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Enantiopure Cyclometalated Rh(III) and Ir(III) Complexes Displaying Rigid Configuration at Metal Center: Design, Structures, Chiroptical Properties and Role of the Iodide Ligand

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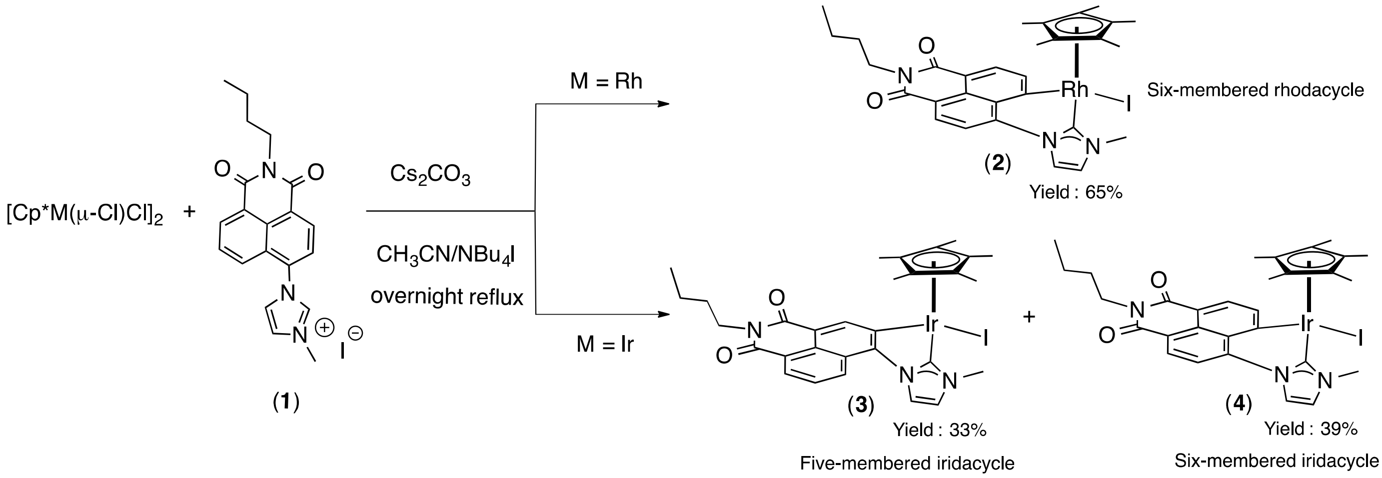
Abstract: Enantiopure *N*-heterocyclic carbene half-sandwich metal complexes of the general formula [Cp*M(C^C:)I] (M = Rh, Ir; C^C: = NI-NHC; NI-H = Naphthalimide; NHC = *N*-heterocyclic carbene) are reported. The rhodium compound was obtained as a single isomer displaying six membered metallacycle and was resolved on chiral column chromatography to the corresponding enantiomers (*S*)-[Cp*Rh(C^C:)I] (*S*)-**2** and (*R*)-[Cp*Rh(C^C:)I] (*R*)-**2**. The iridium congener, however, furnishes a pair of regioisomers, which were resolved into (*S*)-[Cp*Ir(C^C:)I] (*S*)-**3** and (*R*)-[Cp*Ir(C^C:)I] (*R*)-**3** and (*S*)-[Cp*Ir(C^C:)I] (*S*)-**4** and (*R*)-[Cp*Ir(C^C:)I] (*R*)-**4**. These regioisomers differ from each other, only by the size of the metallacycle; five-membered for **3** and six-membered for **4**. The molecular structures of (*S*)-**2** and (*S*)-**4** are reported. Moreover, the chiroptical properties of these compounds are presented and discussed. These compounds display exceptional stable configurations at the metal center in solution with enantiomerization barrier $\Delta G^{\neq}$ up to 124 kJ/mol. This is because the nature of the naphthalimide-NHC clamp ligand and the iodide ligand contribute to their configuration's robustness. In contrast to related complexes reported in the literature, which are often labile in solution.

Keywords: chiral resolution; enantiopure; configurational stability; circular dichroism

1. Introduction

Chirality is an ever-fascinating topic and occurs in many fields of science [1–4]. In the area of transition metal complexes, Brunner [5,6], Gladysz [7,8], von Zelewsky [9], Meggers [10], Constable [11] and others [12,13] have made great contributions to the advancement and comprehension of the elements that control the chirality at metal centers at the molecular and supramolecular levels [11,14]. For instance, octahedral iridium complexes displaying helical chirality (Δ, Λ) show a stable configuration at the metal center [15–19]. Coordination and organometallic complexes with planar chirality also show stable configuration [20–25]. In contrast, half-sandwich rhodium and iridium complexes with piano stool geometry, displaying central chirality are labile in solution, as demonstrated by Brunner and co-workers and others [26–29]. More recently, efforts were devoted to using strongly coordinated *N*-heterocyclic carbene (NHC) ligands to increase the stability at the metal center; however, only a few examples were reported [30–32].

We recently described the synthesis of some half-sandwich iridium complexes displaying stable configuration at the metal center [32]. Such compounds contain Cp*Ir complexes in which the NHC unit is directly attached to a naphthalimide (NI) molecule. The latter strongly chelates the metal center; moreover, an iodide ligand completes the coordination sphere around the metal center. Iodide is known to act as a strong σ-donor and a weak-leaving group [33], thus we anticipated such a combination of ligands should bring rigidity to the configuration of the metal center. In this work, we extended our synthetic procedures to the related rhodium congener. Interestingly only one regioisomer complex is obtained, displaying a six-membered metallacycle. The iridium complexes are obtained as two regioisomers in a rough 1:1 ratio as a mixture of five-membered and six membered iridacycles (Scheme 1).



