



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

Nora Hellou, Monika Srebro-Hooper, Ludovic Favereau, Francesco Zinna, Elsa Caytan, Loic Toupet, Vincent Dorcet, Marion Jean, Nicolas Vanthuyne, J. A. Gareth Williams, et al.

► To cite this version:

Nora Hellou, Monika Srebro-Hooper, Ludovic Favereau, Francesco Zinna, Elsa Caytan, et al.. Enantiopure Cycloiridiated Complexes Bearing a Pentahelicenic N-Heterocyclic Carbene and Displaying Long-Lived Circularly Polarized Phosphorescence. *Angewandte Chemie International Edition*, 2017, 56 (28), pp.8236-8239. 10.1002/anie.201704263 . hal-01539192

HAL Id: hal-01539192

<https://univ-rennes.hal.science/hal-01539192>

Submitted on 16 Apr 2018

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Nora Hellou, Monika Srebro-Hooper,* Ludovic Favereau, Francesco Zinna, Elsa Caytan, Loïc Toupet, Vincent Dorcet, Marion Jean, Nicolas Vanthuyne, J. A. Gareth Williams, Lorenzo Di Bari, Jochen Autschbach, and Jeanne Crassous*

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^[1] have attracted attention due to their applications as phosphors in organic light-emitting devices (OLEDs),^[2] as well as their biological activity.^[3] To date, several classes of enantiopure cycloiridiated systems have been reported.^[1b,4] As for Ir^{III} 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),^[5,6]

chiral NHC-based systems for molecular materials science are almost unknown. Furthermore, no chiral purely π -helical NHC has been reported to date.^[7,8] 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**^{1,2} (Figure 1). 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 ($\pm$)-**5**. First, the [5]helicene-thiadiazole **1**^[9a] was reduced to 1,2-diamino-[4]helicene **2** with LiAlH₄,^[9b] which was then directly cyclized to the precarbenic [5]helicene imidazole **3** by using triethyl orthoformate in the

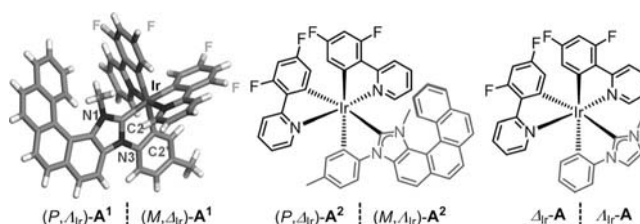
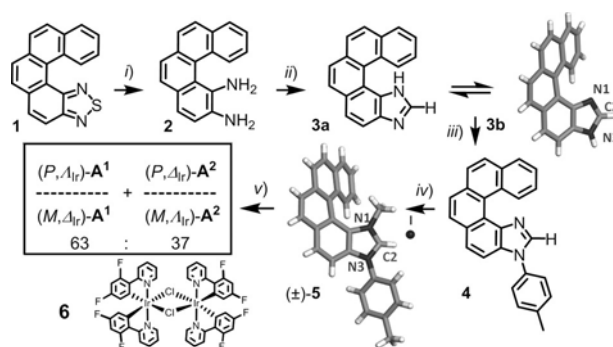


Figure 1. Meridional cycloiridiated complexes **A**^{1,2} bearing a P-[5]helicene-NHC chelating ligand and model NHC complex **A** lacking the helicene unit.^[5c] An X-ray structure of **A**¹ ((P,ΔIr) enantiomer) is shown.



Scheme 1. Preparation of [5]helicene-imidazolium salt ($\pm$)-**5** and of cycloiridiated complexes **A**^{1,2}. i) LiAlH₄, THF, Ar, RT, 5 h; ii) HC(OEt)₃, cat. I₂, CH₃CN, RT, 2 h, 52% (two steps); iii) *p*-tolyl-boronic acid, anhydrous Cu(OAc)₂, pyridine, CH₂Cl₂, air, molecular sieves, RT, 24 h, 69%; iv) CH₃I, CH₃CN, reflux, 18 h, 91%; v) **6**, Ag₂O (2 equiv), 1,2-dichloroethane, 90°C, 16 h, dark, 76%. X-ray structures of tautomer ($\pm$)-**3b** and of ($\pm$)-**5** (*P* enantiomers) are shown.

