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Inorganic Chemistry
Note

Ferrocene Bis(phosphonite)s: Synthesis and Characterization of a Novel Class of Sterically Congested Ligands[1]

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Phosphorus-based ligands continue to play a pivotal role in the development of stereoselective transition-metal-catalyzed reactions. Although phosphine-based ligands have been extensively used in the optimization of catalytic processes, the use of readily modifiable phosphite or phosphonite ligands offers an attractive alternative to phosphine-based ligands. Recently, sterically hindered bis(phosphite) ligands incorporating the seven-membered dibenzo[*d,f*][1,3,2]dioxaphosphepin ring system were reported to be an effective ligand for rhodium-catalyzed hydroformylation reactions (Figure 1).[2] 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.[3] A relationship between the ratio of normal to iso olefin hydroformylation as a function of ligand bite angle has been established.[4] 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.[5] Nevertheless, the ratio of iso to normal olefin hydroformylation has been shown in an elegant study by Casey to be subject to electronic effects.[6] In principle, the facile preparation of aryl phosphites or phosphonites with electron-accepting or -donating groups allows for the tailoring of ligands to meet the electronic requirements for high stereoselectivity in a particular reaction.

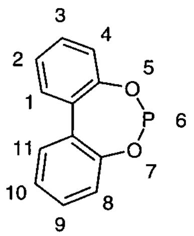
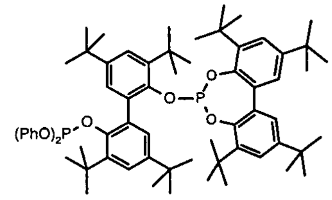


Figure 1. Chemical Abstracts numbering system for the dibenzo[*d,f*][1,3,2]-dioxaphosphepin ring system.



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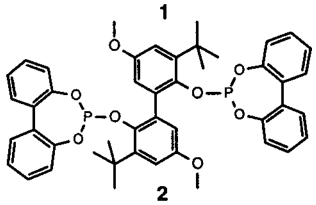

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Ferrocene provides a versatile backbone for the synthesis of chelating ligands.[7] During the course of our work,[8] Reetz[9] and Nifant'ev[10] reported the synthesis of chiral ferrocene diphosphonite ligands that were highly efficient in rhodium-catalyzed hydrogenation and hydrosilation reactions, respectively. Our current interest in seven- and eight-membered cyclic phosphite ligands[11] led to the current investigation of

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sterically congested bis(phosphonite) ligands based upon the ferrocene motif.

Experimental Section

^{1}H NMR (300.08 MHz and 499.84, respectively) spectra were taken on Varian model Gemini-300 or Unity-500 spectrometers. All ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane, where a positive sign is downfield from the standard. ^{31}P NMR spectra (121.47 and 202.33 MHz, respectively) were obtained on a Varian model Gemini-300, or Unity-500 spectrometers. All ^{31}P chemical shifts are reported in ppm relative to 85% phosphoric acid (external), where a positive sign is downfield from the standard. ^{19}F NMR spectra (282.33 MHz) were obtained on a Varian model Gemini-300 spectrometer. Significant ^{1}H NMR data are tabulated in the following order: multiplicity; atom assignments; coupling constant in hertz; number of protons. MALDI TOF MS obtained on a PerSeptive Biosysteme Voyager-DE STR spectrometer. Merck silica gel 60 (200−400 mesh) was used for flash and column chromatography. ICN Silica TSC (60 Å) was used for dry-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 dried apparatus under a dry inert atmosphere of either nitrogen or argon. The Analytical Research Department, Ciba Specialty Chemicals Corp., performed elemental analyses. Detailed procedures for the catalytic reactions carried out in this study are included in the Supporting Information.

