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Central (S) to Central (M = Ir, Rh) to Planar (Metallocene, M = Fe, Ru)

Chirality Transfer Using Sulfoxide Substituted Mesoionic Carbene

Ligands: Synthesis of Bimetallic Planar-Chiral Metallocenes

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Abstract:

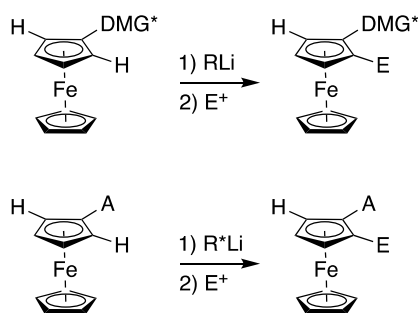
Enantiopure-bimetallic systems containing three different elements of chirality: a main group based chiral center (sulfur), a transition metal-chiral center (Rh, Ir) and a planar chiral element (ferrocene or ruthenocene) were prepared by a sequence of diastereoselective reactions. The chirality of the sulfur chiral center attached to the C5 of 1,2,3-triazolylidene mesoionic carbene ligand (MIC) coordinated to a metal (Ir, Rh), transfers in the formation of bimetallic complexes having a chiral at the metal center and a chiral planar metallocene, through C–H activation of the sandwich moiety (M = Fe,

Ru). The sense of the planar chirality formed in this sequence of reactions depends on the ligand of the achiral at the metal starting complex. The assignment of the configuration of these species has been achieved by a combination of X-ray-diffraction/CD measurements. The electrochemistry of these bimetallic species in coordinating solvents shows an equilibrium between the cationic complexes and the neutral species. The effect of the half sandwich moiety in the oxidation potentials of the system is remarkable, producing notable cathodic displacements. DFT calculations support these findings.

Introduction:

The study of processes of chirality transfer is essential in chemistry.¹ In this regard, the use of chiral sulfoxides in asymmetric synthesis and catalysis is nowadays well-established.² However, sulfoxides as chiral elements to achieve the preparation of chiral-at-metal complexes has been scarcely reported.³ Moreover, the use of these chirality elements to translate the chiral information to a metal center, with the concomitant generation of a planar chiral element is not known. On the other hand, the discovery of ferrocene in the early 1950s marked the beginning of modern organometallic chemistry.⁴ The special properties of ferrocenes have resulted in extensive applications in areas as diverse as optical and redox devices, electrochemical sensors, catalysts or drugs.⁵ In particular, chiral ferrocenes are relevant in asymmetric synthesis, materials science, etc.,⁶ and planar chiral ferrocenes, having an additional stereogenic center, are paramount among the best ligands for asymmetric catalysis.⁷ Thence, methods for introducing planar chirality into ferrocene derived compounds have been widely searched.⁸

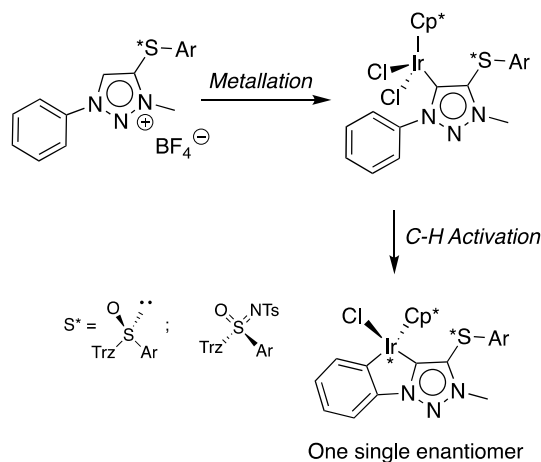
The preparation of planar chiral ferrocenes is achieved mainly by the diastereoselective *ortho*-lithiation of ferrocenes having chiral directing groups. The resulting products keep the additional element of symmetry. Alternatively, the enantioselective lithiation of ferrocene with chiral bases and the subsequent introduction of an electrophile have been extensively used (Scheme 1).⁹ More recently, the catalytic asymmetric C–H activation of the ferrocene moiety has been reported.¹⁰



Scheme 1. Enantioselective lithiation of monosubstituted ferrocenes.

Since its discovery, the interest in chiral-at-metal enantiomerically pure half-sandwich complexes has increased significantly¹¹ mainly due to their similarity with sp^3 -carbon chiral centres, which make them very attractive as chiral catalysts.^{11b,11f} Among the methods to prepare chiral-at-metal half-sandwich complexes, the sequence coordination of a chiral ligand followed by diastereoselective C–H insertion has been used.^{11d} With this purpose, chiral triazolilydene and imidazolylidene carbenes have been reported as ligands producing high levels of selectivity in the synthesis of Ru(III) and Ir(III) complexes.¹²

Pursuing our work in the use of 1,2,3-triazolilydene mesoionic carbenes (MICs) containing enantiopure sulfoxide moieties,¹³ we reported for the first time the use of these MICs in the preparation of enantiopure cyclometallated Ir(III) and Rh(III) half-sandwich complexes.^{3a} The process takes place through the sequence MIC coordination/enantioselective C–H activation (Scheme 2). Metallation to form five-membered metallacycles produce enantiomerically pure complexes, while the formation of the six-membered analogues is not totally diastereoselective.^{3a}



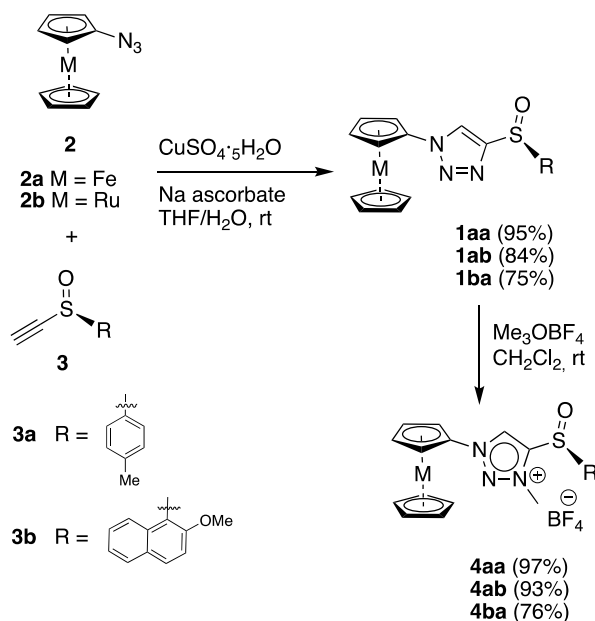
Scheme 2. Enantiopure half-sandwich Ir(III)-metallacycles.

In this regard, recently, Richards has reported the preparation of diastereomerically enriched ferrocene-based planar-chiral iridacycles using enantiopure ferrocenyl oxazolines.¹⁴—In fact, for example, the cycloiridation of an enantiopure (*S*)-valine-derived oxazoline resulted in the highly selective formation of one of the four possible diastereomers. The stereoelectronic effect derived from the iron-iridium interaction in a coordinatively unsaturated intermediate was the responsible of the high selectivity observed.^{14b} Being aware of these results we decide to study the influence of an enantiopure sulfinyl substituent attached to a 1,2,3-triazolyl MIC ligand in the diastereoselective generation of bimetallic complexes having a chiral at the metal half sandwich moiety and a planar chiral metallocene moiety.

Now we report the chirality transfer from an enantiomerically pure sulfoxide in the formation of bimetallic complexes having a chiral at the metal center and a chiral planar metallocene through C–H activation of the sandwich moiety (M = Fe, Ru). Depending on the nature of the ligands at the metal center (carbonate or chlorine) of the starting complex, complexes having identical configuration at the half-sandwich metal, but opposite configuration at the metallocene moiety are obtained. The structural characterization (CD/X-ray) of these new enantiopure hetero-bimetallic species will be thoroughly discussed.

