

η^6 -Hexahelicene Complexes of Iridium and Ruthenium.

Running along the Helix

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Abstract: The first η^6 -complexes of Iridium and Ruthenium coordinated to helicenes have been obtained. Hexahelicene (**1**), 2,15-dimethylhexahelicene (**2**) or 2,15-dibromohexahelicene (**3**) reacts with $[\text{Cp}^*\text{IrCl}_2]_2$ and AgBF_4 in CD_3NO_2 to afford quantitatively the complexes $[\text{Cp}^*\text{Ir}(\eta^6\text{-1})][\text{BF}_4]_2$ (**4A**), $[\text{Cp}^*\text{Ir}(\eta^6\text{-2})][\text{BF}_4]_2$ (**5A**) or $[\text{Cp}^*\text{Ir}(\eta^6\text{-3})][\text{BF}_4]_2$ (**6A**) respectively. In all cases, the final thermodynamic products are similar, and they present coordination between the 12 e^- fragment $[\text{IrCp}^*]^{2+}$ and the terminal ring of the helicene. Monitoring the reaction by NMR shows formation of intermediates, some of them have been fully characterized in solution. These intermediates exhibit the metal fragment coordinated to the internal rings. We have also synthesized the bimetallic complex $[(\text{Cp}^*\text{Ir})_2(\mu_2\text{-}\eta^6\text{:}\eta^6\text{-2})][\text{BF}_4]_4$ (**7**), achieving, at most, coordination between two units $[\text{IrCp}^*]^{2+}$ and the

helicene **2**. Following an analogous methodology, we have prepared the complex $[(\eta^6\text{-cymene})\text{Ru}(\eta^6\text{-2})][\text{BF}_4]_2$ (**8**) which has been studied by X-ray diffraction confirming the preferential binding to the terminal aromatic ring.

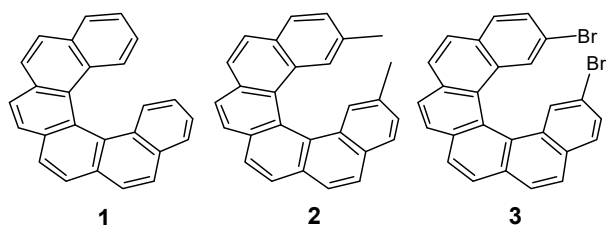


Chart 1

Introduction

Helicenes are a class of polycyclic aromatic molecules with ortho-fused aromatic rings. These organic compounds were long considered as academic curiosities because of their twisted shape due to repulsive steric interactions between terminal rings.¹ In fact, they represent an attractive class of compounds with a fascinating three-dimensional structure and exceptional optical² and electronic³ properties. Perhaps, the most remarkable feature is their inherent chirality, therefore, they have raised attention during years considering potential use as asymmetric catalysts.⁴ This is due to the helicenes have a stereogenic axis which could present left or right handed chiral helical structures with M (-) or P (+) configuration, respectively.⁵ Additionally, these nonplanar condensed aromatics compounds have been employed for molecular recognition,⁶ liquid crystal synthesis⁷ or in material science.⁸ The hexahelicene (**1**) was obtained by Newman and Lednicer in 1956.⁹ Since this first discovery, the synthesis of this helical compounds has been developed significantly from the classical preparation by the oxidative photocyclization of bis(stilbene)s¹⁰ to other non-radiative methodologies.¹¹

In this article, we describe the η^6 -coordination between 12 e⁻ metal fragments $[\text{IrCp}^*]^{2+}$ or $[\text{Ru}(\eta^6\text{-cymene})]^{2+}$ and [6]helicene (**1**) or 2,15-disubstituted [6]helicenes (2,15-dimethylhexahelicene (**2**), 2,15-dibromohexahelicene (**3**)). The η^6 -bis(arene) complexes of p-cymene ruthenium or η^6 -arene complexes of cyclopentadienyl iridium have been widely studied.¹² The coordination of the $[\text{Ru}(\eta^6\text{-cymene})]^{2+}$