Scheme 1. Preparation of the cyclometalated half-sandwich complexes **2**–**4**.

The racemic complexes were all resolved using chiral column chromatography. The chiroptical optical properties were studied and the configurational stability were investigated by measuring the enantiomerization barrier at T = 60 °C for these complexes and were found to be up to $\Delta G^{\neq}{}_{\text{enantiomerization}}$ = 124 kJ/mole, suggesting that these compounds display high configurational stability at room temperature.

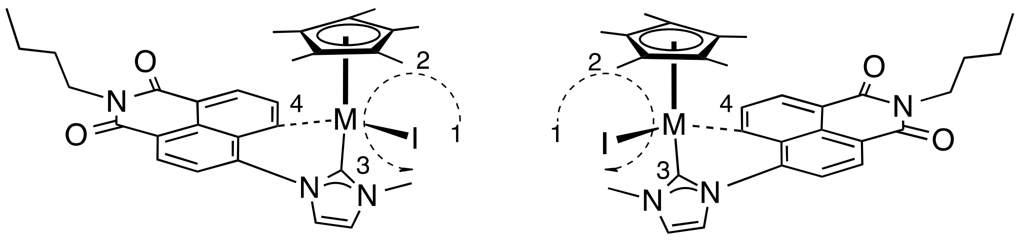
2. Results and Discussions

2.1. Synthesis and Characterization

The target compounds **2**–**4** were prepared by treatment of two equivalents of the imidazolium salt (**1**) with the chloro-bridged dimeric precursor $[Cp^*M(\mu\text{-}Cl)Cl]_2$ in the presence of Cs_2CO_3 and NBu_4I, in CH_3CN under reflux overnight. When $[Cp^*Rh(\mu\text{-}Cl)Cl]_2$ was used as starting material only one single rhodium carbene compound identified as [Cp*Rh(NI-NHC)I] (**2**) (NI-H = Naphthalimide) was obtained in good yield as red microcrystalline solid after eluting on a column chromatography. The ^{1}H-NMR of **2** recorded in $CDCl_3$ showed the presence of a singlet assigned to Cp*Rh protons at δ 1.51 ppm and the aromatic protons of the naphthalimide and NHC moiety appeared in the range of δ 7.1 to δ 8.61 ppm.

Starting with iridium precursor $[Cp^*Ir(\mu\text{-}Cl)Cl]_2$, under similar experimental conditions, two regioisomeric complexes **3** and **4** were obtained. These compounds display the same chemical composition but differ only with the size of the iridacycle. The formation of the two isomers results from the different modes of metallacyclization; (a) whether the cyclization process takes place at the arene attached directly to the NHC moiety to give the five-membered metallacycle. (b) Metallacylization occurs at the other arene ring generating the six-membered metallacycle. Both isomers **3** and **4** were obtained in a 1:1 ratio. The ^{1}H-NMR of **4** recorded in $CDCl_3$ displayed a singlet at δ 1.54 ppm, assigned to the Cp*Ir protons, this upfield shift is a diagnosis to the formation of a six-membered metallacylce. The aromatic protons of the naphthalimide and NHC moiety appeared in the range of δ 7.1 to δ 8.57 ppm. These data are similar to those obtained for complex **2**. The ^{1}H-NMR of compound **3**, on the other hand, displayed a singlet at δ 1.96 ppm to the Cp*Ir protons, which is downfield with respect to the six-membered metallacycle complexes **2** and **4**. Moreover, the aromatic protons of the naphthalimide and NHC moiety appeared downfield in the range

7.1 to 9.2 ppm and displayed a different pattern. Furthermore, 2D COSY, ROESY, HSQC, and HMBC experiments carried out on complexes **3** and **4** allowed us to fully characterize both isomers (Figures S1 and S2, 2D ROESY Spectra of **3** and **4**). In addition, the identity of these molecules was also confirmed by determining the molecular structures of the enantiopure complexes (*S*)-**2** and (*S*)-**4** (Figure 1) (vide infra).

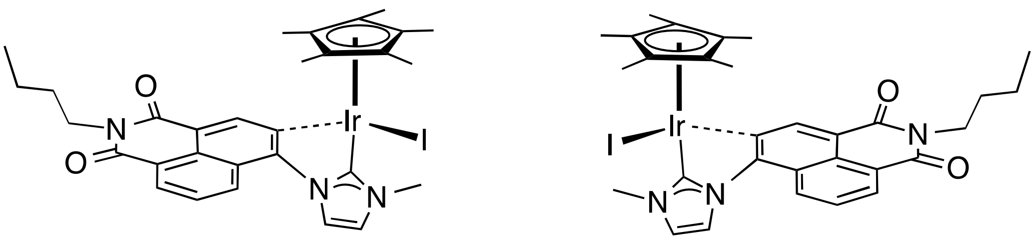


M = Rh, (*S*)-**2**

M = Ir, (*S*)-**4**

M = Rh, (*R*)-**2**

M = Ir, (*R*)-**4**



(*S*)-**3**

(*R*)-**3**

Figure 1. Optically active molecules (*S*)-**2**, (*S*)-**3** and (*S*)-**4**/(*R*)-**2**, (*R*)-**3** and (*R*)-**4** described in this work and priority rule used (I > Cp > C-Carbene > C-arene) to assign the absolute configuration [34,35].

