1



7. X = $CHCH_3$
8. X = CH_2
9. X = Direct Bond

10. X = $CHCH_3$
11. X = CH_2
12. X = Direct Bond

5. X = $CHCH_3$
6. X = CH_2

particular conformation. Careful application of this strategy could be used, in principle, to design ligands that provide a defined coordination sphere about a metal for catalytic reactions. Application of this strategy to chiral bis(phosphite) ligands analogous to **4**, which contain both a stereoaxis and stereocenter, provides a model ligand to investigate the notion of *internal cooperativity of chirality*.[30−32] We report herein our progress in defining the effect of multiple *tert*-alkyl substitution on the conformational freedom of bis(phosphite) ligands.

Results and Discussion

Synthesis and Variable-Temperature $^{31}P\{^1H\}$ Spectral Data. The bis(phosphite) **5** was synthesized to ascertain the effect of substituting an eight-membered 12*H*-dibenzo[*d,g*]-[1,3,2]dioxaphosphocin ring for the seven-membered dibenzo-[*d,f*][1,3,2]dioxaphosphepin ring in **4**. The reaction of the hydroxyaryl-substituted phosphite **7**[33] with an excess of phosphorus(III) chloride using triethylamine as an acid acceptor gave the dichloridite **10** (87% recrystallized). (See Scheme 1.) In the $^{31}P\{^1H\}$ NMR spectrum of **10**, two doublets are observed at δ 139.1 and 203.9 ($^8J_{PP} = 18.3$ Hz), which are in the region expected for a trivalent phosphorus ester and dichloridite, respectively.[34] The reaction of the dichloridite **10** with 2 molar equiv of phenol gave the bis(phosphite) **5**.

In the ^1H NMR spectrum of **5** at 75 °C, eight upfield singlets are observed, which were assigned to the methyl protons of eight nonequivalent *tert*-butyl substituents. This observed nonequivalence is consistent with the presence of a stereocenter in the molecule. In the $^{31}P\{^1H\}$ NMR spectrum of **5** at 100 °C ($C_2D_2Cl_4$), two doublets are observed at δ 140.5 and 137.1 with an eight-bond P−P J coupling of 27.5 Hz. The existence of coupling between the two P atoms in **5** was demonstrated by obtaining the spectrum at two different field strengths and a 2D Homonuclear ^{31}P COSY experiment (Figure 1). The magnitude of the observed ^8J coupling in **5** is considerably smaller than that observed for the analogous bis(phosphite) **4**

---

(30) (a) Pastor, S. D.; Togni, A. *J. Am. Chem. Soc.* **1989**, *111*, 2333. (b) Togni, A.; Pastor, S. D. *J. Org. Chem.* **1990**, *55*, 1649. (c) Pastor, S. D.; Togni, A. *Helv. Chim. Acta* **1991**, *74*, 907. (d) Togni, A.; Pastor, S. D. *Chirality*, **1991**, *3*, 331. (e) Pastor, S. D. *Trends Organomet. Chem.* **1994**, *1*, 63.

(31) (a) Nagel, U.; Rieger, B. *Chem. Ber.* **1988**, *121*, 1123. (b) Nagel, U.; Rieger, B. *Organometallics* **1989**, *8*, 1534. (c) Nagel, U.; Krink, T. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1052. (d) Nagel, U.; Krink, T. *Chem. Ber.* **1993**, *126*, 1091.

(32) Burgess, K.; Ohlmeyer, M. J.; Whitmire, K. H. *Organometallics* **1992**, *11*, 3588.

(33) (a) Pastor, S. D.; Richardson, C. F.; NabiRahni, M. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *90*, 95. (b) See also: Odorisio, P. A.; Pastor, S. D.; Spivack, J. D. *Phosphorus Sulfur* **1984**, *19*, 1.

(34) (a) Tebby, J. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Weinheim, Germany, 1987; p 19. (b) Kleemann, S. G.; Fluck, E.; Tebby, J. C. In *Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*; Tebby, J. C., Ed.; CRC Press: Boca Raton, FL, 1991; pp 49−91.

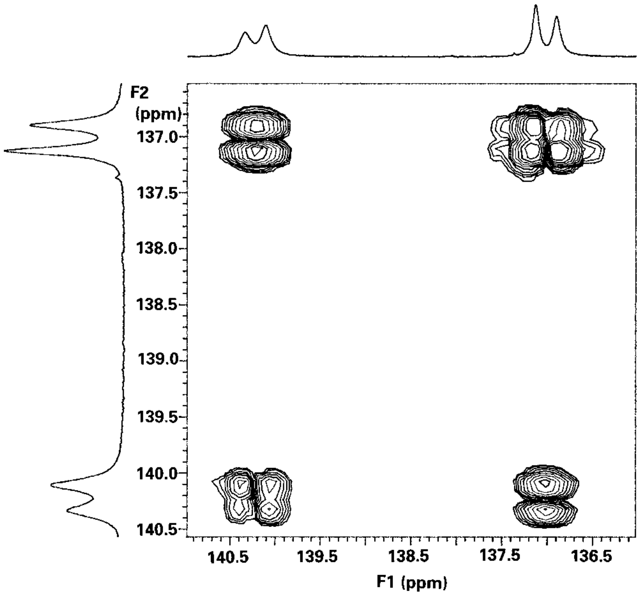


Figure 1. Homonuclear ^{31}P COSY NMR spectrum of **5**.

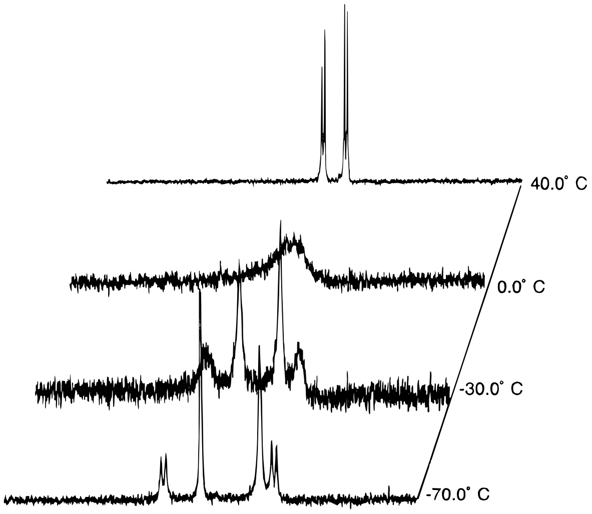


Figure 2. VT $^{31}P\{^{1}H\}$ NMR spectra of **5**.

$(^{8}J_{PP} = 72.8$ Hz). This observation suggests that the substitution of the eight-membered 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring for the seven-membered phosphepin ring results in a significant change in geometry in which the proximity of the phosphorus atoms is reduced.

In the $^{31}P\{^{1}H\}$ NMR spectrum of **5** below 0 °C, the coalescence temperature (T_C), one pair of singlet and one pair of doublet resonances are observed, which were assigned to unequal populations of two diastereoisomeric conformations (Figure 2). The two singlets for the major diastereoisomer are observed at δ 142.4 and 136.4 ($^{8}J_{PP} = 0$). The doublets for the minor diastereoisomer are observed at δ 146.2 and 134.9 with eight-bond P−P *J* coupling of 42.4 Hz. A 2.7:1 ratio of major:minor diastereoisomers ($\Delta G°_{273} = 0.5$ kcal/mol) below T_C was determined by integration of the $^{31}P\{^{1}H\}$ NMR spectrum. Caution, however, must be exercised in the interpretation of integrated ^{31}P NMR spectral resonances because the relaxation times of nonequivalent phosphorus atoms are often significantly different.[35] A weighted average of the ^{31}P NMR chemical shifts and a low-temperature NOESY experiment (−70 °C) indicate that the downfield singlet phosphorus resonance at δ 142.4 corresponds with the upfield doublet signal at δ 134.9. The free energies of activation (ΔG^*) for the process required to render these disastereoisomers equivalent were calculated by the method of Shanan-Atidi and Bar-Eli to be 12.1 and 12.6 kcal/mol.[36] This process can reasonably be assigned to the ΔG^* for inversion of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring. However, a recent VT NMR study[33a] on the hydroxyaryl phosphites **7**−**9** casts doubt on this interpretation; *vide infra*.