fragment to coronene and other polyaromatics compounds has been described.¹³ The preparation of η^6 -polyaromatics complexes is simpler when condensed rings are completely planar and it is also known that the presence of alkyl substituents on the arene facilitates this coordination. Therefore, only a few and exotic examples present this binding type in nonplanar polyaromatic compounds, fundamentally buckybowls derivatives.¹⁴ Particularly interesting are the works of Angelici and co-workers which led to the preparation of η^6 -corannulene complexes.^{14cgh} In such study, they reported the synthesis and structure of a dimetallated buckybowl which presents the coordination of two $12 e^-$ metal fragment $[\text{RuCp}^*]^+$ to each side of corannulene, thereby increasing the flattening of the molecule. There are several structural differences between coronene, corannulene, and helicene. Coronene or [6]circulene is a polyaromatic organic molecule formed by the condensation of six benzene rings presenting a totally planar structure, while corannulene and helicenes show a lack of planarity exhibiting a three dimensional structures (Figure 1). The flattening in nonplanar polyaromatic compounds can be evaluated by the π -orbital axis vector (POAV) analysis,¹⁵ showing that corannulene has a more strained structure than helicenes. Therefore it is reasonable to assume that η^6 -helicenes complexes are more stable and more robust than their corannulene analogues. However, there are no reported examples which present η^6 -coordination complexes to helicenes. For all these reasons, we have considered attractive to explore the chemistry of these η^6 -hexahelicene complexes.

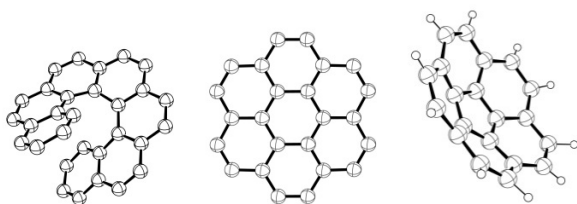


Figure 1. Structures of heptahelicene (left), coronene (middle) and corannulene (right)

Experimental section

General considerations. Synthetic procedures were carried out under an inert atmosphere of nitrogen, in dry solvents (by passage through alumina columns in an IT Solvent Purification System and degassed with N_2), using standard Schlenk techniques, unless otherwise noted. Solution NMR spectra

were obtained on a Bruker AV-400 or a Varian MR 400 spectrometers, using CD₃NO₂ as the solvent, internal lock, and internal reference (δ 4.33 (¹H) 62.8 (¹³C)). For a correct assignment of NMR signals should be noted that the metal fragment is bonded to A, B or C ring as showed in the Figure 2. Crystal evaluation and data collection of **8** were performed on an Oxford Diffraction Supernova diffractometer, equipped with an Atlas CCD area detector and a four-circle kappa goniometer. Elemental analyses were performed on a Perkin-Elmer 2400B CHN analyzer. All reagents and solvents were reagent grade and were used without further purification unless otherwise specified. Nitromethane-d³ (CD₃NO₂) was purchased from Aldrich and subjected to three freeze-pump-thaw cycles before use. Hexahelicene (**1**),¹⁶ 2,15-dimethylhexahelicene (**2**)^{16a,17} and 2,15-dibromohexahelicene (**3**)¹⁸ were prepared according to the literature procedures and the spectral data in agreement with them.

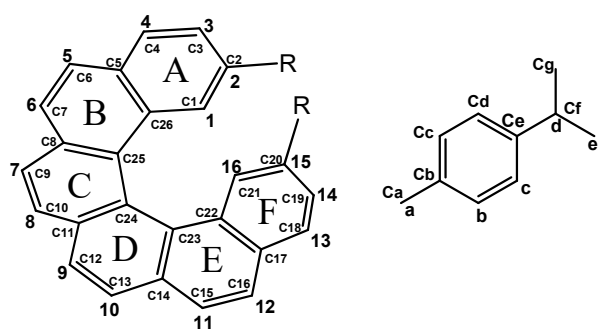


Figure 2. Atom labeling schemes for the cymene and hexahelicene ligands.