*2.2. Chiral Resolution of Complexes [Cp*M(C^C:)I] (M = Rh, (**2**); M = Ir (**3**–**4**) and Chiroptical Properties*

Half-sandwich rhodium and iridium *N*-heterocyclic carbene complexes (**2**–**4**) were resolved on the chiral stationary phase (Experimental details are given in the Supplementary Materials). For the rhodium complex, Chiralpak IF column was chosen using heptane/ethanol/dichloromethane (50/30/20) mixture as eluent. The related iridium complexes **3** and **4** were resolved using (*S*,*S*)-Whelk-O1 chiral column and using the same solvent mixture as eluent. Remarkably all complexes were stable during the resolution process highlighting their robustness and were obtained with >98% ee. The CD spectra of the enantiomers of **2**, **3**, and **4** are given in Figures 2–4. The optical rotations of both enantiomers were monitored as well (experimental details of their resolution are given in the Supplementary Materials).

The CD curves of both enantiomers (Figure 2) displayed an excellent mirror image relationship. For instance, the CD trace of *S*-**2** displayed a positive band at 200 nm (Δε = +42) and a negative band at 265 nm (Δε = −42), followed by a broad positive band at 390 nm (Δε = +36) and a negative band at 445 nm (Δε = −16). The first eluted complex (CD green trace) was crystallized and provided suitable crystals for X-ray diffraction study. The X-ray molecular structure confirmed the identity of the complex (vide infra). Gratifyingly all enantiopure compounds displayed stable configuration in strongly coordinated CH_3CN solution and did not epimerize upon standing for several days in solution as demonstrated by their CD curves (vide infra).

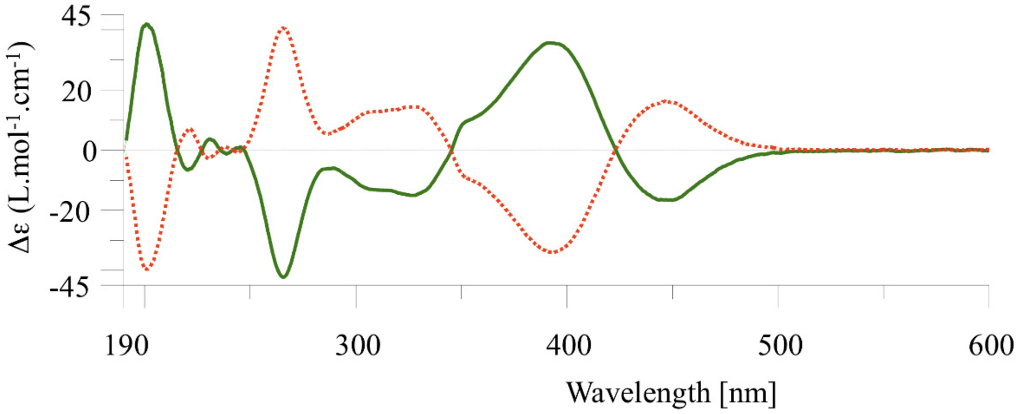


Figure 2. CD spectra of (*S*)-**2** (green) and (*R*)-**2** (red) recorded in CH_3CN at 0.251 mM.

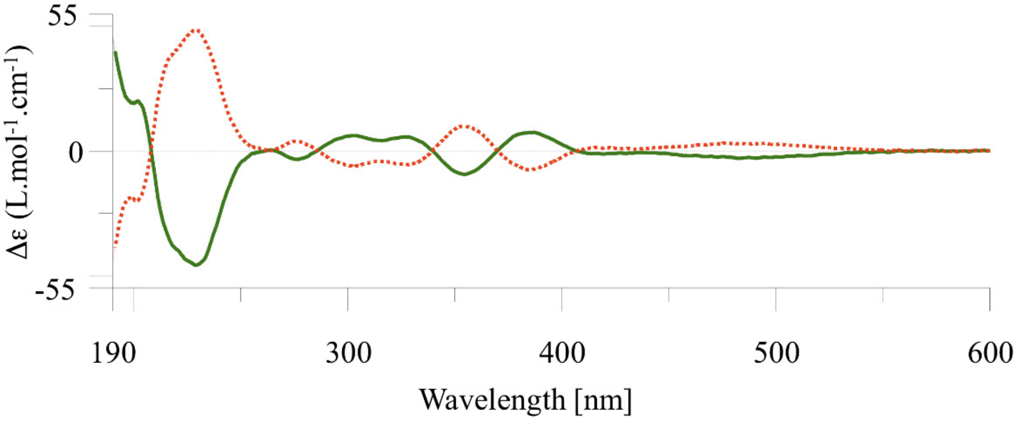


Figure 3. CD spectra of *S*-**3** (green) and *R*-**3** (red) recorded in CH_3CN at 0.24 mM.