[*] Dr. N. Hellou, Dr. L. Favereau, Dr. E. Caytan, Dr. L. Toupet, Dr. V. Dorcet, Dr. J. Crassous
Institut des Sciences Chimiques de Rennes UMR 6226
Institut de Physique de Rennes, UMR 6251
CNRS Université de Rennes 1
Campus de Beaulieu, 35042 Rennes Cedex (France)
E-mail: jean.crassous@univ-rennes1.fr

Dr. M. Srebro-Hooper
Faculty of Chemistry, Jagiellonian University, 30-060 Krakow (Poland)
E-mail: srebro@chemia.uj.edu.pl

Dr. F. Zinna, Prof. L. Di Bari
Dipartimento di Chimica e Chimica Industriale, University of Pisa
via Moruzzi 13, 56124 Pisa (Italy)

M. Jean, Dr. N. Vanthuyne
Aix Marseille University, CNRS, Centrale Marseille, iSm2
Marseille (France)

Prof. J. A. G. Williams
Department of Chemistry, University of Durham
Durham, DH1 3LE (UK)

Prof. J. Autschbach
Department of Chemistry, University at Buffalo
State University of New York, Buffalo, NY 14260 (USA)

Dr. F. Zinna
Present address: Université de Genève
Département de Chimie Organique
Quai Ernest-Ansermet 30, 1211 Genève 4 (Switzerland)

presence of catalytic iodine in acetonitrile.^[9c] To our knowledge **3** is the first fully π -helicenic imidazole, since it displays five *ortho*-fused aromatic rings including the terminal imidazole cycle.

Two tautomeric forms^[10a] (**3a,b** in Scheme 1) are seen by ¹H 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 *Ia* centrosymmetric space group, with both *P* and *M* enantiomers (Scheme 1 and the Supporting Information). The imidazole ring reveals classical metric data (C2–N1 (C2–N3) bond length: 1.320 (1.345) Å),^[10b] 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-boronic acid furnished **4**, the methylation of which with CH₃I in excess gave the imidazolium salt ($\pm$)-**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 1*N* position of **5** blocks the inversion of the helix (see below).^[12] Species ($\pm$)-**5** crystallized in the *P2₁/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 imidazolium cycle (Scheme 1 and the Supporting Information). Species **5** can be regarded as a 1*N*-Me-[5]helicene derivative.^[13]

The heteroleptic cycloiridiated complexes **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 Ag₂O and [Ir(μ -Cl)(dfppy)₂]₂ **6** (Scheme 1).^[5,14] The diastereoisomeric mixture of **A**¹ and **A**² was obtained in a 63:37 ratio, as estimated from ¹H NMR spectroscopy and HPLC (see the Supporting Information), thus suggesting that the cyclometalation is diastereoselective. **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 ¹H-¹H NOESY and ¹H-¹⁹F HOESY NMR studies (see the Supporting Information). X-ray crystallography of the pure diastereoisomer **A**¹ (*I4₁/a* 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 Δ_{Ir} or Λ_{Ir} epimers associated with *M* or *P* helical stereochemistry, respectively [(*M*, Δ_{Ir})-**A**¹ and (*P*, Λ_{Ir})-**A**¹; the other diastereoisomers are (*P*, Δ_{Ir})-**A**² and (*M*, Λ_{Ir})-**A**²]. It also depicts the chiral, purely helical *N*-heterocyclic carbenic ligand, with its five *ortho*-fused rings and the NHC cycle bound to the Ir with a C2–Ir bond length of 2.051 Å, and C2–N1 (C2–N3) of 1.368 (1.366) 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 carbenic cycloiridiated complexes.^[5c–e] The ¹³C NMR spectra of **A**^{1,2}

show the signal of the carbenic carbon at 187.2 ppm (see the Supporting Information).^[5]

(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 carbenic ligand, along with efficient electronic interaction between the [5]helicene-NHC and the metal center. For example, the HOMO (H) and H−2 of **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),^[16b] which revealed a dative NHC–metal bond with the NHC→Ir σ donation and Ir→NHC back-donation typical for carbenic ligands,^[16c] and with the π back-bonding clearly enhanced due to the extended π -helicene system. These electronic features may account for the good stability and unprecedented photophysical and (chir)optical properties of **A**^{1,2} (see below).