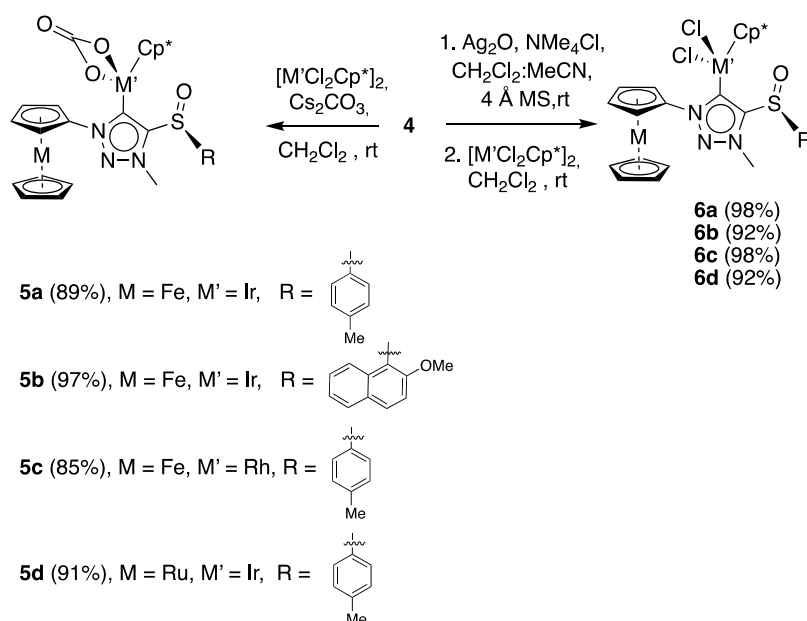
Results and discussion.

Enantiomerically pure sulfinyl triazoles **1** were prepared by reaction of the corresponding sandwich-azides **2** with enantiopure alkoxy sulfoxides **3** using the Cu(I)-catalysed Huisgen cycloaddition.¹⁵ Thus, treatment of azides **2** with alkynes **3**,¹⁶ in the presence of CuSO₄ and sodium ascorbate, in mixtures of THF/water at room temperature, yielded triazoles **1** in excellent yields (75-95%). Reaction of **1** with the Meerwein's salt in dichloromethane at room temperature yielded the corresponding triazolium salts **4** in 76%-97% yields (Scheme 3).^{13a}



Scheme 3. Preparation of enantiomerically pure metallocene derivatives **4**.

Metallation of triazole **4** by treatment with $[\text{M}'\text{Cl}_2\text{Cp}^*]_2$ ($\text{M}' = \text{Ir}, \text{Rh}$) in dichloromethane and in the presence of an excess of Cs_2CO_3 formed half-sandwich M' -carbenes **5**, having a carbonate ligand, in good yields (85-97%) (Scheme 4). In parallel, complexes **6** were obtained also in good yields (92-98%) by reaction of salts **4** with Ag_2O in the dark, followed by addition of $[\text{M}'\text{Cl}_2\text{Cp}^*]_2$ ($\text{M} = \text{Ir}, \text{Rh}$) (Scheme 4).

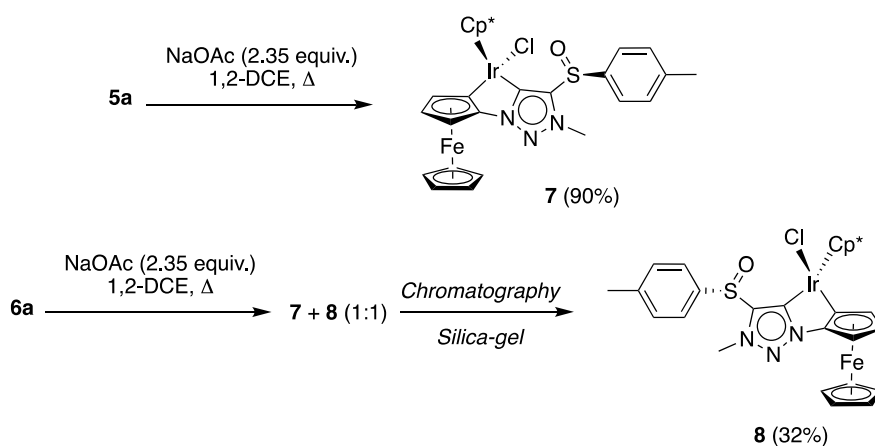


Scheme 4. Metallation of triazoles **4** with $[\text{M}'\text{Cl}_2\text{Cp}^*]_2$ ($\text{M}' = \text{Ir}, \text{Rh}$).

^1H and ^{13}C -NMR data for carbenes **5** and **6** are in accordance with the proposed structures (See Experimental Part). In particular, ^{13}C -NMR spectra for carbene complexes **5a-5d** are characterized by one signal at 161.6-168.0 ppm attributable to the

carbonate ligand.¹⁷ In addition, the Ir(III)-carbene carbon appeared at 163.9-159.5 ppm for **5a-b** and **5d**, while the Rh(III)-carbene carbon in **5c** appears as a doublet ($J_{\text{Rh-C}} = 55.3$ Hz) at 174.3 ppm, in accordance with previously reported chemical shifts for related complexes.^{17b-17d}

Next, the C-H activation of the sandwich fragment was attempted in carbonate complex **5a** and dichlorocarbene complex **6a**. Carbonate **5a** yielded, upon treatment with an excess of NaOAc in refluxing 1,2-dichloroethane, the planar-chiral ferrocene **7** (15:1 diastereomeric mixture, **being 8 the minor component**) that was isolated as a single diastereoisomer in 90% yield (Scheme 5). The structure of **7** was established on spectroscopic means. The ¹H NMR spectra showed three signals, one proton each, at 4.75 (dd), 4.45 (dd) and 4.34 (t) ppm attributable to the three hydrogens of the new 1,2-disubstituted Cp ring of the ferrocene moiety. In addition, the appearance of one signal at 86.3 ppm corresponding to a quaternary carbon was attributed to the ferrocene fragment, and it is in accordance with the new formed C-Ir bond.^{14c,18}



Scheme 5. Synthesis of enantiomerically pure complexes **7** and **8** by a chirality cascade transfer.

Crystals of bimetallic iridacycle **7** were grown from slow evaporation of a dichloromethane/pentane mixture. X-ray analysis confirmed the proposed structure and established the relative and absolute stereochemistry of the new chiral centres as (R_p,S) (Figure 1).¹⁹

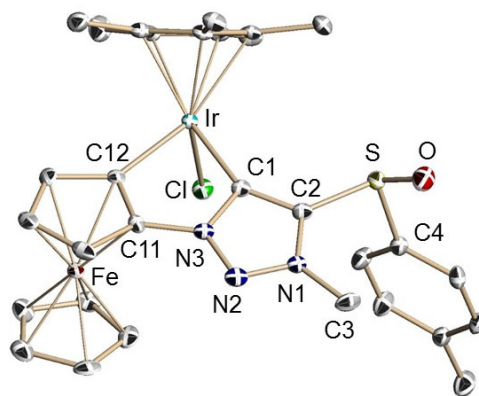


Figure 1. X-Ray of compound **7**. Selected bond lengths [Å] and angles [°]: Ir-C1 2.038(5), Ir-C12 2.066(5), Ir-Cl 2.412(2), C1-C2 1.382(7), C2-N1 1.374(6), N1-N2 1.319(6), N2-N3 1.328(6), N3-C1 1.392(6), N3-C11 1.406(7), N1-C3 1.465(6), C2-S 1.773(5), S-O 1.501(4), S-C4 1.798(5), C1-Ir-C12 78.9(2), C1-Ir-Cl 87.9(2), C12-Ir-Cl 93.9(2).

