

## Metal–Bis(helicene) Assemblies Incorporating $\pi$ -Conjugated Phosphole-Azahelicene Ligands: Impacting Chiroptical Properties by Metal Variation

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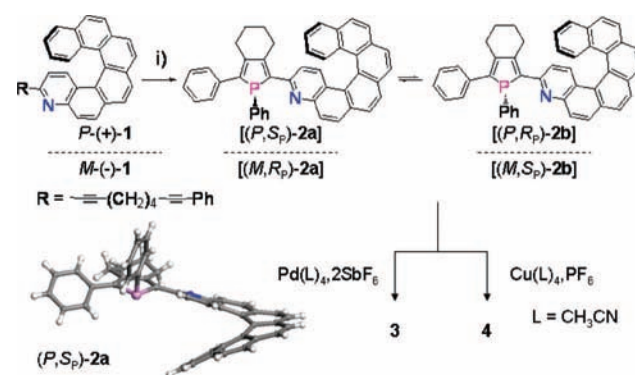
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Helicenes possess a unique screw-shaped  $\pi$ -conjugated structure that provides them with huge optical rotation values.<sup>1</sup> Therefore, there is a growing interest in using helicenes or analogous derivatives as building blocks for the design of chiral ligands for use in asymmetric catalysis,<sup>2a,b</sup> nonlinear optical materials,<sup>2c</sup> and waveguides.<sup>2d</sup> In this context, the development of simple strategies to tune the chiroptical properties of helicene-based derivatives by varying their structures is of great interest.<sup>3</sup> Little is known about the coordination chemistry of helicene derivatives,<sup>2a,3b,4</sup> although metal ions are versatile templates for assembling  $\pi$ -conjugated ligands into supramolecular architectures.<sup>5</sup> We have therefore investigated an unprecedented strategy based on the synthesis of chiral metal–bis(helicene) complexes via stereoselective coordination of aza[6]helicenes bearing a phosphole moiety. The novel diastereomeric ligands **2a** and **2b** (Scheme 1) were designed on the basis of two key properties of phosphole-based  $\pi$ -conjugated systems. First, 2-(2-pyridyl)phospholes are 1,4-P,N chelates that undergo highly stereoselective coordination to metallic ions with different coordination geometries as a result of their heteroditopic nature (trans effect<sup>6a</sup>) and the specific properties of the phosphole ring (ease of inversion at P, steric hindrance provided by the P substituent).<sup>6b,c</sup> Second, in these complexes, the phosphole and pyridine moieties are conjugated, resulting in an intimate electronic interaction between the metal and the  $\pi$ -conjugated P,N-chelates via metal–ligand charge transfer.<sup>6b,c</sup> Herein, we describe the synthesis and chiroptical properties of the phosphole-modified azahelicenes **2a** and **2b** and their Pd<sup>II</sup> and Cu<sup>I</sup> complexes. The interest in modifying azahelicenes by a phosphole moiety and the crucial role played by the metal centers in tuning the chiroptical properties of these novel chiral  $\pi$ -conjugated assemblies are shown and discussed on the basis of first-principles theoretical calculations.

Derivatives **2a** and **2b** were obtained from the newly prepared aza[6]helicene diyne **1** [see the Supporting Information (SI)] according to the Fagan–Nugent route<sup>6,7</sup> (Scheme 1). The starting material **1** was readily resolved into its (+)-**1** (ee 99%) and (–)-**1** (ee 97%) enantiomers using HPLC over a Chiralcel OD-H stationary phase. The intense electronic circular dichroism (CD) band at  $\sim 330$  nm (CH<sub>2</sub>Cl<sub>2</sub>) enabled their absolute configurations to be established.<sup>3,8</sup> It is noteworthy that optically pure functionalized azahelicenes are relatively rare<sup>1,3</sup> and that **1** is the first diyne of this type. *P*-(+)-**1** and *M*-(–)-**1** afforded the corresponding target aza[6]helicene phospholes **2a** and **2b** in  $\sim 50\%$  yield (Scheme 1). It should be noted that the Zr/P exchange required a reaction temperature (40

**Scheme 1.** Synthesis, Solid-State Structures, and Coordination of **2a** and **2b**<sup>a</sup>



<sup>a</sup> (i) Cp<sub>2</sub>ZrCl<sub>2</sub>, 2BuLi, THF, 40°C, then PhPBr<sub>2</sub>, 24 h, rt. X-ray structure of (*P*\*,*S*<sub>P</sub>\*)-**2a** (space group P1).

