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Synthesis and chiroptical properties of organometallic complexes of helicenic *N*-heterocyclic carbenes

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Abstract: Novel [4] and [6]helicenes (**4a**,**b**) bearing a fused imidazolium unit have been prepared from [4] and [6]helicene-2,3-di-*n*-propyl-amines **3a**,**b**. The *in situ* formation of NHC (NHC = N-heterocyclic carbene) derivatives followed by their complexation to iridium(I) or rhodium(I) gave access to complexes **1a**, **1'a** and **1b**, containing mono-coordinated helicene-NHC, chloro and COD (COD = 1,5-cyclooctadiene) ligands. Ir and Rh complexes **1a** and **1'a** were characterized by X-ray crystallography. HPLC and NMR analyses showed that Ir(I) complex **1b** existed as a mixture of two diastereomeric complexes corresponding to enantiomeric pairs *M*-(-)/*P*-(+)-**1b**^{1} and *M*-(-)/*P*-(+)-**1b**^{2} which differ by the position of COD through space. The chiroptical properties (electronic circular dichroism and optical rotation) of the four stereoisomers were measured. These complexes were also tested as catalysts in a transfer hydrogenation reaction.

Keywords: helicenes, *N*-heterocyclic carbenes, iridum, chiroptical properties, transfer hydrogenation

Introduction

The helical topology of helicenes combined with their extended π-conjugation give appealing large-magnitude chiroptical properties such as high optical rotation (OR) values and intense electronic circular dichroism (ECD) spectra.[1] Since several years, our group has been investigating the preparation of chiral organometallic complexes bearing helicenic ligands.[2,3] These compounds display attractivity for many applications, such as in optoelectronic devices,[4,5] chiroptical switches,[6] and asymmetric catalysis.[7,8] The interest of these helicenic organometallic derivatives originates from the association of the inherent properties of the helicene with those of the transition metals (controlled coordination geometry, redox activity, strong spin-orbit coupling, strong emission and absorption, reactivity), giving access to original chiral multifunctional molecules. During the last two decades, organometallic complexes based on *N*-heterocyclic carbenes (NHCs) have experienced a boom due to their important applications in catalysis,[9-11] in medicinal chemistry[12,13] and in molecular materials.[14,15] For these reasons, we have been recently investigating the development of molecular architectures associating helicenes, NHCs and organometallic chemistry, in order to develop a new family of chiral complexes, namely organometallic NHC-helicene complexes (see **A**-**C** in Figure 1).[16-18] This strategy enabled us to create novel chiral molecular materials with unprecedented photophysical properties and potential applications in enantioselective organometallic catalysis.[19,20] In this article, we present novel [4] and [6]helicenic imidazolium salts (**4a**,**b**), and their corresponding helicenic NHC ligands mono-coordinated to iridium(I) (**1a**,**b**) and rhodium(I) (**1'a**) complexes. We describe their synthesis and (chir)optical properties. The catalytic activity of **1b** in the transfer hydrogenation reaction[21] was also examined.

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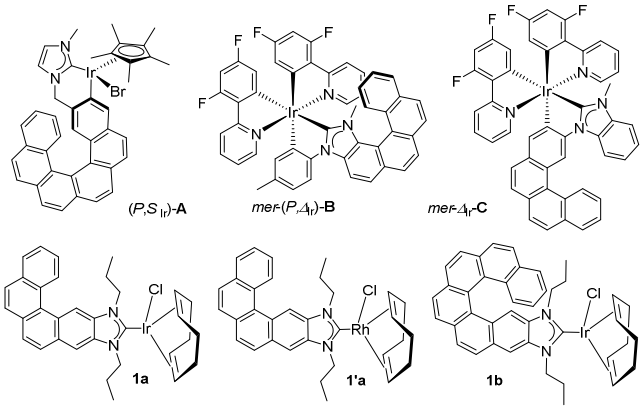
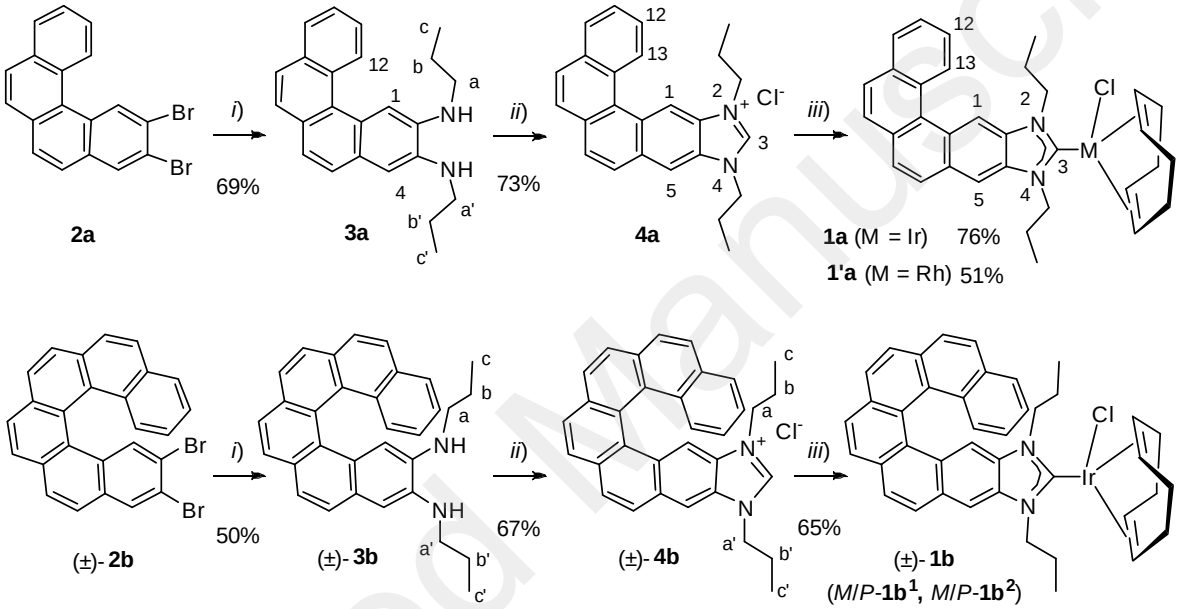


FIGURE 1. Chemical structures of formerly reported iridium complexes coordinated to NHCs bearing a [6]helicene (**A**),[15] [5]helicene (**B**)[16] and [4]helicene (**C**)[17] unit, respectively. Chemical structures of the novel iridium complexes **1a**,**b** and rhodium complex **1'a** reported herein.

