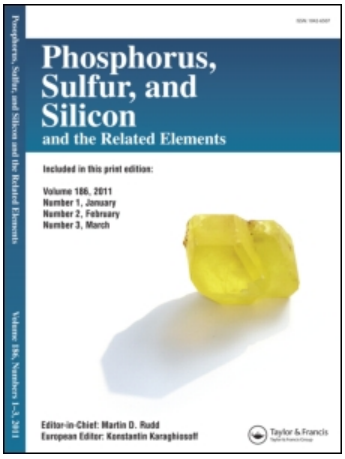

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Sterically Congested Ligands: Synthesis and Solution Conformation of Bisphosphite Ligand Precursors

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STERICALLY CONGESTED LIGANDS: SYNTHESIS AND SOLUTION CONFORMATION OF BISPHOSPHITE LIGAND PRECURSORS

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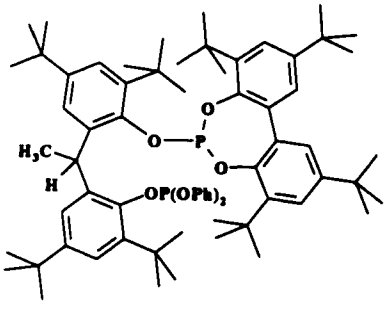
The synthesis and characterization of precursors to sterically hindered bisphosphite ligands containing the dibenzo[*d,f*][1,3,2]dioxaphosphepin and dibenzo[*d,g*][1,3,2]dioxaphosphocin ring system is described. The ΔG^* for ring inversion of the dibenzo[*d,f*][1,3,2]dioxaphosphepin ring was determined by VT $^{31}P\{^1H\}$ NMR spectroscopy. The ^1H NMR spectra of the dibenzo[*d,g*][1,3,2]dioxaphosphocin ligands were consistent with the eight-membered ring adopting a boat-chair conformation in solution.

Key words: Ligand, dibenzo[*d,f*][1,3,2]dioxaphosphepin ring, dibenzo[*d,g*][1,3,2]dioxaphosphocin ring, conformational analysis, ΔG^* for ring inversion.

Chiral phosphorus ligands have played an important role in the design of chiral transition-metal catalysts for asymmetric synthesis.[1] Quite recently, studies have appeared on sterically congested ligands incorporating the dibenzo[*d,f*][1,3,2]dioxaphosphepin and dibenzo[*d,g*][1,3,2]dioxaphosphocin ring systems,[2–4] which are touted as superior ligands for transition-metal-catalyzed hydroformylation reactions.[5] Van Leeuwen *et al.* reported asymmetric rhodium-catalyzed hydroformylation reactions using chiral derivatives of the dibenzo[*d,f*][1,3,2]dioxaphosphepin ring system as ligands.[6] Holmes and co-workers have shown that sterically hindered dibenzo[*d,g*]-[1,3,2]dioxaphosphocin rings may adopt an unusual diequatorial placement in pentaoxyphosphoranes.[7,8] ^{31}P Chemical shift correlations of cyclic oxyphosphoranes containing these and other medium-sized ring systems were reported by Holmes and Prakasha.[9]

Quite interestingly, in the $^{31}P\{^1H\}$ NMR spectrum of the ligand **1**, unprecedented eight-bond P—P J coupling of 72.8 Hz is observed.[2] Crystallographic and semi-



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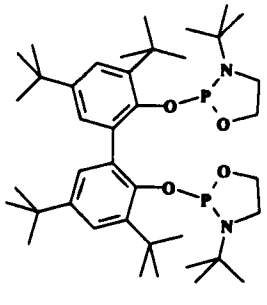

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empirical calculations supported a through-space coupling mechanism in which the close proximity of the two phosphorus atoms to one another is due to restricted conformational freedom because of steric congestion within the molecule. A similar explanation was forwarded to explain the observed ^7J P—P coupling in the highly substituted bis(oxazaphospholidine) **2**.[10-12]

The synthesis and characterization of precursors required for the synthesis of ligands analogous to **1** has not been reported. The synthesis and characterization of these ligand precursors, which are potentially interesting hydroxy-functional phosphite ligands in their own right, as well as our efforts to further elaborate the factors that dictate the conformation of the seven-membered dibenzo-[*d*,*f*][1,3,2]dioxaphosphepin and eight-membered 12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin rings are described herein.

