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Synthesis and Properties of Phospha[5]helicenes Bearing Inner-Rim Phosphorus Center

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Supporting Information Placeholder

ABSTRACT: New phospha[5]helicene derivatives featuring angular fusion of phosphole and carbohelicene moieties have been synthesized using 7-hydroxybenzo[*b*]phosphole oxide as a key intermediate, which can be regioselectively prepared through one-pot multicomponent coupling. The structural behavior of the present phospha[5]helicene oxide, sulfide, and gold complex in the solid- and solution-states, along with DFT calculations, demonstrated close correlation between the P-centered chirality and the helical chirality as well as facile helicity inversion and equilibrium between the diastereomers in solution.

ortho-Fused polyaromatic systems, helicenes, have attracted considerable attention for their unique physicochemical properties due to the inherent helical chirality and the extended π -conjugation, which hold promise in various applications including chiral recognition and sensing, chiroptical switches, and asymmetric catalysis.¹ Incorporation of heteroatoms into the helicene framework offers an attractive means to modulate the structural and electronic properties² as well as to utilize the heteroatom moiety for coordination chemistry³ and asymmetric catalysis.⁴ In this context, notable progress has been made in phosphahelicenes, which feature a phosphorus-containing five-membered ring, phosphole, embedded in the helicene framework (Scheme 1a). Nozaki and Tanaka independently achieved the synthesis of phospha[7]helicene derivatives bearing a phosphorus atom on the middle of the outer rim, using Pd-catalyzed intramolecular P–C coupling and Rh-catalyzed [2 + 2 + 2] cycloaddition, respectively.^{5,6} Nozaki's phospha[7]helicene derivatives were found to form one-dimensional columnar alignment. Marinetti and coworkers used oxidative photocyclization to synthesize a series of chiral phospha[7]helicene and related compounds, where the phosphole moiety is linearly fused to the terminal benzene ring of the [6]helicene framework.^{7,8} Owing to the proximity of the phosphorus center to the inner rim of the helicene framework, tertiary phosphines of this type have proved to serve as efficient chiral ligands for asymmetric gold catalysis^{7c-e} and chiral nucleophilic organocatalysis.^{7f}

Despite the significant progress in the synthesis and application of phosphahelicenes, to our knowledge, phosphahelicenes comprised of angularly fused phosphole and carbohelicene moieties with an inner-rim phosphorus center remain elusive. Such phosphahelicenes are expected to have close interaction between the helical chirality and the P-centered chirality, and thus would serve as attractive scaffolds as chiral ligands and catalysts.⁴ We report here on the synthesis of phospha[5]helicene derivatives of this type that capitalizes on regioselective one-pot synthesis of 7-hydroxybenzo[*b*]phosphole oxide as a key intermediate, followed by Suzuki–Miyaura coupling and iodocyclization as helicene-building steps (Scheme 1b). The structural behavior of the present phospha[5]helicene oxide, sulfide, and gold complex, along with DFT calculations, showed that the helicity and the P-centered chirality are intimately correlated, while helix inversion is a facile process in solution.

Scheme 1. Synthesis of Phosphahelicenes

The present synthesis started with one-pot preparation of 7-hydroxybenzophosphole oxide **3** via sequential assembly of 3-(methoxymethoxy)phenylzinc chloride (**1**), 5-decyne (**2**), and PhPCl_2 (Scheme 2a).⁹ The cobalt-catalyzed migratory arylzincation reaction¹⁰ of **1** (prepared from a 1:1 mixture of the corresponding Grignard reagent and $\text{ZnCl}_2 \cdot \text{TMEDA}$) with **2** was followed by treatment of the resulting *ortho*-alkenylarylzinc intermediate with $\text{CuCN} \cdot 2\text{LiCl}$ and PhPCl_2 , and then with H_2O_2 , thus affording the desired product **3** in 33% yield on a 5 mmol scale. We observed preferential formation of **3** over the other regioisomer (5-hydroxybenzophosphole; ratio = ca. 3:1), which may be ascribed to the secondary directing effect of the alkoxy group on the 1,4-cobalt migration step.^{10,11} The hydroxyl group of **3** was smoothly triflated, and subsequent Suzuki–Miyaura coupling of the triflate **4** with 2-alkynyl-1-naphthylboronic acid **5** afforded an alkynylbiaryl derivative **6** in a moderate yield. Iodocyclization of **6** using ICl ¹² afforded an iodinated phosphahelicene **7** in 56% yield. A CDCl_3 solution of **7** showed two ^{31}P NMR signal (δ 40.2 and 46.3) in a ratio of 5:1, indicating the presence of two diastereomers. Finally, **7** was subjected to Suzuki–Miyaura coupling with phenylboronic acid and 4-(hydroxymethyl)phenylboronic acid, affording phosphahelicenes **8** and **9**, respectively, with diastereomer ratios similar to that of **7**. The treatment of compound **9** with Lawesson's reagent afforded the phosphine sulfide analogue **10** as a single diastereomer (dr >20:1).