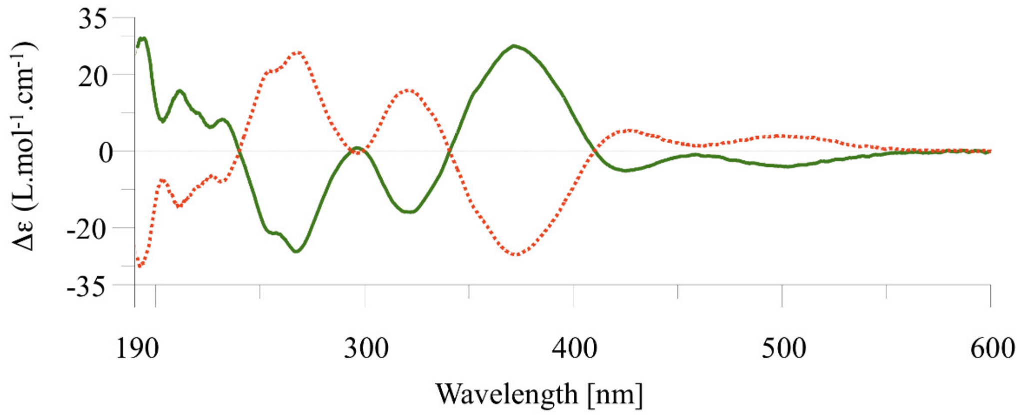


Figure 4. CD spectra of (*S*)-**4** (green) and (*R*)-**4** (red) recorded in CH_3CN at 0.24 mM.

On the other hand, the CD curves of both enantiomers of **3** displayed again an excellent mirror image patterns confirming the enantiomeric relationship between the two complexes (*S*)-**3** and (*R*)-**3**. It is noteworthy that the positive and negative Cotton bands above 350 nm appeared weaker than those observed for the enantiomers of **2** and **4** suggesting perhaps the influence of the size of the five- or six-membered metallacycles (vide infra)

The CD spectra of both enantiomers of **4** are shown in Figure 4. The traces showed opposite image absorption bands, confirming the enantiomeric relationship. Moreover, the absorption profile appears to be comparable to those of complex **2** displaying a six-membered metallacycle. For instance, the CD trace of (*S*)-**4** showed a negative cotton band at 267 nm ($\Delta\varepsilon = -26$), and a broad positive band at 371 nm ($\Delta\varepsilon = +27$) comparable to those observed for (*S*)-**2**. Crystals of the first eluted sample (*S*)-**4** were obtained for X-ray diffraction. The structure is presented and discussed in the next section.

*2.3. Molecular Structures of S-**2** and S-**4***

Single crystals of (*S*)-**2** were obtained by slow diffusion of diethyl ether into a CH_2Cl_2 solution of the complex. X-ray crystallography confirmed the proposed structure of complex (*S*)-**2** (Figure 5).

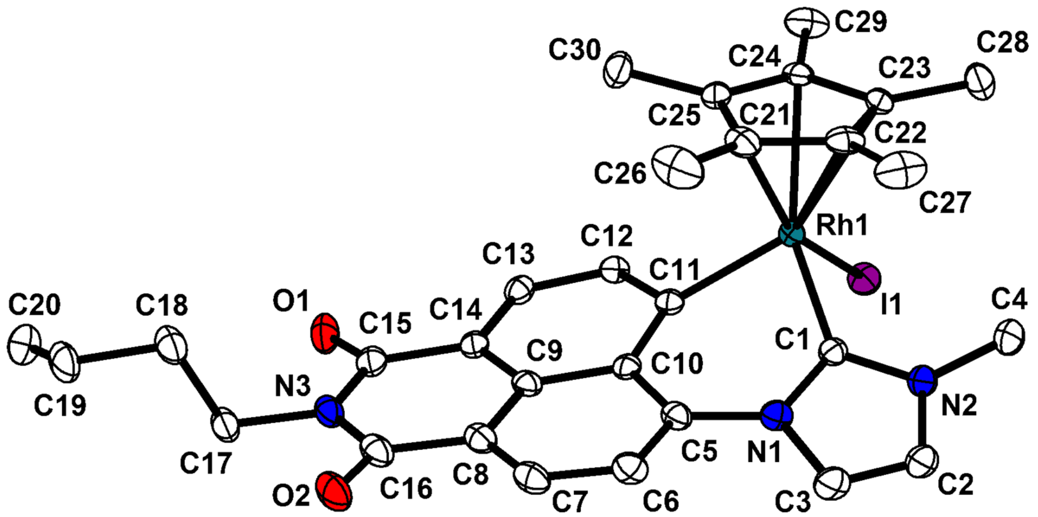


Figure 5. Molecular structure of (*S*)-**2** with thermal ellipsoids drawn at the 30% probability level, hydrogen atoms were omitted for clarity. The asymmetric unit comprises two molecules with the same configuration and almost identical conformations, differing only in their nBu-groups. One molecule was arbitrarily chosen for representation. Selected average bond distances (Å) and angles (deg): Rh1-I1 2.699(**2**), Rh1-C1 1.983(**5**), C1-N1 1.371(**7**), N1-C5 1.414(**6**), C5-C10 1.426(**7**), C10-C11 1.427(**7**), C11-Rh1 2.026(**8**), Rh1-C21 2.154(**5**), Rh1-C22 2.248(**8**), Rh1-C23 2.289(**5**), Rh1-C24 2.276(**5**), Rh1-C25 2.248(**5**), C1-Rh1-C11 86.5(**3**), Rh1-C1-N1 126.0(**6**), Rh1-C11-C10 122.2(**12**), C1-N1-C5 125.8(**4**), C11-C10-C5 123.9(**5**), and N1-C5-C10 120.0(**4**).