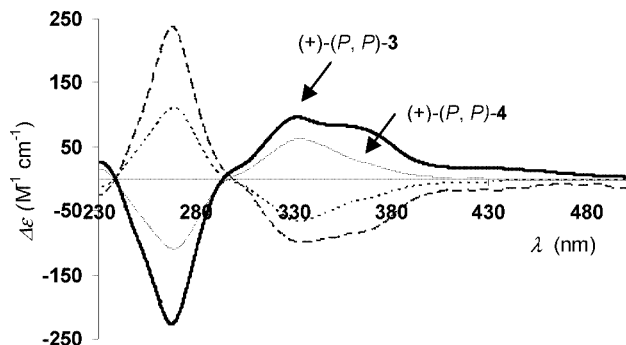
°C) that was low enough to prevent inversion of the aza[6]helicene moiety (inversion barrier  $\sim 36$  kcal mol<sup>-1</sup>).<sup>1</sup> Derivatives **2a** and **2b** possess a novel stereogenic element: the P atom of the phosphole ring (Scheme 1). One key property of phospholes is that their inversion barrier at P ( $\sim 15$ – $16$  kcal mol<sup>-1</sup>) is much lower than that of regular phosphanes ( $\sim 35$ – $36$  kcal mol<sup>-1</sup>) because of the highly aromatic character of planar phospholes.<sup>9</sup> Therefore, the *P*-(+)-diyne **1** afforded a mixture of diastereomers (*P*,*R*<sub>P</sub>)-**2a** and (*P*,*S*<sub>P</sub>)-**2b**, whereas its *M*-(–)-enantiomer gave their (*M*,*S*<sub>P</sub>)-**2a** and (*M*,*R*<sub>P</sub>)-**2b** mirror images (Scheme 1). Indeed, the <sup>31</sup>P NMR spectrum of the reaction mixture displays two singlets of equal intensity at 14.0 and 14.5 ppm. Likewise, the <sup>1</sup>H and <sup>13</sup>C NMR spectra showed expected signals for the aza[6]helicene and the phosphole moieties for each diastereomer. It is worth noting that variable-temperature <sup>31</sup>P NMR spectroscopy confirmed that derivatives **2a** and **2b** interconvert with a barrier of  $\sim 16$  kcal mol<sup>-1</sup>.

Slow crystallization of the diastereomeric mixture of phospholes **2a** and **2b** at room temperature afforded single crystals of **2a** only (Scheme 1).<sup>10</sup> The metric and geometrical data for the azahelicene and phosphole moieties of (*P*\*,*S*<sub>P</sub>\*)-**2a** are fully consistent with those for related derivatives<sup>6b</sup> and fit nicely with the BP/SV(P)- and BP/TZVP-optimized structures.<sup>11</sup> For example, the helical curvature of the aza[6]helicene fragment is classic, with an angle of 45.8° between the pyridine ring and the terminal phenyl ring. It is noteworthy that the twist angle between the phosphole ring and the aza[6]helicene substituent is relatively small (26.3°), in principle allowing an electronic interaction between the two  $\pi$  systems. This is confirmed by the fact that the lower-energy excitation observed by UV–visible spectroscopy appears at 430 nm (see the SI), which

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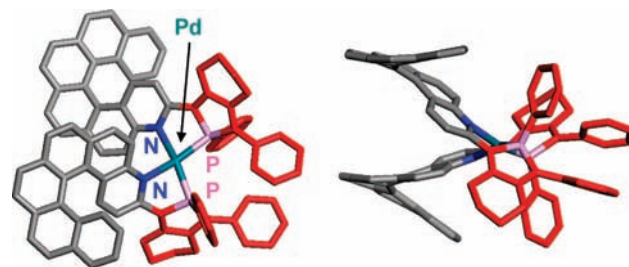


**Figure 1.** CD spectra of (+)-(P,P)-**3** and (+)-(P,P)-**4** (solid lines) and their respective enantiomers (dashed lines) in CH<sub>2</sub>Cl<sub>2</sub> at 293 K.

is red-shifted compared with 2-pyridyl-1,5-diphenylphosphole (390 nm).<sup>9b,c</sup> It should be noted that the calculated<sup>11</sup> UV–visible spectrum well reproduces the experimental one after a red shift of 0.25 eV.