Scheme 2. Synthesis of Phospha[5]helicene

The aromatic region of the ^1H NMR spectra of **7–9** (Figure S1, S2 and S4) showed a major doublet signal at the highest chemical shift of ca. 9 ppm, and a minor apparent triplet signal at the lowest chemical shift of ca. 6 ppm. By contrast, the ^1H NMR spectrum of **10** showed virtually no signal above 8 ppm while displaying a major apparent triplet at 5.9 ppm (Figure S6). These spectral features suggest that the major diastereomers of **7–9** and **10** have different relative configurations. The doublet at ~ 9 ppm can be assigned to the inner rim proton (H^{13}) of the $(R_P,P)/(S_P,M)$ diastereomers, which is significantly deshielded by the nearby aromatic rings (Scheme 2b). On the other hand, the apparent triplet at ~ 6 ppm can be assigned to the H^{12} proton of the $(S_P,P)/(R_P,M)$ diastereomers, which would be under strong shielding effect of the P-Ph group as corroborated by X-ray crystallographic analysis and DFT calculations (vide infra).

While **8** was a gummy material, **9** and **10** were obtained as light yellow solids and could be recrystallized from CH_2Cl_2 . Both of the thus-obtained single crystals proved to consist of racemic mixture of the (S_P,P) and (R_P,M) enantiomers by X-ray diffraction analysis (Figure 1). The P-Ph group is pointed toward the helicene edge, indicating that the H^{12} atom is positioned just below the benzene ring. Presumably due to this structural arrangement, the interplanar angles formed by the phosphole ring and the terminal benzene ring (72.4° and 71.6° for **9** and **10**, respectively) are substantially larger than the corresponding angle of [5]helicene (51.2°).¹³ In the crystal packing, the (S_P,P) and (R_P,M) enantiomers of **9** are paired by mutual hydrogen bonding between the P=O and OH groups, with a relatively short distance (2.720 Å) between the two

oxygen atoms (Figure 1b). An analogous pair of mutually hydrogen-bonded enantiomers is found in the crystal packing of **10** (with S–O distance of 3.277 Å). Notably, redissolution of the crystals of **9** in CDCl₃ reproduced the ³¹P NMR spectra of the as-synthesized **9**, indicating facile helicity inversion in solution at room temperature.

Figure 1. ORTEP drawings of (a) (*R_P,M*)-**9** and (*R_P,M*)-**10** in their racemic single-crystals and (b) a hydrogen-bonded pair of (*R_P,M*)-**9** and (*S_P,P*)-**9**. Thermal ellipsoids are shown at 50% probability.

We next attempted synthesis of a phosphaphelicene–gold complex (Scheme 3). Reduction of the phosphine oxide moiety of **8** was achieved by copper-catalyzed reaction with 1,1,3,3,-tetramethyldisiloxane (TMDS),¹⁴ thus affording the free phosphine derivative **11** in 74% yield as a single diastereomer with (*R_P,M*)/(*S_P,P*) configuration, as assigned by ¹H NMR (Figure S8). Treatment of **11** with AuCl(SMe₂) afforded, upon recrystallization from CH₂Cl₂, the complex **12** in 70% yield. Unlike **9** and **10**, the single crystals of **12** were found to have (*R_P,P*)/(*S_P,M*) configuration. The interplanar angle of the helix was determined to be 61.1°. Upon redissolution in CDCl₃, **12** exhibited two ³¹P NMR peaks (δ 45.5 and 41.9) in a 1.4:1 ratio and characteristic aromatic ¹H NMR signals assignable to (*R_P,P*)/(*S_P,M*) or (*S_P,P*)/(*R_P,M*) isomer (Figure S10), again suggesting facile helicity inversion in solution.