The structure shows the formation of the six-membered rhodacycle, which adopts a boat conformation. The absolute configuration around the metal center was determined to be (*S*) by the refinement of the Flack x parameter (Table 1). The metal center chelated by the (CˆC:) NHC-naphthalimide ligand, is symmetrically bound to η-Cp*. Finally, the iodide ligand completes the coordination sphere around the rhodium and confers a distorted tetrahedral geometry. The iridium complex (*S*)-**4** was found to be isostructural to that of the rhodium complex (*S*)-**2** (Figure 6). We note however the nBu-group of the naphthalimide points downward opposite to that observed for (*S*)-**2**. The absolute configuration of the complex was assigned by refining the Flack × parameter (Table 1).

2.4. Determination of the Enantiomerization Barriers and Configurational Stability

To evaluate the stability of the enantiopure complex, (*R*)-**2** was dissolved in acetonitrile, heated at 60 °C and then analyzed by chiral HPLC. Complex **2** was chemically stable but underwent racemization. Monitoring of the enantiomeric excess versus time revealed a clean first-order reaction and allowed the determination of an enantiomerization barrier of 115.9 kJ/mol. Half-life time was extrapolated at 25 °C by considering zero enantiomerization entropy: 130 days for **2** at 25 °C in acetonitrile. So, enantiopure **2** can be handled and evaporated without any risk of enantiopurity loss. Similar racemization kinetics studies performed on (*S*)-**3** and (*R*)-**4**, provided the enantiomerization barriers in acetonitrile, to be 124.4 kJ/mol and 122.3 kJ/mol, respectively. These values confirm the chemical robustness of these complexes and allowed the estimation of their half-life times at 25 °C, to be 11 and 5 years for **3** and **4**, respectively. Highlighting the role of the metallacycle five-membered size versus six-membered size. The configurational stability is weaker in ethanol, with lower enantiomerization barriers of 4 kJ/mol (see Supporting Information for details). The racemization is faster with rhodium than with iridium, and in protic solvents, this facilitates the iodide decoordination as one might expect. These results underline the importance of iodine on the stabilization of the chiral configuration at the metal center. For comparison purposes, we note that Brunner and co-workers have studied the half-sandwich complexes [Cp*M(N^N*)Cl] (M = Rh, Ir) where N^N* is the anion of (+)-2-N-[(S)-1-phenylethylpyrrolcarbaldimine] and showed that such compounds are configurationally unstable at metal centers. Time-dependent integration of ^{1}H NMR signals of the complexes revealed that the epimerization is a first-order reaction. The half-lives in CD_2Cl_2 solution at −50 °C were 19.4 min for the rhodium complex and 30.6 min for the iridium compound [36].

Table 1. Summary of crystallographic, data collection and refinement parameters for (*S*)-[Cp*Rh(C^C:)I] (*S*)-**2** and (*S*)-[Cp*Ir(C^C:)I] (*S*)-**4**.

Compound	**(*S*)-[Cp*Rh(C^C:)I] (*S*)-2**	**(*S*)-[Cp*Ir(C^C:)I] (*S*)-4**
Empirical formula	C_{30} H_{33} I RhN_3 O_2	C_{30} H_{33} I Ir N_3 O_2
Formula weight	697.40	786.69
Crystal system	Monoclinic	Orthorhombic
Space group	P 2_1	P 2_1 2_1 2_1
Unit cell dimensions	a = 17.2315(4) Å	a = 8.0943(2) Å
	b = 10.6098(2) Å	b = 16.2456(4) Å
	c = 17.2604(4) Å	c = 21.3531(5) Å
	α = 90°	α = 90°
	β = 119.616(1)°	β = 90°
	γ = 90°	γ = 90°
Volume	2743.34(11) Å^3	2807.86(12) Å^3
Z	4	4
Temperature	200(1) K	200(1) K
Wavelength	1.54178 Å	1.54178 Å
θ range for data collection	5.10° to 66.62°	4.96° to 66.64°
Reflections (all/independent)	34,037/9689	15,376/4959
R(int)	2.54%	2.28%
Data/parameters/restraints	4959/340/0	9689/679/1
R1 [I > 2σ(I)]	2.08%	1.79%
wR2 (all data)	5.31%	4.55%
Flack parameter	−0.015(2)	0.001(3)

2.5. Discussion

As mentioned in the introduction of this manuscript, half-sandwich metal complexes continue to attract attention due to their importance in medicinal chemistry [37,38], materials science [39,40] and catalysis [41–43]. Of prime importance is the control of the configurational stability at the metal center. For instance, Brunner [26], White [27] and others [29] demonstrated that half-sandwich metal complexes of rhodium and iridium racemize in solution, because they display labile configuration at the metal center.