The inversion at the phosphole P atom is a clue for obtaining highly stereoselective coordination of (2-pyridyl)phosphole ligands on metallic centers, such as square-planar Pd<sup>II</sup> or tetrahedral Cu<sup>I</sup> ions, since the P atom can adapt its configuration to minimize steric repulsion.<sup>6b</sup> Indeed, a diastereomeric mixture of the interconverting aza[6]helicene phospholes (*P,S<sub>p</sub>*)-**2a** and (*P,R<sub>p</sub>*)-**2b** reacted with Pd(CH<sub>3</sub>CN)<sub>4</sub>·2SbF<sub>6</sub> (2/1 molar ratio) in CH<sub>2</sub>Cl<sub>2</sub> to afford complex **3** (78% yield) as a single stereoisomer (Scheme 1). Its elemental analysis is consistent with a [Pd(azahelicene phosphole)<sub>2</sub>·2SbF<sub>6</sub>] formula. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **3** displays a single peak at 75.0 ppm, and its <sup>1</sup>H and <sup>13</sup>C NMR spectra show only one set of signals assignable to the aza[6]helicene phosphole ligands. These multinuclear NMR data compare well with those of related dicationic Pd<sup>II</sup>(2-pyridylphosphole)<sub>2</sub> complexes having a distorted square-planar coordination sphere in which the P atoms have a mutual syn arrangement, in accordance with the trans effect.<sup>6b,c</sup> The simplicity of these NMR spectra clearly shows that the coordination of aza[6]helicene phospholes **2a** and **2b** to Pd<sup>II</sup> is highly stereoselective. Therefore, complex **3** was obtained as a single enantiomer {[α]<sub>D</sub><sup>23</sup> = +1275 (±2%), (*c* 0.01, CH<sub>2</sub>Cl<sub>2</sub>)}, whereas its mirror image {[α]<sub>D</sub><sup>23</sup> = −1250 (±2%), (*c* 0.01, CH<sub>2</sub>Cl<sub>2</sub>)} was prepared using the mixture of (*M,R<sub>p</sub>*)-**2a** and (*M,S<sub>p</sub>*)-**2b** ligands. The same approach using Cu(CH<sub>3</sub>CN)<sub>4</sub>·PF<sub>6</sub> (2/1 ratio) afforded complex **4** {86% yield, Scheme 1, [α]<sub>D</sub><sup>23</sup> = +910 and −900 (±2%), (*c* 0.01, CH<sub>2</sub>Cl<sub>2</sub>)}, which exhibits a broad <sup>31</sup>P NMR signal (δ 5–6 ppm) in the expected range for dicationic tetrahedral Cu<sup>I</sup>(2-pyridylphosphole)<sub>2</sub> complexes.<sup>6b</sup> This complex was also characterized by high-resolution mass spectrometry and elemental analysis.

The syntheses of complexes **3** and **4** provide a unique opportunity to investigate the impact of the nature of the metal on the chiroptical properties of these chiral metal–bis(helicene) assemblies. The specific molar rotation of the Pd<sup>II</sup> complex **3** measured in CH<sub>2</sub>Cl<sub>2</sub> ([Φ]<sub>D</sub> = 23 100 ± 2%) is much larger than that of its Cu<sup>I</sup> analogue **4** ([Φ]<sub>D</sub> = 13 100 ± 2%). Moreover, their CD spectra are very different. For example, the *P*-helicene-containing complexes **3** and **4**, namely, (+)-(P,P)-**3** and (+)-(P,P)-**4** (Figure 1), both display two intense CD bands at 270 nm (negative) and ~330 nm (positive). However, the magnitude of the CD spectrum of the Pd<sup>II</sup> complex **3** is much larger than that of the Cu<sup>I</sup> complex **4** (Figure 1). Furthermore, the CD spectrum of the Pd<sup>II</sup> assembly **3** displays intense bands at ~370 nm as well as weak bands at lower-energy wavelengths (410–450 nm) that are not observed for the Cu<sup>I</sup> complex **4** (Figure 1). These results clearly show that (i) it is possible to perform a coordination-driven tuning of chiroptical



