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Enantiopure Cycloiridiated Complexes Bearing a Pentahelicenic N-Heterocyclic Carbene and Displaying Long-Lived Circularly Polarized Phosphorescence

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Abstract: A fused π-helical N-heterocyclic carbene (NHC) system was prepared and examined through its diastereoisomerically pure cycloiridiated complexes. The latter display light-green phosphorescence with unusually long lifetimes and circular polarization that depends on both the helical NHC P/M stereochemistry and the iridium Δ/Λ stereochemistry. These unprecedented features are attributed to extended π conjugation within the helical carbenic ligand and efficient helicene-NHC–Ir interaction.

Octahedral cyclometalated iridium(III) complexes have attracted attention due to their applications as phosphors in organic light-emitting devices (OLEDs) as well as their biological activity. To date, several classes of enantiopure cycloiridiated systems have been reported. As for IrIII complexes bearing N-heterocyclic carbene (NHC) ligands, while few examples have been shown to display deep-blue phosphorescence (a challenging target in the OLED area), chiral NHC-based systems for molecular materials science are almost unknown. Furthermore, no chiral purely π-helical NHC has been reported to date. Herein, we describe the synthesis of a π-conjugated ortho-fused [5]helicenic NHC ligand (in which an NHC is incorporated within a helical core) through its diastereoisomerically pure cycloiridiated complexes A[2]. We detail their electronic and structural features, stereochemistry, and photophysical and chiroptical properties experimentally and computationally.

Scheme 1 shows the strategy to prepare the [5]helicene-imidazolium iodide salt ([C6]). First, the [5]helicene-thiadiazole [9a] was reduced to 1,2-diamino-[4]helicene 2 with LiAlH4,[9b] which was then directly cyclized to the precarbenic [5]helical imidazole 3 by using triethyl orthoformate in the presence of I2.

Figure 1. Meridional cycloiridiated complexes A1,2 bearing a P-[5]helicene-NHC chelating ligand and model NHC complex A lacking the helicene unit. An X-ray structure of A (P, enantiomer) is shown.

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presence of catalytic iodine in acetonitrile. To our knowledge, 3 is the first fully π-helical imidazole, since it displays five ortho-fused aromatic rings including the terminal imidazole cycle.

Two tautomeric forms \[10\] (3a,b in Scheme 1) are seen by \(^1\)H NMR spectroscopy (Figure S2 in the Supporting Information) and are in exchange at 75°C on the NMR timescale. X-ray crystallography was used to confirm the helical nature of 3, which crystallized as its 3b tautomer in the \(\text{Ia}\) centrosymmetric space group, with both \(P\) and \(M\) enantiomers (Scheme 1 and the Supporting Information). The imidazolide ring reveals classical metric data (C2–N1 (C2–N3) bond length: 1.320 (1.345) Å),\[10\] while the molecule shows a helicity (dihedral angle between the terminal rings) of 42.27°. A Chan–Lam coupling\[11\] of 3 with \(p\)-tolyl-boric acid furnished 4, the methylation of which with \(\text{CH}_3\text{I}\) in excess gave the imidazolide salt (±)-5. While the [5]helicenic imidazole derivatives 3 and 4 are configurationally unstable in solution (the enantiomers could not be resolved by chiral HPLC at 10°C, which indicates an inversion barrier < 90 kJ mol\(^{-1}\)), the methyl group in the inner 1N position of 5 blocks the inversion of the helix (see below).\[12\] Species (±)-5 crystallized in the \(P_{21}/n\) centrosymmetric space group, with heterochiral dimers of \(P\) and \(M\) enantiomers, and displays a helicity higher than 3 (50.81°), while the \(p\)-tolyl group forms a dihedral angle of 43.67° with the imidazolide cycle (Scheme 1 and the Supporting Information). Species 5 can be regarded as a 1N-Me-[5]helicene derivative.\[13\]