Since the methyl group at the N1 position blocks helical inversion, enantiomerically enriched samples of (*M*, Δ_{Ir})-**A**¹ and (*P*, Λ_{Ir})-**A**¹ and of (*M*, Λ_{Ir})-**A**² and (*P*, Δ_{Ir})-**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]helicenic carbene ligand (inversion barrier > 125 kJ mol^{−1}) and the Ir center. Electronic circular dichroism (ECD) spectra in CH₂Cl₂ are depicted in Figure 2a. Each pair of enantiomers reveal mirror-image spectra. (*P*, Λ_{Ir})-**A**¹ displays a set of two positive

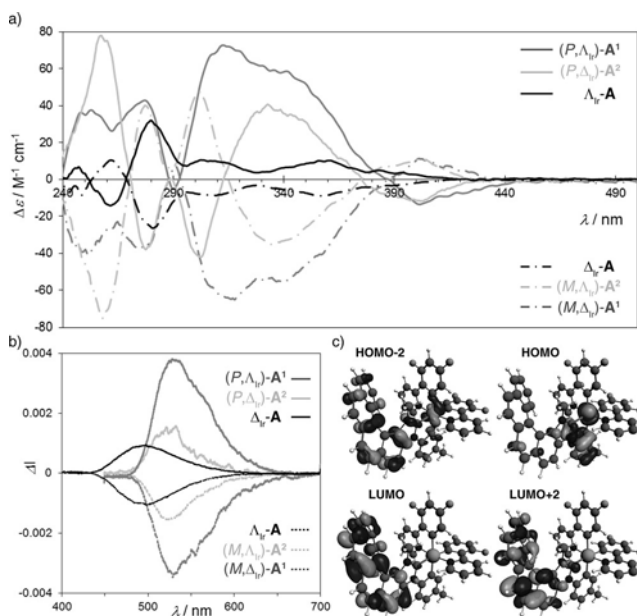


Figure 2. a) ECD spectra of (*P*, Δ_{Ir})-**A**¹ and (*P*, Δ_{Ir})-**A**², their mirror-images (*M*, Δ_{Ir})-**A**¹ and (*M*, Δ_{Ir})-**A**², and Δ_{Ir} -**A**/ Δ_{Ir} -**A**. b) CPL spectra of (*M*, Δ_{Ir})-**A**¹/*(P*, Λ_{Ir})-**A**¹, (*M*, Λ_{Ir})-**A**²/*(P*, Δ_{Ir})-**A**², and Δ_{Ir} -**A**/ Δ_{Ir} -**A** at RT. Each spectrum is normalized to the maximum of its photoluminescence spectrum. c) Isosurfaces (0.04 au) of selected MOs of (*P*, Δ_{Ir})-**A**¹.

ECD bands at 252 nm ($\Delta\epsilon = +38\text{ M}^{-1}\text{ cm}^{-1}$) and 276 (+43), another set of two positive ECD bands at 312 (+73) and 340 (+58), and a weak negative band at 402 (−14). (P,Δ_{Ir})-**A**² shows bands at 257 nm ($\Delta\epsilon = +78\text{ M}^{-1}\text{ cm}^{-1}$), 278 (−38), 302 (−44), 332 (40), and 403 (−13). Interestingly, (P,Δ_{Ir})-**A**¹ and (P,Δ_{Ir})-**A**² possess ECD bands at similar wavelengths but some with an opposite sign (e.g., at ca. 275 and 305 nm). Furthermore, the positive intensity around 255/335 nm is visibly increased/decreased for (P,Δ_{Ir})-**A**² versus (P,Δ_{Ir})-**A**¹. 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**.^[5c] The sign patterns of the bands for $\Delta_{\text{Ir}}\text{-A}$ and (P,Δ_{Ir})-**A**¹ are mostly similar but **A** reveals significantly decreased ECD intensity (not exceeding $30\text{ M}^{-1}\text{ cm}^{-1}$), 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,Δ_{Ir})-**A**¹, 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,Δ_{Ir})-**A**¹ displays a strong positive MR at 436 nm ($+16520^\circ\text{ cm}^2\text{ dmol}^{-1}$) while (P,Δ_{Ir})-**A**² exhibits a negative MR (−2170), thus suggesting that the contribution of the Δ_{Ir} center compensates and even surpasses that from the *P*-[5]helicene-NHC.