Analogously, dichloro-carbene complex **6a** was treated with NaOAc (Scheme 5). After 12 h of reaction in refluxing 1,2-dichloroethane a 1:1 mixture (^1H NMR) of complex **7** together with a new compound **8** was formed. Column chromatography of the mixture allowed the isolation of pure complex **8** in 32% yield, while bimetallic complex **7** could not be recovered. Attempts to improve the yield of compound **8** were unsuccessful. ^1H -NMR of complex **8** showed the same pattern of signals than complex **7** with some differences in the chemical shifts. Thus, one of the hydrogens of the 1,2-substituted ferrocene moves from 4.75 for **7** to 4.90 ppm for **8** and the methyl groups of the Cp* ligand from 1.78 to 2.01 ppm. Therefore, we presumed that both complexes could be diastereomers. The absolute stereochemistry of compound **8** could not be unambiguously established at this stage, but it was inferred using circular dichroism techniques.²⁰ The CD spectrum for carbene **7** (blue in the Figure 2) shows a weak negative Cotton effect around 470 nm, which is attributed to the ferrocene fragment,^{18,21} while the CD for derivative **8** shows positive Cotton effect at the same wavelength. We can conclude that derivatives **7** and **8** should have opposite absolute configurations at ferrocene centre. In addition, CD spectra for **7** and **8** showed negative Cotton effects at 207 and 250 nm for **7** and at 219 and 248 nm for **8**, meaning that both compounds should have the same absolute configuration at Ir-center.^{3a,22} Consequently, on the basis of the CD data and X-ray structure determination, complexes **7** and **8** are diastereomers having opposite configuration at the planar chiral element.²³ **The starting**

sulfoxide defined the configuration of the newly formed iridium-based stereogenic center, while the new element of planar chirality is formed with excellent to medium selectivity.

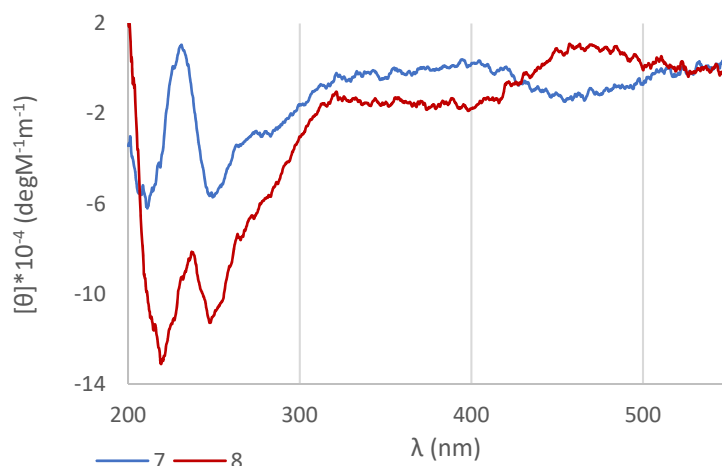
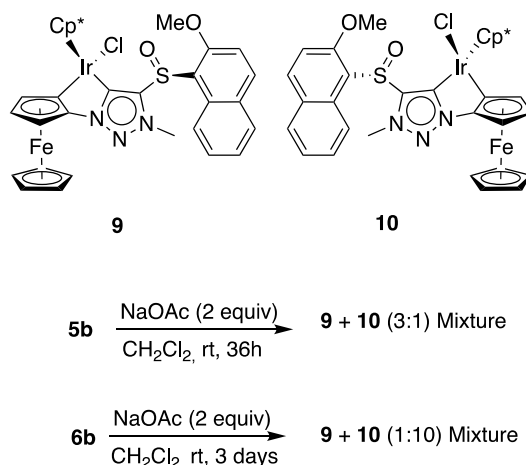


Figure 2. Circular Dichroism of carbene complexes **7** (blue) and **8** (red).

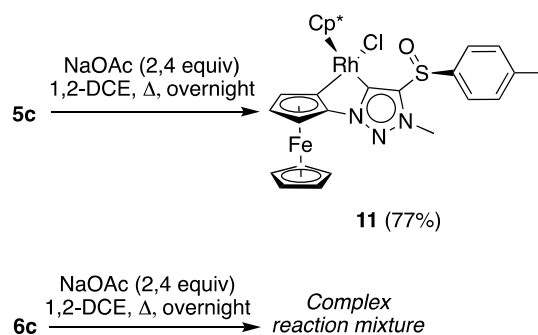
The influence of the steric volume of the substituent at the sulfoxide moiety on the stereoselectivity of the process was next studied. Reaction of complex **5b** with NaOAc in dichloromethane at room temperature²⁴ yielded two diastereomeric products **9** and **10** in a (3:1) ratio after 36 h of stirring (Scheme 6). Moreover, dichlorocarbene **6b** yielded a (2:3) mixture of the iridacycles **9** and **10** under the same reaction conditions. Additional stirring of this mixture for another 3 days, renders an inseparable (1:10) mixture of complexes **9** and **10**. ¹H-NMR data of this mixture suggests that compounds **9** and **10** are diastereoisomers, since the same pattern of signals is observed along the spectra of both complexes. Signals for hydrogens of the 1,2-disubstituted ferrocene Cp ring appeared at 4.89, 4.39 and 4.23 ppm for **10**, the major component of the mixture, while protons for the unsubstituted Cp ferrocene ring appeared at 3.96 ppm as a singlet, and the five methyl groups for the Cp* ligand at 2.00 ppm. Comparison of the chemical shifts of the protons assigned to the ferrocene fragment and to the Cp* ring for compound **10** with those of *p*-tolyl-substituted iridacycles **7** and **8**, suggested that complexes **10** and **8** may have the same absolute stereochemistry in their chiral elements.²⁵



Scheme 6. Synthesis chiral-planar carbenes **9** and **10**.

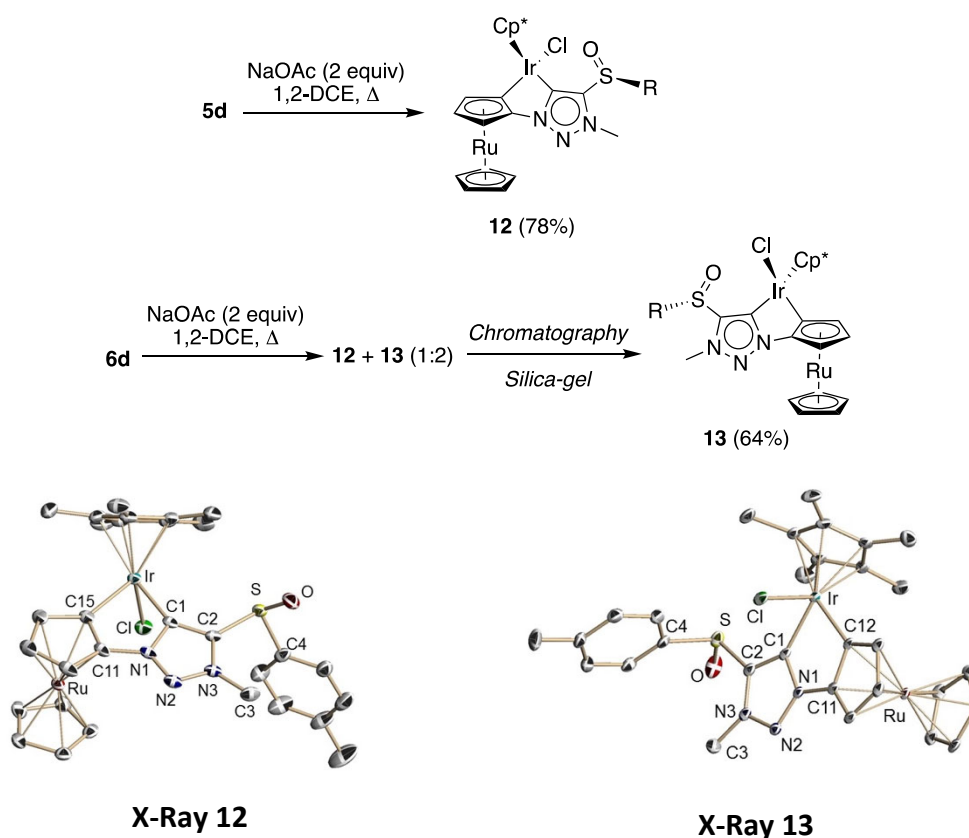
Therefore, substitution of the *p*-tolyl group at sulfur atom by the bulkier 2-methoxynaphthyl group is accompanied by a decrease in the stereoselectivity of the formation of the planar element of chirality (namely the ferrocene moiety) when carbonate complex **5b** is used, while the reaction of dichlorocarbene complex **6b** is more diastereoselective than the analogous process in the *p*-tolyl-substituted complex **6a**.