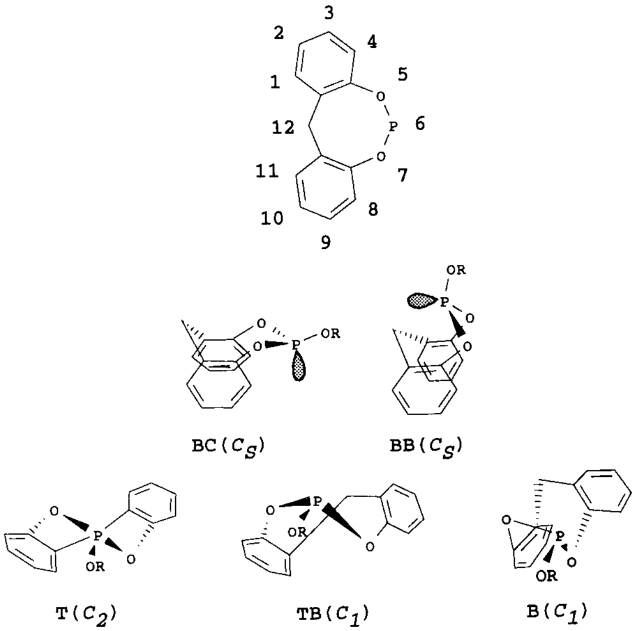


Figure 3. The *Chemical Abstracts* numbering system and conformations of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring system. The lone pair of electrons are illustrated on the BB and BC conformations only. The TB conformation illustrated represents only one member of a family of TB forms.

Studies on the conformation of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring have appeared only within the past 10 years. Quite recently, several reviews have appeared on the subject.[37−41] The commonly accepted nomenclature to describe the conformation of eight-membered rings is used herein; namely the boat−chair (C_s symmetry), boat−boat (C_s symmetry), twist-boat (C_1 symmetry), and twist (C_2 symmetry), which are abbreviated BC, BB, TB, and T, respectively.[42−44] Arshinova has noted that the boat conformer (C_1 symmetry; abbreviated B) should also be considered as it is commonly found in the solid state (Figure 3).[38−41] The B conformation represents a highly distorted TB geometry about halfway between the symmetric C_2 T and BB geometries.[42] Arshinova and co-workers contend that the BB conformer is a transition state (TS) in the conformational equilibrium of 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin and not an energy minimum

---

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

(36) Shanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961.

(37) Quin, L. D. In *Conformational Analysis of Medium-Sized Heterocycles*; Glass, R. S., Ed.; VCH: Weinheim, Germany, 1988; pp 181−216.

(38) Arshinova, R. P.; Danilova, O. I.; Arbusov, B. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1987**, *34*, 1.

(39) Arshinova, R. P. *Russ. Chem. Rev. (Engl. Transl.)* **1988**, 57, 1142.

(40) Arshinova, R. P.; Plyamovatyi, A. Ch.; Kadyrov, R. A.; Gnevashev, S. G.; Arbusov, B. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **1989**, *41*, 449.

(41) Arshinova, R. P. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *68*, 155.

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

(43) Fraser, R. R.; Raza, M. A.; Renaud, R. N.; Layton, R. B. *Can. J. Chem.* **1975**, *53*, 167.

(44) Moore, J. A.; Anet, F. A. L. In *Comprehensive Heterocyclic Chemistry*; Lwowski, W., Ed.; Pergamon: Oxford, U.K., 1984; Vol. 7, pp 653−707.

(semiempirical calculations support this conclusion).[38−41,45,46] The BB conformation has been proposed by several authors in certain cases to explain solution NMR spectral data.[47−50] The BB conformer is observed in the crystal structures in certain transition-metal-containing 12*H*-dibenzo[*d*,*g*][1,3,2]dioxametallocins[51,52] and quite recently for a 12*H*-dibenzo[*d*,*g*][1,3,2]-dioxasilocin.[53] Flexible solid-state conformations, however, can be strongly influenced by crystal-packing forces, and considerable differences between solid-state and solution conformations may exist.[42] The only P(III)-containing 12*H*-dibenzo[*d*,*g*][1,3,2]-dioxaphosphocin reported for which X-ray crystallographic data exist assumes the BC conformation in the solid state with the substituent of phosphorus positioned pseudoequatorially.[54] The pseudoequatorial placement of the substituent on phosphorus is particularly favored by the 4,8-di-*tert*-butyl substitution because this aptitude allows the sterically undemanding lone pair of electrons to be placed pseudoaxially in a cavity between the *tert*-butyl groups. This led to the suggestion that the observation of the TB conformation in 4,8-di-*tert*-butyl-substituted 6-oxo P(V)-containing 12*H*-dibenzo[*d*,*g*][1,3,2]-dioxaphosphocins[38−41,55,56] is due to destabilization of the BC conformer due to steric repulsion between the axial 6-oxo substituent and the *tert*-butyl substituents.[57]

Given the posit that the substituent on P(III)-containing 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocins assumes a pseudoequatorial placement with the lone pair of electrons placed pseudoaxially, the dynamic process observed in the VT $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectra can be assigned to inversion of the dioxaphosphocin ring in **5**. The predominant conformation observed below T_{C} is the BC conformer with both the large aryloxy substituent on phosphorus and the *C*(*12*)-methyl substitutent in a pseudoequatorial position. The absence of P−P coupling in the major species below T_{C} suggests that the P−P intramolecular distance is greater than the sum of the van der Waals radii for phosphorus in this conformation. The minor conformation below T_{C} is either the BC conformer with the C(12) and phosphorus substituent pseudoaxially placed or one of the family of flexible B conformations. A rapid equilibration of several of these species cannot be excluded. The large observed eight-bond P−P *J* coupling (42.4 Hz) suggests that a through-space mechanism is operative for transmission of coupling and that the P−P intramolecular distance in the minor diastereoisomer of **5** below T_{C} is within the sum of the van der Waals radii of phosphorus.

Quite recently, however, a VT $^{31}\text{P}\{^{1}\text{H}\}$ NMR study was reported for the hydroxyaryl phosphites **7**−**9**.[33] Dynamic behavior was observed for the methylene-bridged phosphite **8**, for which an 8.6:1 ratio of major to minor conformational isomers was observed below T_{C}. The ΔG^* of the processes ($\Delta G^*_{213} = 10.0$ and 10.9 kcal/mol) required to render these isomers equivalent was suggested to be either ring inversion or slowing of a single-bond rotational process associated with the exocyclic hydroxyaryl substituent. No dynamic behavior in the VT $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectra was observed for the corresponding C(12)-substituted phosphite **7** down to −90 °C. The absence of dynamic behavior in the C(12)-substituted phosphite **7** compared to the unsubstituted phosphite **8** casts doubt on the explanation that ring inversion is responsible for the VT behavior of **5**. Indeed, some other single-bond rotational process may be responsible for the observed VT spectra, which includes interconversion of conformational isomers (e.g. BC $\rightleftarrows$ B) without a formal ring inversion. Such a comparison must be made with caution, however, because the increased steric interactions in **5** versus **7** may lead to ground-state destabilization with an accompanying lowering of the ΔG^* for ring interconversion processes.

To further investigate what process is responsible for the VT spectral behavior of **5**, the C(12)-bridged methylene bis(phosphite) **6** was prepared. The reaction of excess phosphorus(III) chloride with **8** using triethylamine as an acid acceptor gave the dichloridite **11**. In the $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectrum of **11**, two singlets are observed at δ 202.6 and 137.3, which are in the region expected for the structure illustrated. The reaction of **11** with 2 molar equiv of phenol and triethylamine gave the bis(phosphite) **6** as a white solid. In the $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectrum of **6**, two singlet resonances are observed at δ 137.4 and 134.3. Interestingly, no P−P coupling is observed in the $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectrum of **6**.

