DOI: 10.1002/anie.200905099

Metallahelicenes: Easily Accessible Helicene Derivatives with Large and Tunable Chiroptical Properties**

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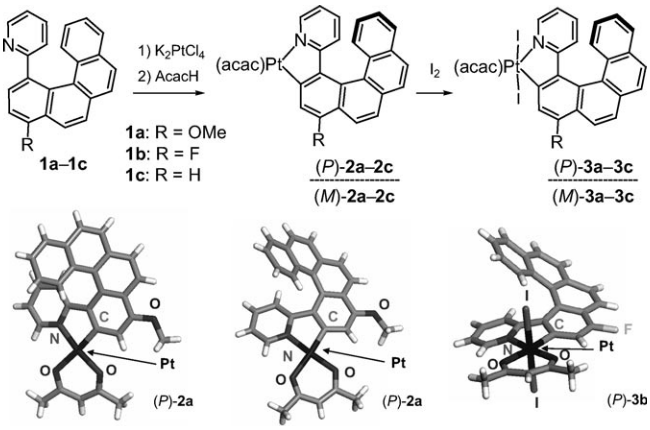
[*n*]Helicene derivatives are *ortho*-annulated, π-conjugated molecules that are endowed with helical chirality.[1] Enantiopure [*n*]helicenes with $n \geq 6$ can be isolated at room temperature and, owing to their unique conjugated screw-shaped structure, they exhibit outstanding chiroptical properties, such as extremely large optical rotations;[2a–c,f–h] these properties make them appealing functional materials, particularly in nonlinear optics and as waveguides.[2d,e,3] One important challenge with regard to further expanding the potential of helicenes is to develop synthetic strategies that provide efficient access to a variety of helical frameworks with tunable chiroptical properties.

Herein, we describe a straightforward synthetic procedure that generates the first reported examples of helicene derivatives with a transition metal incorporated into their *ortho*-annulated π-conjugated backbones.[4] This approach fully exploits the versatility of organometallic chemistry, in that: 1) the construction of the helical backbone is achieved using simple, practical *ortho*-metalation reactions, and 2) structural engineering of the helicene scaffolds can be performed through either undertaking reactions at the incorporated metal center or by varying the nature of the metal. Furthermore, the presence of the metal center provides these helicene-based systems with unusual photophysical properties. Our initial studies employed the platinum(II) ion, which was selected because of its efficient electronic metal–ligand interactions, its large associated spin–orbit coupling, and its redox properties. These chiral platinum helicenes exhibit chiroptical properties that can be fine-tuned by chemical oxidation of the metal center. Moreover, replacing platinum(II) with other metal ions, such as iridium(III), provides access to original [*n*]helicene topologies.

Cyclometalated complexes between heavy late-transition metals and 2-phenylpyridine ligands [(N^C)M, e.g. M = platinum(II), iridium(III)] are readily accessible organometallic species that exhibit high phosphorescent efficiency.[5] Therefore to prepare our target metallahelicenes, we investigated the *ortho*-metalation chemistry of 4-(2-pyridyl)-benzo[g]phenanthrenes **1a**–**1c** (Scheme 1), which can be prepared using a Suzuki-coupling/Wittig/photocyclization reaction sequence. An X-ray diffraction study of **1a** (see the Supporting Information) revealed a helical curvature (hc, the angle between the terminal helicene rings) of 33.4°,[6] a value typical for [4]helicenes.[7a] All attempts to resolve compounds **1a**–**1c** using HPLC failed, showing that **1a**–**1c** are not configurationally stable at room temperature; this is usually the case for [4]helicene derivatives.[8] Compounds **1a**–**1c** were subjected to a classic two-step metalation reaction[5] (Scheme 1), which afforded air-stable platinum(II) complexes **2a**–**2c** (yields > 50%). These results show that *ortho*-metalation is a powerful synthetic route to this family of helicene derivatives, and it can be used to synthesize these species in large quantities (half-gram scale; see the Supporting Information).



Scheme 1. Synthesis of platinum helicenes, and X-ray crystallographic structures of **2a** (two views) and **3b** (stereoisomers with *P*-helices).[6]

An X-ray crystallographic study of complex **2a** confirmed the proposed structure (Scheme 1); this structure is also supported by theoretical calculations (see the Supporting

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[**] We thank the Ministère de l'Education Nationale, de la Recherche et de la Technologie, the CNRS, the ANR (project PHOSHELIX-137104), and the National Science Foundation (CHE 0447321).

Supporting information for this article, including experimental procedures and characterization of the isolated products, is available on the WWW under http://dx.doi.org/10.1002/anie.200905099.