The synthesis of chiral-planar bimetallic ferrocene-rhodacycles was next addressed. Complex **5c** was reacted with NaOAc in refluxing 1,2-dichloroethane affording heterobimetallic rhodacycle **11** in 77% yield and as a single stereoisomer (Scheme 7). Comparison of the ¹H-NMR data for **11** with iridacycles **7** and **8** allows to conclude that **11** possesses the same configuration at the ferrocene and at the Rh(III) than iridacycle **7**.²⁶ Therefore, the stereochemical course of the C–H activation from carbonate complexes is the same in both Rh(III) and Ir(III) complexes. By contrast, Rh-dichlorocarbene **6c** produced only complex reaction mixtures upon treatment with NaOAc under analogous conditions (Scheme 7).



Scheme 7. The synthesis of enantiopure rhodacycle **11**.

Finally, to exemplify the generality of our procedure the preparation of chiral-planar bimetallic ruthenairidacycles was studied. Complexes **5d** and **6d** behave as their ferrocene counterparts. Thus, carbonate carbene **5d** formed the ruthenocene-iridacycle **12** in 78% isolated yield as a single reaction product (Scheme 8). On the contrary, Ir-dichlorocarbene **6d** yielded overnight a (1:2) mixture of iridacycles **12** and **13**. From this mixture we were able to isolate complex **13** in 64% yield. As in the case of bimetallic complex **7** (see above), ruthenocene **12** decomposes on silica-gel. The stereochemistry of both isomers **12** and **13** was assigned by comparison of their ¹H-NMR data with the data of the analogous ferrocene derivatives **7** and **8**. X-Ray analysis of bimetallic metallacycles **12** and **13** unambiguously confirmed this assignment, and by extension the assignation of the stereochemistry of ferrocene derivative **8** (see above).



Scheme 8. The stereodivergent synthesis of enantiopure planar-chiral bimetallic ruthenacycles **12** and **13**. Selected bond lengths [Å] and angles [°] for **12**: Ir-C1 2.013(4), Ir-C15 2.066(4), Ir-Cl 2.425(1), C1-C2 1.383(6), C2-N3 1.371(5), N1-N2 1.322(5), N2-N3

1.319(5), N1-C1 1.386(5), N1-C11 1.421(7), N3-C3 1.462(6), C2-S 1.763(4), S-O 1.489(4), S-C4 1.787(5), C1-Ir-C15 78.0(2), C1-Ir-Cl 85.7(1), C15-Ir-Cl 94.0(2). Selected bond lengths [Å] and angles [°] for **13**: Ir-C1 2.021(5), Ir-C12 2.061(4), Ir-Cl 2.424(2), C1-C2 1.390(7), C2-N3 1.364(6), N1-N2 1.323(5), N2-N3 1.329(5), N1-C1 1.376(6), N1-C11 1.414(7), N3-C3 1.457(6), C2-S 1.774(5), S-O 1.485(5), S-C4 1.792(5), C1-Ir-C12 78.3(2), C1-Ir-Cl 84.3(2), C12-Ir-Cl 84.9(2).

Once established the structure of the compounds prepared through this work, we investigated the interconversion between complexes **7** and **8**. Therefore, the chiral sulfur to metal center chirality transfer follows a pattern like the one reported recently by us.^{3a} The transfer of chirality involves the formation of the planar element of chirality, with the subsequent isomerization of the less stable (kinetic) diastereomer to the most stable one (thermodynamic diastereomer). This is consistent with the isolation of both diastereomers (having opposite configurations at the chiral-planar metallocene) during the formation of complexes **7** and **8** (see above) from **5a** and **6a**, respectively.

To shed some light into this isomerization, we carried out interconversion and deuteration experiments. Thus, complex **7** was heated in boiling 1,2-dichloroethane in the presence of NaOAc (Table 1). The product remained unaltered after 18 h. Conversion into its diastereomer **8** (having opposite configuration in the ferrocene chiral element) was not observed. Subsequently, enantiomerically pure complex **8** was reacted under similar conditions, rendering a (1:5) mixture of diastereomeric complexes **7** and **8** after 18 h of heating. Therefore, it can be concluded that complex **7** is the thermodynamic product. Similar experiments carried out with Ru-complex **12** afforded a (1:1) mixture of complexes **12** and **13**, while complex **13** formed a (1:10) mixture of **12** and **13**. Next, we carried out the interconversion of ruthenocenes **12** and **13** in deuterated solvents at room temperature. Pure complexes **12** and **13** afforded, upon dissolution in methanol-*d*₄, mixtures (2.5:1) and (6:1), respectively of these compounds. These mixtures evolved to (1:1) ratio from **12** and (1:2) from **13** after 6 additional hours (Table 1).²⁷

Table 1. Interconversion experiments of carbenes **7**, **8**, **12** and **13**.

<i>Compound</i>	<i>Solvent</i>	<i>Time (h)</i>	<i>Products (ratio)</i>
7	1,2-DCE ^a	18	7
8	1,2-DCE ^a	18	7+8 (1:5)

12	1,2-DCE ^a	18	12+13 (1:1)
13	1,2-DCE ^a	18	12+13 (1:10)
12	Methanol- <i>d</i> ₄ ^b	0 to 6	12+13 (2.5:1) to (1:1)
13	Methanol- <i>d</i> ₄ ^b	0 to 6	12+13 (6:1) to (1:2)
7	Acetonitrile- <i>d</i> ₃ ^c	0	7
8	Acetonitrile- <i>d</i> ₃ ^c	0	8
12	Acetonitrile- <i>d</i> ₃ ^c	0	12
13	Acetonitrile- <i>d</i> ₃ ^c	0	13

^{a)} Cyclometalated carbenes **7**, **8**, **12** and **13** were treated with NaOAc (2.35 equiv) in refluxing 1,2-dichloroethane. ¹H NMR of the crude mixtures were recorded in CDCl₃.

^{b)} ¹H NMR samples were prepared by dissolving 7 mg of carbenes **12** or **13** in methanol-*d*₄.

^{c)} Samples of carbenes **7**, **8**, **12** and **13** were prepared dissolving 10 mg, 10 mg, 9 mg and 7 mg, respectively, in 0.5 mL of deuterated solvent. Final ¹H NMR spectra were obtained in CDCl₃.

Interconversion experiments were also carried out in CD₃CN, a coordinating solvent. Upon dissolution of complex **7** at room temperature two products were detected. The ¹H NMR spectra is congruent with a mixture of starting material **7** and the cationic complex derived from the interchange of a Cl-ligand with CD₃CN.²⁸ Upon removal of the solvent, complex **7** was recovered unaltered (See SI). Similar behavior was observed for ruthenocene **12**, while the degree of conversion for complexes **8** and **13** was lower.

We can conclude from these experiments that cyclometallated complexes **8**, **12** and **13** interconvert in solution in non-coordinating solvents. Ru-complexes **12** and **13** are more prone to isomerize than their Fe-counterparts.²⁹ However, in the presence of more coordinating solvents like MeCN the formation of the putative cationic intermediates hampered the inversion of the configuration of the planar-chiral element.

Finally, we submitted complexes **5a** and **6a** to the C-H activation reaction in deuterated 1,2 dichloroethane. Thus, complex **5a** was treated in boiling 1,2-dichloroethane-*d*₄ in the presence of NaOAc. After 2.5 hours complete conversion into complex **7** was observed, and no deuterium incorporation was not detected in **7** (¹H NMR). In parallel, complex **6a** was treated under analogous conditions yielding a (1:1) mixture of carbenes **7** and **8**. Deuteration was not observed either (¹H NMR). Moreover, treatment of complex **8** in boiling 1,2-dichloroethane-*d*₄ for 18 hours shows no deuteration (partial decomposition of **8** was detected without formation of complex **7**). Similar results were obtained when complex **8** was stirred at 50 °C in CDCl₃ containing methanol-*d*₄. These facts suggest that hydrogen transfer from the solvent did not occur either during the cyclometallation step or during the isomerization.