The heteroleptic cycloiridiated complexes \(\text{A}^{1,2}\), which bear a [5]helicene-NHC-N-tolyl and two 2-(2,4-difluorophenyl)-pyridyl (dfppy) ligands, were obtained by reacting 5 with \(\text{Ag}_2\text{O}\) and \([\text{Ir}(\mu-\text{Cl})(\text{dfppy})]_2\) \(\text{L}\) (Scheme 1).\[5,14\] The diastereomeric mixture of \(\text{A}^{1}\) and \(\text{A}^{2}\) was obtained in a 63:37 ratio, as estimated from \(^1\)H NMR spectroscopy and HPLC (see the Supporting Information), thus suggesting that the cyclometalation is diastereoselective. \(\text{A}^{1,2}\) correspond to the meridional geometric isomers, thus indicating that the mutually trans configuration of the pyridyl rings of the precursor 6 is retained,\[5,14\] as further evidenced by \(^1\)H-1H NOESY and \(^1\)H-13F HOESY NMR studies (see the Supporting Information). X-ray crystallography of the pure diastereoisomer \(\text{A}^{1}\) (4a/\(\text{Ia}\) centrosymmetric space group; Figure 1 and the Supporting Information) shows pseudo-octahedral geometry around the iridium center and a trans relationship between the pyridyl rings of the two dfppy ligands, whereas the [5]helicene-NHC chelate can be oriented in two ways around the Ir\(^{III}\), defining either the \(\Delta\_\text{H}\) or \(\Lambda\_\text{H}\) epimers associated with \(M\) or \(P\) helical stereochemistry, respectively \(([\text{M(}\Delta\_\text{H})]\text{A}^{1}\) and \(\text{P(}\Delta\_\text{H})\text{A}^{1}\)). The other diastereoisomers are \(\text{P(}\Delta\_\text{H})\text{A}^{2}\) and \(\text{M(}\Delta\_\text{H})\text{A}^{2}\). It also depicts the chiral, purely helical N-heterocyclic carbene ligand, with its five orthofused rings and the NHC cycle bound to the Ir with a C2–Ir bond length of 2.051 Å, and C2–Ni \(2.102\) Å.\[15\] Furthermore, the C2 of the tolyl group is coordinated to the metal (C2–Ir: 2.102 Å) and is almost coplanar with the NHC cycle (dihedral angle: 3.92°). These metric data correspond to classical values for carbene cycloiridiated complexes.\[5c-e\] The \(^13\)C NMR spectra of \(\text{A}^{1,2}\) show the signal of the carbene carbon at 187.2 ppm (see the Supporting Information).\[9\]

(Time-dependent) DFT calculations\[16\] (see the Supporting Information) demonstrate extended π conjugation between the NHC unit and the other fused phenyl rings within the π-helical carbene ligand, along with efficient electronic interaction between the [5]helicene-NHC and the metal center. For example, the HOMO (H) and H–2 of \(\text{A}^{1,2}\), span over the Ir and the helicene-NHC-tolyl, while the LUMO (L) and L+2 correspond almost purely to the helicene-NHC π-helical system (Figure 2c and the Supporting Information). The strong interaction between the π-helical NHC and Ir\(^{III}\) was confirmed with ETS-NOCV charge and bonding-energy decomposition analysis (see the Supporting Information).\[10\] which revealed a dative NHC-metal bond with the NHC—Ir σ donation and Ir—NHC back-donation typical for carbene ligands\[10\] and with the π back-bonding clearly enhanced due to the extended π-helical system. These electronic features may account for the good stability and unprecedented photophysical and (chir)optical properties of \(\text{A}^{1,2}\) (see below).

Since the methyl group at the N1 position blocks helical inversion, enantiomerically enriched samples of \(\text{P(}\Delta\_\text{H})\text{A}^{1}\) and \(\text{P(}\Delta\_\text{H})\text{A}^{2}\) and of \(\text{M(}\Delta\_\text{H})\text{A}^{2}\) were prepared by HPLC separation over chiral stationary phases (ee 96–99%, see the Supporting Information).\[17\] Refluxing of stereoisomerically pure samples in chloroform for several hours did not lead to any epimerization, thus showing the high configurational stability of the [5]helicen carbene ligand (inversion barrier > 125 kJ mol\(^{-1}\)) and the Ir center. Electronic circular dichroism (ECD) spectra in CH\(_2\)Cl\(_2\) are depicted in Figure 2a. Each pair of enantiomers reveal mirror-image spectra. \((\text{P(}\Delta\_\text{H})\text{A}^{1}\) displays a set of two positive

