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Metal−Bis(helicene) Assemblies Incorporating π-Conjugated Phosphole-Azahelicene Ligands: Impacting Chiroptical Properties by Metal Variation

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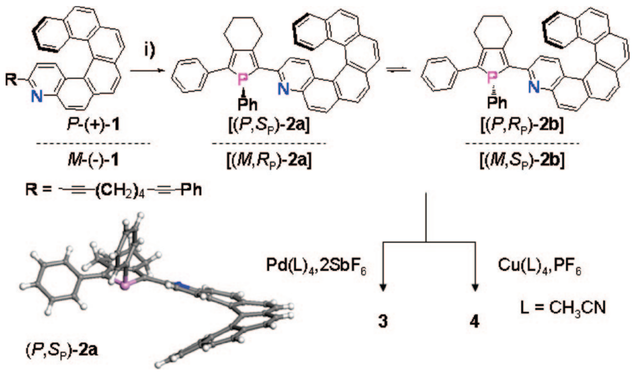
Helicenes possess a unique screw-shaped π-conjugated structure that provides them with huge optical rotation values.[1] Therefore, there is a growing interest in using helicenes or analogous derivatives as building blocks for the design of chiral ligands for use in asymmetric catalysis,[2a,b] nonlinear optical materials,[2c] and waveguides.[2d] 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.[3] Little is known about the coordination chemistry of helicene derivatives,[2a,3b,4] although metal ions are versatile templates for assembling π-conjugated ligands into supramolecular architectures.[5] 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 π-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[6a]) and the specific properties of the phosphole ring (ease of inversion at P, steric hindrance provided by the P substituent).[6b,c] Second, in these complexes, the phosphole and pyridyne moieties are conjugated, resulting in an intimate electronic interaction between the metal and the π-conjugated P,N-chelates via metal−ligand charge transfer.[6b,c] Herein, we describe the synthesis and chiroptical properties of the phosphole-modified azahelicenes **2a** and **2b** and their Pd^{II} and Cu^{I} 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 π-conjugated assemblies are shown and discussed on the basis of first-principles theoretical calculations.

Scheme 1. Synthesis, Solid-State Structures, and Coordination of **2a** and **2b**[a]



[a] (i) Cp$_2$ZrCl$_2$, 2BuLi, THF, −40°C, then PhPBr$_2$, 24 h, rt. X-ray structure of (P*,S_P*)-**2a** (space group P$\bar{1}$).

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[6,7] (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 ~330 nm (CH$_2$Cl$_2$) enabled their absolute configurations to be established.[3,8] It is noteworthy that optically pure functionalized azahelicenes are relatively rare[1,3] 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 ~50% yield (Scheme 1). It should be noted that the Zr/P exchange required a reaction temperature (40 °C) that was low enough to prevent inversion of the aza[6]helicene moiety (inversion barrier ~36 kcal mol^{-1}).[1] 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 (~15−16 kcal mol^{-1}) is much lower than that of regular phosphanes (~35−36 kcal mol^{-1}) because of the highly aromatic character of planar phospholes.[9] Therefore, the P-(+)-diyne **1** afforded a mixture of diastereomers (P,R_P)-**2a** and (P,S_P)-**2b**, whereas its M-(−)-enantiomer gave their (M,S_P)-**2a** and (M,R_P)-**2b** mirror images (Scheme 1). Indeed, the ^{31}P NMR spectrum of the reaction mixture displays two singlets of equal intensity at 14.0 and 14.5 ppm. Likewise, the ^{1}H and ^{13}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 ^{31}P NMR spectroscopy confirmed that derivatives **2a** and **2b** interconvert with a barrier of ~16 kcal mol^{-1}.