The electrochemical properties of complexes **7** and **8** were finally studied (Figure 3 and Table 2). Bimetallic complex **7** shows two quasi-reversible oxidation waves at $E_{1/2} = 0.19$ and 0.39 V; and two irreversible waves at $E_{pa} = 0.82$ V and 0.99 V. Analogously, complex **8** shows two quasi-reversible oxidation waves at $E_{1/2} = 0.26$ V and 0.39 V and one irreversible wave at $E_{pa} = 1.19$ V. Complexes **5a** and **6a** show single quasi-reversible oxidation waves at $E_{1/2} = 0.70$ and 0.69 V attributable to Fe(II)–Fe(III) process, respectively, and the additional irreversible oxidative wave at $E_{pa} = 1.25$ V and $E_{pa} = 1.23$ V, attributable to the Ir(III)-Ir(IV) oxidation, respectively.³⁰ Compared with the standard Fe(II)-Fe(III) oxidation of ferrocene in MeCN ($E_{1/2} = 0.97$ V),³¹ the Fe(II)-Fe(III) process in complexes **5a** and **6a** becomes much easier, owing to a combined inductive and delocalization effect caused by the MIC-Ir-half-sandwich.³²

The apparition of two strongly cathode-displaced half-waves in complexes **7** and **8** between 0.19 V and 0.39 V instead of the single wave observed in complexes **5a** and **6a** pointed to the existence of an equilibrium between closed complexes **7** and **8** and the corresponding cationic complexes in MeCN.²⁸ This equilibrium is congruent with NMR data (see above) and discard that formation of cationic complexes stem from electrochemical oxidation. The first oxidation wave at 0.19 V and 0.26 V can be attributed to the Fe(II)-Fe(III) oxidation in the cationic complex to yield the corresponding cation-radicals; the second wave at 0.39 V should be assigned the reversible oxidation Fe(II)-Fe(III) oxidation in the neutral complexes **7** and **8**, again to yield the corresponding cation-radicals. Finally, the irreversible Ir(III)-Ir(IV) oxidation of the cationic species appears anodically shifted regarding to the standard apparition of these waves.³²

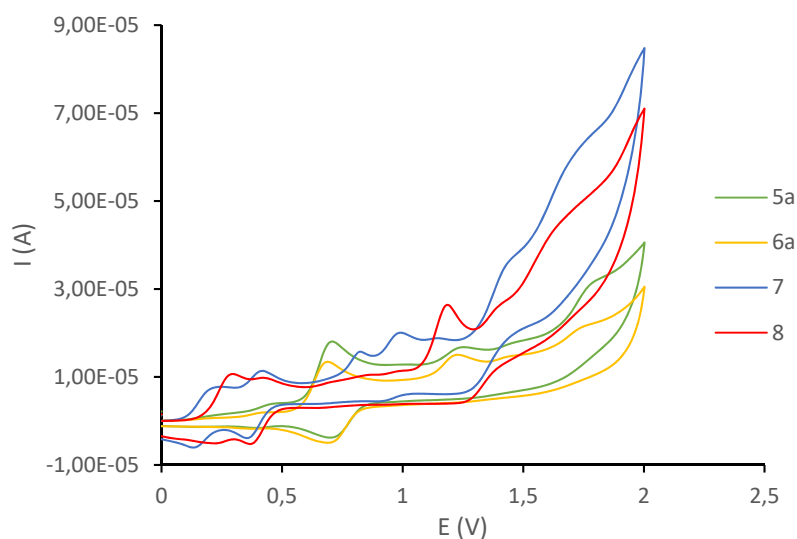


Figure 3. CVs obtained in MeCN for complexes **5a**, **6a**, **7** and **8** obtained in the conditions indicated in Table 1.

Table 2. CV data for compounds **5a**, **6a**, **7** and **8**.^a

Compound	Epa1	Epc1	$\Delta E1$	$E_{1/2}$	Epa2	Epc2	$\Delta E2$	$E_{1/2}$	Epa3	Epa4
5a	0.71	0.70	0.002	0.70	1.25	-	-	-	-	-
6a	0.69	0.69	0.002	0.69	1.23	-	-	-	-	-
7 (MeCN)	0.24	0.13	0.11	0.19	0.42	0.35	0.07	0.39	0.82	0.99
7 (DCM)	0.29	0.13	0.16	0.21	1.25	-	-	-	-	-
8 (MeCN)	0.30	0.22	0.08	0.26	0.42	0.37	0.06	0.39	1.19	-
8 (DCM)	0.41	0.10	0.30	0.25	1.41	-	-	-	-	-

^a) Data obtained from 1×10^{-3} M in the indicated solvents, containing 0.1 M $[N(nBu)_4]PF_6$ as supporting electrolyte at 20 °C. Data are given in V. Counter-electrode: Pt; working electrode: Glassy Carbon; Reference electrode: Ag/AgCl; scan rate: 100 mV/s.

To support these hypotheses, we repeated the electrochemistry of complexes **7** and **8** in a low coordinating solvent like dichloromethane (DN = 1, compared with DN = 14.1 for MeCN)³³ (Figure 4). Now complexes **7** and **8** show a single quasi-reversible oxidation wave at $E_{1/2} = 0.21$ V and 0.25 V, respectively, and one irreversible wave at Epa = 1.25 and 1.41 V, respectively. These results obtained in a non-coordinating solvent coupled together with the data obtained from NMR,²⁸ support the hypothesis of the existence

of cationic species in more coordinating solvents like MeCN which are responsible for the apparition of two waves in the electrochemistry of complexes **7**, **8**, **12** and **13** (see SI).

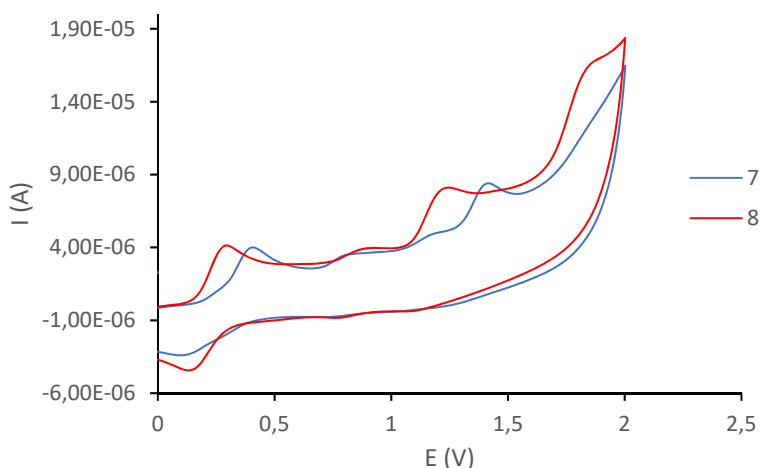


Fig. 4. Data obtained from 10⁻³ M 1,2-dichloroethane solutions, containing 0.1 M [N(nBu)₄]PF₆ as supporting electrolyte at 20 °C. Data are given in V. Counter-electrode: Pt; working electrode: Glassy Carbon; Reference electrode: Ag/AgCl; scan rate: 100 mV/s.

DFT calculations (B3LYP-D3/6-31G**&LANL2DZ/PCM-Cl₂C₂H₄) were performed to assist in the understanding of the electrochemistry of complexes **7**, **8**, **12** and **13**. The starting coordinates were taken from X-ray diffraction data of complex **7**. The HOMO in complex **7** is clearly shared by the ferrocene and the irida-segment, while the HOMO of the **7**⁺ is associated to the iridacycle with nearly nil contribution of the ferrocene fragment (Figure 5). Therefore, we may conclude that the first oxidation wave can be associated with Fe(II)-Fe(III) oxidation with a strong contribution for the Ir-moiety, which explains the cathodic shift observed in this wave, while the second wave (from **7**⁺ to **7**²⁺) is associated with the Ir(III)-Ir(IV) oxidation.