The efficient interaction between the π -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 at 498 nm. Particularly striking are the phosphorescence lifetimes of around 300 μs observed for **A**^{1,2}, which are much longer than the values of 1 μs typically recorded for tris-cyclometalated Ir^{III} complexes, or the 3.1 μs observed for **A**. The measured lifetimes are amongst the longest reported for cycloirradiated 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 $8.5 \times 10^8\text{ M}^{-1}\text{ s}^{-1}$ (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_2Cl_2 continuum solvent model, see the Supporting Information) calculations^[16a] 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 π conjugation in the helical NHC ligand. For **A**, the phosphorescence transition is Ir $\rightarrow$ dfppy metal–ligand charge transfer (MLCT).^[5c] In contrast, the T₁ excited states of **A**^{1,2}, which exhibit mixed Ir-NHC-tolyl-helicene,dfppy $\rightarrow$ NHC-helicene ML/intraligand/ligand–ligand CT character, is strongly delocalized across the

[5]helicene-NHC, which lowers its energy. Lesser Ir orbital participation (lesser MLCT character) in the T₁ emission for **A**^{1,2} versus **A** is consistent with an increase in the emission lifetime for the former and indicates that the spin-orbit coupling at the metal ion in **A**^{1,2} is attenuated, yet still sufficient to promote the formally spin-forbidden T₁ $\rightarrow$ S₀ process to the extent that it can compete with non-radiative decay.^[18] The result is interesting to compare with platina-helicenes, which reveal relatively long-lived phosphorescence in an even more red-shifted region (620 nm) but with shorter lifetimes (20 μs).^[21a,b]

Circularly polarized luminescence (CPL) spectra of all enantiopure stereoisomers of **A** and **A**^{1,2} were measured in deoxygenated CH_2Cl_2 samples ($C \approx 10^{-5}\text{ M}$) and are depicted in Figure 2b.^[21c–h] Each pair of enantiomers display mirror-image CP phosphorescence with dissymmetry factors^[22] g_{lum} of $+9 \times 10^{-4}$ at 493 nm for (Δ_{Ir})-**A**, and $+3.7 \times 10^{-3}$ and $+1.5 \times 10^{-3}$ at 530 nm for (P,Δ_{Ir})-**A**¹ and (P,Δ_{Ir})-**A**², respectively, thus revealing that the stereochemistry of the π -helical NHC ligand controls the sign of the CPL signal with a value 3 times higher for epimer (P,Δ_{Ir})-**A**¹ versus (P,Δ_{Ir})-**A**². Here again, manipulating the Ir^{III} stereochemistry enables the CPL to be modified.

In summary, this new diversification in organometallic helicene chemistry provides molecules with unprecedented features and opens a new field, namely NHCs in helicenes. The Ir–NHC-helicene complexes display very long-lived CP blue-green phosphorescence, which may lead to future applications as chiral dopants in CP-OLEDs,^[23a] singlet-oxygen sensitizers, or selective photooxidizing agents.^[4j,20,23b]

Acknowledgements

This work was supported by the ANR (12-BS07-0004-METALHEL-01) and the Chirafun CNRS network. Thibault Reynaldo is thanked for technical support and Dr. Marc Mauduit and Dr. Gilles Muller for fruitful discussions. M.S.-H. acknowledges the young researchers' T-subsidy from the Ministry of Science and Higher Education in Poland. JA acknowledges NSF Grant CHE-1560881 and the Center for Computational Research in Buffalo.

-
- [1] a) H. Amouri, M. Gruselle, *Chirality in Transition Metal Chemistry: Molecules, Supramolecular Assemblies and Materials*, Wiley-VCH, Weinheim, **2009**; b) M. Helms, Z. Lin, L. Gong, K. Harms, E. Meggers, *Eur. J. Inorg. Chem.* **2013**, 4164 and references therein.