Slow crystallization of the diastereomeric mixture of phospholes **2a** and **2b** at room temperature afforded single crystals of **2a** only (Scheme 1).[10] The metric and geometrical data for the azahelicene and phosphole moieties of (P*,S_P*)-**2a** are fully consistent with those for related derivatives[6b] and fit nicely with the BP/SV(P)- and BP/TZVP-optimized structures.[11] 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 π 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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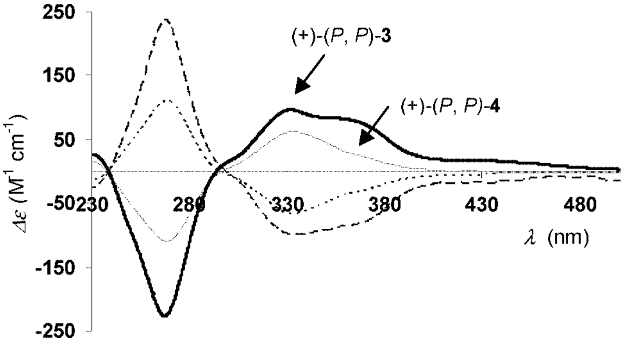

Figure 1. CD spectra of (+)-(*P*,*P*)-**3** and (+)-(*P*,*P*)-**4** (solid lines) and their respective enantiomers (dashed lines) in CH_2Cl_2 at 293 K.

is red-shifted compared with 2-pyridyl-1,5-diphenylphosphole (390 nm).[9b,c] It should be noted that the calculated[11] 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^{II} or tetrahedral Cu^{I} ions, since the P atom can adapt its configuration to minimize steric repulsion.[6b] Indeed, a diastereomeric mixture of the interconverting aza[6]helicene phospholes (*P*,S_P)-**2a** and (*P*,R_P)-**2b** reacted with $Pd(CH_3CN)_4,2SbF_6$ (2/1 molar ratio) in CH_2Cl_2 to afford complex **3** (78% yield) as a single stereoisomer (Scheme 1). Its elemental analysis is consistent with a [Pd(azahelicene phosphole)$_2$•2SbF_6] formula. The $^{31}P\{^1H\}$ NMR spectrum of **3** displays a single peak at 75.0 ppm, and its ^1H and ^{13}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^{II}(2-pyridylphosphole)$_2$ complexes having a distorted square-planar coordination sphere in which the P atoms have a mutual syn arrangement, in accordance with the trans effect.[6b,c] The simplicity of these NMR spectra clearly shows that the coordination of aza[6]helicene phospholes **2a** and **2b** to Pd^{II} is highly stereoselective. Therefore, complex **3** was obtained as a single enantiomer {$[\alpha]_D^{23} = +1275$ (±2%), (*c* 0.01, CH_2Cl_2)}, whereas its mirror image {$[\alpha]_D^{23} = -1250$ (±2%), (*c* 0.01, CH_2Cl_2)} was prepared using the mixture of (*M*,R_P)-**2a** and (*M*,S_P)-**2b** ligands. The same approach using $Cu(CH_3CN)_4,PF_6$ (2/1 ratio) afforded complex **4** {86% yield, Scheme 1, $[\alpha]_D^{23} = +910$ and -900 (±2%), (*c* 0.01, CH_2Cl_2)}, which exhibits a broad ^{31}P NMR signal (δ 5−6 ppm) in the expected range for dicationic tetrahedral Cu^{I}(2-pyridylphosphole)$_2$ complexes.[6b] 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^{II} complex **3** measured in CH_2Cl_2 ($[\Phi]_D = 23\,100 \pm 2\%$) is much larger than that of its Cu^{I} analogue **4** ($[\Phi]_D = 13\,100 \pm 2\%$). 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^{II} complex **3** is much larger than that of the Cu^{I} complex **4** (Figure 1). Furthermore, the CD spectrum of the Pd^{II} 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^{I} complex **4** (Figure 1). These results clearly show that (*i*) it is possible to perform a coordination-driven tuning of chiroptical properties of phosphole-modified azahelicenes and (*ii*) it is more efficient to organize these heteroditopic ligands around a square-planar Pd^{II} metal center than around a tetrahedral Cu^{I} center.[12]

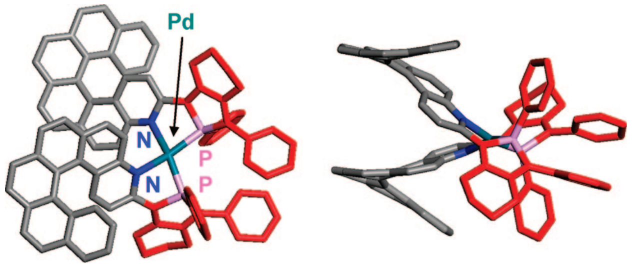

Figure 2. Optimized[11] structure of complex $Pd(\mathbf{2a})_2^{2+}$ (**3′**).