Materials and Methods

General. THF was freshly distilled under argon from sodium / benzophenone. Heptane refers to a mixture of isomers. All commercially available chemicals were used without further purification. Column chromatography purifications were performed over silica gel (Acros, 0.063–0.200 mm). NMR spectra were recorded at room temperature on a Bruker AV III 400 MHz equipped with a tunable BBFO probe, and a Bruker Avance I 500 MHz fitted with a TCI cryoprobe (Biosit platform, Université de Rennes 1). ^{1}H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to Me_4Si as external standard. Assignment of proton and carbon signals is based on standard and band-selective HSQC and HMBC, COSY and NOESY (500ms mixing time). Mass spectrometry was performed by the CRMPO, University of Rennes 1, by ESI or by MALDI-TOF. Melting points were measured on a melting point apparatus Stuart SMP10. Specific rotations (in deg cm^3 g^{-1}) were measured in a 1 dm thermostated quartz cell on a Perkin Elmer-341 polarimeter. Circular dichroism (in M^{-1} cm^{-1}) was measured on a Jasco J-815 Circular Dichroism Spectrometer IFR140 facility (Biosit platform, Université de Rennes 1). UV/vis spectroscopy was conducted on a Varian Cary 5000 spectrometer. Chiral high-performance liquid chromatography (HPLC) was performed by iSm2, Aix Marseille University, on an Agilent Technologies 1260 Infinity with Igloo-Cil ovens, using CD-2095 as circular dichroism detector. The conditions for HPLC separations are described in the SI part. The starting precursors **2a**,**b** were prepared according to literature procedures.[20] Complexes **1a**,**b** and **1'a** were prepared according to Scheme 1. Single crystals were grown by slow evaporation of *n*-pentane into a dichloromethane solution of the compounds.



SCHEME 1. Synthesis of iridium(I) complexes 1a,b and of rhodium(I) complex 1'a. *i*) *n*-propylamine, Pd_2dba_3/*rac*-BINAP, *t*-BuONa, toluene, 135 °C, 48 hrs; *ii*) HCl, $(EtO)_3CH$; *iii*) $[M(COD)Cl]_2$ (M = Ir, Rh), *t*-BuOK, THF, rt, 13 hrs.

***N,N'*-dipropyl[4]helicene-2,3-diamine 3a**. In a Schlenk tube under argon, were placed Pd_2dba_3 (57 mg, 0.02 mmol, 16 mol%) and *rac*-BINAP (68 mg, 0.03 mmol, 28 mol%) in dry toluene (5 mL). The solution was degassed for 10 min then heated at 135 °C for 15 min. After cooling down to room temperature. *t*-BuONa (76 mg, 0.78 mmol, 6 eq.), *n*-propylamine (0.13 mL, 1.62 mmol, 12.5 eq.) and 2.3-dibromo[4]helicene **2a** (150 mg, 0.13 mmol, 1 eq.) in toluene (5 mL) were added. After stirring and heating at 135°C for 48 hours, the reaction mixture was cool down to room temperature poured into dichloromethane and filtered over Celite®. The solvent was stripped off and the obtained brown oil was purified by chromatography over silica gel (heptane : ethyl acetate 98:2, as the eluent) yielding **3a** as a white solid (119 mg, 69%). Mp = 94-96°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14 (td, J_1 = 0.8 Hz, J_2 = 7.2 Hz, 6H, $H_{c,c'}$); 1.87 (sept, J = 7.2 Hz, 4H, $H_{b,b'}$); 3.3 (br s, 4H, $H_{a,a'}$); 4.12 (ls, 2H, NH); 7.15 (s, 1H, H_4); 7.58-7.68 (m, 3H); 7.75 (d, J = 8.4 Hz, 1H). 7.79 (s, 2H); 8.00 (dd, J_1 =1.2 Hz, J_2 = 8 Hz,1H); 8.38 (s, 1H, H_1); 9.24 (d, J = 8.4 Hz, 1H, H_{12}). ^{13}C NMR (101 MHz, $CDCl_3$): δ 11.9 (CH_3); 11.95 (CH_3); 22.65 (2 $CH_{2'}$); 46.6 (2 CH_2); 108.15 (C); 109.5 (C); 125.25 (2 CH); 125.4 (2 CH); 125.6 (2 CH); 127.3 (2 CH); 128.45 (2 CH); 129.7 (2 C); 130.5 (C); 133.4 (2C); 137.3 (C). HRMS (MALDI-TOF) $[M+H]^+$($C_{24}H_{27}N_2$): calcd. 343.2174; found 343.2177.

(±)-*N,N'*-dipropyl[6]helicene-2,3-diamine 3b. Racemic compound **3b** was prepared according to the same Buchwald-Harthwig conditions as for **3a**, and was obtained as a yellow solid, with a 50% yield. This aromatic diamine showed low stability and was thus used directly to the next step. ^{1}H NMR (400 MHz, $CDCl_3$): δ0.83 (t, J = 7.6 Hz, 3H, H_c); 1.06 (t, J = 7.6 Hz, 3H, $H_{c'}$); 1.29-1.32 (m, 2H, 2H_b); 1.70 (sex, J = 7.2 Hz, 2H, 2$H_{b'}$); 1.87-1.94 (m, 1H, H_a); 2.09-2.15 (m, 1H, H_a); 2.97-3.23 (m, 4H, NH and $H_{a'}$); 6.76-6.82 (m, 2H); 6.94 (s, 1H); 7.24 (d, J =

8Hz, 1H); 7.76-7.85 (m, 4H); 7.87-7.90 (m, 2H), 7.94-8.012 (m, 4H). HRMS (MALDI-TOF) $[M+H]^+$($C_{32}H_{31}N_2$): calcd. 443.2482; found 443.2478.