RESULTS AND DISCUSSION

The phosphite **4** was prepared by the reaction of two molar equivalents of **3** with one molar equivalent of phosphorus(III) chloride using triethylamine as an acid acceptor in 82% isolated yield using a modification of the method reported by Odorisio *et al.*[13] In the $^{31}P\{^1H\}$ NMR spectrum of **4**, a singlet was observed at δ 144.1, which is in the region expected for a tricoordinate P(III) ester.[14] Interestingly, in the ^1H NMR spectrum (500 Hz) of **4**, the protons of the eight *tert*-butyl groups as well as the eight aromatic protons are nonequivalent.[15] The observed ^1H NMR spectrum is consistent with the presence of a stereoaxis in **4**. This would be the case if either ring inversion of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepin ring or rotation about the single bond connecting the exocyclic aryl groups is slow on the NMR time scale. The previously measured free energy barriers for dioxaphosphepin ring inversion ($\Delta G^{\ddagger}_{232}$ = 10.2 and 10.8 kcal/mole; T_C = −41.5°C)[2] in **1** and the hindered rotation[10] about the single bond connecting the two aryl groups in **2** suggest that the latter is the case.

In the variable temperature (VT) $^{31}P\{^1H\}$ NMR spectrum of **4** below −15.1°C, the coalescence temperature (T_C), two singlets were observed at δ 143.6 and δ 148.4, which were assigned to two unequal populations of diastereoisomers (1.35 to 1 ratio by integration of the ^{31}P resonances; $\Delta G^{\ddagger}_{203}$ = 0.1 kcal/mol) (Figure 1).[16] Slow inversion on the NMR time scale of the dioxaphosphepin ring in **1** below the T_C would lead to the observation of two diastereoisomers, $R^*_{Axial}R^*_{Axial}$ and $R^*_{Axial}S^*_{Axial}$, because of the presence of a stereoaxis about the single bond connecting the aryl groups in both the dioxaphosphepin ring and the exocyclic substituent on phosphorus. The free energies of activation of the process required to render these diastereoisomers equivalent are $\Delta G^{\ddagger}_{258}$ = 11.4 and 11.6 kcal/mol, which were calculated by the method of Shanan-Atidi and Bar-Eli for unequal populations of exchanging species.[17] This process can reasonably be assigned to the ΔG^* for ring inversion of the dioxaphosphepin ring in **4**. The observed barrier observed for dioxaphosphepin ring inversion in **4** is about 1 kcal/mol higher than that observed for **1**. A small increase in ΔG^* for rotational processes in hydroxyaryl molecules due to hydrogen bonding was previously reported.[18]

The dioxaphosphocin derivative **6a**, previously isolated in low yield as the side