Synthesis. [Cp*Ir(η^6 -**1**)] [BF₄]₂ (**4A**). To a flask containing [Cp*IrCl₂]₂ (6.1 mg, 0.008 mmol), **1** (5.0 mg, 0.015 mmol) and an excess of AgBF₄ (19.5 mg, 0.100 mmol) was added CD₃NO₂ (1 ml). The solution was stirred for 1 hour at room temperature, and the AgCl precipitate was removed by filtration. The resulting solution was transferred by cannula to NMR tube for monitoring. The reaction was completed 15 days after and the solution formed was evaporated to dryness under vacuum obtained an orange precipitate of **4A**. This reaction is nearly quantitative by NMR spectroscopy. ¹H NMR (400 MHz, CD₃NO₂, 298 K): δ 8.88 (d, ³J(H,H) = 9.0 Hz, 1H, H6), 8.65 (d, ³J(H,H) = 8.2 Hz, 1H, H8), 8.39 (d, ³J(H,H) = 8.2 Hz, 1H, H7), 8.35 (d(AB system), ³J(H,H) = 8.3 Hz, 1H, H9 or H10), 8.33 (d(AB system), ³J(H,H) = 8.3 Hz, 1H, H10 or H9), 8.21 (d(AB system), ³J(H,H) = 8.6 Hz, 1H, H11 or H12),

8.19 (d(AB system), $^3J(\text{H,H}) = 8.6$ Hz, 1H, H12 or H11), 8.11 (dd, $^3J(\text{H,H}) = 8.0$ Hz and $^5J(\text{H,H}) = 1.0$ Hz, 1H, H13), 7.97 (d, $^3J(\text{H,H}) = 9.0$ Hz, 1H, H5), 7.96 (d, $^3J(\text{H,H}) = 6.1$ Hz, 1H, H4), 7.75 (d, $^3J(\text{H,H}) = 8.5$ Hz, 1H, H16), 7.51 (m, 1H, H14), 7.43 (d, $^3J(\text{H,H}) = 6.7$ Hz, 1H, H1), 7.32 (m, 1H, H3), 7.05 (m, 1H, H15), 6.58 (m, 1H, H2), 1.51 (s, 15H, Cp*). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CD_3NO_2 , 298 K): δ 140.80 (C7), 136.30 (C11), 136.03 (C10), 135.97 (C8), 134.79 (C14), 134.29 (C17), 131.92 (C12 or C13), 131.46 (C15 or C16), 130.49 (C18), 129.51 (C22), 129.09 (C9), 128.90 (C12 or C13), 128.45 (C21), 128.43 (C2), 128.37 (C1), 127.92 (C15 or C16), 126.23 (C23), 125.42 (C24), 123.66 (C6), 122.12 (C25), 111.39 (C26), 105.27 (C_5Me_5), 100.32 (C5), 98.14 (C3), 96.50 (C4), 95.03 (C2), 90.48 (C1), 8.91 (C_5Me_5). Anal. Calcd for $\text{C}_{36}\text{H}_{31}\text{B}_2\text{F}_8\text{Ir}$: C, 52.13; H, 3.77. Found: 52.17; H 3.88.