Imidazolium chloride 4a. In a round-bottom flask, were placed *N*,*N'*-dipropylbenzo[*c*]phenanhtrene-2.3-diamine **3a** (50 mg, 0.14 mmol, 1 eq.) and triethyl orthoformate $(EtO)_3CH$ (2 mL). Then an aqueous solution of HCl 12N (28 µL, 0.34 mmol, 2.4 eq.) was added dropwise. The resulting suspension was stirred under argon at room temperature for 30 min then heated under air atmosphere at 80 °C for 12 hours. After cooling down to room temperature, the obtained precipitate was washed with diethyl ether to give **4a** as a pale yellow solid (40 mg. 73%). Mp **=** 180-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.12 (br s, 6H, $H_{c,c'}$); 2.23 (br s, 4H, $H_{b,b'}$); 4.75 (br s, 4H, $H_{a,a'}$); 7.67-7.74 (m, 2H); 7.85-7.92 (m, 2H); 7.99-8.10 (m, 3H); 8.30 (s, 1H); 8.93 (d, *J* = 7.2 Hz, 1H, H_{13}); 9.27 (s, 1H, H_1); 11.84 (s, 1H, H_3). ^{13}C NMR (101 MHz, $CDCl_3$): δ11.1 (CH_3); 11.2 (CH_3); 22.8 (CH_2); 22.9 (CH_2); 49.1 (CH_2); 49.3 (CH_2); 111.05 (CH); 111.2 (CH); 126.3 (CH); 126.5 (CH); 126.6 (CH); 127.05 (CH); 127.2 (CH); 128.6 (CH); 128.8 (C); 128.9 (CH); 129.2 (CH); 129.65 (C); 129.8 (C); 130.3 (C); 131.1 (C); 132.1 (C); 133.7 (2C); 146.4 (C_3). HRMS (ESI) $[M^+]$ ($C_{25}H_{25}N_2^+$): calcd. 353.2012; found 353.2011(1).

Imidazolium chloride 4b. Compound **4b** was prepared from **3b**, according to the same procedure as for **4a**. The final salt was washed with ethyl acetate to give **4b** as a pale yellow solid (26 mg, 67%). Mp = 200 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.75 (t, *J* = 7.6 Hz, 3H, H_c); 1.02 (t, *J* = 7.2 Hz, 3H, $H_{c'}$), 1.26-1.29 (m, 1H, H_b); 1.37-1.41 (m, 1H, H_b); 2.08-2.17 (m, 2H, $H_{b'}$); 3.70-3.84 (m, 2H, H_a); 4.54-4.66 (m, 2H, $H_{a'}$); 6.53 (t, *J* = 7.6 Hz, 1H); 7.13 (t, *J* = 7.2 Hz, 1H); 7.41 (d, *J* = 8.4 Hz, 1H); 7.77 (d, *J* = 8 Hz, 1H); 7,87 (s, 1H); 7.91 (d, *J* = 8.4 Hz, 1H); 7.97-8.08 (m, 6H); 8.11 (d, *J* = 8 Hz, 2H); 11.71 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ10.8 (CH_3); 11.0 (CH_3); 22.0 (CH_2); 22.6 (CH_2); 48.4 (CH_2); 48.95 (CH_2); 110.05 (CH); 111.25 (CH); 123.6 (C); 125.0 (CH); 126.3 (CH); 126.8 (C); 126.9 (CH); 127.2 (C); 127.3 (CH); 127.3 (CH); 127.4 (2CH); 127.7 (CH); 127.9 (CH); 127.9 (CH); 128.5 (2CH); 128.5 (C); 128.9 (C); 129.1 (C); 129.2 (C); 130.6 (C); 131.4 (C); 131.9 (C); 131.9 (C); 133.6 (C); 145.9 (C_3). HRMS (MALDI-TOF) $[M^+]$ ($C_{33}H_{29}N_2^+$): calc. 353.2325; found 353.2320.

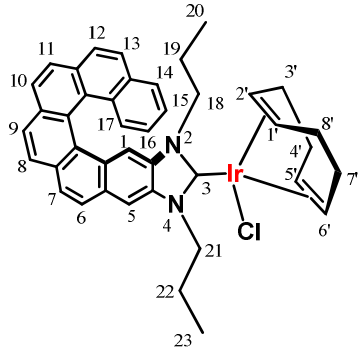
Iridium complex of [4]helicene-NHC 1a. In a Schlenk tube under argon, were placed successively $[Ir(COD)Cl]_2$ (48.4 mg, 0.07 mmol, 0.6 eq.), *t*-BuOK (13.5 mg, 0.12 mmol, 1 eq.) and dry THF (5 mL). After stirring for 10 min at room temperature, imidazolium salt **4a** (50 mg) was added and the solution was stirred at room temperature for 13 hours. The solvent was stripped off and the crude mixture was purified by flash chromatography over silica gel (diethyl ether as the eluent) to give complex **1a** (63 mg, 76%) as a yellow solid. Mp **=** 252-254 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20-1.25 (m, 6H, $H_{c,c'}$); 1.73-1.80 (m, 2H, COD); 1.86-1.95 (m, 2H, COD); 2.04-2.17 (m, 2H, $2H_b$); 2.28-2.39 (m, 6H, 4H from COD and $2H_{b,b'}$); 3.08 (s, 2H, COD); 4.73-4.93 (m, 6H, 2H from COD and $4H_{a,a'}$); 7.65-7.74 (m, 2H); 7,79 (d, *J* = 8.4 Hz, 1H); 7.84-7.86 (m, 2H); 7.92-7.96 (m, 2H); 8.07 (dd, J_1 =1.6 Hz, J_2 = 8 Hz,1H); 8.98 (s, 1H, H_1); 9.08 (d, *J* = 8.4 Hz, 1H, H_{13}). ^{13}C NMR (101 MHz, $CDCl_3$): δ11.9 (CH_3); 11.95 (CH_3); 23.0 (CH_2), 23.2 (CH_2), 29.4 (CH_2); 29.5 (CH_2); 33.6 (CH_2); 33.7 (CH_2); 50.3 (CH_2); 50.4 (CH_2); 52.7 (CH); 52.7 (CH); 87.2 (CH); 87.3 (CH); 107.0 (CH); 107.7 (CH); 125.9 (C); 126.0 (CH); 126.25 (CH); 126.3 (CH); 126.85 (2CH); 127.2 (C); 127.3 (CH); 127.4 (CH); 128.8 (CH); 129.6 (C); 130.2 (C); 130.45 (C); 133.5 (C); 134.0 (C); 134.70 (C); 197.0 (C_3). HRMS (ESI MS) $[M+Na]^+$ ($C_{33}H_{36}N_2{}^{35}ClNa^{193}Ir$): calcd. 711.2089; found 711.2079.