In the VT $^{31}\text{P}\{^{1}\text{H}\}$ NMR spectra of **6** below −50 °C, the T_{C}, two pairs of singlet resonances are observed, which were assigned to two unequal populations of stereoisomeric conformations. At −85 °C, a 7.7:1 ratio of major to minor diastereoisomers ($\Delta G°_{223} = 0.9$ kcal/mol) is observed by integration of the ^{31}P signals. The two singlets for the major diastereoisomer are observed at δ 138.4 and 132.2 ($^{8}J_{\text{PP}} = 0$). Two singlet resonances for the minor diastereoisomer are observed at δ 135.4 and 140.1. The ΔG^* values for the processes required to render these diastereoisomers equivalent are 10.1 and 11.0 kcal/mol, which are similar to those observed for the precursor hydroxyaryl phosphite **8**. A reasonable explanation for the lack of observable $^{8}J_{\text{PP}}$ coupling in **6** is that the increased conformational mobility due to removal of the methyl substituents in both the exocyclic hydroxyaryl group and the dioxaphosphocin ring relative to **5** leads to populations of conformations where the intramolecular P−P distance is greater than the sum of the

---

(45) Danilova, O. I.; Arshinova, R. P.; Kadyrova, V. Kh.; Mukmeneva, N. A.; Arbusov, B. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1987**, *57*, 2381.

(46) Arshinova, R. P.; Danilova, O. I.; Ovodova, O. V. *Dokl. Chem. (Engl. Transl.)* **1986**, *287*, 852.

(47) Odorisio, P. A.; Pastor, S. D.; Spivack, J. D.; Steinhuebel, L.; Rodebaugh, R. K. *Phosphorus Sulfur* **1983**, *15*, 9.

(48) Goddard, J. D.; Payne, A. W.; Cook, N.; Luss, H. R. *J. Heterocycl. Chem.* **1988**, *25*, 575.

(49) Rzepa, H. S.; Sheppard, R. N. *J. Chem. Res., Synop.* **1988**, 102.

(50) (a) Reddy, C. D.; Reddy, R. S.; Reddy, M. S.; Krishnaiah, M.; Berlin, K. D.; Sunthankar, P. *Phosphorus, Sulfur Silicon Relat. Elem.* **1991**, *62*, 1. (b) Reddy, C. D.; Reddy, R. S.; Raju, C. N. *Asian J. Chem.* **1991**, *3*, 63. (c) Reddy, C. D.; Reddy, R. S. N.; Raju, C. N.; ElMasri, M.; Berlin, K. D.; Subramanian, S. *Magn. Reson. Chem.* **1991**, *29*, 1140. (d) Reddy, C. D.; Berlin, K. D.; Reddy, R. S.; Raju, C. N.; Elmasri, M.; Subramanian, S. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *81*, 61. (e) Reddy, B. S.; Reddy, C. D.; Reddy, P. M. *Heteroatom Chem.* **1994**, *5*, 507.

(51) (a) Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 66. (b) Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1991**, *30*, 145.

(52) (a) Toscano, P. J.; Schermerhorn, E. J.; Dettelbacher, C.; Macherone, D.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1991**, 933. (b) For application of seven- and eight-membered metallocycles as polymerization and cyclotrimerization catalysts, see: van der Linden, A.; Schaverien, C. J.; Meijboom; N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008.

(53) Clarke, F. A.; Fuhrer, H.; Meier, H.; Pastor, S. D.; Rist, G.; Shum, S. P. *Helv. Chim. Acta* **1993**, *76*, 1476.

(54) Litvinov, I. A.; Struchkov, Yu. T.; Arbusov, B. A.; Arshinova, R. P.; Ovodova, O. V. *J. Struct. Chem. (Engl. Transl.)* **1984**, *25*, 943.

(55) (a) Arbusov, B. A.; Arshinova, R. P.; Danilova, O. I.; Kadyrova, V. Kh.; Mukmeneva, N. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1986**, 1601. (b) Arshinov, R. P.; Danilova, O. I.; Ovodova, O. V. *Chem. (Engl. Transl.)* **1986**, *287*, 99. (c) Danilova, O. I.; Arshinova, R. P. *J. Gen. Chem. USSR (Engl. Transl.)* **1987**, *57*, 2393. (d) Said, M. A.; Swamy, K. C. C.; Mohan, K. C.; Lakshmi, N. V. *Tetrahedron* **1994**, *50*, 6989. For related work on dibenzo[*d*,*g*][1,3,2]-diazaphosphocines, see: (e) Cameron, T. S.; Cheng, C. Y.; Demir, T.; Howlett, K. D.; Keat, R.; Porte, A. L.; Prout, C. K.; Shaw, R. A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 510. (f) Cameron, T. S. *J. Chem. Soc., Perkin Trans. 2* **1972**, 591. (g) Demir, T.; Shaw, R. A. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1547.

(56) Pastor, S. D.; Spivack, J. D. *J. Heterocycl. Chem.* **1991**, *28*, 1561.

(57) Pastor, S. D. *Trends Heterocycl. Chem.* **1993**, *3*, 1993.

van der Waals radii of phosphorus; *vide ante*. A similar explanation was advanced for the lack of observable eight-bond P−P coupling in **3c** relative to **3b**.[12]

Given the previous observations for the bis(oxazaphospholidines) **3a**−**c**, replacement of the C(12) ethylidene in **5** by a direct C−C bond would not necessarily be expected to increase the conformational freedom of the molecule. The phosphorodichloridite **12** was prepared by the reaction of **9** with an excess of phosphorus(III) chloride using triethylamine as an acid acceptor. In the $^{31}P\{^1H\}$ NMR spectrum of **12**, two doublets are observed at δ 203.9 and 142.2 ($^7J_{PP}$ = 4.8 Hz). The bis(phosphite) **1** was prepared by the reaction of **12** with 2 mol of phenol using triethylamine as an acid acceptor (71% recrystallized).

In the $^{31}P\{^1H\}$ NMR spectrum of **1** at 40 °C, two doublets are observed at δ 143.1 and 140.1 ($^7J_{PP}$ = 4.6 Hz). In the 500 MHz ^1H NMR spectrum of **1**, nonequivalence of all eight *tert*-butyl substituent protons as well as all eight aromatic protons is observed. This observation is consistent with the presence of a stereoaxis in **1** because of hindered rotation about the single bond connecting the two aryl rings in the exocyclic substituent of the dioxaphosphepin ring. Similar observations have been previously reported for closely related sterically hindered molecules.[12,14,15,33]

In the $^{31}P\{^1H\}$ NMR spectrum of **1** below −30 °C, the coalescence temperature (T_C), one pair of singlet and one pair of doublet resonances are observed that were assigned to unequal populations of two diastereoisomers (Figure 2). The two singlets for the major diastereoisomer are observed at δ 144.0 and 141.4 ($^7J_{PP}$ = 0). The doublets are observed for the minor diastereoisomer at δ 139.7 and 122.7 with seven-bond P−P *J* coupling of 26.6 Hz. A 1.5:1 ratio of major:minor diastereoisomers ($\Delta G°_{243}$ = 0.2 kcal/mol) below T_C was determined by integration of the $^{31}P\{^1H\}$ NMR spectrum. The ΔG^* values for the processes required to render these diastereoisomers equivalent are 11.0 and 11.2 kcal/mol. The process rendering these diastereomers equivalent may reasonably be assigned to inversion of the seven-membered dibenzo[*d,f*][1,3,2]dioxaphosphepin ring.

X-ray Crystal Structures and Solid-State ^{31}P NMR. Crystals of **5** suitable for obtaining an X-ray structure were grown from a mixture of toluene and acetonitrile. Bis(phosphite) **5** has 80 non-hydrogen atoms and a triclinic crystal, which required 15 000 reflections to solve the structure. Refinement of the structure was further complicated by the fact that four of the *tert*-butyl substituents were disordered and the degree of disorder was different for each. At first the disorder appeared too difficult to solve, with each cycle of refinement taking nearly 2 days to complete. A technique was devised to allow further refinement of the structure. First, the ideal distance constraints were derived from a molecule of *tert*-butylbenzene whose energy was minimized with the MM2* force field in MacroModel. Two molecules of *tert*-butylbenzene were then superimposed such that one was rotated about the bond between the aromatic and aliphatic groups by 180°. The interatomic distances which define this idealized disordered *tert*-butylbenzene were measured in MacroModel and applied as constraints to each of the disordered *tert*-butyl substituents in the refinement. After assignment of this idealized geometry, the next step involved obtaining the relative occupancy of the disorder for each of the four groups, which differed significantly. The percentage of one rotamer in each of these groups was 83% for C(50)−C(52), 91% for C(54)−C(56), 80% for C(57)−C(59), and 45% for C(63)−C(65). The occupancy was then fixed and the refinement continued, carried out in blocks of 40 non-hydrogen atoms because of the number of variables allowed (for atomic numbering scheme, see Figure 4). One of the carbon atoms with 9% occupancy, C(54), did not refine anisotropically, but the other carbon atoms refined satisfactorally. Hydrogen atoms were not added to the disordered *tert*-butyl substituents.[59] Using this methodology allowed refinement *R* = 0.0845 and R_w = 0.1484.