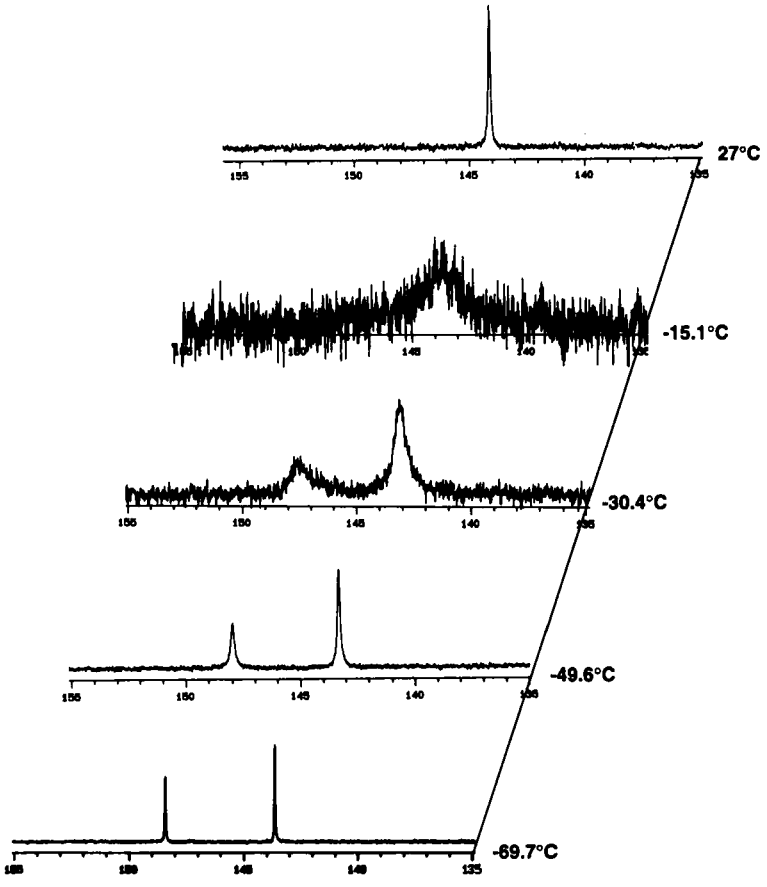
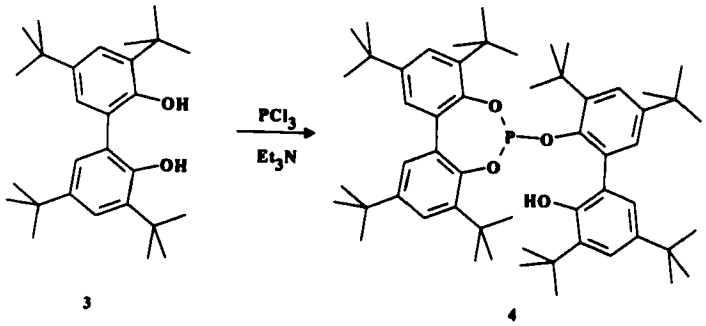
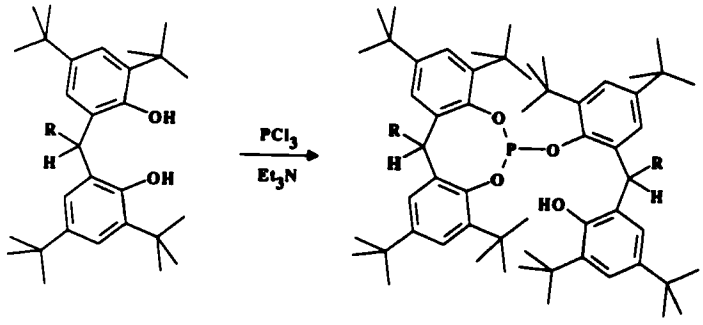


FIGURE 1 Variable temperature $^{31}P\{^1H\}$ NMR Spectra of **4**.

product of a reaction,[13] was prepared by the reaction of two molar equivalents of the methylenebisphenol **5a** with one molar equivalent of phosphorus(III) chloride using triethylamine as an acid acceptor. In the $^{31}P\{^1H\}$ NMR spectrum of **6a**, a singlet was observed at δ 137.7, which is in the region expected for a tricoordinate P(III) ester.[14] In the ^1H NMR spectrum of **6a**, the C(12) methylene protons of the dioxaphosphocin ring (the methylene group bonded to both aryl groups in the eight-membered ring) are nonequivalent and appear as a doublet at δ 3.49 ($^2J_{HCH}$ = 12.8 Hz) and doublet of doublets ($^5J_{HP}$ = 2.8 Hz) at δ 4.50. The observed geminal coupling ($^2J_{HCH}$ = 12.8 Hz) for the C(12) methylene protons and five-bond coupling of the C(12) proton to phosphorus are those expected for the dioxaphosphocin ring in **6a** adopting a boat-chair conformation (BC) commonly found for the trivalent phosphorus containing ring.[19-21] The observation of five-bond J coupling of the downfield C(12) proton to phosphorus is consistent with a pseudoaxial placement for this proton and the lone pair of electrons on phosphorus.[20,21] The observation of two equivalent pairs of *tert*-butyl substituents and aromatic protons in the ^1H NMR spectrum requires that a σ plane of symmetry pass through the phosphorus atom and C(12) methylene protons, consistent with the C_S sym-