Scheme 3. Synthesis and X-ray Structure of Phosphaphelicene–Gold Complex^a

^aThermal ellipsoids are shown at 50% probability.

To gain insight into the structural behaviors of the present phosphaphelicene derivatives, we performed DFT calculations (B3LYP/6-31G(d)) on a model compound **Ao**, which was generated by replacing the peripheral Ph and Bu groups of **8** with H and Me groups, respectively (Figure 2). (*R_P,P*)-**Ao** is calculated to be more stable than (*R_P,M*)-**Ao** by 4.1 kcal/mol presumably due to steric repulsion between the P-Ph group and the helicene edge, which is qualitatively (though not quantitatively) in line with the relative configuration of the major diastereomers of **7–9** assigned by ¹H NMR. Note that the H¹² atom of (*R_P,M*)-**Ao** is positioned right below the benzene ring of the P-Ph group, with the distances between H¹² and the phenyl carbons of 3.31–3.41 Å. These diastereomers are connected by the transition state of helix inversion (**TS-Ao**), with a low activation energy of 16.9 kcal/mol from (*R_P,P*)-**Ao**. Given this energy profile, selective crystallization of the (*R_P,M*)/(*S_P,P*) isomers of **9** may be ascribed to facile interconversion between the diastereomers and favorable intermolecular interactions, including hydrogen bonding, in the crystal packing. Replacement of the oxygen atom of **Ao** with a sulfur atom (**As**) was found to significantly affect the relative energies of the diastereomers, favoring (*R_P,M*)-**As** over (*R_P,P*)-**As** by 0.6 kcal/mol (Figure S12). This energy trend, which is qualitatively consistent with the relative configuration of **10**, may be ascribed to greater steric clash between S and the helicene terminal in (*R_P,P*)-**As** than that between O and the helicene terminal in (*R_P,P*)-**Ao**. We also studied the structural behavior of a model free phosphaphelicene **A**, which showed: (1) (*R_P,M*)/(*S_P,P*) isomers are more stable than (*R_P,P*)/(*S_P,M*) isomers by 5.4 kcal/mol, and (2) isomerization between these isomers can take place through either helix inversion (Δ*G*[‡] = 17.3 kcal/mol) or phosphorus inversion (Δ*G*[‡] = 23.0 kcal/mol) (Figure S13).¹⁵ This would suggest difficulty in optical resolution of **11**.

Figure 2. Free energy diagram (kcal/mol) for the isomerization of model phospha[5]helicene oxide **A_o** (B3LYP/6-31G(d)).

The absorption and emission spectra of the compound **9** are shown in Figure 3. The absorption profile of **9** was rather broad and tailing with absorption maxima at 322 nm, 338 nm, and 390 nm (shoulder), which might be ascribed to the presence of two diastereomers and also to the contribution from vibronic progression. The compounds **8**, **10** and **12** also showed similarly complex absorption profiles (Figures S14 and S15). The emission color of **9** was light-blue, with a broad peak at 454 nm and a quantum yield of 0.42 (referenced to quinine sulfate). The compound **8** also showed light-blue emission with somewhat lower emission wavelength (431 nm) with similar quantum yield (0.44). On the other hand, the sulfide derivative **10** and the gold complex **12** were virtually non-emissive, likely due to the heavy atom effect.

Figure 3. Absorption (dashed line) and emission (solid line) spectra of **9** (5×10^{-6} M in CH_2Cl_2).

In summary, we have synthesized phospha[5]helicene derivatives that feature angularly fused phosphole and carbohelicene units and an inner-rim phosphorus center using 7-hydroxybenzo[*b*]phosphole as the precursor, which is nontrivial to access by typical methods for benzo[*b*]phosphole synthesis.¹⁶ The X-ray crystallographic structures of the phospha[5]helicene oxide, sulfide, and gold complex demonstrated their inherent helical and P-centered chirality. Their behavior in solution and DFT calculations suggest significant impact of the phosphorus center on the diastereomer ratio as well as facile equilibration between the diastereomers through helix inversion. We expect that the present synthetic approach could be extended to access analogous phospha[6]helicenes or more extended derivatives with stable helicity, which would be amenable to optical

resolution¹⁷ and hold promise as chiral scaffolds for catalysis and chiroptical applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Detailed experimental procedures and spectral data for new compounds (PDF)

Accession Codes

CCDC 1903363–1903365 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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