Low-temperature studies of the reaction between $[\text{Cp}^\text{IrCl}_2]_2$, AgBF_4 and **1**.* To a flask containing **1** (5.0 mg, 0.015 mmol), $[\text{Cp}^*\text{IrCl}_2]_2$ (6.1 mg, 0.008 mmol) and an excess of AgBF_4 (19.5 mg, 0.100 mmol) was added CD_3NO_2 (1 ml) slowly in a bath at -78°C . The resulting solution was filtrated and transferred by cannula to NMR tube. The characterization could be performed by low temperature NMR experiments exhibiting the formation of three isomers, **4A**, **4B** and **4C**. ^1H NMR (400 MHz, CD_3NO_2 , 253 K, **4A**): δ 8.85 (d, $^3J(\text{H,H}) = 9.0$ Hz, 1H, H6), 8.63 (d, $^3J(\text{H,H}) = 8.2$ Hz, 1H, H8), 8.39 (d, $^3J(\text{H,H}) = 8.2$ Hz, 1H, H7), 8.34 (s(AB system), 2H, H9 and H10), 8.22 (s(AB system), 2H, H11 and H12), 8.12 (d, $^3J(\text{H,H}) = 8.0$ Hz, 1H, H13), 7.96 (d, $^3J(\text{H,H}) = 9.0$ Hz, 1H, H5), 7.95 (d, $^3J(\text{H,H}) = 6.1$ Hz, 1H, H4), 7.76 (d, $^3J(\text{H,H}) = 8.5$ Hz, 1H, H16), 7.52 (m, 1H, H14), 7.44 (d, $^3J(\text{H,H}) = 6.7$ Hz, 1H, H1), 7.30 (m, 1H, H3), 7.05 (m, 1H, H15), 6.57 (m, 1H, H2), 1.47 (s, 15H, Cp*). ^1H NMR (400 MHz, CD_3NO_2 , 253K, **4B**): δ 8.95 (d, $^3J(\text{H,H}) = 9.0$ Hz, 1H, H6), 8.80 (d, $^3J(\text{H,H}) = 8.5$ Hz, 1H, H8), 8.64 (d, $^3J(\text{H,H}) = 8.2$ Hz, 1H, H7), 8.32 (d(AB system), $^3J(\text{H,H}) = 8.6$ Hz, 1H, H12), 8.31 (d(AB system), $^3J(\text{H,H}) = 8.6$ Hz, 1H, H9 or H10), 8.29 (d(AB system), $^3J(\text{H,H}) = 8.6$ Hz, 1H, H10 or H9), 8.22 (d(AB system), $^3J(\text{H,H}) = 8.6$ Hz, 1H, H11), 8.19 (d, $^3J(\text{H,H}) = 8.0$ Hz, 1H, H13), 8.18 (d, $^3J(\text{H,H}) = 9.0$ Hz, 1H, H5), 8.09 (d, $^3J(\text{H,H}) = 6.3$ Hz, 1H, H4), 7.66 (d, $^3J(\text{H,H}) = 8.5$ Hz, 1H, H16), 7.62 (d, $^3J(\text{H,H}) = 7.0$ Hz, 1H, H1), 7.47 (m, 2H, H3 and H14), 6.92 (m, 2H, H2 and H15), 1.53 (s, 15H, Cp*). ^1H NMR (400 MHz, CD_3NO_2 , 253K, **4C**): δ 8.72 (d, $^3J(\text{H,H}) = 8.8$ Hz, 1H, H10), 8.59 (d, $^3J(\text{H,H}) = 8.2$ Hz, 1H, H12), 8.57

(d, $^3J(\text{H,H}) = 8.5$ Hz, 1H, H5), 8.25 (d, $^3J(\text{H,H}) = 8.2$ Hz, 1H, H11), 8.17 (d, $^3J(\text{H,H}) = 8.5$ Hz, 1H, H4), 8.16 (d, $^3J(\text{H,H}) = 8.8$ Hz, 1H, H9), 8.15 (d, $^3J(\text{H,H}) = 8.0$ Hz, 1H, H13), 8.04 (s(AB system), 2H, H7 and H8), 7.91 (d, $^3J(\text{H,H}) = 8.5$ Hz, 1H, H6), 7.59 (m, 1H, H3), 7.54 (m, 1H, H14), 7.25 (d, $^3J(\text{H,H}) = 7.5$ Hz, 1H, H1), 7.20 (d, $^3J(\text{H,H}) = 9.0$ Hz, 1H, H16), 7.06 (m, 1H, H2), 6.99 (m, 1H, H15), 1.43 (s, 15H, Cp*). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CD_3NO_2 , 253 K): 140.7 (C6, **4C**), 139.1 (C7, **4A**), 138.4 (C7, **4B**), 137.3, 136.5 (C16, **4C**), 136.3 (C13, **4C**), 135.7, 135.6 (C10, **4B**), 134.7, 134.5, 134.4 (C10, **4A**), 133.7, 133.2, 132.8, 132.7, 132.0, 131.3 (C3, **4C**), 130.5 (C9, **4B**), 130.2 (C12 or C13, **4A**), 129.9 (C18, **4B**), 129.6 (C15 or C16, **4A**), 129.2, 128.9 (C2, **4C**), 128.8 (C18, **4A**), 128.0, 127.9 (C19, **4C**), 127.7 (C9, **4A**), 127.6 (C12 or C13, **4B**; C16, **4B**), 127.5 (C1, **4C**), 127.4 (C15 or C16, **4A**), 127.3 (C12 or C13, **4A**), 126.9 (C21, **4A**; C15, **4C**), 126.8 (C15, **4B**), 126.7 (C20, **4A**; C12 or C13, **4B**; C20, **4C**), 126.6 (C21, **4B**), 126.5 (C21, **4C**), 126.3 (C19, **4A**), 125.7 (C6, **4B**), 124.8, 123.9, 123.7 (C3 or C19, **4B**), 123.3, 123.1, 122.4 (C6, **4A**), 120.6, 118.8 (C7, **4C**), 118.7, 115.21 (C2 or C15, **4B**), 109.5, 108.3, 104.6 (C_5Me_5 , **4B**), 103.6 (C_5Me_5 , **4A**), 102.5 (C_5Me_5 , **4C**), 99.6, 98.8, 98.1 (C3 or C19, **4B**), 96.7 (C3, **4A**), 95.6 (C4, **4B**; C2 or C20 **4B**), 95.3 (C9 or C10, **4C**), 94.9 (C4, **4A**), 93.5 (C2, **4A**), 91.3 (C9 or C10, **4C**), 88.8 (C1, **4A**), 88.7 (C1, **4B**), 7.6 (C_5Me_5 , **4B**), 7.4 (C_5Me_5 , **4A**), 6.9 (C_5Me_5 , **4C**). Some carbon atoms of isomer **4C** could not be detected.