In order to gain more insight into the role of the Pd^{II} 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 $Pd(\mathbf{2a})_2^{2+}$ assembly is 81.6 kJ/mol more stable than its diastereoisomer $Pd(\mathbf{2b})_2^{2+}$. This large value is in agreement with the experimental observation that the coordination of interconverting **2a** and **2b** to Pd^{II} 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^{II} coordination sphere of $Pd(\mathbf{2b})_2^{2+}$ is much more distorted than that of $Pd(\mathbf{2a})_2^{2+}$ (twist angles between the N−Pd−P planes: $Pd(\mathbf{2b})_2^{2+}$, 54.8°; $Pd(\mathbf{2a})_2^{2+}$, 24.7°).[13] In fact, the metric data for the PdN_2P_2 core of $Pd(\mathbf{2a})_2^{2+}$ (**3′**) (Figure 2) fit well with those of other dicationic Pd(2-pyridylphosphole)$_2$ complexes established by X-ray diffraction studies.[6b,14] 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[11] 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 $\pi-\pi^*$ 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.[8a,c] The Pd^{II} 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^{I} complex **4** (Figure 1), clearly showing the impact of the metal ions on the CD properties. The long-wavelength

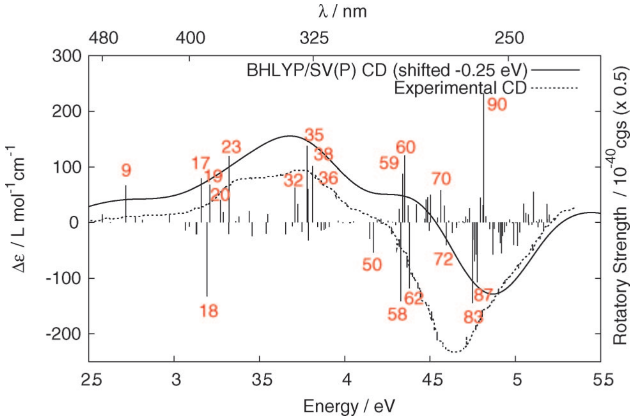

Figure 3. Comparison of the experimental (dashed line) and TD-DFT (solid line) CD spectrum of **3′** at the BHLYP/SV(P) level. The numbered excitations correspond to those with high rotatory strength that were analyzed in detail (see the SI).

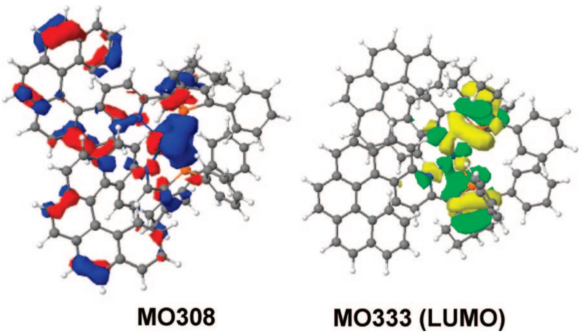

Figure 4. Two MOs of **3′** involved (14%) in excitation 9 in Figure 3.

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 π systems, etc.),[9] 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 π-conjugated structures. The theoretical analysis confirmed the process of stereoselective coordination of phosphole-modified azahelicenes to Pd^{II} 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 crystallographic 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_P^*)-**2a** and (P^*,R_P^*)-**2b** and afforded single crystals of racemic (P^*,S_P^*)-**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.[6b]

(13) It is noteworthy that the overlapping of two *P*-helices induces a distorted square-planar geometry with a Δ configuration around the Pd center (Figure 2) while *M*-helices induce a Λ configuration.

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