Information). As expected, the d^8 platinum(II) ion adopts a slightly distorted square-planar geometry; the metric data of the platinum(II) coordination sphere is within the typical range previously reported for other [(N^C)Pt(acac)] complexes (acacH = 2,4-pentanedione).[5] The phenyl and pyridine rings that are coordinated have a twist angle of 7.3°, and the consecutive twist angles between the fused aromatic rings (24.7°, 31.0°, and 13.4°) lead to a hc value of 52.3° in the metalla[6]helicene-like skeleton (Scheme 1); these values are similar to those reported in organic or heteroatomic [6]helicene systems (hc ~ 50°).[7b,9] Indeed, derivatives **2a**–**2c** possess this targeted, inherently chiral, *ortho*-annulated π-conjugated framework.

The electronic properties of these metallahelicenes were investigated using UV/Vis spectroscopy and theoretical calculations. The electronic absorption spectra of complexes **2a**–**2c** displayed several intense absorption bands between 250 and 350 nm that were red-shifted compared to those of the free ligands **1a**–**1c** ($\lambda_{max} = 290$ nm), and two weaker, lower-energy broad bands below 450 nm (Figure 1). The intense bands indicate the presence of an extended π-conjugated system within the metallahelicenes, whilst the lower energy bands are thought to arise from orbitals involving the metal and the N^C-ligands. These assignments are supported by time-dependent DFT calculations (BHLYP/SV(P) level of theory), which accurately reproduced the experimental spectra of **2a**–**2c** after a modest red shift of 0.25 eV (Figure 1). For example, the long-wavelength band is essentially a HOMO–LUMO transition (3 eV, 89.2%; Figure 1), involving two molecular orbitals (MOs) that consist of a mixture of platinum orbitals and extended N^C π-orbitals (Figure 1). In fact, the orbitals on the metal atom are involved in many π-MOs (Figure 1; see the Supporting Information for an excitation analysis in terms of MO-to-MO contributions). These experimental and theoretical results reveal the unique structural properties of **2a**–**2c**, in which a conjugated helicoidal system is intimately electronically coupled with an integrated transition metal center.

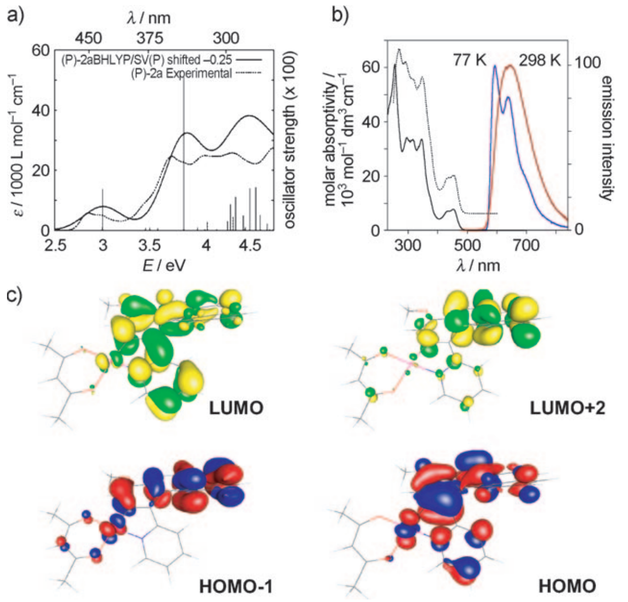


Figure 1. a) Experimental spectrum (•••••) and calculated UV/Vis spectrum for **2a** shifted by −0.25 eV (BHLYP/SV(P),——). b) Normalized emission spectra of **2a** at 298 K (dichloromethane; red line) and at 77 K (diethyl ether/isopentane/ethanol; 2:2:1 v/v; blue line; $\lambda_{ex} = 450$ nm). The absorption (——) and excitation spectra ($\lambda_{em} = 640$ nm,•••••) at 298 K are shown on the same wavelength scale. c) Views of selected MOs of **2a**.

Metallahelicenes **2a**–**2c** exhibit an emission behavior that differs considerably from that of typical organic helicenes, such as the free ligands **1a**–**1c**. Compounds **1a**–**1c** all have blue fluorescence in dichloromethane solvent at room temperature (see the Supporting Information). In a rigid glass matrix at 77 K, the fluorescence is accompanied by long-lived green phosphorescence. In contrast, even at room temperature, platinum helicenes **2a**–**2c** display phosphoresce only, in the red region of the spectrum (Figure 1; see also the Supporting Information); indeed, with luminescence quantum yields of up to 10%, the metallahelicenes (**2a**–**2c**) are efficient (N^C)platinum(II) red phosphors.[5] The absence of fluorescence in platinum helicenes **2a**–**2c** can be attributed to the effective spin-orbit coupling associated with the platinum center, favoring rapid intersystem crossing from the singlet to the triplet state. The fact that the phosphorescence of the complexes is substantially lower in energy than that of the free ligands is testament to the involvement of the metal in the emitting excited state. The influence of spin–orbit coupling and the efficient mixing of metal orbitals and ligand orbitals is also manifest in the much shorter lifetimes of triplet emission in the complexes (see the Supporting Information). Compounds **2a**–**2c** are the first reported helicene derivatives to exhibit strong phosphorescence at room temperature,[10] a property induced by the incorporation of a heavy metal atom within the helicene π-conjugated framework. Indeed, the heavy metal plays a dual role, both forming the [*n*]helicene skeleton upon *ortho*-metalation (Scheme 1), and dramatically impacting on the optical properties of the helicoidal π-conjugated system.