$[\text{Cp}^*\text{Ir}(\eta^6\text{-2})][\text{BF}_4]_2$ (**5A**). To a flask containing $[\text{Cp}^*\text{IrCl}_2]_2$ (5.6 mg, 0.007 mmol), **2** (5.0 mg, 0.014 mmol) and an excess of AgBF_4 (19.5 mg, 0.100 mmol) was added CD_3NO_2 (1 ml). The solution was stirred for 1 hour at room temperature, and the AgCl precipitate was removed by filtration. The resulting solution was transferred by cannula to NMR tube for monitoring. The reaction was completed 6 days after and the solution formed was evaporated to dryness under vacuum obtained an orange precipitate of **5A**. This reaction is nearly quantitative by NMR spectroscopy. ^1H NMR (400 MHz, CD_3NO_2 , 298 K): δ 8.88 (d, $^3J(\text{H,H}) = 8.9$ Hz, 1H, H6), 8.68 (d, $^3J(\text{H,H}) = 8.2$ Hz, 1H, H8), 8.39 (d, $^3J(\text{H,H}) = 8.2$ Hz, 1H, H7), 8.35 (d(AB system), $^3J(\text{H,H}) = 8.3$ Hz, 1H, H9 or H10), 8.34 (d(AB system), $^3J(\text{H,H}) = 8.3$ Hz, 1H, H10 or H9), 8.18 (d(AB system), $^3J(\text{H,H}) = 8.6$ Hz, 1H, H11 or H12), 8.13 (d(AB system), $^3J(\text{H,H}) = 8.6$ Hz, 1H, H12 or H11), 8.03 (d, $^3J(\text{H,H}) = 8.2$ Hz, 1H, H13), 7.93 (d, $^3J(\text{H,H}) = 8.9$ Hz, 1H, H5),

7.87 (d, $^3J(\text{H,H}) = 6.4$ Hz, 1H, H4), 7.51 (s, 1H, H16), 7.43 (d, $^3J(\text{H,H}) = 8.2$ Hz, 1H, H14), 7.31 (s, 1H, H1), 7.20 (d, $^3J(\text{H,H}) = 6.4$ Hz, 1H, H3), 2.07 (s, 3H, 2-Me), 1.97 (s, 3H, 15-Me), 1.51 (s, 15H, Cp*). Due to the poor solubility of **5** in CD₃NO₂, we were unable to obtain satisfactory ¹³C {¹H} NMR spectrum. Anal. Calcd for C₃₈H₃₅B₂F₈Ir: C, 53.22; H, 4.11. Found: 53.05; H 4.00.