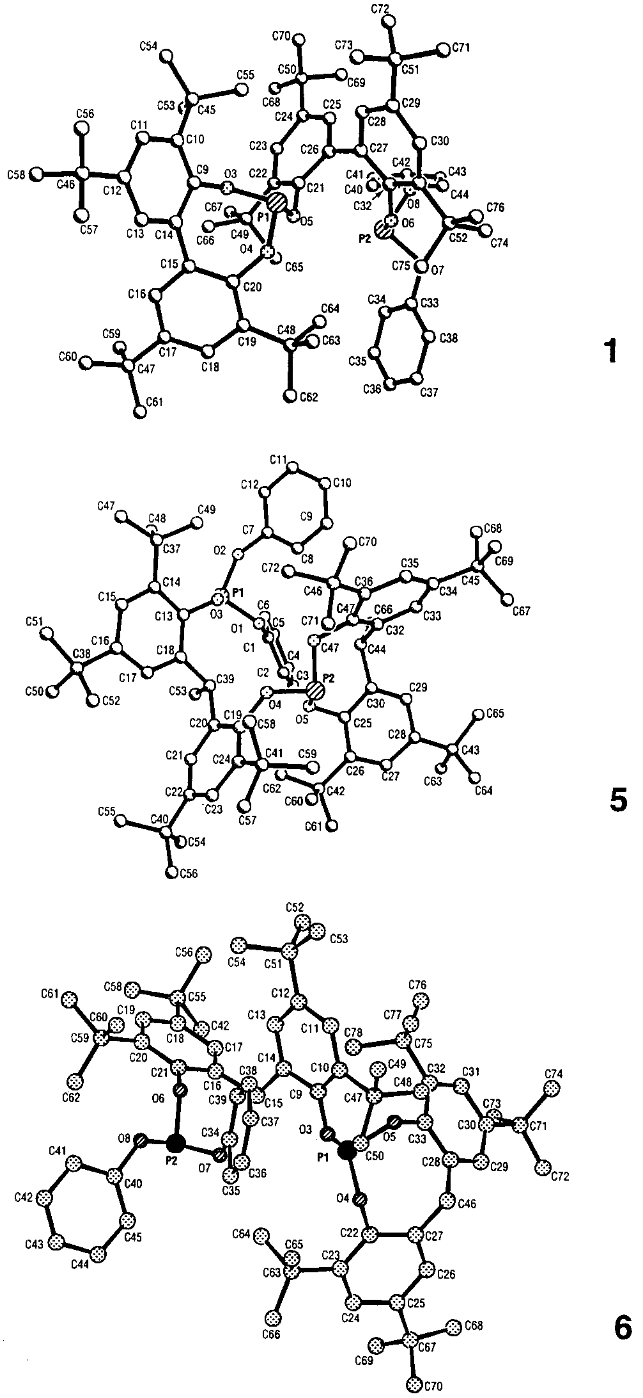


Figure 4. Molecular structures of **1**, **5**, and **6**.

The solution to the structure of **5** provides a rare example of an X-ray crystal structure of a 12*H*-dibenzo[*d,g*][1,3,2]-dioxaphosphocin ring containing tricoordinate P(III).[54] The 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin ring of **5** exists in a BC conformation in the solid state as defined by the signs of

---

(58) The resonance at δ 140.1 was partially obscured by a minor impurity resonance at δ 140.3.

(59) A molecule of solvent was located in the difference map but was not identified. The refinement includes only two of its atoms with the occupancy fixed at 0.5.

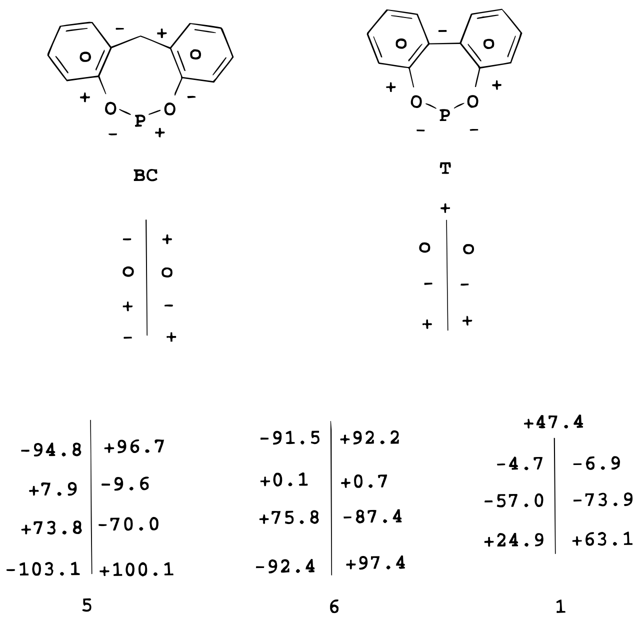


Figure 5. The T and BC conformations of the 12*H*-dibenzo[*d*,*f*][1,3,2]-dioxaphosphocin and 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring systems specified by the signs of the torsional angles according to the formalism of Hendrickson.[60]

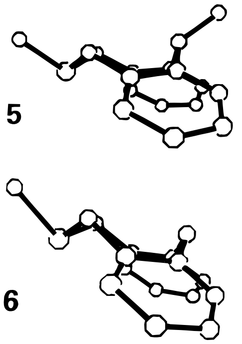


Figure 6. The BC conformations of the 12*H*-dibenzo[*d*,*g*][1,3,2]-dioxaphosphocin ring systems of **5** and **6** (ring, C(12)- and P-substituent atoms, only).

the torsional angles according to the formalism of Hendrickson (Figure 5).[60] The exocyclic oxygen atom bonded to phosphorus assumes a pseudoequatorial placement on the ring (Figure 6). The pseudoequatorial placement of the ring substituent on phosphorus provides an example of the difference between conformational energies of substituents in six- and eight-membered rings.[61] The sum of the O−P−O bond angles about phosphorus is 296.3°, which is nearly midway between pyramindal (270° for "pure" p character) and tetrahedral (328.5° for sp^3 hybridization) geometries. The geometry about the P(1) atom is similar (298.0°). The endocyclic O(5)−P(2)−O(6) bond angle (104.1°) is larger than the two exocyclic O−P−O bond angles (92.0 and 100.2°, respectively). The methyl carbon atom bonded to the C(12) bridging methylene carbon atom is also pseudoequatorially placed on the ring. This is consistent with the P−H five-bond *J* coupling observed for the pseudoaxial C(44) methine proton, which is observed in the ^{1}H NMR spectrum of **5** at δ 5.53 as a doublet of quartets ($^5J_{HP} = 1.2$ Hz).[48,49,57,62]

Quite interestingly, the intramolecular distance between P(1) and P(2) is 5.56 Å, which is larger than the sum of the van der Waals radii of phosphorus (3.7 Å).[63] The large intramolecular P−P distance found in the solid-state conformation of **5** strongly suggests that this conformation corresponds to the major diastereomer in the VT $^{31}P\{^1H\}$ NMR below the T_C *without observable* $^8J_{P-P}$ *coupling.*

Caution must be exercised in the comparison of conformations obtained from X-ray structural data with those 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, for a range of pentacoordinated phosphorus compounds, Maciel *et al.* showed that the ^{31}P chemical shifts obtained in the solid state differed little from those obtained in solution. The conclusion was reached that the solid-state and solution conformations did not vary significantly.[64] Similar conclusions were reached by Holmes and co-workers.[23,65]

In the solid-state CP-MAS ^{31}P NMR spectrum of **5** two singlets are observed at δ 135.2 and 143.7 that are similar in chemical shift to those observed in dichloromethane (δ 136.4 and 142.4, respectively). Assuming that the integrity of the solid-state conformation is maintained in solution, the similarity of the chemical shifts observed supports the suggestion that the major conformation observed below T_C is the same as the conformer observed in the solid-state crystallographic study. The large intramolecular P−P distance observed supports the lack of through-space $^8J_{PP}$ coupling.