3,3′,5,5′-Tetrakis(1,1-dimethylethyl)-2,2′-dihydroxy-1,1′-biphenyl (3). To a stirred mixture of 2,4-di-*tert*-butylphenol (20.6 g, 0.1 mole) and potassium hydroxide (44.0 g, 0.8 mol) in 250 mL of distilled water at 85−90 °C was added dropwise over 1 h a 30% aqueous solution of hydrogen peroxide (30 mL, 0.27 mol). The reaction mixture was slowly cooled to room temperature, and then the aqueous phase was decanted. The precipitate was collected by filtration, and the filter cake was washed sequentially with water (1 L), 3 M hydrochloric acid (300 mL), and water (300 mL). The wet filter cake was partitioned between a mixture of diethyl ether (100 mL), toluene (50 mL), and water (50 mL). The organic phase was extracted sequentially with 6 M hydrochloric acid (4 × 30 mL), 5% sodium bicarbonate (50 mL), and water (50 mL). The organic phase was dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. The product was purified by tritration with acetonitrile (50 mL) to give 12.8 g (63%) of a white solid, mp 197 °C (lit.[12] mp 195−196.5 °C). ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 18 H), 1.47 (s, 18 H), 5.22 (exchangeable s, OH, 2 H), 7.12 (d, ^4J = 2.5 Hz, 2 H), 7.41 (d, ^4J = 2.5 Hz, 2 H). MS: m/z 410 (molecular ion). Anal. Calcd for $C_{28}H_{42}O_2$: C, 81.90; H, 10.31. Found: C, 82.08; H, 10.34.

1,1′-Bis[2,4,8,10-tetrakis(1,1-dimethylethyl)dibenzo[*d,f*][1,3,2]-dioxaphosphepin-6-yl]ferrocene (6). Synthesis. To a stirred solution of 9.5 g (50 mmol) of ferrocene in 250 mL of hexane was added dropwise 67 mL (107 mmol) of a 1.6 M solution of *n*-butyllithium in hexane at ambient temperature. The reaction mixture was stirred for 20 min, and then to the resultant red suspension was added 12.0 g (103 mmol) of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (*exothermic*). The reaction mixture was heated at reflux for 2 h during which time an orange suspension formed. The reaction mixture was allowed to cool to ambient temperature, and 100 mL of tetrahydrofuran (THF) was added to the reaction mixture. To the resultant reaction mixture cooled to −40 °C was added dropwise a solution of 51.8 g (109 mmol) of **4** in 100 mL of THF. The reaction mixture was allowed to warm slowly to ambient temperature, and then it was heated at reflux for 6 h. The reaction mixture was allowed to cool to ambient temperature, and any insoluble precipitate was removed by filtration. The volatiles were removed in vacuo, and the residue was triturated with 150 mL of hexane. The resultant solid was recrystallized from a mixture of acetonitrile and THF to give 25 g (47.7%) of a light brown solid, mp 356 °C (under nitrogen). ^{31}P{^{1}H} NMR (benzene-d_6): δ 193.2. ^{1}H NMR (benzene-d_6; 80 °C): δ 1.28 (s, 36 H), 1.43 (s, 36 H), 4.42 (unresolved m, 4 H), 4.50 (m, 4 H), 7.26 (d, 4 H), 7.46 (d, 4 H). ^{13}C{^{1}H} NMR (benzene-d_6): δ 31.3 (s), 31.4 (s), 34.3 (s), 35.4 (s), 71.5 (d, J = 4 Hz), 72.4 (d, J = 21 Hz), 80.0 (d, J = 40 Hz), 124.1 (s), 126.7 (s), 134.5 (d, J = 4 Hz), 140.1 (d, J = 1 Hz), 146.2 (s), 147.8 (d, J = 6 Hz). MS: m/z 1064 ($M^{+\bullet}$). Anal. Calcd for $C_{66}H_{88}FeO_4P_2$: C, 74.56; H, 8.34; P, 5.83. Found: C, 74.13; H, 8.04; P, 5.83.

X-ray Structural Analysis. Crystals suitable for X-ray crystallographic analysis were grown by slow evaporation of a THF solution of **6**. Crystal data: $C_{66}H_{88}FeO_4P_2\cdot 4C_4H_8O$; formula weight = 1351.15; monoclinic system; crystal size = 0.54 × 0.54 × 0.13 mm; cell parameters a = 33.419(6) Å, b = 10.678(1) Å, c = 22.684(6) Å, β = 102.08(2)°; V = 7916(3) Å^3; space group = $C2/c$; d_{calc} = 1.135 Mg·m^{-3}; Z = 4; θ range from data collection = 2.7−74.2°; intensity variation = ±2%; μ = 2.250 mm^{-1}; Nonius CAD4 diffractometer; Cu Kα radiation; graphite crystal monochromator; number of variables 330; number of reflections measured 8297; number of reflections in least squares 6660; R = 0.081; largest difference peak/hole 1.425/−0.367; structure solution solved by direct methods (Siemens SHELXS) and parameters refined by full-matrix least-squares calculations (SHELXS) with anisotropic displacement parameters for all non-H atoms. The difference Fourier map showed 30 of 44 hydrogen atoms, with the positions of the remaining ones calculated by assuming normal geometry (H atom parameters idealized and not refined). The Fourier map showed four disordered THF molecules/ferrocene ligand. The parameters of the THF atoms could not be refined.