Rhodium complex of [4]helicene-NHC 1'a. In a Schlenk tube under argon, were placed successively $[Rh(COD)Cl]_2$ (38.9 mg, 0.08 mmol, 0.6 eq.), *t*-BuOK (14.75 mg, 0.13 mmol, 1eq.) and dry THF(5 mL). After stirring for 10 min at room temperature, imidazolium salt **3a** (51 mg) was added, and the solution was stirred at room temperature for 13 hours. The solvent was stripped off and the crude mixture was purified by flash chromatography over silica gel (diethyl ether as the eluent) to give complex **1'a** (40 mg, 51%) as a yellow solid. Mp **=** 240-243 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ1.25-1.30 (m, 6H, $H_{c,c'}$); 2.07-2.19 (m, 6H, 2H from COD and $2H_b$); 2.37-2.57 (m, 6H, 2H from COD and $2H_{b'}$); 3.48 (s, 2H, COD); 4.88-5.06 (m, 4H, $H_{a,a'}$); 4.73-5.25 (s, 2H, COD); 7.65-7.78 (m, 2H); 7.80-7.86 (m, 3H); 8.06 (dd, J_1 =1.2 Hz, J_2 = 8 Hz, 1H, H_{13}); 8.97 (s, 1H, H_1); 9.08 (d, *J* = 8.4 Hz, 1H, H_{13}). HRMS (ESI MS) $[M+Na]^+$ ($C_{33}H_{36}N_2{}^{35}ClNa^{193}Rh$): calcd. 607.1489; found 607.14845.

Iridium complex of [6]helicene-NHC 1b. In a Schlenk tube under argon, were placed successively $[Ir(COD)Cl]_2$ (48.4 mg, 0.07 mmol, 0.6 eq.), *t*-BuOK (13.5 mg, 0.12 mmol, 1 eq.) and dry THF (5 mL). After stirring for 10 min at room temperature, imidazolium salt **4b** (58.5 mg, 1 eq.) was added and the solution was stirred at room temperature for 13hours. The solvent was stripped off and the crude mixture was purified by flash chromatography over silica gel (diethyl ether as the eluent) to give complex **1b** (62 mg, 65%) as a yellow solid. Mp **=** 269 °C. HRMS (ESI) $[M+Na]^+$ ($C_{41}H_{40}N_2{}^{35}ClNa^{193}Ir$): calcd. 811.24016; found 811.2404(0).

The mixture of four diastereomers was then separated by HPLC over a chiral stationnary phase (Chiralpak IG, eluent: hexane/ethanol/dichloromethane (80/10/10), see SI) to yield complexes **1b^1** and **1b^2**. First eluted: (*P*)-**1b^1**, > 99% *ee*, $[\alpha]_D^{23}$ = +2287; second eluted: (*M*)-**1b^1** > 98% *ee*, $[\alpha]_D^{23}$ = -1860; third eluted: (*P*)-**1b^2**, > 98% *ee*, $[\alpha]_D^{23}$ = +2750; fourth eluted: (*M*)-**1b^2**, > 98% *ee*, $[\alpha]_D^{23}$ = -2121 (CH_2Cl_2, 5 × 10^{-5} M). Some isomerization process between **1b^1** and **1b^2** stereoisomers was observed (see below and in SI).

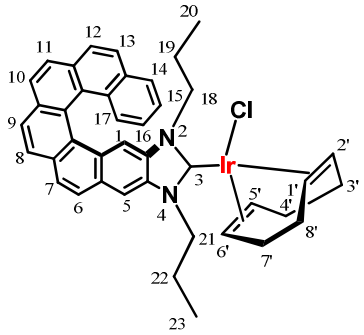
Complex 1b^1



^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.73 (t, *J* = 7.5 Hz, 3H, H_{20}); 1,09 (t, *J* = 7.5 Hz, 3H, H_{23}); 1.12-1.26 (m, 2H); 1.69-1.77 (m, 2H, H_{19}); 1.79-1.86 (m, 2H); 1.88-1.96 (m, 1H, H_{22}); 2.07-2.15 (m, 1H, H_{22}); 2.17-2.32 (m, 4H); 2,80 (td, J_1 = 2.5 Hz, J_2 = 7 Hz, 1H, $H_{2'}$); 2.96-2.98 (m, 1H, $H_{1'}$); 3.69-3.75 (m, 1H, H_{18}); 4.05-4.10 (m, 1H, H_{18}); 4.52-4.58 (m, 2H, H_{21} and $H_{5'/6'}$); 4.59-4.63 (m, 1H, $H_{5'/6'}$); 4.68-4.74 (m, 1H, H_{21}); 6.50-6.53 (m, 1H, H_{16}); 7.10 (td, J_1