Interestingly, in the solid-state conformation of **4**, the lone pair of electrons on the two phosphorus atoms point toward one another and the intramolecular P−P distance is within the sum of their van der Waals radii. In the solid-state conformation of **5**, however, the lone pair of electrons on the two phosphorus atoms do not mutually point toward one another. Whether a specific orientation of the lone pair of electrons on the two phosphorus atoms of **5** is a geometric requirement for $^8J_{P-P}$ coupling is unclear, because through-space coupling is not expected for this conformation in any case due to the large intramolecular P−P distance.[66] The involvement of the oxygen lone-pair in the transmission of coupling data cannot be excluded.[67,68] The presence of an sp^3 carbon atom connecting the aryl groups argues against a coupling mechanism involving the π system.[69] Our previous observation that coupling is lost

---

(60) Hendrickson, J. B. *J. Am. Chem. Soc.* **1964**, *86*, 4854.

(61) Gallagar, M. J. In *Phosphorus-31 Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Weinheim, Germany, 1987, pp 310−322.

(62) For related studies supporting this conclusion, see: (a) Lansbury, P. T.; Bieron, J. F.; Klein, M. *J. Am. Chem. Soc.* **1966**, *88*, 1477. (b) Lansbury, P. T.; Bieron, J. F.; Lacher, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 1482. (c) Lansbury, P. T.; Lacher, A. J.; Saeva, F. D. *J. Am. Chem. Soc.* **1967**, *89*, 4361. (d) Rabideau, P. W.; Marcinow, Z. *J. Org. Chem.* **1986**, *51*, 2949.

(63) Values of van der Waals radii from: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(64) Dennis, L. W.; Bartuska, V. J.; Maciel, G. E. *J. Am. Chem. Soc.* **1982**, *104*, 230.

(65) Holmes, R. R.; Prakasha, T. K. *Phosphorus, Sulfur Silicon Relat. Elem.* **1993**, *80*, 1.

(66) For a study on the geometric dependence of P−P coupling, see: Pascal, R. A., Jr.; West, A. P., Jr.; Van Engen, D. *J. Am. Chem. Soc.* **1990**, *112*, 6406.

(67) For general references on the through-space coupling mechanism, see: (a) Petrakis, L.; Sederholm, C. H. *J. Chem. Phys.* **1961**, *35*, 1243. (b) Ng, S.; Sederholm, C. H. *J. Chem. Phys.* **1964**, *40*, 2090. (c) Hilton, J.; Sutcliffe, L. H. *Prog. NMR Spectrosc.* **1975**, *10*, 27. (d) Szalontai, G.; Bakos, J.; Tóth, I.; Pelczer, I.; Scharar, P. *Phosphorus Sulfur* **1987**, *30*, 734. (e) Szalontai, G.; Bakos, J.; Tóth, I.; Heil, B. *Magn. Reson. Chem.* **1987**, *25*, 761. (f) Holah, D. G.; Hughes, A. N.; Knudsen, K. L.; Perrier, R. *J. Heterocycl. Chem.* **1988**, *25*, 155. (g) Mallory, F. B.; Mallory, C. W.; Baker, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 2577 and references therein. (h) Perera, S. D.; Shaw, B. L.; Thornton-Pett, M.; Vessey, J. D. *Inorg. Chim. Acta* **1993**, *207*, 175.

(68) For P-H coupling suggested to be mediated by the lone pair of electrons on oxygen, see: Goddard, J. D.; Payne, A. W.; Cook, N.; Luss, H. R. *J. Heterocycl. Chem.* **1988**, *25*, 575.

in the P−sulfide derivative of **3a** strongly suggests that the lone pair of electrons on phosphorus is involved.[15]

Triclinic crystals of **6** suitable for X-ray crystallography were grown from a mixture of toluene and hexane. The 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring of **6** is seen to be in a BC conformation in the solid state. The observation of five-bond ^5J H−P coupling in the solution ^{1}H NMR spectrum of **6** is consistent with the solid-state BC ring conformation being maintained in solution.[48,49,57,62] The exocyclic oxygen atom bonded to phosphorus assumes a pseudoequatorial placement on the ring (Figure 6). The sum of the O−P−O bond angles about phosphorus is 296.0°, which is essentially the same as found for the ring phosphorus atom in **5**. The endocyclic O(4)−P(1)−O(5) bond angle (105.2°) is larger than the two exocyclic O−P−O bond angles (90.4 and 97.4°, respectively).

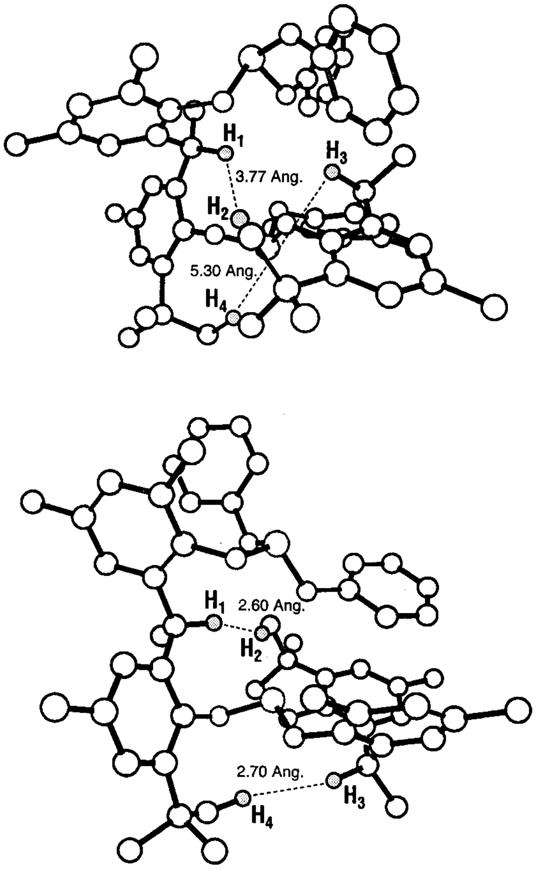
Quite interestingly, the intramolecular distance between P(1) and P(2) in the solid-state conformation of **6** is 5.48 Å, which is larger than the sum of the van der Waals radii of phosphorus (3.7 Å).[63] If this conformation is maintained in solution, the large P−P intramolecular distance is consistent with the lack of observable $^8J_{PP}$ coupling.

Monoclinic crystals of **1** suitable for X-ray crystallography were grown from a mixture of toluene and acetonitrile. Even considering the low refinement of **1** due to disorder, the intramolecular P−P distance of 4.64 Å is larger than the sum of the van der Waals radii of phosphorus. If a significant time-averaged population of this solid-state conformation is maintained in solution, the large P−P intramolecular distance is consistent with the lack of $^8J_{PP}$ coupling observed for the major diastereoisomer below the T_C.

In the solid-state, the seven-membered dibenzo[*d*,*f*][1,3,2]-dioxaphosphepin assumes a nonplanar twist conformation. The C(13)−C(14)−C(15)−C(16) torsion angle about the single bond joining the two aryl rings is 47.4°, which is similar in magnitude to that found in the seven-membered ring in **4**. This observation is consistent with our previous contention that substitution of the aryl groups of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepin ring increases the nonplanarity of the ring, presumably because of steric interactions within the ring. This contention is supported by crystallographic studies on unsubstituted dibenzo[*d*,*f*][1,3,2]-dioxaphosphepin rings[22,70−72] and semiempirical geometry calculations on model compounds.[14]

The endocyclic O(3)−P(1)−O(4) bond angle (102.7°) is larger than the exocyclic O−P−O bond angles (94.9 and 100.7°). The sum of the O−P−O bond angles about phosphorus is 297.8°, consistent with a pyramidal geometry about phosphorus.

Solution NOE Studies and Conformational Search. Although the two species observed for **5** below the T_C might be assigned to a conformational equilibrium due to ring inversion of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring, the slowing on the NMR time scale of other single-bond-rotational processes could account for the observed spectra; *vide ante*. In particular, a rotation about the P(2)−O(4) and O(4)−C(19) bonds can be envisioned that leads to the conformational rotamer $\mathbf{5_{rot}}$ with the lone pair of electrons on phosphorus pointing toward P(1) (Figure 7). A random conformational search performed with the AMBER*[73,74] force field showed that $\mathbf{5_{rot}}$ is indeed a global energy minimum on the potential energy surface.