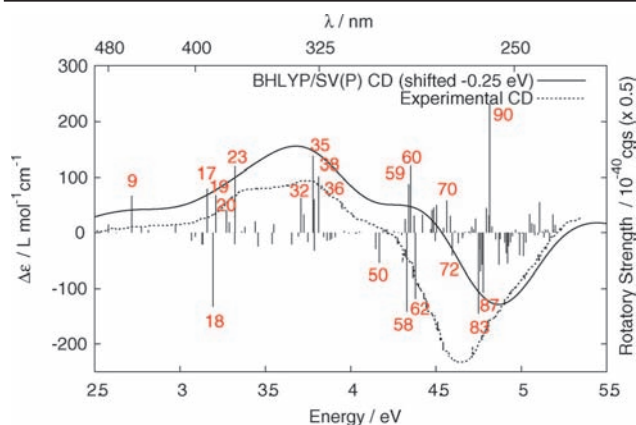
**Figure 2.** Optimized<sup>11</sup> structure of complex Pd(**2a**)<sub>2</sub><sup>2+</sup> (**3'**).

properties of phosphole-modified azahelicenes and (ii) it is more efficient to organize these heteroditopic ligands around a square-planar Pd<sup>II</sup> metal center than around a tetrahedral Cu<sup>I</sup> center.<sup>12</sup>

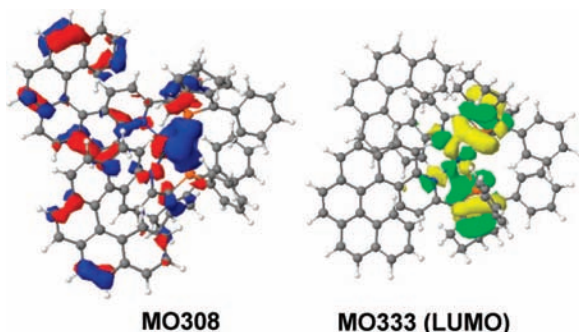
In order to gain more insight into the role of the Pd<sup>II</sup> ion, complex **3** was investigated using theoretical calculations. The first issue was to confirm the absolute configuration of the P centers of enantiomerically pure assembly **3**. Calculations at the BP/SV(P) level of theory for the ligand having a *P*-helix revealed that the Pd(**2a**)<sub>2</sub><sup>2+</sup> assembly is 81.6 kJ/mol more stable than its diastereoisomer Pd(**2b**)<sub>2</sub><sup>2+</sup>. This large value is in agreement with the experimental observation that the coordination of interconverting **2a** and **2b** to Pd<sup>II</sup> is highly stereoselective (Scheme 1).

The difference in the energies of these two diastereomeric complexes can be attributed to steric factors, as suggested by the fact that the square-planar Pd<sup>II</sup> coordination sphere of Pd(**2b**)<sub>2</sub><sup>2+</sup> is much more distorted than that of Pd(**2a**)<sub>2</sub><sup>2+</sup> (twist angles between the N–Pd–P planes: Pd(**2b**)<sub>2</sub><sup>2+</sup>, 54.8°; Pd(**2a**)<sub>2</sub><sup>2+</sup>, 24.7°).<sup>13</sup> In fact, the metric data for the PdN<sub>2</sub>P<sub>2</sub> core of Pd(**2a**)<sub>2</sub><sup>2+</sup> (**3'**) (Figure 2) fit well with those of other dicationic Pd(2-pyridylphosphole)<sub>2</sub> complexes established by X-ray diffraction studies.<sup>6b,14</sup> Significant parameters are the twist angle between the N–Pd–P planes (**3'**, 24.7°; X-ray, 13.7–19.5°), the lengths of the Pd–P (**3'**, 2.319 and 2.302 Å; X-ray, 2.25–2.26 Å) and Pd–N (**3'**, 2.200 and 2.190 Å; X-ray, 2.12–2.16 Å) bonds, and the P,N bite angles (**3'**, 79.9 and 79.7°; X-ray, 81.0–82.8°). The curvature of the helices is retained in the coordination sphere of the metal (**2a**, 45.8°; **3'**, 49.5°), and the two twist angles between the coordinated phosphole and the pyridine rings are 19.4 and 23.4°, allowing an electronic interaction between the phosphole and the azahelicene π systems to take place. For example, the shape of the LUMO+1 and HOMO-4 molecular orbitals (MOs) clearly reflects the conjugation between the coordinated P- and N-heterocycles (see the SI). It is noteworthy that the orbitals of both the metal and the π-conjugated P,N ligands are involved in many of the MOs (LUMO, LUMO+2, LUMO+4,...; see the SI), showing the intimate electronic interaction between these two fragments.