With these unusual systems in hand, it was crucial to elucidate whether these organometallic helicenes would possess the important chiroptical properties of [6]helicenes. In other words, could they be resolved, and do they exhibit large optical rotations and intense circular dichroism (CD) bands? Derivatives **2a** and **2b** were selected for this study because they are configurationally stable in solution at room temperature,[11] thus allowing their enantiomers to be separated by chiral stationary phase HPLC (*ee* values of 98%–99.5%). They display very high specific and molar optical rotations [(+)-**2a**:$[\alpha]_D^{23} = 1300$, $[\phi]_D^{23} = 8170$ (±5%) ($c = 2.85 \times 10^{-3}$, dichloromethane); (+)-**2b**: $[\alpha]_D^{23} = 1240$, $[\phi]_D^{23} = 7420$ (±5%) ($c = 1.8 \times 10^{-3}$, dichloromethane)]. For comparison, the molar optical rotations for *P*-[6]carbohelicene[2h] ($[\phi]_D^{23} = 11950$) is of a similar order of magnitude; the calculated[2f,g] gas phase values for *P*-**2a** ($[\phi]_D = 10281$, BHLYP/SV(P)) is in the range of the experimental measurements. The mirror-image CD spectra of complexes **2a** and **2b** are intense (Figure 2a; also see the Supporting Information), and are very similar for both complexes. The (+) enantiomers show an intense negative band at 250 nm and a strong positive band with several maxima tailing down to 410 nm. Together, these data demonstrate that metallahelicenes **2a** and **2b** exhibit the important chiroptical properties that make helicene derivatives unique and appealing compounds.

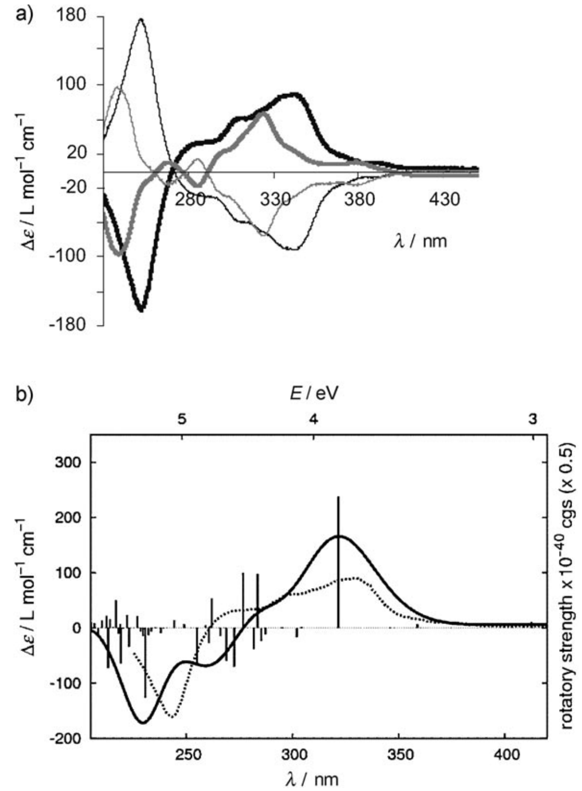
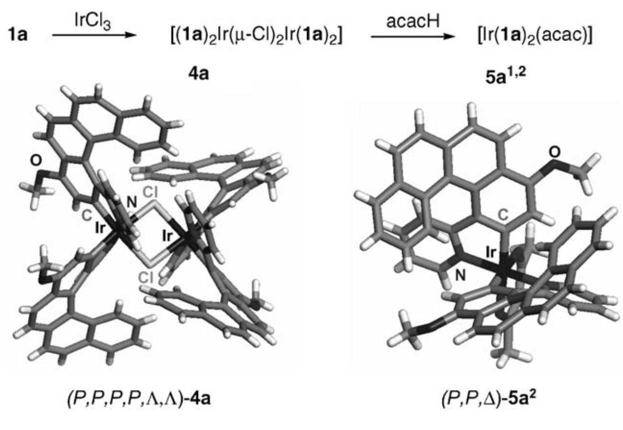


Figure 2. a) Mirror-image CD spectra of platinum(II)-**2a** (black), and platinum(III)-**3a** (gray; thick lines: (+)-derivatives; thin lines: (−)-derivatives). b) Comparison between the experimental CD spectrum (•••••) and BHLYP/SV(P) spectrum shifted by −0.25 eV (——) of *P*-(+)-**2a**.