5

$\mathbf{5_{rot}}$

Figure 7. Comparison of selected internuclear distances in the solid-state conformation of **5** and the single-bond rotamer $\mathbf{5_{rot}}$.

Spectral studies in solution support the contention that a significant population of this conformation exists in solution. A combination of decoupling and DNOE experiments was used to assign the individual peaks in the 500 MHz ^{1}H NMR spectrum of **5**, which were generated at both NMR probe temperature and 75 °C. Eight distinct singlets are observed for the methyl protons of the eight nonequivalent *tert*-butyl substituents, as well as distinct doublets for the eight nonequivalent aromatic protons. The resonance at δ 1.65 was assigned to the methyl group protons of the *tert*-butyl group bonded to C(14) by the observation of an NOE from the *ortho* protons of the phenoxy groups bonded to P(1) (refer to Figures 4 and 7 for atom designation). Quite interestingly, the *C*(*39*)-methine proton was observed as a doublet of doublets of quartets, which was a result of five-bond coupling to both the P(1) and P(2) atoms.

The key NOE's observed that support the existence of a conformation similar to $\mathbf{5_{rot}}$ are 2-fold.[75] An NOE is observed upon irradiation of the *tert*-butyl group bonded to the C(36) atom of the ring to the methine proton H(1) bound to the acyclic bridging C(39) atom (Figure 7). An NOE is observed between

---

(69) For nine-bond P−P coupling mediated by π-electron contributions, see: Ernst, L. *J. Chem. Soc., Chem. Commun.* **1977**, 375.

(70) Baker, M. J.; Harrison, K. N.; Orpen, A. G.; Pringle, P. G.; Shaw, G. *J. Chem. Soc., Chem. Commun.* **1991**, 803.

(71) Meyer, T. G.; Fischer, A.; Jones, P. C.; Schmutzler, R. *Z. Naturforsch.* **1993**, *48B*, 659.

(72) For early studies in solution, see: (a) Pastor, S. D.; Spivack, J. D.; Steinhuebel, L. P.; Matzura, C. *Phosphorus Sulfur* **1983**, *15*, 253. (b) Arbusov, B. A.; Kadyrov, R. A.; Arshinova, R. P.; Mukmeneva, N. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1981**, 784.

(73) (a) Weiner, S. J.; Kollman, P. A.; Case, D. A.; Singh, U. C.; Ghio, C.; Alagona, G.; Profeta, S., Jr.; Weiner, P. *J. Am. Chem. Soc.* **1984**, *106*, 765 and references therein. (b) Weiner, S. C.; Kollman, P.; Nguyen, D. T.; Case, D. A. *J. Comput. Chem.* **1986**, *7*, 230.

(74) Mohamadi, F.; Richards, N. G. J.; Guida, W. C.; Liskamp, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440.

(75) Typically, a NOE is observed for protons within 5 Å of each other. (a) For a concise discussion and caveats, see: Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; pp 30−31. (b) For a detailed monograph, see: Neuhaus, D.; Williamson, M. *The Nuclear Overhauser Effect in Structural and Conformational Analysis*; VCH: Weinheim, Germany, 1989.

the methyl group protons of *tert*-butyl group bonded to the C(24) and the methine proton H(3) bonded to C(44) of the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring. These NOE's are consistent with conformation **5**$_{\mathbf{rot}}$ illustrated. Measurement of the intramolecular H(1)−H(2) and H(3)−H(4) distances (2.60 and 2.70 Å, respectively) in **5**$_{\mathbf{rot}}$ [H(2) is bonded to C(72) and H(4) is bonded to C(59)] supports the observed NOE's. In the solid-state conformation of **5,** the H(1)−H(2) and H(3)−H(4) distances after idealized geometrical attachment of the protons to the appropriate carbon atoms are significantly larger (3.77 and 5.30 Å, respectively). The intramolecular P−P bond distance is 4.50 Å in **5**$_{\mathbf{rot}}$ versus 5.56 Å observed in the solid-state conformation.

Conclusions

The solution DNOE NMR spectral data suggest that the VT ^{31}P NMR spectral data obtained for **5** are best explained by diastereomeric conformations interconverted primarily by hindered rotation(s) about the single bond(s) connecting the 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin ring to the substituted-diphenoxydiaryl exocyclic group, rather than a ring inversion process. This explanation suggests that eight-bond P−P coupling is observed in solution for a population of rotamer **5**$_{\mathbf{rot}}$ in which the intramolecular P−P distance is within the sum of the van der Waals radii. The conformation in the solid state corresponds to the diastereomer below T_C for which P−P coupling in solution is not observed.

Although the VT ^{31}P NMR spectral data obtained for **5** can be reasonably attributed to a process involving hindered rotation(s) about a single bond (or bonds), the ring inversion process cannot be totally excluded. Regardless of the exact process occurring, the important conclusion from this study is that *restriction of molecular motion by steric congestion can be used to rationally design a ligand favoring a particular disposition of phosphorus atoms.* The uniquely designed coordination spheres that these ligands provide are expected to lead to enhanced selectivity in transition-metal-catalyzed reactions.[76]

Experimental Section

All melting points were determined in open capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR (499.84 and 300.08 MHz, respectively) spectra were taken on a Varian Model Gemini-300 or Unity-500 spectrometer. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. ^{31}P NMR (80.98, 121.47, and 202.33 MHz, respectively) were obtained on a Varian Model XL-200, Gemini-300, or Unity-500 spectrometer. All ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. Significant ^{1}H NMR data are tabulated in the following order: multiplicity (m, multiplet; s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dq, doublet of quartets; dt, doublet of triplets; ddq, doublet of doublet of quartets), atom assignments, coupling constant in hertz, and number of protons. Merck silica gel 60 (200−400 mesh) was used for column chromatography. Merck precoated (0.25 mm) silica gel F-254 plates were used for TLC. Reagents were purchased from commercial laboratory supply houses. Solvents were dried prior to use when necessary with appropriate drying agents. Reactions were carried out in flame-dried apparatus under a dry inert atmosphere of either nitrogen or argon. Elemental analyses were performed by the Analytical Research Department, Ciba-Geigy Corp. Calculations were performed using MacroModel[74] version 4.0 on a Silicon Graphics Personnel Iris Model 4D/35.

2-{1-{3,5-Bis(1,1-dimethylethyl)-2-[(2,4,8,10-tetrakis(1,1-dimethylethyl)-12-methyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin-6-yl)-oxy]phenyl}ethyl}-4,6-bis(1,1-dimethylethyl)phenol (7). Compound **7** was prepared using a modified procedure reported by Pastor *et al*.[33] To a solution of 87.7 g (200 mmol) of 2,2′-ethylidenebis(4,6-di-*tert*-butylphenol) and 41.8 mL (300 mmoL) of triethylamine in 300 mL of toluene was added dropwise a solution of 8.7 mL (100 mmol) of phosphorus(III) chloride in 50 mL of toluene. The reaction mixture was stirred at ambient temperature for 23 h, and the resultant suspension of triethylamine hydrochloride was removed by filtration. The solvent was removed *in vacuo*, and the residue was triturated with acetonitrile (300 mL) to give 79.4 g (86%) of a white solid, mp 219−221 °C (lit.[33] 223−227 °C). ^{31}P{^{1}H} NMR (202.33 MHz) (benzene-d_6): δ 134.4. ^{1}H NMR (300.08 MHz) (benzene-d_6): δ 1.13 (s, 9 H), 1.15 (s, 9 H), 1.20 (s, 9 H), 1.28 (s, 9 H), 1.40 (s, 9 H), 1.42 (s, 9 H), 1.42 (d, 3 H), 1.59 (s, 9 H), 1.63 (s, 9 H),1.97 (d, 3 H), 5.30 (dq, C(12)H, $^{3}J_{\mathrm{HCCH}} =$ 6.5 Hz, $^{5}J_{\mathrm{HP}} =$ 2.0 Hz, 1 H), 5.57 (s, OH, 1 H), 5.79 (dq, 1 H), 7.29 (d, 1 H), 7.32 (d, 1 H), 7.36 (d, 1 H), 7.41 (d, 1 H), 7.42 (d, 1 H), 7.57 (d, 2 H), 7.60 (d, 1 H). Anal. Calcd for $C_{60}H_{89}O_4P$: C, 79.6; H, 9.9. Found: C, 79.1; H, 10.2.