The computed<sup>11</sup> CD spectrum of **3'** agrees very well with the experimental one for complex **3** after a red shift of 0.25 eV (Figure 3). According to these calculations, the most intense CD bands involve π–π\* transitions of the extended phosphole–azahelix π systems (see Figure 3 and Tables S4 and S5 in the SI). The over- and underestimation of the CD intensities of the bands at 330 and 250 nm, respectively, are similar to those for free hexahelicene.<sup>8a,c</sup> The Pd<sup>II</sup> center is involved in many transitions and contributes in particular to the low-energy tail of the first CD band through partial metal–ligand charge transfer (see the SI). For example, the dominant contribution (14%) to excitation 9 in Figure 3 is essentially a transition from a metal-centered MO (MO308, Figure 4) to a metal–ligand MO (MO333, Figure 4). It should be noted that these low-energy CD bands involving the metal center are not observed for the Cu<sup>I</sup> complex **4** (Figure 1), clearly showing the impact of the metal ions on the CD properties. The long-wavelength



**Figure 3.** Comparison of the experimental (dashed line) and TD-DFT (solid line) CD spectrum of **3'** at the BHLYP/SV(P) level. The numbered excitations correspond to those with high rotatory strength that were analyzed in detail (see the SI).



**Figure 4.** Two MOs of **3'** involved (14%) in excitation 9 in Figure 3.

tail of the first CD band is likely a major contributor to the huge molar rotation of **3**. Further details and additional computations will be reported in a follow-up article.

In conclusion, because of their peculiar properties (ease of inversion at P, polarizable  $\pi$  systems, etc.),<sup>9</sup> phospholes are unique building blocks for the tailoring of azahelicene derivatives that can be assembled on metal centers. The nature of the metal center has a profound impact on the chiroptical properties of the assemblies, opening a novel and potent means of tuning this key property of chiral screw-shaped  $\pi$ -conjugated structures. The theoretical analysis confirmed the process of stereoselective coordination of phosphole-modified azahelicenes to Pd<sup>II</sup> and revealed the intimate metal–helix electronic interactions that impact the chiroptical properties of the metal–bis(helicene) assembly.

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**Supporting Information Available:** Experimental procedures and spectroscopic data (UV–vis and CD spectra) for **1–4**, X-ray crystal-

lographic data and a CIF file for **2a**, and computational details for **3'**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) It should be noted that the crystallization was performed with a mixture of (*P*\*,*S*<sub>P</sub>\*)-**2a** and (*P*\*,*R*<sub>P</sub>\*)-**2b** and afforded single crystals of racemic (*P*\*,*S*<sub>P</sub>\*)-**2a**.
- (11) The computations used DFT/TD-DFT with the BP and BHLYP functionals and were performed with the Turbomole program (see the SI for details and references).
- (12) The BP/SV(P)-optimized structures of **3** show that the coordination sphere is distorted, as observed for related model complexes.<sup>6b</sup>
- (13) It is noteworthy that the overlapping of two *P*-helices induces a distorted square-planar geometry with a  $\Delta$  configuration around the Pd center (Figure 2) while *M*-helices induce a  $\Lambda$  configuration.
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