= 1 Hz, J_2 = 8 Hz, 1H, H_{15}); 7.46 (s, 1H, H_1); 7.48 (d, J = 8,5 Hz, 1H, H_{17}); 7.70 (s, 1H, H_5); 7.84 (d, J = 7.5 Hz, 1H, H_{14}); 7.94 (d, J = 8.5 Hz, 1H); 7.98 (d, J = 8.5 Hz, 1H); 8.01-8.09 (m, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 11.65 (C_{20}); 12.0 (C_{23}); 22.8 (C_{19}), 23.4 (C_{22}), 29.8 (CH_2); 30.0 (CH_2); 33.9 (CH_2); 34.1 (CH_2); 50.15 (C_{18}); 50.55 (C_{21}); 53.,0 ($C_{1'/2'}$); 53.05 ($C_{1'/2'}$); 86.9 ($C_{5'/6'}$); 87.0 ($C_{5'/6'}$); 106.8 (C_5); 108.3 (C_1); 124.3; 125.1; 126.1; 126.2; 126.2; 127.25; 127.3; 127.7; 127.8; 127.8; 127.8; 127.9; 127.9; 128.07; 128.3; 128.4; 128.7; 130.0; 131.5; 132.1; 132.45; 133.8; 134.1; 133.7; 196.6 (C_3).

Complex 1b[2]



^{1}H NMR (500 MHz, CD_2Cl_2): δ 0.70-0.76 (m, 1H, H_{19}); 0.79 (t, J = 6.5 Hz, 3H, H_{20}); 0.85-0.89 (m, 1H); 1.11 (t, J = 7,5 Hz, 3H, H_{23}); 1.26-1.31 (m, 1H); 1.33-1.42 (m, 1H, H_{19}); 1.73-1.78 (m, 2H); 1.93-2.00 (m, 1H, H_{22}); 2.08-2.22 (m, 5H, H_{22} + $4H_{COD}$); 2.64-2.67 (m, 1H, $H_{5'}$); 2.77-2.79 (m, 1H, $H_{6'}$); 3.70-3.76 (m, 1H, H_{18}); 4.06-4.12 (m, 1H, H_{18}); 4.56-4.62 (m, 3H, H_{21} + $2H_{COD}$); 4.63-4.70 (m, 1H, H_{21}); 6.64-6.68 (m, 1H, H_{16}); 7.23 (t, J = 7.5 Hz, 1H, H_{15}); 7.56 (s, 1H, H_1); 7.61 (d, J = 8.5 Hz, 1H, H_{17}); 7.72 (s, 1H, H_5); 7.83 (d, J = 8 Hz, 1H, H_{14}); 7.93 (d, J = 9 Hz, 1H); 7.96 (d, J = 8.5 Hz, 1H); 8.02-8.06 (m, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ11.28 (C_{20}); 11.45 (C_{23}); 23.0 (C_{19}), 23.8 (C_{22}), 29.3 (CH_2); 29.3 (CH_2); 33.3 (CH_2); 33.4 (CH_2); 59.5 (C_{18}); 50.05 (C_{21}); 52.4 ($C_{6'}$); 52.6 ($C_{5'}$); 86.4 (CH); 86.45 (CH); 106.5 (C_5); 107.3 (C_1); 123.7; 125.2; 125.6; 125.95; 126.1; 126.4; 126.7; 127.0; 127.1; 127.3; 127.35; 127.45; 127.7; 127.9; 128.0; 128.1; 128.1; 129.2; 131.0; 131.6; 131.9; 133.2; 133.6; 133.7; 196.2 (C_3).

General procedure for catalytic transfer hydrogenation

Acetophenone (1.0 mmol), *t*-BuOK (0.1 mmol) and catalyst (0.01 mmol or 0.02 mmol) were introduced into an oven-dried Schlenk tube. Dry *i*-PrOH (3.0 mL) was then added and the mixture was refluxed, for the specified time, under argon. The efficiencies of the reactions were determined by ^{1}H NMR and the enantioselectivities by chiral HPLC.

Results and Discussion

SYNTHESIS

The synthesis of iridium(I) complex **1a** bearing a [4]helicenic NHC ligand was first investigated. It started with the preparation of 2,3-dibromo-carbo[4]helicene **2a** according to a known procedure,[22] which was then transformed into 2,3-di-*n*-propylamino-carbo[4]helicene **3a**, by a Buchwald-Hartwig coupling using classical conditions (69% yield, see Scheme 1). Upon reaction with triethylorthoformate and HCl, diamine **3a** then afforded helical imidazolium chloride salt **4a** with 73% yield. Compounds **3a** and **4a** were characterized by NMR spectroscopy and mass spectrometry. For example, the ^{1}H NMR spectrum of salt **4a** displayed characteristic signals coming from the helicenic unit and the imidazolium part. Indeed, a singlet at 9.27 ppm and a doublet 8.93 ppm correspond to H_1 and H_{13} protons, respectively, while the highly deshielded proton at 11.84 ppm corresponds to proton of the precarbenic CH. Both types of methylenes and methyls of the *n*-propyl chain were found to be isochronous and appeared as large singlets. The ^{13}C NMR also confirmed the imidazolium formation with the tertiary pre-carbenic carbon C_3 resonating at 196.9 ppm. The chemical structure of **4a** was finally confirmed by X-ray crystallography (*P*-1 space group), which showed *i*) the helical structure with a small helicity (dihedral angle between terminal rings) of 29.94 degrees (a typical value for [4]helicene units),[1] *ii*) the imidazolium cycle fused to the helical core, *iii*) the heterochiral assembly in a head-to-tail fashion, and *iv*) the *n*-propyl chains. Interestingly, the chloride ions form channels all along the z axis (see Figure 2).