2-{1-{3,5-Bis(1,1-dimethylethyl)-2-[(2,4,8,10-tetrakis(1,1-dimethylethyl)-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin-6-yl)oxy]phenyl}-methyl}-4,6-bis(1,1-dimethylethyl)phenol (8). The procedure for compound **7** was repeated using 84.9 g (200 mmol) of 2,2′-methylenebis(4,6-di-*tert*-butylphenol),[77] 41.8 mL (300 mmol) of triethylamine, and 8.7 mL (100 mmol) of phosphorus(III) chloride in 300 mL of toluene (18 h at reflux temperature). The residue was triturated with acetonitrile (200 mL) give 80.4 g (92% yield) of a white solid, mp 243-246 °C (lit.[33] 246−253 °C). ^{31}P{^{1}H} NMR (121.47 MHz) (benzene-d_6): δ 137.0. ^{1}H NMR (499.84 MHz) (CDCl$_3$): δ 1.23 (s, 18 H), 1.25 (s, 9 H), 1.29 (s, 9 H), 1.31 (s, 18 H), 1.37 (s, 9 H), 1.53 (s, 9 H), 3.49 (d, C(12)H, $^{2}J_{\mathrm{HCH}} =$ 12.8 Hz, 1 H), 4.33 (s, CH$_2$, 2 H), 4.50 (dd, C(12)H, $^{2}J_{\mathrm{HCH}} =$ 12.8 Hz, $^{5}J_{\mathrm{HP}} =$ 2.8 Hz, 1 H), 5.72 (s, OH, 1 H), 7.05 (overlapping d, 2 H), 7.18 (d, 1 H), 7.25 (d, 2 H), 7.28 (d, 1 H), 7.34 (d, 2 H). Anal. Calcd for $C_{58}H_{85}O_4P$: C, 79.4; H, 9.8. Found: C, 79.2; H, 10.0.

2-{3,5-Bis(1,1-dimethylethyl)-2-[(2,4,8,10-tetrakis(1,1-dimethylethyl)dibenzo[*d*,*f*][1,3,2]dioxaphosphepin-6-yl)oxy]phenyl}-4,6-bis-(1,1-dimethylethyl)phenol (9). The procedure of compound **7** was repeated using 120 g (252 mmol) of 3,3′5,5′-tetrakis(1,1-dimethylethyl)-1,1′-biphenyl-2,2′-diol,[78] 81.6 mL (431 mmol) of triethylamine, and 19.2 mL (220 mmol) of phosphorus(III) chloride in 310 mL of toluene (24 h at ambient temperature). The residue was triturated with acetonitrile (500 mL) to give 31.69 g (26%) of a white solid, mp 245−250 °C (lit.[33] 245−250 °C). ^{31}P{^{1}H} NMR (202.33 MHz) (benzene-d_6): δ 144.2. ^{1}H NMR (300.08 MHz) (benzene-d_6): δ 1.12 (s, 9 H), 1.21 (s, 9 H), 1.23 (s, 9 H), 1.29 (s, 9 H), 1.39 (s, 9 H), 1.40 (s, 9 H), 1.48 (s, 9 H), 1.65 (s, 9 H), 5.70 (s, OH, 1 H), 7.22 (d, 1 H), 7.23 (d, 1 H), 7.31 (d, 1 H), 7.46 (d, 1 H), 7.47 (d, 1 H), 7.50 (d, 1 H), 7.54 (d, 1 H), 7.60 (d, 1 H). Anal. Calcd for $C_{56}H_{81}O_4P$: C, 79.2; H, 9.6. Found: C, 79.3; H, 10.0.

2-{3,5-Bis(1,1-dimethylethyl)-2-{[2,4,8,10-tetrakis(1,1-dimethylethyl)dibenzo[*d*,*f*][1,3,2]-dioxaphosphepin-6-yl]oxy}phenyl}-4,6-bis-(1,1-dimethylethyl)phenyl Diphenyl Phosphite (1). To a solution of 26.7 g (31.5 mmol) of **9** and 8.8 mL (63 mmol) of triethylamine in 200 mL of toluene was added dropwise a solution of 5.5 mL (63 mmol) of phosphorus(III) chloride in 20 mL of toluene. After the addition was complete, the reaction mixture was heated at reflux for 28 h. The reaction mixture was filtered to remove triethylamine hydrochloride, and the volatiles were removed *in vacuo*. The residue was triturated with acetonitrile (200 mL) to give 25.3 g (85%) of **12** as an off-white solid, mp 220−231 °C. ^{31}P{^{1}H} NMR (80.98 MHz) (benzene-d_6): δ 203.9 (d, $^{7}J_{\mathrm{PP'}} =$ 4.6 Hz), 142.2 (d). The phosphorodichloridite **12** was converted to the bis(phosphite) without further purification.

To a solution of 20.0 g (21 mmol) of **12** in 150 mL of toluene was added dropwise a solution of 4.0 g (42 mmol) of phenol and 5.9 mL (42 mmol) of triethylamine in 40 mL of toluene. The reaction mixture was stirred for 2 h at ambient temperature, and then the resultant precipitate of triethylamine hydrochloride was removed by filtration. The residue was purified by flash chromatography[79] (silica gel; 99.5: 0.5 hexane:ethyl acetate eluent) to give 15.9 g (71%) of **1** as white

---

[76] Wink, D. J.; Kwok, T. W.; Yee, A. *Inorg. Chem.* **1990**, *29*, 5006.

[77] Odorisio, P. A.; Pastor, S. D.; Spivack, J. D.; Bini, D.; Rodebaugh, R. K. *Phosphorus Sulfur* **1984**, *19*, 285−293.

[78] Kushioka, K. *J. Org. Chem.* **1983**, *48*, 4948.

[79] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

solid, mp 141−145 °C. ^{31}P{^{1}H} NMR (202.33 MHz) (benzene-d_6): δ 140.1 (d, $^7J_{PP}$ = 4.6), 143.1 (d). ^{1}H NMR (499.84 MHz) (benzene-d_6): δ 1.17 (s, 9 H), 1.21 (s, 9 H), 1.30 (s, 9 H), 1.32 (s, 9 H), 1.34 (s, 9 H), 1.37 (s, 9 H), 1.70 (s, 9 H), 1.80 (s, 9 H), 7.23 (d, 1 H), 7.27 (d, 1 H), 7.30 (d, 1 H), 7.47 (d, 1 H), 7.52 (d, 1 H), 7.59 (d, 1 H), 7.60 (d, 1 H), 7.72 (d, 1 H). Anal. Calcd for $C_{68}H_{90}O_6P_2$: C, 76.7; H, 8.5. Found: C, 77.0; H, 8.9.

Suitable crystals for X-ray analysis (colorless prisms) were grown from a 9:1 acetonitrile:toluene mixture (v/v). Crystal data: $C_{68}H_{72}O_6P_2$; fw = 1047.2; crystal size (mm) 0.1 × 0.1 × 0.4; crystal system monoclinic; cell parameters a = 14.591(6) Å, b = 19.846(4) Å, c = 24.885(6) Å, β = 99.60(2)°, V = 7105(3) Å^3; space group $P2_1/n$; d_{calc} = 0.979 Mg·m^{-3}; F_{000} = 2232; absorption coefficient = 0.871 mm^{-1}; Z = 4. Data collection: 2θ range = 3.15−115.0°; temperature = 23 °C; Siemens R3m/V diffractometer; Cu Kα (λ = 1.541 78 Å) radiation; highly oriented graphite crystal monochromator; scan type $2\theta-\theta$; scan speed (variable) = 3.00−14.65° min^{-1} in ω; independent reflections 9673; observed reflections 6329 ($F > 3.0\sigma(F)$). R indices (observed): R = 0.0842, R_w = 0.1220. R indices (all data): R = 0.1187, R_w = 0.1332. Solution: direct methods. Refinement method: full-matrix least-squares; Siemens SHELXTL PLUS (VMS) system.