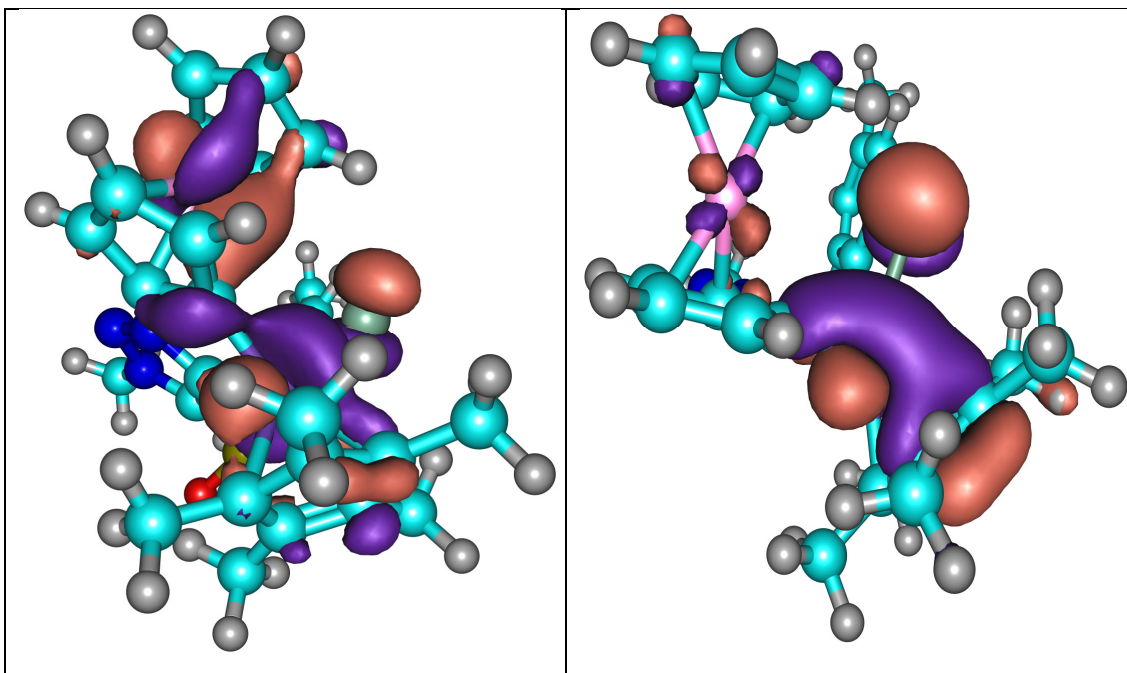


Figure 5. HOMO orbitals of **7** (left) and **7⁺** (right).

Conclusions.

The cyclometallation of ferrocene-containing enantiomerically pure half-sandwich metallacycles is an efficient entry to enantiopure-bimetallic systems containing three different elements of symmetry: a main group based chiral center (sulfur); a transition metal-chiral center (Rh, Ir) and a planar chiral element (ferrocene or ruthenocene). The generation these elements of symmetry is achieved by the concomitant formation of the half sandwich chiral at the metal moiety, and of the chiral-planar element at the metallocene moiety. Thus, beginning with an easily available sulfur chiral center attached to a MIC, prepared through a standard Cu-catalyzed alkyne-azide cycloaddition, trimetallic enantiopure compounds containing three chiral elements are easily available. Depending on the nature of the ligands at the metal center (carbonate or chlorine) of the starting complex, complexes having the same configuration at the half-sandwich metal, but opposite configuration at the metallocene moiety were obtained. The assignment of the configuration of these species has been achieved by a combination of X-ray-diffraction/CD measures.

In addition, an inversion process in the planar chiral element (that may occur in an intramolecular way) has been uncovered. Although much remains to be done to fully

understand these processes, deuteration and interconversion experiments rule out the possibility of the participation of open species in this isomerization processes.

Finally, electrochemistry of these bimetallic species has shown the formation of cationic and neutral complexes in coordinating solvents. This fact has been also determined by NMR experiments that show that the formation of cationic species is reversible. DFT calculations show the strong delocalization effect caused by a MIC-Ir-half-sandwich cyclometallated complex resulting in a strong cathodic displacement of the oxidation waves of the cyclometallated species.

Overall, the possibility of using a chiral sulfoxide to achieve the sequential preparation of enantiopure bimetallic complexes is demonstrated. Efforts to fully understand the underlying mechanisms of stereo-discrimination as well as to understand the isomerization processes in the chiral planar systems are now underway.

Experimental Section.

General methods.

Unless noted otherwise, all manipulations were carried out under an argon atmosphere using standard Schlenk techniques. CH₃CN, THF and dichloromethane were dried by passage through solvent purification columns containing activated alumina. Other solvents were HPLC grade and were used without purification. All reagents were obtained from commercial sources and used without additional purification, unless noted otherwise. Flash column chromatography was performed using silica gel (Merck, n° 9385, 230-400 mesh). ¹H and ¹³C NMR spectra were recorded at 300, 400 or 500 MHz (¹H NMR) and at 75 or 100 MHz (¹³C NMR) using CDCl₃ as solvent with the residual solvent signal as internal reference (CDCl₃, 7.26 and 77.2 ppm). The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), and br s (broad singlet). High-resolution mass spectrometry (HRMS) by the ESI technique was performed with an Agilent 6500 accurate mass apparatus with a Q-TOF analyser. IR spectra were recorded on a Perkin-Elmer 681 spectrophotometer. Optical rotations were measured on a Jasco P-2000 polarimeter using a sodium lamp. Melting points were determined on a Koffler block.

The products tend to decompose in solution, making it difficult to perform NMR with

good quality, the signals start being very broad and undefined. To fix this, the crude product can be filtered in AcOEt through a small pad of SiO₂, where the decomposed fraction will be retained. If the product is very polar, precipitations can be made using dichloromethane/pentane, separating the decomposed fraction as the solid, and the proper product as the supernatant.

Computational details: Geometry optimizations without symmetry constraints were carried out by using the Gaussian 16 suite of programs³⁴ using the B3LYP functional³⁵ in conjunction with the D3 dispersion correction suggested by Grimme,³⁶ and the 6-31G** basis set for the C, H, N, O, S, and Cl atoms and LANL2DZ effective core potential for Fe and Ir. All structures were fully optimized in Cl₂C₂H₄ as the solvent and using the polarizable continuum model (PCM) method.³⁷

General procedure for the synthesis of 1,2,3-triazoles.

Ferrocenyl/ruthenocenyl azide (1.00 equiv) and alkyne (1.00 equiv), were dissolved in THF and water. Then, a solution of CuSO₄·5H₂O (1.00 equiv) in water and a solution of sodium ascorbate (2.00 equiv) in water were added. The reaction mixture was stirred at rt overnight. THF was removed under vacuum, and dichloromethane and an aqueous solution of ammonia (15%) were added. The mixture was stirred for 10 min. The organic phase was washed with water and brine and filtered through a Celite pad. The solvent was removed under vacuum. The crude product was purified by column chromatography (SiO₂) to afford the pure triazole.

Compound (S)-1aa.

Ferrocenyl azide **2a** (323 mg, 1.03 mmol, 1.05 equiv) and alkyne **3a** (223.7 mg, 0.99 mmol, 1.00 equiv), were dissolved in THF (17.0 mL) and water (6.0 mL). Then, a solution of CuSO₄·5H₂O (246 mg, 0.99 mmol, 1.00 equiv) in water (6.0 mL) and a solution of sodium ascorbate (390 mg, 1.97 mmol, 2.00 equiv) in water (4.0 mL) were added. Flash chromatography (SiO₂ hexanes/AcOEt 3:2) yielded **1aa** as an orange-brown solid (368 mg, 95%).

¹H NMR (400 MHz, CDCl₃): δ 8.03 (s, 1H, N₃C=CH), 7.69 (d, *J* = 7.9 Hz, 2H, Ar *p*-tol), 7.34 (d, *J* = 7.9 Hz, 2H Ar *p*-tol), 4.83 (b s, *J* = 2.8, 1.4 Hz, 1H, Fc), 4.75 (b s, 1H, Fc), 4.27 (b s, 2H, Fc), 4.20 (s, 5H, Fc), 2.40 (s, 3H, CH₃ *p*-tol). ¹³C NMR (101 MHz, CDCl₃): δ 153.2 (C, N₃C=CH), 142.3 (C, *p*-tol), 140.1 (C, *p*-tol), 130.3 (2CH, Ar *p*-tol), 124.9 (2CH, Ar *p*-tol),

123.5 (CH, N₃C=CH), 93.3 (C, Fc), 70.5 (5CH, Fc), 67.3 (CH, Fc), 67.1 (CH, Fc), 62.7 (CH, Fc), 62.5 (CH, Fc), 21.6 (CH₃, *p*-tol). **IR (KBr):** ν_{max} 3433, 1084, 817 cm⁻¹. $[\alpha]_{\text{D}}^{25} = + 228.44$ (*c* 0.68, CHCl₃). **HRMS (ESI) *m/z*** calculated for C₁₉H₁₈FeN₃OS: 392.0515[M+H]⁺; found 392.0510. **Mp:** 103-106 °C.

