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From Hetero- to Homochiral Bis(metallahelicene)s Based on a $Pt^{III}-Pt^{III}$ Bonded Scaffold: Isomerization, Structure, and Chiroptical Properties

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S *Supporting Information*

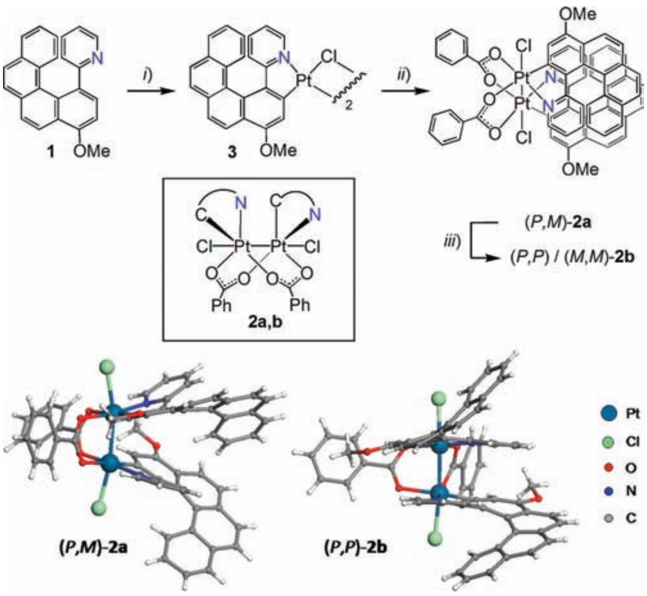
ABSTRACT: Hetero- and homochiral diastereomeric bis(metallahelicene)s have been synthesized. They possess a rare $Pt^{III}-Pt^{III}$ scaffold bridged by benzoato ligands. It is shown that heterochiral (*P*,*M*)-bis(Pt^{III}-[6]helicene) can isomerize into the homochiral (*P*,*P*)- and (*M*,*M*)-bis(Pt^{III}-[6]helicene). A theoretical study shows a unique $\sigma-\pi$ conjugation between the two π-helices and the σ-$Pt^{III}-Pt^{III}$ scaffold that impacts the strong chiroptical properties.

[*n*]Helicenes are polycyclic π-conjugated systems that consist of *n* *ortho*-fused aromatic rings with helical chirality.[1] This unique helical conjugated structure endows [*n*]helicenes with fascinating attributes, such as huge molecular chiroptical properties and the ability to self-organize within supramolecular aggregates, that are potentially of great interest in chiral material sciences.[2] Although remarkable progress has recently been made in helicene chemistry using organic synthesis,[3] other approaches allowing a straightforward access to novel well-defined molecular helical structures, as well as an understanding of the factors controlling their structure and properties, are crucial to the development of [*n*]helicenes toward functional materials.

In this paper, we report an organometallic approach toward unprecedented helical structures resulting from the close *superimposition* of two [6]helicenes using an original $Pt^{III}-Pt^{III}$ scaffold.[4] Diastereoisomeric complexes having the two possible *heterochiral* (*P*,*M*)-**2a** and *homochiral* (*P*,*P*)/(*M*,*M*)-**2b** arrangements (Scheme 1) have been structurally characterized, and it is shown that the *heterochiral* assembly **2a** isomerizes into its *homochiral* diastereoisomer **2b**. Density functional theory (DFT) calculations reveal a certain degree of conjugation between the two metalla[6]helicene moieties through the Pt—Pt σ-bond for the two dinuclear complexes **2a**,**b**. A route leading to the enantiopure homochiral bis(metallahelicene) **2b** is described, and structure—chiroptical property relationships are established based on experimental and theoretical data.