2-{1-{3,5-Bis(1,1-dimethylethyl)-2-{[2,4,8,10-tetrakis(1,1-dimethylethyl)-12-methyl-12*H*-dibenzo[*d,f*][1,3,2]dioxaphosphocin-6-yl]-oxy}phenyl}ethyl}-4,6-bis(1,1-dimethylethyl)phenyl Diphenyl Phosphite (5). By the procedure used to prepare compound **1**, compound **10** was prepared from 50.0 g (55mmol) of **7**, 16.0 mL (114 mmol) of triethylamine, and 9.9 mL (114 mmol) of phosphorus(III) chloride in 250 mL of toluene (20 h at reflux temperature). The residue was triturated with acetonitrile (200 mL) to give 48.6 g (87%) of a white solid, mp = 195−200 °C. ^{31}P{^{1}H} NMR (80.98 MHz) (benzene-d_6): δ 203.9 (d, $^8J_{PP'}$ = 18.3 Hz), 139.1 (d). The phosphorodichloridite **10** was converted to the bis(phosphite) without further purification.

Compound **5** was prepared from 35.0 g (35mmol) of **10**, 6.6 g (70 mmol) of phenol, and 9.8 mL (70 mmol) of triethylamine in 300 mL of toluene (16 h at ambient temperature). The residue was triturated with acetonitrile (200 mL) to give 33.8 g (86%) of **5** as a white solid, mp 152-156 °C. Spectral assignments were supported by appropriate DEC, DNOE, and NOESY experiments. P−P coupling was demonstrated by a 2D homonuclear ^{31}P COSY experiment in benzene-d_6. Carbon atoms are designated according to the crystal structure numbering scheme. ^{31}P{^{1}H} NMR (121.47 MHz) ($C_2D_2Cl_4$)(100 °C): δ 137.1 (d, $^8J_{PP}$ = 27.5 Hz), 140.5 (d). ^{1}H NMR (499.84 MHz) (benzene-d_6): δ 1.18 (s, 9 H), 1.26 (s, 9 H), 1.30 (s, 9 H), 1.31 (s, 9 H), 1.37 (s, 9 H), 1.41 (s, 9 H), 1.54 (d, C(12)CH$_3$, 3 H), 1.65 (s, 9 H), 1.73 (s, 9 H), 5.53 (dq, C(44)H, $^5J_{HP}$ = 1.2 Hz, 1 H), 4.65 (ddq, C(39)H, $^5J_{HP}$ = 5.2 Hz, $^5J_{HP'}$ = 5.2 Hz, 1 H), 6.61 (t, 2 H), 6.65 (d, 2 H), 6.66 (t, 1 H), 6.72 (t, 1 H), 6.75 (d, 2 H), 6.82 (t, 2 H), 7.03 (d, 1 H), 7.20 (d, 1 H), 7.28 (d, 1 H), 7.33 (d, 1 H), 7.49 (d, 1 H), 7.52 (d, 1 H), 7.60 (d, 1 H), 7.64 (d, 1 H). Anal. Calcd for $C_{72}H_{98}O_6P_2$: C, 77.1; H, 8.8. Found: C, 77.5; H, 9.1.

Suitable crystals for X-ray analysis (colorless prisms) were grown from an 8:2 acetonitrile:toluene mixture (v/v). Crystal data: $C_{72}H_{98}O_6P_2$; fw = 1098.2; crystal size (mm) 0.4 × 0.5 × 0.5; crystal system triclinic; cell parameters a = 11.530(3) Å, b = 13.751(3) Å, c = 24.134(4) Å, α = 83.480(10)°, β = 89.70(2)°, γ = 67.46(2)°, V = 3508.3(12) Å^3; space group $P\bar{1}$; d_{calc} = 1.040 Mg·m^{-3}; F_{000} = 1156; absorption coefficient = 0.912 mm^{-1}; Z = 2. Data collection: 2θ range = 3.2−115.0°; temperature = 23 °C; Siemens R3m/V diffractometer; Cu Kα (λ = 1.541 78 Å) radiation; highly oriented graphite crystal monochromator; scan type $2\theta-\theta$; scan speed (variable) = 3.00−14.65° min^{-1} in ω; reflections collected 15 334; independent reflections 9574; observed reflections 9567 ($F > 3.0\sigma(F)$). R indices (observed): R = 0.0845, R_w = 0.1484. R indices (all data): R = 0.0939, R_w = 0.1561. Solution: direct methods. Refinement method: full-matrix least-squares; Siemens SHELXTL PLUS (VMS) system.

2-{1-{3,5-Bis(1,1-dimethylethyl)-2-{[2,4,8,10-tetrakis(1,1-dimethylethyl)-12*H*-dibenzo[*d,f*][1,3,2]dioxaphosphocin-6-yl]oxy}phenyl}-methyl}-4,6-bis(1,1-dimethylethyl)phenyl Diphenyl Phosphite (6). By the procedure used to prepare compound **1**, compound **11** was prepared from 40.0 g (45.6mmol) of **8**, 7.9 mL (57 mmol) of triethylamine, and 5.0 mL (57 mmol) of phosphorus(III) chloride in 210 mL of toluene (3 h at reflux temperature). The residue was triturated with 200 mL of acetonitrile to give 33.2 g (75%) of **11**. ^{31}P-{^{1}H} NMR (200 MHz) (benzene-d_6): δ 202.6, 137.2. The phosphorodichloridite **11** was converted to the bis(phosphite) without further purification.

Compound **6** was prepared from 9.77 g (10 mmol) of **11**, 1.88 g (20 mmol) of phenol, and 2.8 mL (20 mmol) of triethylamine in 100 mL of toluene (1 h at ambient temperature). The residue was triturated with 200 mL of acetonitrile to give 8.7 g (79.8%) of **6** as a white solid, mp 112−117 °C. MS: m/z 1094 (M$^{\bullet+}$). ^{31}P{^{1}H} NMR (80.98 MHz) (benzene-d_6): δ 137.4 (s), 134.3 (s). ^{1}H NMR (300.08 MHz) (benzene-d_6): δ 1.19 (s, 9 H), 1.23 (s, 9 H), 1.24 (s, 18 H), 1.28 (s, 18 H), 1.59 (s, 9 H), 1.77 (s, 9 H), 3.24 (d, C(12)H, $^2J_{HCH}$ = 12.8 Hz, 1 H), 4.65 (dd, C(12)H, $^2J_{HCH}$ = 12.8 Hz, $^5J_{HP}$ = 2.7 Hz, 1 H), 5.10 (d, $^5J_{HP}$ = 2.3, 2 H), 6.51 (d, 1 H), 6.70 (m, 4 H), 6.82 (m, 1 H), 6.99 (m, 4 H), 7.24 (d, 4 H), 7.29 (m, 3 H), 7.46 (d, 1 H). Anal. Calcd for $C_{71}H_{96}O_6P_2$: C, 76.9; H, 8.7. Found: C, 77.2; H, 8.7.

Suitable crystals for X-ray analysis were grown form a 95:5 hexane: toluene mixture (v/v). Crystal data: $C_{70}H_{94}O_6P_2$; fw = 1093.46; crystal size (mm) 0.31 × 0.14 × 0.03; crystal system triclinic; cell parameters a = 14.318(2) Å, b = 14.636(2) Å, c = 18.264(2) Å, α = 69.19(1)°, β = 71.86(1)°, γ = 83.87(1)°, V = 3400(1) Å^3; space group $P\bar{1}$; d_{calc} = 1.068 Mg·m^{-3}; Z = 2. Data collection: 2θ range = 3−55°; temperature = −80 °C; Enraf-Nonius CAD4 diffractometer; Cu Kα (λ = 1.541 78 Å) radiation; highly orientated graphite crystal monochromator; reflections measured 9791; observed reflections 4018 ($F > 3.0\sigma(F)$); R = 0.082, R_w = 0.101; weighting scheme $w = 1/\sigma^2(|F_o|)$. Solution: direct methods. Refinement method: full-matrix least-squares (SHELXTL).

Acknowledgment. The authors thank Ciba-Geigy for support and permission to publish this work and Ms. S. Loggins and Mr. B. Mason (Ciba Additives Scientific Documentation Department) for on-line computer literature searches.

Supporting Information Available: Additional structural diagrams and data from X-ray crystallographic analysis of the bis(phosphites) **1**, **5**, and **6**, including tables of crystal data, thermal parameters, bond angles, bond lengths, torsion angles, and atomic parameters (35 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead for ordering information and Internet access instructions.

IC9509286