[(6)Rh^{I}AcAc] (7). Synthesis. To a stirred solution of 2.1 g (1.9 mmol) of **6** in 5 mL of benzene-d_6 was added portionwise 0.5 g (1.9 mmol) of (acetylacetonato)dicarbonylrhodium(I). (*Caution! Vigorous evolution of carbon monoxide is observed after each addition.*) The reaction mixture was allowed to stir until gas evolution was complete (2 h). Upon standing for 72 h, the resultant precipitate was collected by filtration to give 1.27 g (53%) of a yellow crystalline solid, mp 240−245 °C. ^{31}P{^{1}H} NMR (benzene-d_6): δ 178.4 (d, $^1J_{PRh}$ = 266.8 Hz). ^{1}H NMR (benzene-d_6) (300 MHz): δ 1.26 (s, 36 H), 1.88 (s, 36 H), 1.59 (s, CH_3, 6 H), 3.84 (unresolved m, 4 H), 4.81 (m, 4 H), 5.24 (, 1 H), 7.27 (d, ^4J = 2.5, 4 H), 7.47 (d, ^4J = 2.5, 4 H). Matrix-assisted laser desorption ionization (MALDI) time-of-flight MS [2-(2*H*-benzotriazol2-yl)-4-methylphenol matrix]: m/z 1264. The MS spectrum displays the isotope pattern consistent with that expected for the presence of iron and rhodium. Anal. Calcd for $C_{71}H_{95}FeO_6P_2Rh$: C, 67.40; H, 7.57. Found: C, 66.91; H, 7.45.

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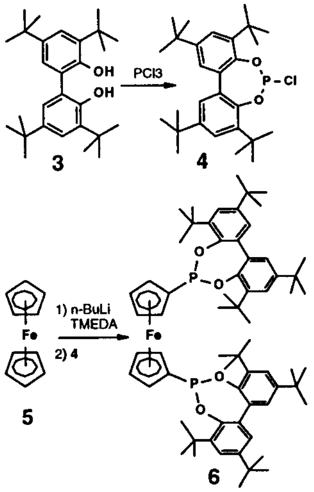
X-ray Structural Analysis. Crystals suitable for X-ray crystallographic analysis were grown from a saturated solution of **7** in a mixture of benzene and dichloromethane. Crystal data: $C_{71}H_{95}FeRhO_6P_2\cdot4(C_6H_6)(CH_2Cl_2)$; formula weight = 1548.42; monoclinic system; crystal size = 0.63 × 0.54 × 0.08 mm; cell parameters $a = 19.462(2)$ Å, $b = 36.482(4)$ Å, $c = 12.124(1)$ Å, $\beta = 93.07(1)°$; $V = 8596(2)$ Å^3; space group = $P2_1/c$; $d_{calc} = 1.224$ Mg·m^{-3}; $Z = 4$; θ range from data collection = 3.7−54.5°; intensity decay = ±22%; $\mu = 4.213$ mm^{-1}; Philips PW1100 automatic diffractometer; Mo Kα radiation; graphite crystal monochromator; number of variables 919; number of reflections measured 11 197; number of reflections in least squares 9532; $R = 0.057$; largest difference peak/hole 0.826/−0.642; structure solution solved by direct methods (Siemens SHELXS) and parameters refined by full-matrix least-squares calculations (SHELXS) with anisotropic displacement parameters for all non-H atoms. Hydrogen atom positions were calculated and not refined.

Results and Discussion

Synthesis. The bisphenol **3** was prepared by the oxidative coupling of 2,4-di-*tert*-butylphenol with hydrogen peroxide under alkaline conditions. The phosphorochloridite **4** was prepared by the reaction of the bisphenol **3** with phosphorus(III) chloride as reported in the literature.[11a] The ferrocenylbis(phosphonite) **6** was prepared by the reaction of 1,1′-dilithioferrocene, which was prepared in situ from ferrocene (**5**) and *n*-butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine, with 2 equiv of **4** (48% recrystallized).