We have recently described the first family of organometallic helicenes in which the metal center is incorporated within the helical backbone.[5] The precursor of these novel helicene derivatives is the di-μ-chloro Pt^{II}-dimer **3** (Scheme 1), which is readily obtained by a simple *ortho*-metalation reaction involving 1-methoxy-4-(2-pyridyl)benzo[*g*]phenanthrene **1**.[5] Inspired by the reactivity of related cyclometalated [(2-phenylpyridinato)(μ-Cl)Pd]$_2$ complexes,[6] **3** was reacted with 2 equiv of silver benzoate with the aim to obtain Pt dimers in which the metalla[6]helicene moieties will be superimposed on a bimetallic scaffold supported by bridging $PhCO_2^-$ ligands. The reaction (**3**:$PhCO_2Ag$ = 1/2 molar ratio) was conducted in a mixture of $CHCl_3$/THF

Scheme 1. Synthesis, Schematic, and X-ray Crystallography Structures of (*M*,*P*)-2a and (*P*,*P*)-2b Benzoato-Bridged Pt^{III}-Dimers[a]



[a] Only one enantiomer is shown. Reagents and conditions: (i) K_2PtCl_4, 2-ethoxyethanol, reflux, Ar, 16 h; (ii) $PhCO_2Ag$, $CHCl_3$/THF, rt, 12 h, Ar, 57%; (iii) toluene, 80 °C, Ar, 3 days.

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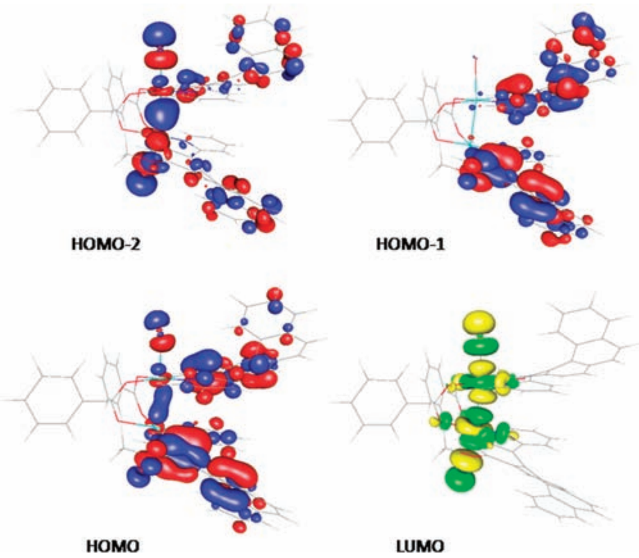


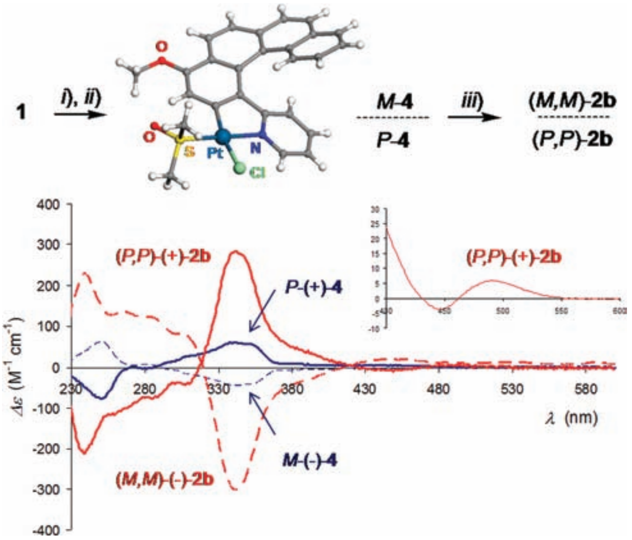
Figure 1. Isosurfaces (0.03 au) of selected molecular orbitals of (*M*,*M*)-**2b**.