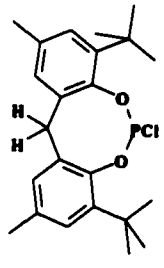


3 4



5
a. R = H
b. R = Me

6
a. R = H
b. R = Me



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metry of the BC conformation. The presence of twisted conformations that rapidly pass through the required symmetry plane (either as a transition state or intermediate) or the boat-boat (BB) conformation cannot be rigorously excluded.[22]

In the VT $^{31}P\{^1H\}$ NMR spectra of **6a** below $-60°C$, the coalescence temperature, two singlets were observed at δ 139.3 and δ 140.3, which were assigned to two unequal populations of diastereoisomeric conformations (8.6 to 1 ratio by integration of the ^{31}P resonances; $\Delta G^{\circ}_{183} = 0.8$ kcal/mol) (Figure 2). The free energies of activation for the process required to render these diastereoisomers equivalent are $\Delta G^{\neq}_{213} = 10.0$ and 10.9 kcal/mol. This process can reasonably be assigned to the $\Delta G^{\neq}$ for ring inversion of the dioxaphosphocin ring in **6a**. The observed $\Delta G^{\neq}$ is similar to that reported by Arshinova for the chloridite **7** ($\Delta G^{\neq}_{235} = 10.9$ kcal/mol and $\Delta G^{\circ}_{195} = 0.1$ kcal/mol).[23,24] Previous studies, however, suggest that 2,10-di-

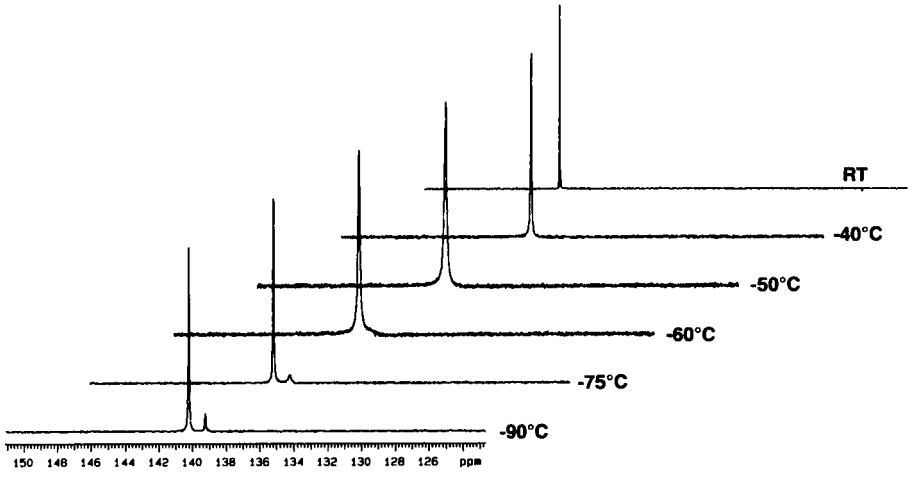

FIGURE 2 Variable temperature $^{31}P\{^1H\}$ NMR Spectra of **5a**.

tert-butyl-substituted 12*H*-dibenzo[*d*,*g*][1,3,2]dioxa-phosphocin rings with a tricoordinate P(III) atom are conformationally biased with a pseudoequatorial substituent on phosphorus.[20,25] Coalescence was observed in the VT ^1H NMR spectra of **6a**, but solubility problems at low temperature prevented obtaining resolved spectra below the T_C. Indeed, the low ΔG^* observed for **6a** may not be ring inversion, but rather the slowing of a single-bond rotation in the exocyclic substituent on phosphorus or an equilibration process with one or more of the possible flexible boat conformations.[20,21] At present, the nature of the minor isomer remains unresolved.