3 **4** **5** **6**

In the $^{31}P\{^1H\}$ NMR spectrum (benzene-d_6) of **6** a singlet was observed at δ 193.2, which was assigned to the two equivalent phosphorus atoms of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepinyl substituents. This observation is consistent with rapid ring inversion of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepinyl rings (atropisomerization about the C−C bond connecting the two aryl rings) on the NMR time scale. If ring inversion was slow on the NMR time scale, two atropisomers with nonequivalent phosphorus atoms would be expected to be observable with relative absolute configurations of (*R**, *R**) and (*R**, *S**), which refers throughout this paper to the relative absolute configurations the two stereoaxes.[13,14]

The rhodium(I) complex **7** was prepared by the reaction of **6** with (acetylacetonato)dicarbonylrhodium(I) in benzene.

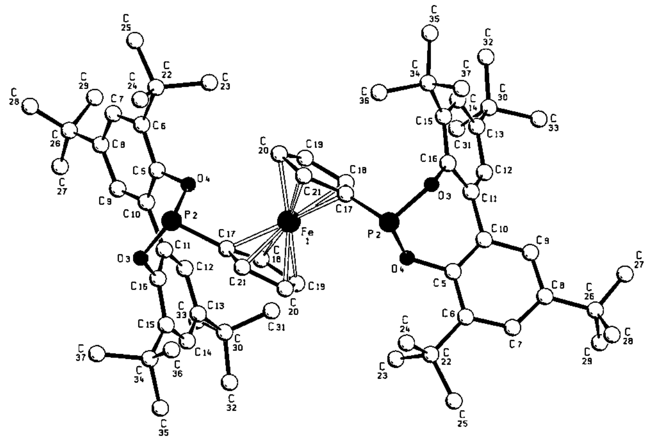
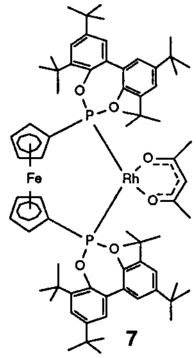


Figure 2. Molecular structure of **6** showing the crystallographic numbering scheme.

Upon standing, crystals of the rhodium(I) complex **7** separated from solution. In the $^{31}P\{^1H\}$ NMR spectrum (benzene-d_6) of **7**, a doublet was observed at δ 178.4, which was assigned to the two equivalent phosphorus atoms of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepinyl substituents bonded to rhodium with $^1J_{PRh} = 266.8$ Hz. As in the free ligand, the observation of only one phosphorus signal in the $^{31}P\{^1H\}$ NMR spectrum is consistent with rapid ring inversion of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepinyl rings on the NMR time scale.



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X-ray Crystallography. Crystals of **6** were obtained by slow evaporation of a tetrahydrofuran solution. In the solid state, the molecule of **6** has C_2 symmetry with the 2-fold axis running through the iron atom (see Figure 2). All of the bond lengths are within the expected ranges.[15] The Fe−C bond distances are between 2.030 and 2.046 Å, which is in the range found in ferrocene.[16] The planes defined by the two cyclopentadienyl rings are parallel to each other. The C(5)−C(10)−C(11)−C(16) dihedral angle about the single

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(13) The examination of a Drieding molecular model suggests that the alternate explanation of a planar ring conformation is highly unlikely. The formation of a single diastereoisomer cannot be rigourously excluded; albiet, in this case the four *tert*-butyl substituents of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepinyl ring are nonequivalent. For examples, see ref 11.

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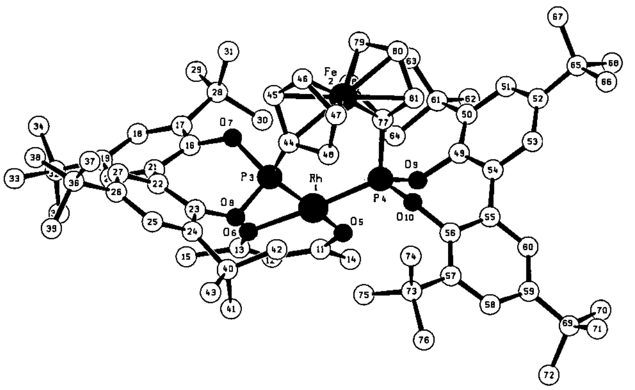

Figure 3. Molecular structure of **7** showing the crystallographic numbering scheme.

bond connecting the two aryl rings of the dibenzo[*d*,*f*][1,3,2]-dioxaphosphepin ring is 54.2(8)°, which is in the range found for other sterically hindered dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings.[11a,11b,17,18] Given the posit that pyramidal geometry is achieved when the sum of the requisite bond angles about phosphorus is 270° (for "pure" p character), the two equivalent phosphorus atoms (301.8°) are midway between pyramidal and tetrahedral geometry.