(95/5) at room temperature for 12 h under argon (Scheme 1). After purification by column chromatography, a mixture of two species, **2a** and **2b** (9/1 molar ratio), was isolated (57% yield). The ^{1}H and ^{13}C NMR data of the main species **2a** reveal that this compound has a C_1 symmetry. For example, two singlets at 3.9 and 3.8 ppm for the methoxy groups are recorded in its ^{1}H NMR spectrum. In contrast, the minor derivative **2b** has a C_2 symmetry; one signal only is observed for the methoxy moiety (^{1}H NMR, 3.7 ppm). Single crystals of pure **2a** were grown from an *i*-Pr$_2$O/CH$_2$Cl$_2$ solution of this 9/1 mixture of **2a**,**b**. X-ray analysis revealed that **2a** consisted of two platina[6]helicenes assembled by two bridging μ^2-benzoato ligands, with the N-atoms having a mutual *anti* arrangement (Scheme 1). Each metal ion is linked to a Cl atom and is therefore formally a d^7 Pt^{III} center (Scheme 1). The Pt−Cl bond lengths are classic [2.426(3), 2.428(3) Å], and the metal−metal distance [2.5952(6) Å] is consistent with a Pt^{III}−Pt^{III} single bond.[4] Pt^{III}-dimers are quite rare species,[4] and the first Pt^{III}-dimer supported by μ^2-carboxylate bridging donors (i.e., acetato ligands) has been only very recently obtained via *ortho*-metalation of functionalized phenylpyridines by PtCl$_2$(dmso)$_2$ performed in refluxing AcOH.[4a] The individual Pt^{III}-[6]helicenes of dimer **2a** have opposite handedness and display helical curvatures (dihedral angle between the two terminal rings, 49° ± 1°) that are comparable to those of monomeric Pt^{II}- and Pt^{IV}-[6]helicenes (54 ± 2°).[5] Overall, this heterochiral (*P*,*M*)-bis-platina(III)-[6]helicene complex is not a pure *meso* compound, since it displays a C_1 symmetry due to the *anti* arrangement of the two orthometalated phenylpyridine moieties (Scheme 1). Note that the NMR data are fully consistent with this solid-state structure (see SI).[7] This compact heterochiral arrangement results in steric congestion, as indicated by the large angle between the two five-membered platinacycles (46.5°) and the nonlinearity of the Cl−Pt−Pt−Cl fragment (Scheme 1 and Table S2 in SI). The synthesis of **2a** (Scheme 1) nicely illustrates that organometallic chemistry allows us to obtain original helicene-based architectures, since this unusual (Pt^{III})$_2$ scaffold endows complex **2a** with an unprecedented structure in which two [6]helicene moieties of opposite handedness are superimposed.

Interestingly, heating the mixture of **2a**,**b** (9/1 molar ratio) in toluene at 80 °C under an inert atmosphere results in the transformation of **2a** into **2b** (Scheme 1). This transformation, which can be easily followed by ^{1}H NMR spectroscopy (see SI), is rather slow but can be conducted until completion (3 days). An X-ray diffraction study performed on single crystals shows that **2b** features a Pt^{III}-dimer scaffold supported by two μ^2-benzoato ligands (Scheme 1), as observed for **2a**, but with the two Pt^{III}-[6]helices having the same handedness (Scheme 1)! Overall, complex **2b** displays a unique helix structure resulting from two metal−metal bonded, superimposed metallohelices with identical configuration. The helical curvatures of the metallahelicenes of (*P*,*P*)- and (*M*,*M*)-**2b** are classic (37.7−53.0°), and this complex exhibits an overall C_2 symmetry, in line with the NMR data (see SI). Note that, due to the short Pt^{III}−Pt^{III} intermetallic distance [2.5788(9) Å], the two phenylpyridine moieties are engaged in intramolecular $\pi-\pi$ interaction (centroid−centroid distance, 3.464 Å; Scheme 1). This *homochiral* assembly **2b** seems to be less constrained than its *heterochiral* precursor **2a**, as indicated by the modest angle between the two five-membered platinacycles (19.8°) and the linearity of the Cl−Pt−Pt−Cl fragment (Scheme 1 and Table S2 in SI). Indeed, *heterochiral* bis(metallahelicene) **2a** can isomerize into its *homochiral* analogue **2b**, although DFT calculations indicate that the energy difference between these two species is rather small.[8] The computations revealed that, within complexes **2a**,**b**, the metalla[6]helicene moieties are electronically coupled through the Pt^{III}−Pt^{III} σ-scaffold. This $\sigma-\pi$ conjugation is apparent in many molecular orbitals. For example, in the HOMO-2 and HOMO of **2a** (see SI, MOs 271 and 273) and **2b** (Figure 1), there is an extensive mixing of the π-orbitals of the two metallohelicenes with the σ-orbitals of the Cl−Pt−Pt−Cl fragment. This type of interaction is unprecedented in helicene chemistry and prompted us to investigate its impact on the chiroptical property of these bis(metallahelicene) complexes.