Upon reaction of **4a** with $[Ir(COD)Cl]_2$ in the presence of *t*-BuOK as the base, the iridium(I) complex **1a** bearing COD, chloro ligands and monodentate [4]helicenic carbene was obtained with 76% yield. This complex was fully characterized by NMR spectroscopy, mass spectrometry and X-ray crystallography. The X-ray structure of racemic **1a** (*P-1* centro-symmetric space group, Figure 2 and SI) shows a pseudotetrahedral geometry around the iridium center, with the two double bonds of COD, the chlorine and the carbenic C forming the tetrahedron. Complex **1a** displays a typical C^3–Ir bond length of 2.011Å. These metric data are similar to corresponding values for other reported carbenic cycloiridiated complexes.[23] The [4]helicenic part shows a helicity of 27.36° in the solid state, but it is not configurationally stable in solution.

The analogous rhodium(I) complex **1'a** was also prepared with 51% yield according to the same procedure as **1a** but using $[Rh(COD)Cl]_2$ as the Rh(I) organometallic precursor. Its structure was ascertained by X-ray crystallography. Very similar features as for **1a** were found for **1'a** which also crystallized in the *P*-1 space group (C^3-Rh bond length of 2.011 Å, helicity 27.20°).

Similarly to **4a**, [6]helicenic imidazolium salt **4b** was prepared in two steps from 2,3-dibromo-carbo[6]helicene **2b**,[22] according to Scheme 1, *i.e.* through a Buchwald-Hartwig coupling giving 2,3-dipropylamino-carbo[6]helicene **3b** followed by a cyclization forming the imidazolium unit. Compounds **3b** and **4b** were also fully characterized by NMR spectroscopy and mass spectrometry. For example, the ^{1}H NMR spectrum of diamine **3b** displayed a set of six distinguished signals for shielded and deshielded protons $H_{a,b,c}$ and $H_{a',b',c'}$, respectively, of the *n*-propyl chains due to their different positions relative to the helicene inner core.

Compound **3b** crystallized into single crystals and its X-ray crystallographic structure is depicted in Figure 3a which shows the heterochiral (*P* and M) pair (*P*-1 space group)**.** Compound **3b** arranges along the y axis into homochiral columns in a head-to-tail fashion (Figure 3b). The hexahelicenic diamine is now configurationally stable and displays a helicity of 58.65°.

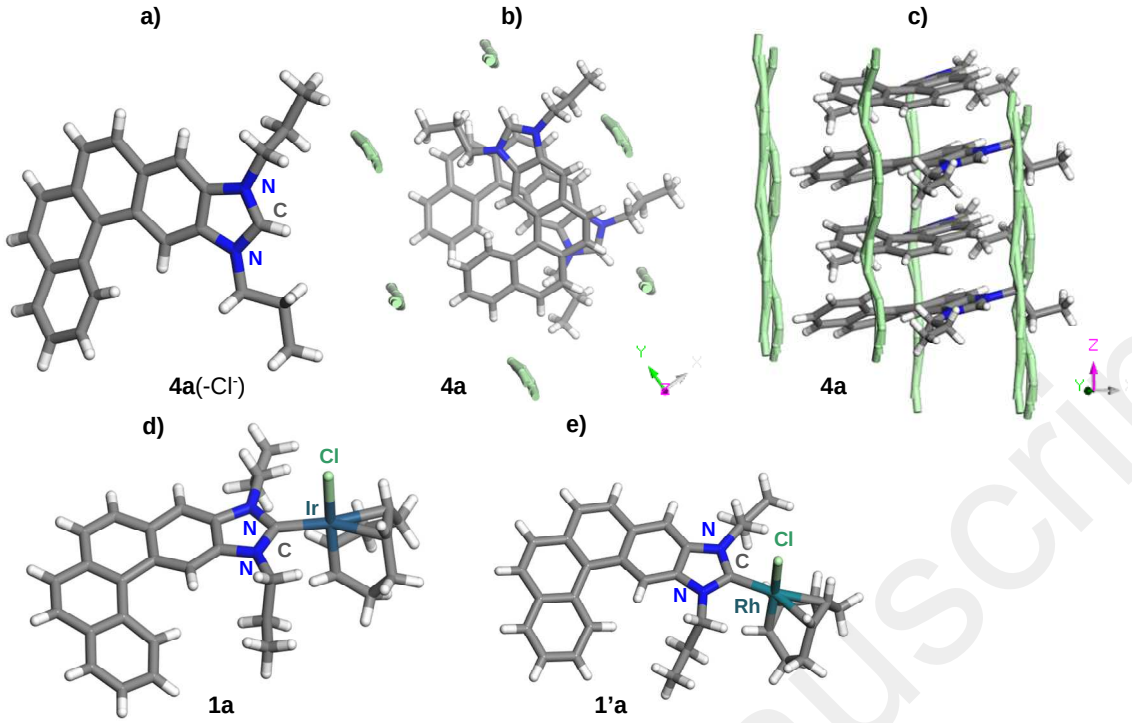


FIGURE 2. X-ray crystallographic structures of imidazolium salt 4a (a) and its views along the z (b) and y (c) axes, of iridium complex 1a (d) and rhodium complex 1'a (e).

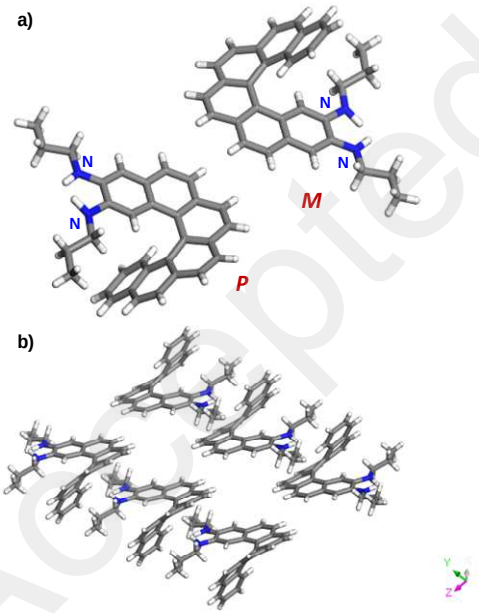


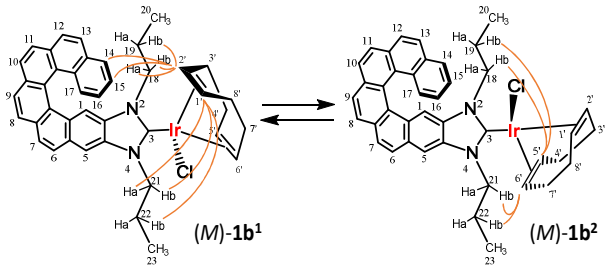
FIGURE 3. X-ray crystallographic structure of [6]helicenic diamine 3b. a) Heterochiral pair; b) head-to-tail organisation into homochiral columns.