[Cp*Ir(η^6 -**3**)](BF₄)₂ (**6A**). To a flask containing [Cp*IrCl₂]₂ (4.1 mg, 0.005 mmol), **3** (5.0 mg, 0.010 mmol) and an excess of AgBF₄ (19.5 mg, 0.100 mmol) was added CD₃NO₂ (1 ml). The solution was stirred for 1 hour at room temperature, and the AgCl precipitate was removed by filtration. The resulting solution was transferred by cannula to NMR tube for monitoring. The reaction was completed 14 days after and the solution formed was evaporated to dryness under vacuum obtained an orange precipitate of **6A**. This reaction is nearly quantitative by NMR spectroscopy. ¹H NMR (400 MHz, CD₃NO₂, 298 K): δ 8.95 (d, $^3J(\text{H,H}) = 9.0$ Hz, 1H, H6), 8.72 (d, $^3J(\text{H,H}) = 8.2$ Hz, 1H, H8), 8.44 (d, $^3J(\text{H,H}) = 8.2$ Hz, 1H, H7), 8.40 (d(AB system), $^3J(\text{H,H}) = 8.4$ Hz, 1H, H9 or H10), 8.38 (d(AB system), $^3J(\text{H,H}) = 8.4$ Hz, 1H, H10 or H9), 8.24 (s(AB system), 2H, H11 and H12), 8.09 (d, $^3J(\text{H,H}) = 8.6$ Hz, 1H, H13), 8.06 (d, $^3J(\text{H,H}) = 6.6$ Hz, 1H, H4), 8.04 (d, $^3J(\text{H,H}) = 9.0$ Hz, 1H, H5), 7.80 (d, $^4J(\text{H,H}) = 1.8$ Hz, 1H, H16), 7.72 (dd, $^3J(\text{H,H}) = 6.6$ Hz and $^4J(\text{H,H}) = 1.8$ Hz, 1H, H3), 7.71 (dd, $^3J(\text{H,H}) = 8.6$ Hz and $^4J(\text{H,H}) = 1.5$ Hz, 1H, H14), 7.64 (d, $^4J(\text{H,H}) = 1.5$ Hz, 1H, H1), 1.54 (s, 15H, Cp*). ¹³C {¹H} NMR (100 MHz, CD₃NO₂, 298 K): δ 141.5 (C7), 137.2 (C10), 136.8, 136.5, 135.7, 133.1, 132.7 (C18), 132.2 (C12 or C13), 131.7 (C19), 131.3 (C15 or C16), 131.1 (C21), 130.6, 129.9 (C12 or C13), 129.4 (C9), 128.8 (C15 or C16), 125.5, 124.5, 123.3 (C6), 122.1, 120.4, 112.8, 106.4 (C₅Me₅), 101.6 (C3), 98.9, 97.2, 96.3 (C4), 92.8 (C1), 8.54 (C₅Me₅). Quaternary carbons of helicene could not be assigned. Anal. Calcd for C₃₆H₂₉B₂Br₂F₈Ir: C, 43.80; H, 2.96. Found: 43.62; H 3.05.

Intermediate [Cp*Ir(η^6 -**3**)](BF₄)₂ (**6C**). To a flask containing **3** (5.0 mg, 0.010 mmol), [Cp*IrCl₂]₂ (4.1 mg, 0.005 mmol) and an excess of AgBF₄ (19.5 mg, 0.100 mmol) was added CD₃NO₂ (1 ml) slowly in a bath at -78°C. The resulting solution was filtrated and transferred by cannula to NMR tube. The characterization of intermediate **6C** could be performed by low temperature NMR studies on a Bruker AV400 spectrometer. ¹H NMR (400 MHz, CD₃NO₂, 253 K): δ 8.78 (d, $^3J(\text{H,H}) = 8.6$ Hz, 1H, H10),