General procedure for the synthesis of triazolium salts.

Triazole (1.00 equiv) and Meerwein's salt (1.30 equiv) were stirred under argon at rt in dichloromethane until complete consumption of the starting material (TLC analysis). The reaction was quenched with some drops of methanol. The solvent was removed under *vacuum* and the resulting residue was solved in the minimum amount of dichloromethane and precipitated with Et₂O. The solvents were decanted, the solid was washed with Et₂O (x3) and vacuum-dried to yield the corresponding pure reaction products.

Compound (S)-4aa

Overnight treatment of triazole **1aa** (200 mg, 0.51 mmol, 1.00 equiv) with Meerwein's salt (113.4 mg, 0.77 mmol, 1.30 equiv) in dichloromethane (15.0 mL), afforded pure **4aa** as a red-brown solid (245 mg, 97%).

¹H NMR (400 MHz, CDCl₃): δ 8.41 (s, 1H, N₃C=CH), 7.83 (d, *J* = 7.9 Hz, 2H, Ar *p*-tol), 7.46 (d, *J* = 7.7 Hz, 2H, Ar *p*-tol), 5.18 (b s, 2H, Fc), 4.53 (b s, 7H, Fc), 4.32 (s, 3H, N-CH₃), 2.45 (s, 3H, CH₃ *p*-tol). **¹³C NMR** (101 MHz, CDCl₃): δ 146.5 (C, N₃C=CH), 144.6 (C, *p*-tol), 135.1 (C, *p*-tol), 131.2 (2CH, Ar *p*-tol), 129.7 (CH, N₃C=CH), 125.4 (2CH, Ar *p*-tol), 92.1 (C, Fc), 72.2 (5CH, Fc), 69.7 (2CH, Fc), 64.3 (2CH, Fc), 39.7 (CH₃, N-CH₃), 21.6 (CH₃, *p*-tol). **IR (KBr):** ν_{max} 3107, 1518, 1492, 1222, 1105, 1084, 1051, 1030, 876, 808 cm⁻¹. $[\alpha]_{\text{D}}^{25} = - 76.87$ (*c* 0.66, CHCl₃). **HRMS (ESI) *m/z*** calculated for C₂₀H₂₀FeN₃OS: 406.0671 [M]⁺; found 406.0677. **Mp:** 176-178 °C.

General procedure for the synthesis of iridium and rhodium carbenes.

Method 1.

To a solution of triazolium salt (1.00 equiv) in dichloromethane, [MCl₂Cp*]₂ (M= Ir, Rh) (0.50 equiv) and Cs₂CO₃ (5.00 equiv) were added. The reaction mixture was stirred at rt overnight (¹H NMR analysis). It was filtered through Celite and the volatiles were removed under *vacuum* to afford the reaction products.

Method 2.

In a flask charged with 4 Å molecular sieves, a mixture of triazolium salt (1.00 equiv),

NMe₄Cl (1.50 equiv) and Ag₂O (0.75 equiv) in CH₃CN/dichloromethane (1:10 v/v) was stirred at rt in the dark until the complete formation of the silver carbene (¹H NMR analysis). The mixture was filtered through a pad of celite and the volatiles were removed. The residue was dissolved in dichloromethane and stirred at rt with the corresponding metallic compound, [MCl₂Cp*]₂ (M= Ir, Rh) (0.50 equiv) until completion of the reaction (¹H NMR analysis). The reaction mixture was filtered through Celite and the volatiles were removed under vacuum to afford the reaction products.

Compound (S)-5a.

¹H NMR (500 MHz, CDCl₃): δ 8.03 (d, *J* = 8.2 Hz, 2H, Ar *p*-tol), 7.40 (d, *J* = 8.0 Hz, 2H, Ar *p*-tol), 5.77 (bs, 1H, ferroc), 4.60 (bs, 1H, ferroc), 4.27 (b s, 1H, ferroc), 4.24 (s, 5H, ferroc), 4.23 (overlapped, 1H, ferroc), 3.88 (s, 3H, N-CH₃), 2.38 (s, 3H, CH₃ *p*-tol), 1.54 (s, 15H, 5CH₃ Cp*). ¹³C NMR (126 MHz, CDCl₃): δ 167.9 (C, C=O, CO₃²⁻), 163.5 (C, N₃C=Clr), 148.0 (C, N₃C=Clr), 141.6 (C, *p*-tol), 136.4 (C, *p*-tol), 130.5 (2CH, Ar *p*-tol), 126.2 (2CH, Ar *p*-tol), 96.5 (C, Fc), 86.3 (5C, Cp*), 70.9 (5CH, Fc), 68.7 (CH, Fc), 67.5 (CH, Fc), 66.8 (CH, Fc), 66.5 (CH, Fc), 38.1 (CH₃, N-CH₃), 21.5 (CH₃, *p*-tol), 9.5 (5CH₃, Cp*). IR (KBr): ν_{max} 2921, 1659, 1634, 1610, 1384, 1079, 1043, 823 cm⁻¹. [α]_D²⁵ = + 32.03 (c 0.49, CHCl₃). HRMS (ESI) *m/z* calculated for C₃₀H₃₄FeIrN₃OS: 365.5687 [M]⁺²; found 365.5696. Mp: Decomposes before melting.

Compound (S)-6a.

Following general method 2, treatment of triazolium salt **4aa** (100 mg, 0.20 mmol, 1.00 equiv) with NMe₄Cl (33 mg, 0.30 mmol, 1.50 equiv) and Ag₂O (35 mg, 0.15 mmol, 0.75 equiv) in CH₃CN/dichloromethane (1:10 mL) for 14h, followed by reaction with [IrCl₂Cp*]₂ (80 mg, 0.10 mmol, 0.50 equiv) for additional 4h, afforded pure **6a** as an orange solid (158 mg, 98%).

¹H NMR (400 MHz, CDCl₃): δ 8.05 (d, *J* = 8.4 Hz, 2H, Ar *p*-tol), 7.31 (d, *J* = 8.6 Hz, 2H, Ar *p*-tol), 6.39 (br s, 1H, Fc), 4.43 (br s, 1H, Fc), 4.25 (s, 5H, Fc), 4.26 (overlapped, 2H, Fc), 3.74 (s, 3H, N-CH₃), 2.40 (s, 3H, CH₃ *p*-tol), 1.49 (s, 15H, 5 CH₃ Cp*). ¹³C NMR (101 MHz, CDCl₃): δ 159.0 (C, N₃C=Clr), 151.1 (C, N₃C=Clr), 141.3 (C, *p*-tol), 138.3 (C, *p*-tol), 129.8 (2CH, Ar *p*-tol), 127.3 (2CH, Ar *p*-tol), 96.9 (C, Fc), 89.5 (5C Cp*), 70.9 (CH, Fc), 70.7 (5CH, Fc), 69.2 (CH, Fc), 66.9 (CH, Fc), 66.5 (CH, Fc), 38.3 (CH₃, N-CH₃), 21.4 (CH₃, *p*-tol), 9.2 (5CH₃, Cp*) IR (KBr): ν_{max} 2916, 1450, 1333, 1035, 813 cm⁻¹ [α]_D²⁵ = - 12.75 (c 0.67,

CHCl₃). **HRMS** (ESI) *m/z* calculated for C₃₀H₃₄ClFeIrN₃OS: 768.1077 [M-Cl]⁺; found 768.1078. **Mp**: Decomposes before melting

General procedure for the synthesis of iridium and rhodium cyclometallated carbenes.