The experimental CD spectrum of **2a** agreed well with a computed spectrum red shifted by 0.25 eV (Figure 2b). The calculated CD spectrum of the *P*-platinum helicene also compared well with that of (+)-**2a**, enabling its absolute configuration to be assigned as *P*-(+)/*M*-(−). Of particular interest is that the platinum orbitals are involved in almost all CD-intense transitions, even those of high energy. For example, the dominant contributions to the intense CD band at 321 nm ($R = 475 \times 10^{-40}$ esu^{2}cm^2) are transitions from HOMO to LUMO + 2 (47%) and from HOMO-1 to LUMO (40%; Figure 1). Likewise, the CD band at 283 nm ($R = 195 \times 10^{-40}$ esu^{2}cm^2) involves two main transitions (16% and 13%), implying that there is an occupied d_{z^2}-like orbital centered on the metal ion (MO no. 119; see the Supporting Information). Note that the low energy CD band at 412 nm displayed a low rotatory strength ($R = 21 \times 10^{-40}$ esu^{2}cm^2) and is essentially a HOMO–LUMO transition (89%). The calculations revealed the crucial contribution of the metal center to the chiroptical properties of metallahelicenes. This prompted us to modify the oxidation state and coordination sphere of the platinum(II) ion with the aim of tuning this key property.

Enantiopure (+)-platinum(II) helicenes **2a** and **2b** were reacted with iodine in dichloromethane to afford the corresponding air-stable platinum(IV) helicenes **3a** and **3b** in good yields (60–70%; Scheme 1).[12] The molecular structure of **3b**[13] has an octahedral geometry around the platinum(IV) center with two iodine atoms occupying the apical positions (Scheme 1). The bond lengths and angles about the metal center are comparable to those for platinum(II) complex **2a** (see the Supporting Information). The value of hc of the coordinated N^C ligand (56°) remains unchanged upon oxidation of the metal ion. Notably, chiral HPLC revealed that this oxidation process afforded complexes **3a** and **3b** as single enantiomers (**3a**: *ee* > 99.8%, **3b**: *ee* > 99.5%; see the Supporting Information). This result is of great importance as it shows that it is possible to modify the coordination geometry and the oxidation number of the metal center whilst maintaining the helicity and enantiopurity of the metallahelicene. Moreover, the shape and intensity of the CD spectra of platinum(II) and platinum(IV) metallahelicene derivatives are markedly different. For example, the oxidation of *P*-(+)-**2a** into *P*-(+)-**3a** results in a decrease in the intensity of the CD bands at high energy (approx. 230–250 nm) and those at 340–360 nm, and also an inversion in sign of the CD bands at 280 nm (Figure 2a). Note that complex **3a** can be reduced to its platinum(II) precursor (**2a**) upon treatment with zinc powder. Indeed, the presence of a reactive platinum center within the helicoidal π-conjugated skeleton allows redox-modulated structural engineering to be achieved, which impacts the chiroptical properties of these novel types of helicene derivatives.

Finally, to illustrate the scope of this organometallic approach to unusual helicenes, the synthesis of their corresponding iridium helicene derivatives was investigated.[5] The reaction of **1a** with $IrCl_3$ afforded μ-chloro-bridged iridium dimers **4a**, which could be further reacted with acacH to give two isomeric monometallic species (**5a**^{1} and **5a**^{2}; Scheme 2), which were isolated in 22% yield. These monometallic and bimetallic complexes feature an unprecedented structural motif in which two helicene moieties are connected by an octahedral center (i.e., the iridium(III) ion; Scheme 2). These preliminary results illustrate that *ortho*-metalation is a power-



Scheme 2. Synthesis of iridium helicenes, and X-ray crystallographic structures of **4a** and **5a**^{2} (stereoisomers with *P*-helices).[6]

ful synthetic tool for the generation of original helicene structures.

In conclusion, helicenes with unprecedented structural and chiroptical properties can be readily obtained using a straightforward and practical ligand *ortho*-metalation procedure. As illustrated with platinum(II) derivatives, the incorporation of metal centers within the helicoidal conjugated framework results in intimate metal–helix electronic interactions, which confers multiple functionality upon these derivatives, including efficient phosphorescence and tunable chiroptical properties. This synthesis of the first metallahelicene derivatives shows that exploiting the potential of organometallic chemistry opens up promising new perspectives in helicene chemistry.

Received: September 11, 2009
Published online: November 30, 2009

Keywords: chirality · helicenes · optical rotation · organometallic compounds · π interactions

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