The obtention of [6]helicene-benzimidazolium chloride **4b** was confirmed by ^{1}H and ^{13}C NMR analyses which showed the typical highly deshielded signal at 11.7 ppm for H_3 and at 145.9 for C_3.

Similarly to **1a**, [6]helicene-NHC-Ir complex **1b** was prepared from **4b** upon reaction of $[Ir(COD)Cl]_2$ in the presence of *t*-BuOK and was obtained with 65 % yield. This compound showed a peak at 811.2404(0) in the ESI-HRMS corresponding to $[M+Na]^+$ and its ^{1}H NMR spectrum corresponded to a mixture of two sets of signals.

SEPARATION OF STEREOISOMERS

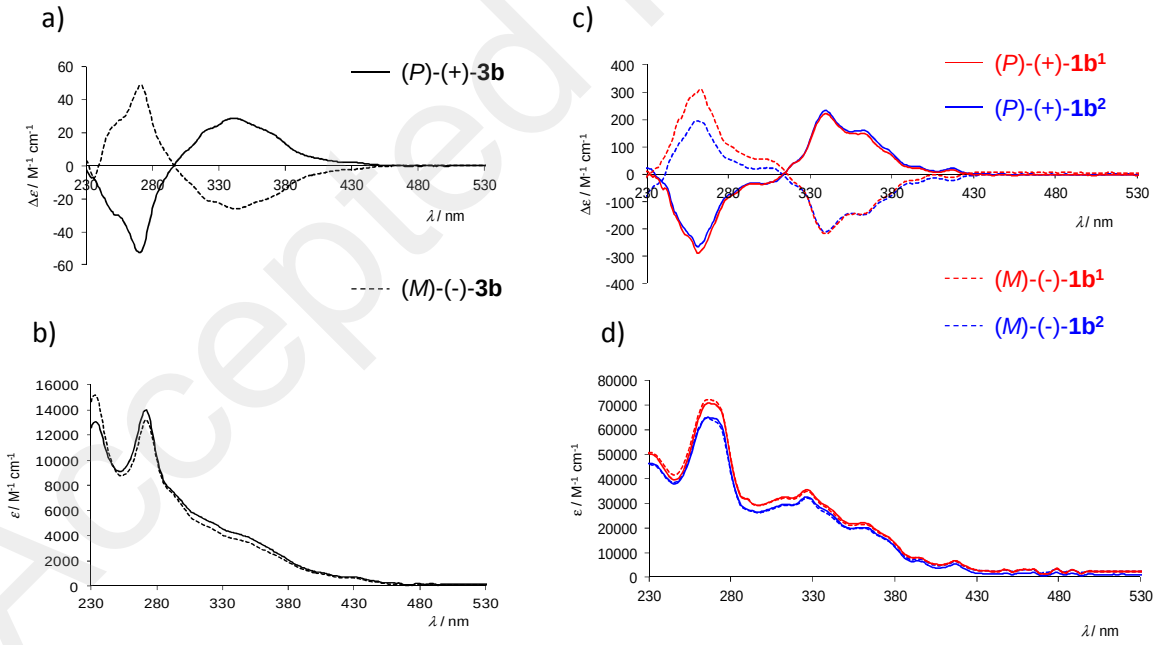
Complex **1b** was then subjected to chiral HPLC separation (see experimental part and SI). A set of four signals was obtained, corresponding to enantiomeric pairs (*M*)-(-)/(*P*)-(+)-**1b^1** and (*M*)-(-)/(*P*)-(+)-**1b^2**. The final structures of **1b^1** and **1b^2** were clarified by NOESY experiments, which revealed that the COD ligand could adopt two positions, one directed towards the helical moiety (**1b^1**) and one on the opposite direction (**1b^2**). Indeed, complex **1b^1** shows spatial proximity between 14 and 15 protons from helicene terminal aromatic ring and one of the COD double bound, whereas compound **1b^2** only shows spatial proximity of COD ligand with protons from the alkyl chains on the opposite side of the helicene. Moreover, NOESY correlations reveal that orientation of alkyl chains from the imidazole moiety relative to helicene changes slightly according to the position of the COD ligand (see SI). The interconversion barrier between **1b^1** and **1b^2** was estimated to 104 kJ/mol at 25°C (see SI), so that exchange takes only a few hours at ambient temperature.



SCHEME 2. Stereochemistry of diastereomeric complexes $1b^1$ and $1b^2$ that are in slow equilibrium. NOESY correlations are shown in orange.