Unfortunately, all attempts to resolve the enantiomers of **2a** and **2b** using chiral HPLC failed. Therefore, another synthetic route based on the recent work of Bruce et al. was investigated.[4a] Monomeric Pt^{II}-complex **4**, bearing a dmso ligand, was readily prepared by reacting **1** with *cis*-[Pt^{II}(dmso)$_2$Cl$_2$] in toluene at 110 °C (85% yield, Scheme 2). This complex was fully characterized by multinuclear NMR spectroscopy and X-ray diffraction study (Scheme 2). The *P* and *M* enantiomers of **4a** were separated by HPLC over Chiralpak IA (*P*-**4a**, ee 93%; *M*-**4a**, ee 90%; see SI). As observed for the only other known Pt^{II}-metallahelicenes,[5] their experimental specific and molar rotation values are high ($[\alpha]_D^{23}$ = +1100 (±5%), *c* 0.01, CH$_2$Cl$_2$; $[\phi]_D^{23}$ = +7060 (±5%) for *P*-(+)-**4**).[9] Their CD spectra display a strong band at 240 nm and a broader one centered at 350 nm and tailing down to 440 nm (Scheme 2). Addition of silver benzoate to these Pt^{II}-complexes **4** in acetone at room temperature, followed by a flash chromatography over silica gel (AcOEt/heptane, 8/2), afforded the optically active homochiral (*M*,*M*) and (*P*,*P*) complexes **2b** in 40% yield (Scheme 2).[10] The experimental specific and molar rotation values for (*P*,*P*)-(+)-**2b** are large ($[\alpha]_D^{23}$ = +2060 (±5%), *c* 0.04, CH$_2$Cl$_2$; $[\phi]_D^{23}$ = +28 200 (±9%)). For comparison, the molar rotation of this bis(metallahelicene) **2b** is 3 times higher than those of monometallic Pt^{II}-[6]helicenes ($[\phi]_D^{23}$ = 7060−8170),[5] showing that superimposing two metallahelicenes on a Pt^{III}−Pt^{III} scaffold is an efficient approach for enhancing chiroptical properties of helicene derivatives. The CD spectra for complexes

Scheme 2. (Top) Synthesis of Enantioenriched Complexes *M*-4/*P*-4 and (*M*,*M*)-2b/(*P*,*P*)-2b[a] and (Bottom) CD Spectra[b]



[a] Reagents and conditions: (i) Pt(dmso)$_2$Cl$_2$, toluene, 110 °C, Ar, 16 h, 85%; (ii) HPLC separation over Chiralpak IA; (iii) PhCO$_2$Ag, acetone, rt, 12 h, Ar, flash chromatography over SiO$_2$, heptane/EtOAc 8:2, 40%. The X-ray crystallographic structure of the *M* isomer of **4** is shown. [b] CD spectra in CH$_2$Cl$_2$ at 293 K of (*P*,*P*)-(+)-**2b** and *P*-(+)-**4** (plain lines) and their respective enantiomers (dashed lines). Inset: CD spectrum of (*P*,*P*)-(+)-**2b** in the 400−600 nm region.

(*P*,*P*)-(+)- and (*M*,*M*)-(−)-**2b** are mirror-image and much more intense than those of their respective monometallic precursors **4** (Scheme 2). The (+)-enantiomer displays two intense bands, a negative one at 240 nm and a broad positive one centered at 350 nm. Two weak bands at low energy (440 and 490 nm, Scheme 2 insert) and three weak bands at higher energy (260, 285, and 305 nm, Scheme 2) are also observed.