- [2] a) *Highly Efficient OLEDs with Phosphorescent Materials* (Ed.: H. Yersin), Wiley-VCH, Weinheim, **2008**; b) C. Ulbricht, B. Beyer, C. Friebe, A. Winter, U. S. Schubert, *Adv. Mater.* **2009**, *21*, 4418.
- [3] a) J. M. Hearn, I. Romero-Canelon, B. Qamar, Z. Liu, I. Hands-Portman, P. J. Sadler, *ACS Chem. Biol.* **2013**, *8*, 1335; b) L. Lu, L.-J. Liu, W.-C. Chao, H.-J. Zhong, M. Wang, X.-P. Chen, J.-J. Lu, R.-N. Li, D.-L. Ma, C.-H. Leung, *Sci. Rep.* **2015**, *5*, 14544.
- [4] a) C. Schaffner-Hamann, A. von Zelewsky, A. Barbieri, F. Barigelletti, G. Muller, J. P. Riehl, A. Neels, *J. Am. Chem. Soc.* **2004**, *126*, 9339; b) F. J. Coughlin, M. S. Westrol, K. D. Oyler, N. Byrne, C. Kraml, E. Zysman-Colman, M. S. Lowry, S. Bernhard, *Inorg. Chem.* **2008**, *47*, 2039; c) L. Yang, A. von Zelewsky, H. P. Nguyen, G. Muller, G. Labat, H. Stoeckli-Evans, *Inorg. Chim. Acta* **2009**, *362*, 3853; d) C.-H. Leung, H.-J. Zhong, H. Yang, Z. Cheng, D. S. H. Chan, V. P.-Y. Ma, R. Abagyan, C.-Y. Wong, D. L. Ma, *Angew. Chem. Int. Ed.* **2012**, *51*, 9010; *Angew. Chem.* **2012**, *124*, 9144; e) E. Marchi, R. Sinisi, G. Bergamini, M. Tragni, M. Monari, M. Bandini, P. Ceroni, *Chem. Eur. J.* **2012**, *18*, 8765; f) T.-Y. Li, Y.-M. Jing, X. Liu, Y. Zhao, L. Shi, Z. Tang, Y.-X. Zheng, J. L. Zuo, *Sci. Rep.* **2015**, *5*, 14912; g) C. Citti, U. M. Battisti, G. Ciccarella, V. Maiorano, G. Gigli, S. Abbate, G. Mazzeo, E. Castiglioni, G. Longhi, G. Cannazza, *J. Chromatogr. A* **2016**, *1467*, 335; h) G. Mazzeo, M. Fusè, G. Longhi, I. Rimoldi, E. Cesarotti, A. Crispini, S. Abbate, *Dalton Trans.* **2016**, *45*, 992; i) T.-Y. Li, Y.-X. Zheng, Y.-H. Zhou, *Dalton Trans.* **2016**, *45*, 19234; j) L. Zhang, E. Meggers, *Acc. Chem. Res.* **2017**, *50*, 320.
- [5] a) T. Sajoto, P. I. Djurovich, A. Tamayo, M. Yousufuddin, R. Bau, M. E. Thompson, R. J. Holmes, S. R. Forrest, *Inorg. Chem.* **2005**, *44*, 7992; b) C.-F. Chang, Y.-M. Cheng, Y. Chi, Y.-C. Chiu, C.-C. Lin, G.-H. Lee, P.-T. Chou, C.-C. Chen, C.-H. Chang, C.-C. Wu, *Angew. Chem. Int. Ed.* **2008**, *47*, 4542; *Angew. Chem.* **2008**, *120*, 4618; c) T.-Y. Li, X. Liang, L. Zhou, C. Wu, S. Zhang, X. Liu, G.-Z. Lu, L.-S. Xue, Y.-X. Zheng, J.-L. Zu, *Inorg. Chem.* **2015**, *54*, 161; d) J. Lee, H.-F. Chen, T. Batagoda, C. Coburn, P. I. Djurovich, M. E. Thompson, S. R. Forrest, *Nat. Mater.* **2016**, *15*, 92; e) P.-H. Lanoë, J. Chan, G. Gontard, F. Monti, N. Armaroli, A. Barbieri, H. Amouri, *Eur. J. Inorg. Chem.* **2016**, 1631.
- [6] Reviews on applications of NHC metal complexes: a) M. Merics, M. Albrecht, *Chem. Soc. Rev.* **2010**, *39*, 1903; b) R. Visbal, M. C. Gimeno, *Chem. Soc. Rev.* **2014**, *43*, 3551; c) I. Omae, *Coord. Chem. Rev.* **2016**, *310*, 154.