CHIROPTICAL PROPERTIES

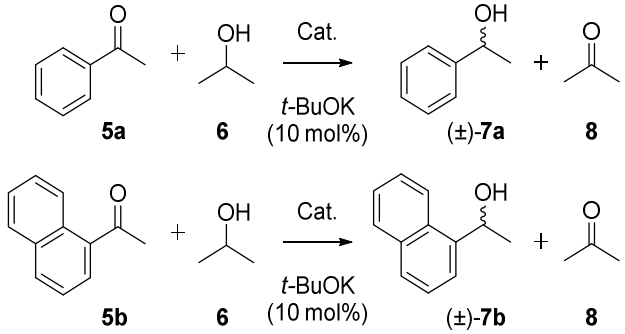
The chiroptical properties (OR and ECD) of pure stereoisomers (*P*)-(+) and (*M*)-(-)-**$1b^1$** / **$1b^2$** were then investigated. For comparison, pure enantiomers (*P*)-(+) and (*M*)-(-)-**3b** (*ee*'s > 99.5 and 98%) were also prepared by chiral HPLC over Chiralpak IA stationary phase (Heptane/ethanol/dichloromethane (80/10/10) as the eluent, see SI). (*P*)-(+) and (*M*)-(-)-**3b** display specific rotations values $[\alpha]_D^{23}$ of +760 and -733 ° cm^2 g^{-1} (±5%, CH_2Cl_2, 5×10^{-5} M), which are moderate values for hexahelicenic structures.[1] Similarly, their UV-vis and ECD spectra show moderate intensities, as depicted on Figure 4. Indeed, the UV-vis spectrum of **3b** shows one intense band at 270 nm (ε = 14 $\times$ 10^3 M^{-1} cm^{-1}) and moderate ones (4×10^3 M^{-1} cm^{-1} < ε < 8×10^3 M^{-1} cm^{-1}) at 295, 320, 341 and 350 nm, while the ECD spectrum of (*P*)-(+)-**3b** displays two main bands, one negative at 279 nm ($\Delta\varepsilon$ = -52 M^{-1} cm^{-1}) and one positive at 341 nm ($\Delta\varepsilon$ = +29 M^{-1} cm^{-1}), with some unresolved vibronic progression. We interpret this peculiar behavior by the presence of quinoidal forms that may coexist in such a compound. Oxidized impurities cannot be excluded due to the poor stability of such aromatic diamine derivative. On the contrary, the pure enantiomers (*P*)-(+) and (*M*)-(-)-**$1b^1$** display very intense UV-vis and ECD spectra, with UV-vis spectra showing one intense band at 265 nm (ε > 70×10^3 M^{-1} cm^{-1}) and other intense ones (16×10^3 M^{-1} cm^{-1} < ε < 35×10^3 M^{-1} cm^{-1}) at 310, 325, 341, 361, and 375. Two other weak bands at 395 and 420 nm are also present. The ECD spectrum of (*P*)-(+)-**$1b^1$** displays one strong negative band at 261 nm ($\Delta\varepsilon$ = -288 M^{-1} cm^{-1}) and two main strong positive bands at 341 nm ($\Delta\varepsilon$ = +219 M^{-1} cm^{-1}) and 361 nm ($\Delta\varepsilon$ = +148 M^{-1} cm^{-1}), with some vibronic progression, accompanied by two weak ECD bands at 395 and 420 nm (15 M^{-1} cm^{-1} < ε < 23 M^{-1} cm^{-1}). Diastereomeric complex (*P*)-(+)-**$1b^1$** displays very similar UV-vis and ECD responses. Note that the (*P*)-(+) and (*M*)-(-) absolute configurations can be clearly assigned for all enantiopure compounds thanks to comparison of their typical ECD signatures with those of already known helicenes.[16-18] Compounds **$1b^1$** and **$1b^2$** display strong specific rotation values ((*P*)-**$1b^1$**: $[\alpha]_D^{23}$ = +2750° cm^2 g^{-1}; (*P*)-**$1b^2$**: $[\alpha]_D^{23}$ = +2703° cm^2 g^{-1} (±5%, CH_2Cl_2, 5×10^{-5} M).



FIGRE 4. ECD (a, c) and UV-vis (b,d) spectra of enantiomers (*P*)-(+) and (*M*)-(-)-3b and (*P*)-(+) and (*M*)-(-)-$1b^1$/$1b^2$ in CH_2Cl_2 (conc. between 3.10^{-4} and 2.10^{-5} M) .

CATALYTIC ACTIVITY

Rhodium and iridium complexes bearing chiral NHCs can be applied as catalysts in asymmetric hydrogenations. Indeed, such complexes have been used in the transfer hydrogenation of various ketones with very good enantioselectivities.[21,24-26] As depicted on Scheme 3, the catalytic activity of complexes **1a** and **1b**[1] was evaluated using the transfer hydrogenation reaction on acetophenone **5a** and 1-acetyl-naphthalene **5b**, to their corresponding alcohols **7a** and **7b**, using isopropanol (**6**) as both the solvent and the hydrogen source. Very good reaction yields were obtained, with rather low loadings of catalyst (Table 1). However no enantioselectivity was observed when using (*P*)-**1b**[1] as the chiral catalyst, as evidenced by chiral HPLC analysis of the final alcohol. Most probably, the low steric hindrance of the N-substituents on the NHC moiety combined with the fluxionality around the metal preclude any chiral discrimination during the catalytic reaction.



SCHEME 3. Catalytic tests on hydrogen transfer from isopropanol to aromatic ketones.

TABLE 1: experimental conditions and results of catalytic tests.

Entry	Ketone	Cat. (X mol%)	Temp.	Time	Conversion
1	**5a**	**1a** (2)	60 °C	5 hrs	94%
2	**5b**	**1a** (1)	60°C	3 d	99%
3	**5a**	(*P*)-**1b**[1] (2)	60°C	6 hrs	99%

CONCLUSION

In conclusion, we have prepared novel Ir(I) and Rh(I) complexes bearing monodentate [4]- or [6]helicene-NHC complexes. These compounds were fully characterized, especially by X-ray crystallography for [4]helicenic derivatives **1a** and **1'a** and by chiroptical activity for [6]helicenic derivative **1b**. They appeared as efficient catalysts in the transfer hydrogenation of acetophenone and 1-acetyl-naphthatene. Further efforts will be pursued in the future to achieve efficient enantioselective catalysis of similar enantiopure helicenic NHC-based organometallic complexes.

Acknowledgements

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Supporting information

Additional supporting information on NMR, HPLC and X-ray crystallographic data may be found in the online version of this article at the publisher's website.

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Graphical Abstract