Crystals of **7** suitable for X-ray crystallography were prepared by crystallization from a mixture of benzene and dichloromethane (see Figure 3). In the solid state, all of the bond lengths are within the expected ranges.[15] The Fe−C bond distances are between 2.006 and 2.071 Å, which is in the range found in ferrocene.[16] The planes defined by the two cyclopentadienyl rings are tilted 5.2° relative to each other. The geometry about Rh(I) in **7** is square planar. The Rh−P bond lengths (2.161 and 2.177 Å) and Rh−O bond lengths (2.060 and 2.069 Å) are similar to those found in other Rh(I) acetylacetonate complexes.[19] The C(16)−C(21)−C(22)−C(23) and C(49)−C(54)−C(55)−C(56) dihedral angles about the single bonds connecting the two aryl rings of the dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings are −52.83 (0.91) and −55.68 (0.89)°, which is in the range found for other sterically hindered dibenzo[*d*,*f*][1,3,2]dioxaphosphepin rings.[11a,11b,17,18] The solid-state conformation of **7** is that of the (*R**, *R**) atropisomer. However, caution should be exercised in the comparison of solution with solid-state conformations determined by X-ray structural analysis. Anet and Yavari warned that lattice energy, along with the resultant crystal-packing effects in the solid state, could render the solid-state conformation different from that observed in solution.[20]

Given the posit that pyramidal geometry is achieved when the sum of the requisite bond angles about phosphorus is 270° (for "pure" p character), the two phosphorus atoms (sum of the angles about P(3) = 304.9°; P(4) = 302.4°) are midway between pyramidal and tetrahedral geometry. The coordination geometry about the rhodium atom in **7** is square planar within 0.08 Å of the best-calculated plane through the Rh, P(3), P(4), O(5), and O(6) atoms. The acetylacetonate chelate ring [Rh, O(5), C(11), C(12), C(13), and O(6)] is planar and is tilted 0.4° to the rhodium coordination plane.

Catalytic Reactions. The ferrocene bis(phosphonite) **6** was screened as a ligand for transition-metal-catalyzed hydrosilation,[11f,21] hydrogenation, and cross-coupling (C−C bond formation) reactions (Suzuki reaction).[22] The hydrosilation of acetophenone with diphenylsilane catalyzed by the Rh(I) complex **7** followed by hydrolysis of the silyl ether gave phenethyl alcohol in 93% isolated yield (eq 1). However, the actual catalytic species may be different from **7** and be formed in situ under the reaction conditions. The hydrosilation of acetophenone with diphenylsilane using the Rh(I) complex formed in situ from **6** and chloro(1,5-cyclooctadiene)rhodium(I) dimer[23] followed by hydrolysis of the silyl ether gave phenethyl alcohol in 90% isolated yield.

Hydrogenation of the α,*β*-unsaturated C−C double bond of dimethyl itaconate with a cationic Rh complex prepared from **6** and bis(bicyclo[2.2.1]hepta-2,5-diene)rhodium(I) perchlorate gave the saturated succinate ester in 99% isolated yield (eq 2). The ferrocenylbis(phosphonite) **6** was evaluated as a ligand for C−C bond formation (Suzuki reaction) following the experimental protocol of Buchwald.[24,25] 3-Trifluoromethyl-1,1′-biphenyl[26] was formed in 90% isolated

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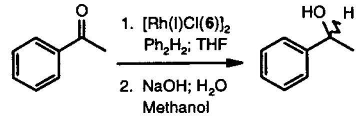
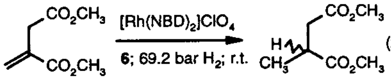
yield by reaction of 3-(trifluoromethyl)phenylboronic acid with bromobenzene using the catalyst formed in situ from **6** and palladium(II) acetate (eq 3).



(1)



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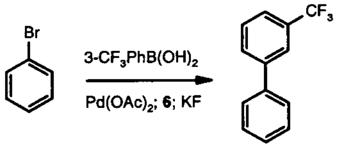

(3)

In summary, the synthesis and characterization of the first ferrocenylbis(phosphonite) **6** and Rh(I) complex **7** containing a sterically congested tetralkyl-substituted dibenzo[*d*,*f*][1,3,2]-dioxaphosphepin ring system is reported. The high yields of products obtained in three different transition-metal-catalyzed reactions suggest that **6** is a robust ligand useful in a wide variety of reactions.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format, and detailed experimental procedures for the catalytic reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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