The C(12)-substituted dioxaphosphocin derivative **6b** was prepared in 78% yield (recrystallized) by the analogous reaction of two molar equivalents of **5b** with one molar equivalent of phosphorus(III) chloride using triethylamine as an acid acceptor. In the $^{31}P\{^1H\}$ NMR spectrum of **6b**, a singlet was observed at δ 134.7. In the ^1H NMR spectrum of **6b** nonequivalence of all the *tert*-butyl and aromatic protons is observed. This is expected to be the case because of the presence of a stereocenter in **6b**. The methine carbon atom connecting the aryl groups of the exocyclic substituent bonded to phosphorus is both stereogenic and chirotopic. A doublet of quartets is observed at δ 5.08, which is assigned to the C(12)-methine proton with $^3J_{HCCH} = 8$ Hz and $^5J_{HP} = 2$ Hz. No change was observed in the VT $^{31}P\{^1H\}$ NMR spectra (300 MHz) down to -90°C. The magnitude of the observed five-bond phosphorus-proton J coupling and the VT $^{31}P\{^1H\}$ NMR spectra is consistent with a conformationally biased ring system adopting a BC conformation with a pseudoequatorial C(12)-methyl substituent and a pseudoequatorial aryloxy substituent bonded to phosphorus.

EXPERIMENTAL

All melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. IR spectra were obtained on 1% solutions in Perkin Elmer NaCl cells using a Perkin-Elmer Model 1430 IR spectrophotometer. ^1H NMR and ^{31}P NMR spectra were taken on a Varian Model XL-200,

Gemini 300 or Unity 500 spectrometer. VT ^{31}P NMR spectra were obtained on a Varian Gemini 300 spectrometer in CD_2Cl_2 solvent. All ^1H chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. 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 ^1H 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), atom assignments, coupling constant in Hertz, and number of protons. Merck precoated (0.25 mm) silica gel F-254 plates were used for TLC. Reagents were purchased from commercial laboratory supply houses. Solvents were dried prior to use when necessary with appropriate drying agents. Reactions were carried out in flame-dried apparatus under a dry inert atmosphere of either nitrogen or argon.

3,3',5,5'-Tetra-tert-butyl-2-[(2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g][1,3,2]dioxaphosphepin-6-yl)oxy]-2'-hydroxy-1,1'-biphenyl (**4**). To a solution of 0.69 g (5 mmol) of phosphorus(III) chloride in 10 mL of toluene cooled with an ice bath was added dropwise a solution of 4.11 g (10 mmol) of **3** and 1.52 g (15 mmol) of triethylamine in 30 mL of toluene. The resultant reaction mixture was heated at 60°C for 2 hours. The reaction mixture was allowed to cool and then the suspension of triethylamine hydrochloride removed by filtration. The solvent was removed *in vacuo* and the residue recrystallized from 20 mL of acetonitrile to give 3.50 g (82%) of a white solid, mp 245–250°C (lit[13] 237–247°C).