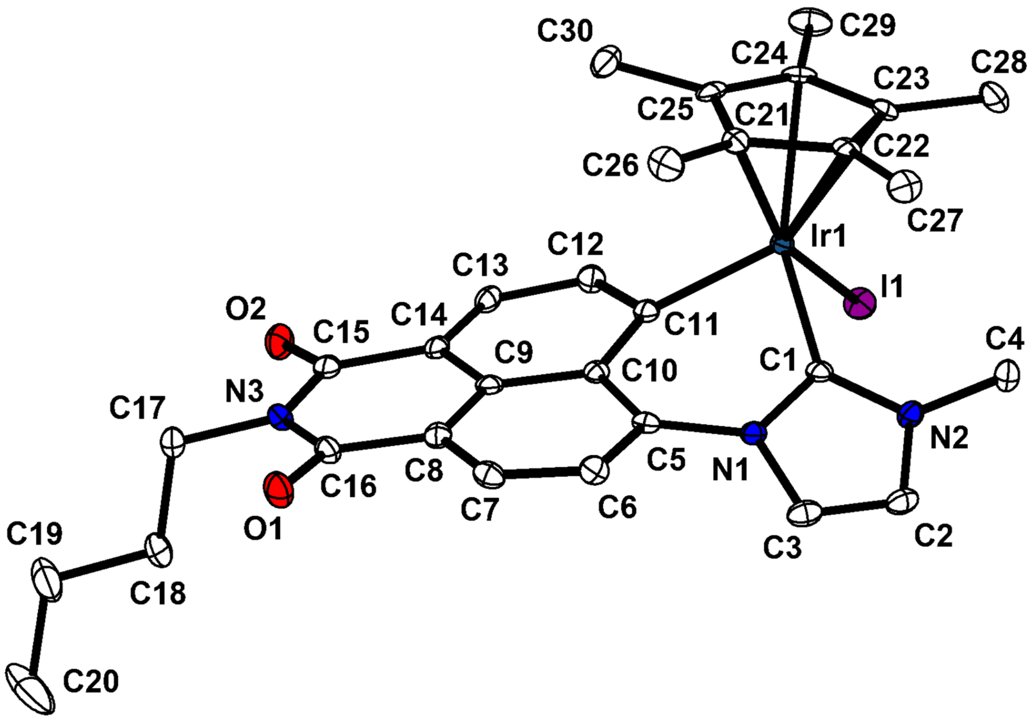


Figure 6. Molecular structure of (*S*)-**4** with thermal ellipsoids drawn at the 30% probability level, hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Ir1-I1 2.702(**1**), Ir1-C1 1.982(**5**), C1-N1 1.367(**6**), N1-C5 1.430(**6**), C5-C10 1.422(**7**), C10-C11 1.422(**7**), C11-Ir1 2.053(**4**), Ir1-C21 2.168(**5**), Ir1-C22 2.230(**5**), Ir1-C23 2.271(**4**), Ir1-C24 2.279(**4**), Ir1-C25 2.246(**4**), C1-Ir1-C11 86.6(**2**), Ir1-C1-N1 125.1(**3**), Ir1-C11-C10 121.0(**4**), C1-N1-C5 125.8(**4**), C11-C10-C5 123.8(**4**), and N1-C5-C10 119.7(**4**).

More recently, efforts were made to use strong donor NHC ligands [44,45] associated with helicene [31] or other elements of chirality to increase the configurational rigidity at the metal center with some success. Thus, our complexes presented in this work display only one stereogenic element of chirality. This is a rare example of chiral half-sandwich metal complexes displaying exceptional rigidity at the metal center. The data obtained from the determination of the free energy of enantiomerization confirm this behavior.

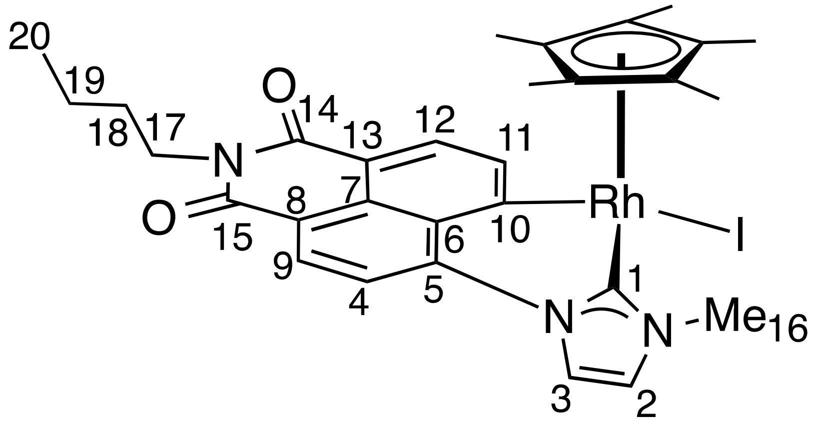
We feel this unique class of complexes owe their rigid configuration to the nature of the NI-NHC (CˆC:) ligand that acts as a clamp and strongly chelates the metal center. Moreover, the iodide ligand is known to act as a strong donor ligand but a weak-leaving group [46], which contributes to the robustness of the configuration at the metal center in these complexes. Therefore, our judicious choice to combine strongly NHC-chelating (CˆC:) ligands and iodide generate a novel class of chiral cyclometalated complexes with exceptional configuration at the metal center which might show interesting applications in a variety of fields, spanning from medical chemistry, organometallic catalysis to materials science.

3. Materials and Methods

General Synthetic Procedure

All synthetic manipulations were carried out under argon using Schlenk tube techniques. The ^{1}H and ^{13}C, and spectra were recorded in CD_2Cl_2 and CD_3CN using a Bruker Avance 400 and 300 NMR spectrometer at 400.13 and 100.61 and 76.31 MHz, respectively. The azolium salt [IMZ-NI-H][I] (**1**) was prepared according to our procedure published in the literature [47–49].

Synthesis of **2**. In a dry Schlenk tube, imidazolium salt (**1**) (150 mg, 0.33 mmol), $[Cp^{*}Rh(\mu Cl)Cl]_2$ (60 mg, 0.11 mmol), Cs_2CO_3 (82 mg, 0.253 mmol) and NBu_4I (243 mg, 0.66 mmol) were mixed in 15 mL of distilled and degassed acetonitrile, the solution was refluxed overnight. The resulting solution was cooled at r.t., filtered to remove a precipitate and washed with distilled acetonitrile. After evaporation of the solvents, the crude solid was purified by chromatography column (SiO_2) with a mixture of CH_2Cl_2/Acetone (99/1). The desired fractions were then concentrated to give product **2** as orange miscrocrystalline solid in 65% yield.