The chiroptical properties of bimetallic complexes **2a**,**b** were investigated by TD-DFT calculations. We have shown previously that the type of calculations employed here can provide useful insight into structure−property relationships of organometallic helicene derivatives.[5,11] The calculated electronic optical activity compares well with experiment. For example, the computed (BHLYP/SV(P)) molar rotation for (*M*,*M*)-**2b** is $[\phi]_D^{23} = -26.7 \times 10^3$ [experimental $[\phi]_D^{23} = -27 \times 10^3$ (±9%)], and the shape of the calculated CD spectrum matches the experimental one (Figure 2). The occupied MOs involved in the intense transitions in the CD spectrum result from a mixing of both metallahelicene π-systems and Pt^{III}−Pt^{III} σ-scaffold orbitals (see transitions 9, 18, 21, and 22 in the SI).[12] For example, the dominant contribution (74%) to the most red-shifted and strongest CD band (ca. 350 nm, $R = -538 \times 10^{-40}$ esu^2 cm^2, no. 9) is a HOMO-2 to LUMO transition (Figures 1 and 2). The fact that the two π-helices interact through the σ-Pt^{III}−Pt^{III} scaffold has clearly an impact on the resulting chiroptical properties of these novel *homochiral* superimposed bis-helicene derivatives.

In conclusion, these results show that organometallic chemistry allows us to obtain unusual chiral structures (superimposed helicene moieties), reactivity (heterochiral−homochiral isomerization), and electronic properties (σ−π conjugation) in helicene chemistry. The resulting strong CD and large magnitude of the optical rotation of these novel assemblies based on metal−metal bonded scaffolds open up promising perspectives for the molecular engineering of helicene-based chiroptical materials.

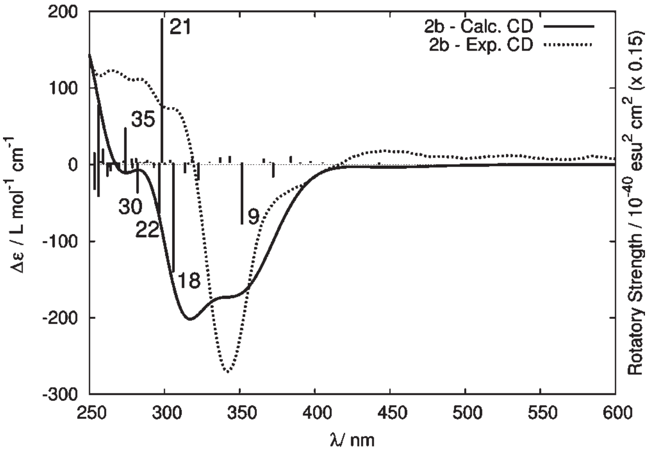


Figure 2. Experimental (CH$_2$Cl$_2$) and TD-DFT calculated CD spectra for (*M*,*M*)-**2b**. The numbered excitations correspond to those with high rotatory strength that were analyzed in detail (see SI).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures, spectroscopic data, X-ray crystallographic data and CIF files for **2a**,**b** and **4**; computational details for theoretical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) X-ray diffraction study reveals an intramolecular CH···aryl π interaction between the H^6 atom of one helix and an aromatic cycle of the other helix (2.63 Å, see SI), resulting in a strong shielding of its ^1H NMR chemical shift (4.4 ppm).

(8) At the RI-BP86/SV(P) level of theory (gas phase), **2b** is more stable than **2a** by 0.6 kcal·mol^{-1}. Calculations with BP86 and the larger TZVP basis placed the energy difference at 0.4 kcal·mol^{-1}, and at 0.5 kcal·mol^{-1} using computations with TZVP and the conductor-like screening model (COSMO) using the dielectric constant of toluene (ε = 2.38).

(9) For comparison, the molar rotation of *P*-6-carbohelicene is $[\phi]_D^{23}$ = 11 950: Grimme, S. *Chem. Phys. Lett.* **2001**, *339*, 380–388.

(10) These data suggest that the oxidation of **3** or **4** into **2a**,**b** (Schemes 1 and 2) involves the Ag$^+$ ions. For oxidation of Pt(II)- into P(III)-complexes by Ag$^+$, see: (a) Steele, B. R.; Vrieze, K. *Trans. Met Chem.* **1977**, *2*, 169–174. (b) Bancroft, D. P.; Cotton, F. A. *Inorg. Chem.* **1988**, *27*, 4022–4025.

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(12) Note that MOs of **2b** where the two helical π-systems do not interact through the Pt—Pt bond also impact the CD spectrum (see for example HOMO-1 involved in transition 21, Figures 1 and 2).