MS (CI) 850 (MH^+); $^{31}P\{^1H\}$ NMR (202.33 MHz) ($CDCl_3$) δ 142.2; $^{31}P\{^1H\}$ NMR (121.47 MHz) (CD_2Cl_2) (27°C) δ 144.1; $^{31}P\{^1H\}$ NMR (121.47 MHz) (CD_2Cl_2) (−69.7°C) δ 143.6 (major), 148.4 (minor); ^1H NMR (499.84 MHz) ($CDCl_3$) δ 0.97 (s, 9 H), 1.26 (s, 9 H), 1.32 (overlapping s, 18 H), 1.33 (s, 9 H), 1.34 (s, 9 H), 1.42 (s, 9 H), 1.47 (s, 9 H), 5.44 (s, OH, 1 H), 7.09 (d, 1 H), 7.11 (d, 1 H), 7.16 (d, 1 H), 7.17 (d, 1 H), 7.36 (overlapping d, 2 H), 7.41 (d, 1 H), 7.43 (d, 1 H); IR (CH_2Cl_2) ν 3560 cm^{-1}.

1-[3,5-Di-tert-butyl-2-[(2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g][1,3,2]dioxaphosphocin-6-yl)oxy]phenyl]-1-(3,5-di-tert-butyl-2-hydroxyphenyl)methane (**6a**). Following the procedure used to prepare compound **4**, compound **6a** was prepared from 0.69 g (5 mmol) of phosphorus(III) chloride, 4.25 g (10 mmol) of **5a**, and 1.52 g (15 mmol) of triethylamine in 35 mL of toluene (7 h at 70°C). The residue was recrystallized from a mixture of 30 mL of acetonitrile and 23 mL of toluene to give 2.42 g (55%) of a white solid, mp 253–257°C (lit[13] 246–253°C).

$^{31}P\{^1H\}$ NMR (121.47 MHz) ($CDCl_3$) δ 137.7; $^{31}P\{^1H\}$ NMR (121.47 MHz) (CD_2Cl_2) (−90°C) δ 140.3 (major), 139.3 (minor); ^1H 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, $^2J_{HCH}$ = 12.8 Hz, 1 H), 4.50 (d, C(12)H, $^2J_{HCH}$ = 12.8 Hz, $^5J_{HP}$ = 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); IR (CH_2Cl_2) ν 3520 cm^{-1}.

1-[3,5-Di-tert-butyl-2-[(2,4,8,10-tetra-tert-butyl-12-methyl-12H-dibenzo[d,g][1,3,2]dioxaphosphocin-6-yl)oxy]phenyl]-1-(3,5-di-tert-butyl-2-hydroxyphenyl)ethane (**6b**). Following the procedure used to prepare compound **4**, compound **6b** was prepared from 0.69 g (5 mmol) of phosphorus(III) chloride, 4.39 g (10 mmol) of **5b**, and 2.02 g (20 mmol) of triethylamine in 35 mL of toluene (3 h at 85°C). The residue was recrystallized from a mixture of 25 mL of acetonitrile and 5 mL of toluene to give 3.54 g (78%) of a white solid, mp 223–227°C.

$^{31}P\{^1H\}$ NMR (202.33 MHz) ($CDCl_3$) δ 134.8; ^1H NMR (499.84 MHz) ($CDCl_3$) δ 1.08 (s, 9 H), 1.31 (s, 9 H), 1.35 (s, 9 H), 1.38 (s, 9 H), 1.385 (s, 9 H), 1.388 (s, 9 H), 1.538 (s, 9 H), 1.543 (s, 9 H), 1.69 (d, $^3J_{HCCH}$ = 8 Hz, 3 H), 1.85 (d, $^3J_{HCCH}$ = 8 Hz, 3 H), 5.08 (dq, C(12)H, $^3J_{HCCH}$ = 8 Hz, $^5J_{HP}$ = 2 Hz, 1 H), 5.42 (q, C(12)H, $^3J_{HCCH}$ = 8 Hz, 1 H), 6.97 (s, OH, 1 H), 7.195 (d, 1 H), 7.23 (d, 1 H), 7.25 (d, 1 H), 7.26 (d, 1 H), 7.32 (d, 1 H), 7.41 (d, 1 H), 7.49 (d, 1 H), 7.51 (d, 1 H); IR (CH_2Cl_2) ν 3510 cm^{-1}.

Anal. Calcd: C, 79.6; H, 9.9.
Found: C, 79.5; H, 10.1.

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