![Figure 2](image_url)
ECD bands at 252 nm ($\Delta e = +38 \text{m}^{-1} \text{cm}^{-1}$) and 276 (+43), another set of two positive ECD bands at 312 (+73) and 340 (+88), and a weak negative band at 402 (−14). ($P_{A_0} - A_1^2$) shows bands at 257 nm ($\Delta e = +78 \text{m}^{-1} \text{cm}^{-1}$), 278 (−38), 302 (−44), 332 (40), and 403 (−13). Interestingly, ($P_{A_0} - A_1^2$) and ($P_{A_0} - A_2^2$) possess ECD bands at similar wavelengths but some with an opposite sign (e.g., at 275 and 305 nm). Furthermore, the positive intensity around 255/355 nm is visibly increased/decreased for ($P_{A_0} - A_2^2$) versus ($P_{A_0} - A_1^2$). All these features reflect the impact of the pseudo-octahedral iridium stereochemistry. Effects of both Ir and helicene-NHC chirality are further demonstrated by a comparison of the ECD spectra for $A_1^2$ and for the model NHC complex $A_3$.[5b] The sign patterns of the bands for $A_0 - A_1^2$ and ($P_{A_0} - A_1^2$) are mostly similar but $A_1$ reveals significantly decreased ECD intensity (not exceeding 30 m$^{-1}$ cm$^{-1}$), evidently due to the lack of the helicene (Figure 2a). Note also that the calculated ECD spectra for the parent $P_5$-helicene-NHC species are blue-shifted and less intense compared to ($P_{A_0} - A_1^2$), which confirms the reinforcing effect of the metal and helicene-NHC stereochemistry. See the Supporting Information for all simulated spectra and molecular orbital analysis. The experimental molar rotations (MRs) also reflect differences between the two epimers. ($P_{A_0} - A_1^2$) displays a strong positive MR at 436 nm (+16 520° cm$^{-2}$ dmol$^{-1}$) while ($P_{A_0} - A_2^2$) exhibits a negative MR (−2170), thus suggesting that the contribution of the $A_0$ center compensates and even surpasses that from the $P_5$-helicene-NHC.

The efficient interaction between the $\pi$-helical NHC and Ir$^{III}$ is also reflected in the emission properties of $A_1^2$ (see the Supporting Information). Both complexes display vibrationally structured light-green phosphorescence with the 0,0 band maximum at 525 nm, and quantum yields of ca. 9–13%. The $A_1^2$ emission is red-shifted compared to that of the NHC model A, which displays a blue-green phosphorescence with the 0,0 band maximum at 498 nm. Particularly striking are the phosphorescence lifetimes of around 300 ms typically recorded for tris-cyclometalated Ir$^{III}$ complexes, or the 3.1 ms observed for A. The measured lifetimes are amongst the longest reported for cycloiridiatid systems.[18, 19] As a result, the luminescence of these complexes is extremely sensitive to oxygen. Lifetimes decrease by a factor of greater than 500 upon aeration of the samples in solution at RT (Table S2 in the Supporting Information). The bimolecular rate constants for quenching by oxygen are of the order of $8.5 \times 10^9 \text{m}^{-1} \text{s}^{-1}$ (estimated from the lifetimes under these conditions), which is typical of diffusional quenching for molecular phosphors in solution. Efficient sensitization of singlet oxygen may be anticipated.[20] Time-dependent DFT (PBE0/SV(P), CH$_2$Cl$_2$ continuum solvent model, see the Supporting Information) calculations[21a] correctly reproduce changes in the phosphorescence energies for $A_1^2$ versus A and link the emission features of $A_1^2$ to the extended $\pi$ conjugation in the helical NHC ligand. For A, the phosphorescence transition is Ir$^{III}$-dppy metal–ligand charge transfer (MLCT).[22] In contrast, the T$_1$ excited states of $A_1^2$, which exhibit mixed Ir-NHC-tolyl-helicene,dppy-→NHC-helicene ML/inaltaligand/ligand-CT character, is strongly delocalized across the.