A solution of iridium or rhodium carbene (1.00 equiv) was treated under argon with solid NaOAc (2.35 equiv) in dichloromethane or 1,2-dichloroethane, as specified, until completion of the reaction (¹H NMR analysis). The reaction mixture was filtered through a pad of celite and the solvent was removed under vacuum to afford reaction products. When needed, the resulting crude product was purified by silica gel chromatography.

Compound (S_s,S_{Ir},R_p)-7.

A solution of iridium carbene **5a** (100 mg, 0.126 mmol, 1.00 equiv) was treated overnight with solid NaOAc (25 mg, 0.30 mmol, 2.35 equiv) in refluxing 1,2-dichloroethane, yielding **7** as a red solid (87 mg, 90%).

¹H NMR (500 MHz, CDCl₃): δ 8.02 (d, *J* = 8.3 Hz, 2H, Ar *p*-tol), 7.38 (d, *J* = 8.0 Hz, 2H, Ar *p*-tol), 4.75 (dd, *J* = 2.2, 0.9 Hz, 1H, Fc), 4.45 (dd, *J* = 2.3, 0.9 Hz, 1H, Fc), 4.34 (t, *J* = 2.2 Hz, 1H, Fc), 4.22 (s, 5H, Fc), 3.84 (s, 3H, N-CH₃), 2.41 (s, 3H, CH₃ *p*-tol), 1.78 (s, 15H, 5CH₃ Cp*). ¹³C NMR (126 MHz, CDCl₃): δ 156.6 (C, N₃C=Clr), 143.9 (C, N₃C=Clr), 141.5 (C, *p*-tol), 137.5 (C, *p*-tol), 130.4 (2CH, Ar *p*-tol), 125.7 (2CH, Ar *p*-tol), 101.3 (C, Fc), 90.7 (5C, Cp*), 86.3 (C, Fc), 69.6 (5CH, Fc), 69.3 (CH, Fc), 66.1 (CH, Fc), 54.5 (CH, Fc), 38.0 (CH₃, N-CH₃), 21.5 (CH₃, *p*-tol), 9.7 (5CH₃, Cp*). **IR (KBr)**: ν_{max} 2914, 1451, 1106, 1082, 1049, 816 cm⁻¹. **[α]²⁵_D** = + 38.28 (*c* 0.67, CHCl₃). **HRMS** (ESI) *m/z* calculated for C₃₀H₃₃FeIrN₃OS: 732.1318 [M-Cl]⁺; found 732.1338. **Mp**: Decomposes before melting.

Compound (S_s,S_{Rh},R_p)-11.

A solution of rhodium carbene **5c** (200 mg, 0.28 mmol, 1.00 equiv) was treated overnight with solid NaOAc (54 mg, 0.66 mmol, 2.35 equiv) in refluxing 1,2-dichloroethane, yielding **11** as a red solid (147 mg, 77%).

¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, *J* = 8.3 Hz, 2H, Ar *p*-tol), 7.37 (d, *J* = 8.2 Hz, 2H, Ar *p*-tol), 4.81 (dd, *J* = 2.2, 0.9 Hz, 1H, Fc), 4.59 (dd, *J* = 2.2, 0.9 Hz, 1H, Fc), 4.29 (t, *J* = 2.3 Hz, 1H, Fc), 4.19 (s, 5H, Fc), 3.88 (s, 3H, N-CH₃), 2.40 (s, 3H, CH₃ *p*-tol), 1.70 (s, 15H, 5CH₃ Cp*). ¹³C NMR (101 MHz, CDCl₃): δ 174.6 (C, d, *J* = 51.0 Hz, N₃C=CRh), 145.2 (C, d, *J* = 2.7 Hz, N₃C=CRh), 141.6 (C, *p*-tol), 137.5 (C, *p*-tol), 130.4 (2CH, Ar *p*-tol), 125.7 (2CH, Ar *p*-tol), 102.8 (C, d, *J* = 42.2 Hz, Fc), 100.8 (C, Fc), 97.30 (5C, d, *J* = 5.4 Hz, Cp*), 70.5 (CH, Fc),

70.3 (5CH, Fc), 65.8 (CH, Fc), 55.1 (CH, Fc), 38.1 (CH₃, N-CH₃), 21.5 (CH₃, *p*-tol), 9.9 (5CH₃, Cp*). **IR (KBr):** ν_{\max} 2914, 1447, 1082, 1049, 816 cm⁻¹. **[α]²⁵_D** = - 161.96 (*c* 0.10, CHCl₃). **HRMS (ESI) *m/z*** calculated for C₃₀H₃₃FeN₃ORhS: 642.0744 [M-Cl]⁺; found 642.0730. **Mp:** Decomposes before melting.

Compound (S_S,S_{Ir},R_p)-12.

A solution of iridium carbene **5d** (100 mg, 0.12 mmol, 1.00 equiv) was treated overnight with solid NaOAc (24 mg, 0.28 mmol, 2.35 equiv) in refluxing 1,2-dichloroethane, yielding **12** as an orange solid (75 mg, 78%).

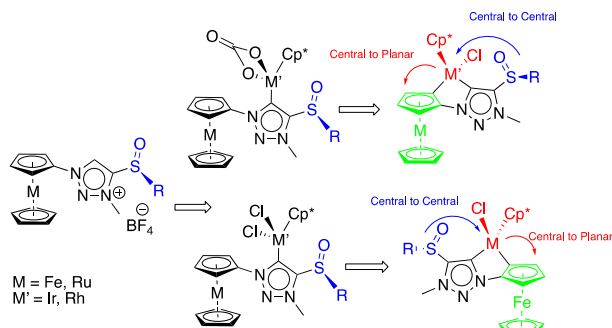
¹H NMR (300 MHz, CDCl₃): δ 7.93 (d, *J* = 8.4 Hz, 2H, Ar *p*-tol), 7.35 (d, *J* = 8.1 Hz, 2H, Ar *p*-tol), 5.14 (d, *J* = 2.2 Hz, 1H, Rc), 4.83 (d, *J* = 2.1 Hz, 1H, Rc), 4.59 (s, 5H, Rc), 4.58 (overlapping, 1H, Rc), 3.80 (s, 3H, N-CH₃), 2.40 (s, 3H, CH₃ *p*-tol), 1.83 (s, 15H, 5CH₃ Cp*). **¹³C NMR** (75 MHz, CDCl₃): δ 156.4 (C, N₃C=Clr), 143.7 (C, N₃C=Clr), 141.5 (C, *p*-tol), 137.4 (C, *p*-tol), 130.3 (2CH, Ar *p*-tol), 125.7 (2CH, Ar *p*-tol), 105.1 (C, Rc), 90.7 (5C, Cp*), 89.9 (C, Rc), 72.2 (CH, Rc), 71.2 (5CH, Rc), 68.1 (CH, Rc), 56.9 (CH, Rc), 38.0 (CH₃, N-CH₃), 21.5 (CH₃, *p*-tol), 9.8 (5CH₃, Cp*). **IR (KBr):** ν_{\max} 2918, 2005, 1449, 1369, 1048, 815 cm⁻¹. **[α]²⁵_D** = - 146.04 (*c* 0.18, CHCl₃). **HRMS (ESI) *m/z*** calculated for C₃₀H₃₃IrN₃ORuS: 778.1014 [M-Cl]⁺; found 778.1016. **Mp:** 160-163 °C.

Crystallographic data: The crystallographic details concerning the structures of **7**, **12** and **13** are in the supporting information. Deposition Numbers 1914377-1914379 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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²⁵ ¹H-NMR of derivative **8** showed signals at 4.90, 4.44 and 4.38 ppm, for the 1,2-disubstituted Cp ring, and at 4.05 ppm for the unsubstituted one. Additionally, the methyls of the Cp* ring appeared at 2.01; while for compound **7** shifts are: 4.75, 4.45 and 4.34; 4.22 and 1.78 ppm, respectively.

²⁶ In particular chemical shifts for the *p*-tolyl, the 1,2-disubstitued ferrocene Cp ring and for the Cp* ligand for **11** showed a very good coincidence with shifts for **7**. CD measurements support this assignation (see Figure S1). See Supporting Information.

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