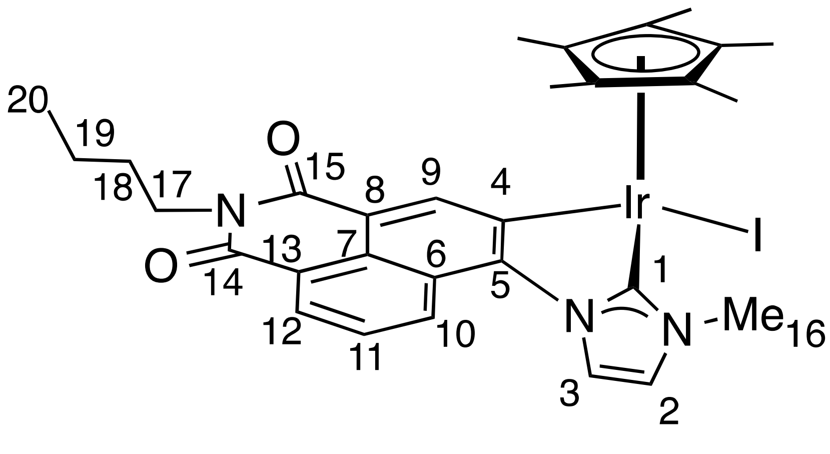


(2)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 8.0, 2.1 Hz, 2H, $H_{9,11napht}$), 8.21 (d, *J* = 7.8 Hz, 1H, $H_{12napht}$), 7.78 (d, *J* = 2.4 Hz, 1H, H_{3imid}), 7.65 (d, *J* = 8.0 Hz, 1H, H_{4napht}), 7.28 (q, *J* = 2.3 Hz, 1H, H_{2imid}), 4.20 (t, *J* = 7.7 Hz, 2H, H_{17}), 4.06 (d, *J* = 2.2 Hz, 3H, H_{16}), 1.76 (t, *J* = 8.2 Hz, 2H, H_{18}), 1.51 (s, 15H, CH_3 Cp*), 1.28 (m, 2H, H_{19}), 1.01 (m, *J* = 6.4, 5.7, 3.8 Hz, 3H, H_{20}).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.02 (C_{14}), 177.58 (C_{15}), 165.12 (C_1), 163.22 (C_{10}), 144.34 (C_{11}), 141.09 (C_5), 129.84 (C_9), 128.66 (C_6), 128.28 (C_7), 125.07 (C_2), 122.44 (C_8), 119.86 (C_3), 116.92 (C_{13}), 112.96 (C_4), 99.55 (*Cq* Cp*), 41.29 (C_{16}), 39.85 (C_{17}), 30.27 (C_{18}), 20.43 (C_{19}), 13.65 (C_{20}), 9.37 (CH_3 Cp*). Anal. calcd. for **2** C 51.67, H 4.77, N 6.03; Found: C 51.99, H 4.77, N 5.72.

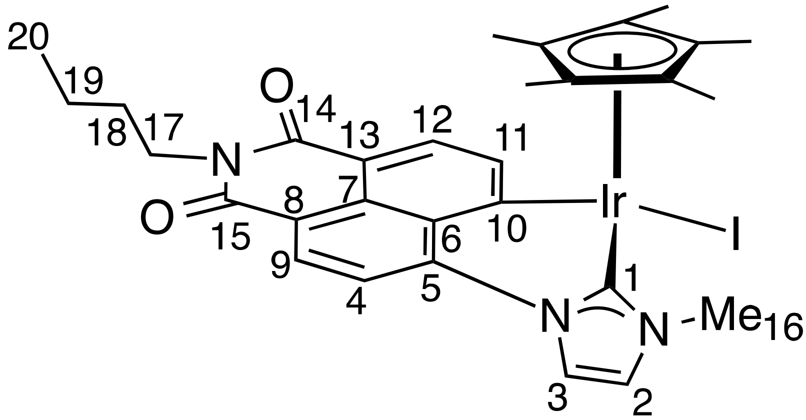
*Synthesis of **3** and **4***. In a dry Schlenk tube, imidazolium salt (**1**) (88 mg, 0.185 mmol), [Cp*Ir(μCl)Cl]$_2$ (50 mg, 0.061 mmol), Cs_2CO_3 (46 mg, 0.14 mmol) and NBu_4I (137 mg, 0.37 mmol) were mixed in 15 mL of distilled and degassed acetonitrile, the solution was refluxed overnight. The resulting solution was cooled at r.t., filtered to remove a precipitate and washed with distilled acetonitrile. After evaporation of the solvents, the crude solid was purified by chromatography column (SiO_2) with a mixture of CH_2Cl_2/Acetone (99/1). The desired fractions were then concentrated to give products **3** and **4** in almost 1/1 ratio.