- [7] Reviews on chiral NHCs: a) V. César, S. Bellemin-Laponnaz, L. H. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619; b) F. Wang, L.-J. Liu, W. Wang, S. Li, M. Shi, *Coord. Chem. Rev.* **2012**, *256*, 804.
- [8] Pseudo-helicenic Ir/Rh complexes: W. A. Herrmann, D. Baskakov, E. Herdtweck, S. D. Hoffmann, T. Bunlaksanansorn, F. Rampf, L. Rodefeld, *Organometallics* **2006**, *25*, 2449.
- [9] a) T. Biet, K. Martin, J. Hankache, N. Hellou, A. Hauser, T. Bürgi, N. Vanthuyne, T. Aharon, M. Caricato, J. Crassous, N. Avarvari, *Chem. Eur. J.* **2017**, *23*, 437; b) A. J. McConnell, M. H. Lim, E. D. Olmon, H. Song, E. E. Dervan, J. K. Barton, *Inorg. Chem.* **2012**, *51*, 12511; c) Z.-H. Zhang, J.-J. Li, Y.-Z. Gao, Y.-H. Liu, *J. Heterocycl. Chem.* **2007**, *44*, 1509.
- [10] a) C. I. Nieto, P. Cabildo, M. Á. García, R. M. Claramunt, I. Alkorta, J. Elguero, *Beilstein J. Org. Chem.* **2014**, *10*, 1620; b) A. Escande, J. L. Galigné, *Acta Crystallogr. Sect. B* **1974**, *30*, 1647.
- [11] J. X. Qiao, P. Y. S. Lam in *Boronic Acids: Preparation and Applications in Organic Synthesis Medicine and Materials*, 2nd ed. (Ed.: D. G. Hall), Wiley-VCH, Weinheim, **2011**, pp. 315–361.
- [12] Attempts to enantiomerically resolve **5** failed. Indeed, semi-preparative and analytical separations of helical salts are very rare. a) D. Koval, L. Severa, L. Adriaenssens, J. Vavra, F. Teply, V. Kasicka, *Electrophoresis* **2011**, *32*, 2683; b) G. M. Labrador, J. Bosson, Z. S. Breitbach, Y. Lim, E. R. Francotte, R. Sabia, C. Villani, D. W. Armstrong, J. Lacour, *Chirality* **2016**, *28*, 282.
- [13] K. Yamamoto, M. Okazumi, H. Suemune, K. Usui, *Org. Lett.* **2013**, *15*, 1806.
- [14] A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau, M. E. Thompson, *J. Am. Chem. Soc.* **2003**, *125*, 7377.
- [15] We recently reported the first cycloiridiated complex bearing a [6]helicene-CH₂-NHC ligand: N. Hellou, C. Jahier-Diallo, O. Baslé, M. Srebro-Hooper, L. Toupet, T. Roisnel, E. Caytan, C. Roussel, N. Vanthuyne, J. Autschbach, M. Mauduit, J. Crassous, *Chem. Commun.* **2016**, *52*, 9243; See also: I. G. Sánchez, M. Šámal, J. Nejedlý, M. Karras, J. Klívar, J. Rybáček, M. Buděšínský, L. Bednárová, B. Seidlerová, I. G. Stará, I. Starý, *Chem. Commun.* **2017**, *53*, 4370.
- [16] a) “Calculating electronic optical activity of coordination compounds”: J. Autschbach in *Comprehensive Inorganic Chemistry II*, Vol. 9 (Eds: K. Poeppelmeier, J. Reedijk), Elsevier, Oxford, **2013**, pp. 407–426; b) M. P. Mitoraj, A. Michalak, T. Ziegler, *J. Chem. Theory Comput.* **2009**, *5*, 962; c) M. Srebro, A. Michalak, *Inorg. Chem.* **2009**, *48*, 5361.