(3)

3: A crystalline red powder. Yield 32 mg (33%).^{1}H NMR (500 MHz, $CDCl_3$)). *δ* 9.09 (s, 1H, $H_{9\ napht}$), 8.48 (dd, *J* = 8.7; 0.9 Hz, 1H, $H_{10\ napht}$), 8.45 (dd, *J* = 7.3; 0.9 Hz, 1H, $H_{12\ napht}$), 8.07 (d, *J* = 2.3 Hz, 1H, $H_{3\ imid}$), 7.71 (dd, *J* = 8.7, 7.3 Hz, 1H, $H_{11\ napht}$), 7.19 (d, *J* = 2.3 Hz, 1H, $H_{2\ imid}$), 4.23–4.15 (m, 2H, H_{17}), 3.98 (s, 3H, H_{16}), 1.96 (s, 15H, CH_3 Cp*), 1.76–1.70 (m, 2H, H_{18}), 1.50–1.42 (m, 2H, H_{19}), 0.98 (t, *J* = 7.4 Hz, 3H, H_{20})^{13}C NMR (125 MHz, Chloroform-*d*)

δ 169.4 (C_1), 165.0 (C_{14}), 164.3 (C_{15}), 145.9 (C_5), 143.4 (C_9), 142.3 (C_4), 128.0 (C_{12}), 127.0 (C_7), 125.8 (C_{11}), 125.3 (C_{10}), 123.5 (C_{13}), 122.2 (C_2), 120.0 (C_6), 118.8 (C_3), 117.9 (C_8), 93.0 (C_q.Cp*), 40.3 (C_{17}), 38.4 (C_{16}), 30.4 (C_{18}), 20.6 (C_{19}), 14.0 (C_{20}), 10.5 (CH_3.Cp*). Anal. calcd. for **3** C 45.74, H 4.35, N 5.21; Found: C 45.71, H 4.39, N 5.08.



(4)

4: A crystalline red powder. Yield 38 mg (39%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, J = 8.1 Hz, 1H, $H_{9\ napht}$), 8.38 (d, J = 7.8 Hz, 1H, $H_{11\ napht}$), 8.16 (d, J = 7.8 Hz, 1H, $H_{12\ napht}$), 7.69 (d, J = 2.3 Hz, 1H, $H_{3\ imid}$), 7.54 (d, J = 8.1 Hz, 1H, $H_{4\ napht}$), 7.22 (d, J = 2.3 Hz, 1H, $H_{2\ imid}$), 4.18–4.14 (m, 2H, H_{17}), 3.98 (s, 3H, H_{16}), 1.76–1.70 (m, 2H, H_{18}), 1.54 (s, 15H, CH_3 Cp*), 1.50–1.42 (m, 2H, H_{19}), 0.98 (t, J = 7.4 Hz, 3H, H_{20}). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4 (C_{14}), 163.8 (C_{15}), 158.5 (C_1), 158.4 (C_{10}), 145.5 (C_{11}), 141.6 (C_5), 130.2 (C_{12}), 129.8 (C_9), 128.5 (C_6), 128.3 (C_7), 124.0 (C_2), 122.2 (C_8), 118.8 (C_3), 116.5 (C_{13}), 112.8 (C_4), 93.7 (C_q.Cp*), 40.9 (C_{16}), 40.1 (C_{17}), 30.4 (C_{18}), 20.6 (C_{19}), 14.0 (C_{20}), 9.4 (CH_3.Cp*). Anal. calcd. for **4** C 45.74, H 4.35, N 5.21; Found: C 45.65, H 4.30, N 5.09.

X-ray crystal structure determination. A single crystal was selected, mounted and transferred into a cold nitrogen gas stream. Intensity data were collected with a Bruker Kappa-APEX2 system using micro-source Cu-Kα radiation. Unit-cell parameters determination, data collection strategy, integration and absorption correction were carried out with the Bruker APEX2 suite of programs. The structure was solved with SHELXT and refined anisotropically by full-matrix least-squares methods with SHELXL using WinGX. Absolute structure was determined by anomalous scattering effects analysis and chemical absolute configuration was then deduced. The structures were deposited at the Cambridge Crystallographic Data Centre with numbers CCDC 2,145,150 and 2,145,151 which can be obtained free of charge via www.ccdc.cam.ac.uk, accessed on 10 February 2022.

4. Conclusions

In this work, we reported a novel procedure to prepare half-sandwich piano stool complexes of rhodium and iridium. These complexes were resolved using chiral column chromatography into the corresponding enantiomers. The enantiomerization barrier was measured in acetonitrile and ethanol and was up to 124 kJ/mol at 60 °C. These data suggest that our compounds display rigid configuration at the metal center in solution. Our choice to combine a strong chelating (C^C:) ligand with a strong donor/weak-leaving iodide ligand [33,46] generates complexes with strong configuration at the metal center. Due to the presence of an organic chromophore, these complexes might be used to preparer novel luminescent materials or as photocatalysts; the results will be disclosed in due course.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/chemistry4010014/s1, Figure S1. 2D ROESY spectrum of 3 recorded in CDCl3; Figure S2. 2D ROESY spectrum of 4 recorded in $CDCl_3$; Resolution of complexes **2**, **3** and **4** on chiral stationary phase; UV-vis and CD spectra of complexes **2**, **3** and **4**; Determination of free energy of enantiomerisation performed in CH_3CN and EtOH.

Author Contributions: The synthesis and spectroscopic characterization of the new complexes were performed by A.G. and J.-P.T. The X-ray structural determination was carried out by G.G., M.J. and N.V. performed the chiral separation of the enantiomers and determined the optical rotation and CD spectra. All authors participated in the discussion. Preparation and writing of the manuscript were made by H.A., who also directed the project. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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