- [17] The diastereomeric mixture of **A**¹ and **A**² was eluted with hexane/2-PrOH/chloroform (7:1:2 v/v/v) on Chiralpak IA to obtain (*M*, Δ _{ir})-**A**¹, (*M*, Δ _{ir})-**A**² and the mixture of (*P*, Δ _{ir})-**A**¹ and (*P*, Δ _{ir})-**A**², which was subsequently separated on (*S,S*)-Whelk-O1 column. See the Supporting Information for details.
- [18] Some Ir complexes with π -extended chromophores and long-lived triplet states are suitable as triplet–triplet annihilation, but not as luminophores. See: J. F. Sun, F. F. Zhong, X. Y. Yi, J. Z. Zhao, *Inorg. Chem.* **2013**, *52*, 6299.
- [19] Non-cyclometalated, N₆-coordinated Ir^{III} complexes may display lifetimes of comparable magnitude, where the metal orbitals lie too low in energy to mix effectively with ligand-centred excited states. See: W. Leslie, A. S. Batsanov, J. A. K. Howard, J. A. G. Williams, *Dalton Trans.* **2004**, 623.
- [20] R. Gao, D. G. Ho, B. Hernandez, M. Selke, D. Murphy, P. I. Djurovich, M. E. Thompson, *J. Am. Chem. Soc.* **2002**, *124*, 14828.
- [21] a) L. Norel, M. Rudolph, N. Vanthuyne, J. A. G. Williams, C. Lescop, C. Roussel, J. Autschbach, J. Crassous, R. Réau, *Angew. Chem. Int. Ed.* **2010**, *49*, 99; *Angew. Chem.* **2010**, *122*, 103; b) C. Shen, E. Anger, M. Srebro, N. Vanthuyne, K. K. Deol, T. D. Jefferson, Jr., G. Muller, J. A. G. Williams, L. Toupet, C. Roussel, J. Autschbach, R. Réau, J. Crassous, *Chem. Sci.* **2014**, *5*, 1915; Selected other examples of CPL-active helicenes: c) J. E. Field, G. Muller, J. P. Riehl, D. Venkataraman, *J. Am. Chem. Soc.* **2003**, *125*, 11808; d) K. E. S. Phillips, T. J. Katz, S. Jockusch, A. J. Lovinger, N. J. Turro, *J. Am. Chem. Soc.* **2001**, *123*, 11899; e) K. Nakamura, S. Furumi, M. Takeuchi, T. Shibuya, K. Tanaka, *J. Am. Chem. Soc.* **2014**, *136*, 5555; f) N. Saleh, M. Srebro, T. Reynaldo, N. Vanthuyne, L. Toupet, V. Y. Chang, G. Muller, J. A. G. Williams, C. Roussel, J. Autschbach, J. Crassous, *Chem. Commun.* **2015**, *51*, 3754; g) I. H. Delgado, S. Pascal, A. Wallabregue, R. Duwald, C. Besnard, L. Guénée, C. Nançoz, E. Vauthey, R. C. Tovar, J. L. Lunkley, G. Muller, J. Lacour, *Chem. Sci.* **2016**, *7*, 4685; h) T. Katayama, S. Nakatsuka, H. Hirai, N. Yasuda, J. Kumar, T. Kawai, T. Hatakeyama, *J. Am. Chem. Soc.* **2016**, *138*, 5210.
- [22] a) F. Zinna, L. Di Bari, *Chirality* **2015**, *27*, 1; b) E. M. Sánchez-Carnerero, A. R. Agarrabeitia, F. Moreno, B. L. Maroto, G. Muller, M. J. Ortiz, S. de la Moya, *Chem. Eur. J.* **2015**, *21*, 13488.
- [23] a) J. R. Brandt, X. Wang, Y. Yang, A. J. Campbell, M. J. Fuchter, *J. Am. Chem. Soc.* **2016**, *138*, 9743; b) S. C. J. Meskers, H. P. J. M. Dekkers, *Spectrochim. Acta Part A* **1999**, *55*, 1857.