8.66 (d, $^3J(\text{H,H}) = 8.5$ Hz, 1H, H12), 8.62 (d, $^3J(\text{H,H}) = 9.0$ Hz, 1H, H5), 8.32 (d, $^3J(\text{H,H}) = 8.5$ Hz, 1H, H11), 8.25 (d, $^3J(\text{H,H}) = 8.6$ Hz, 1H, H9), 8.19 (d, $^3J(\text{H,H}) = 8.6$ Hz, 1H, H4), 8.14 (d, $^3J(\text{H,H}) = 8.5$ Hz, 1H, H13), 8.13 (d(AB system), $^3J(\text{H,H}) = 6.5$ Hz 1H, H7 or H8), 8.10 (d(AB system), $^3J(\text{H,H}) = 6.5$ Hz 1H, H8 or H7), 7.99 (d, $^3J(\text{H,H}) = 9.0$ Hz, 1H, H6), 7.88 (dd, $^3J(\text{H,H}) = 8.6$ Hz and $^4J(\text{H,H}) = 1.7$ Hz, 1H, H3), 7.72 (dd, $^3J(\text{H,H}) = 8.5$ Hz and $^4J(\text{H,H}) = 1.5$ Hz, 1H, H14), 7.41 (s, br, 1H, H16), 7.31 (s, br, 1H, H1), 1.51 (s, 15H, Cp*). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CD_3NO_2 , 253 K): δ 141.2 (C6), 139.7, 138.6, 137.8 (C13 and C16), 136.0 (C3), 134.4, 133.7 (C4), 132.9, 132.6 (C19), 132.3 (C18), 132.0, 131.0 (C1), 130.5 (C21), 129.8, 129.7, 129.2 (C12), 128.2 (C15), 127.9, 124.2, 121.1 (C7), 110.4, 104.1 (C_5Me_5), 97.5 (C9 or C10), 93.7 (C9 or C10), 93.1, 86.6, 8.2 (C_5Me_5). Quaternary carbons of helicene could not be assigned.

$[(\text{Cp}^*\text{Ir})_2(\mu_2-\eta^6:\eta^6\text{-2})][\text{BF}_4]_4$ (**7**). To a flask containing $[\text{Cp}^*\text{IrCl}_2]_2$ (11.2 mg, 0.014 mmol), **2** (5.0 mg, 0.014 mmol) and an excess of AgBF_4 (19.5 mg, 0.100 mmol) was added CD_3NO_2 (1 ml). The solution was stirred for 1 hour at room temperature, and the AgCl precipitate was removed by filtration. The resulting solution was transferred by cannula to NMR tube for monitoring. The reaction was completed 3 hours after and the solution formed was evaporated to dryness under vacuum obtained an orange precipitate of **7**. This reaction is nearly quantitative by NMR spectroscopy. ^1H NMR (400 MHz, CD_3NO_2 , 298 K): δ 8.91 (d, $^3J(\text{H,H}) = 9.1$ Hz, 2H, H6 and H11), 8.78 (d, $^3J(\text{H,H}) = 8.3$ Hz, 2H, H8 and H9), 8.60 (d, $^3J(\text{H,H}) = 8.3$ Hz, 2H, H7 and H10), 8.12 (d, $^3J(\text{H,H}) = 9.1$ Hz, 2H, H5 and H12), 8.04 (d, $^3J(\text{H,H}) = 6.8$ Hz, 2H, H4 and H13), 7.38 (s, 2H, H1 and H16), 7.37 (d, $^3J(\text{H,H}) = 6.8$ Hz, 2H, H3 and H14), 2.29 (s, 6H, Me), 1.50 (s, 30H, Cp*). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CD_3NO_2 , 298 K): δ 139.8 (C7 and C15), 139.0, 137.0 (C11 or C24), 136.9 (C10 and C12), 131.9 (C9 and C13), 126.5 (C6 and C16), 125.0 (C11 or C24), 119.5, 113.8, 110.7, 105.9 (C_5Me_5), 100.2 (C3 and C19), 99.2, 96.7 (C4 and C18), 89.9 (C1 and C21), 18.4 (Me), 8.6 (C_5Me_5). Quaternary carbons of helicene could not be assigned. Anal. Calcd for $\text{C}_{48}\text{H}_{50}\text{B}_4\text{F}_{16}\text{Ir}_2$: C, 42.44; H, 3.71. Found: 42.60; H 3.82.

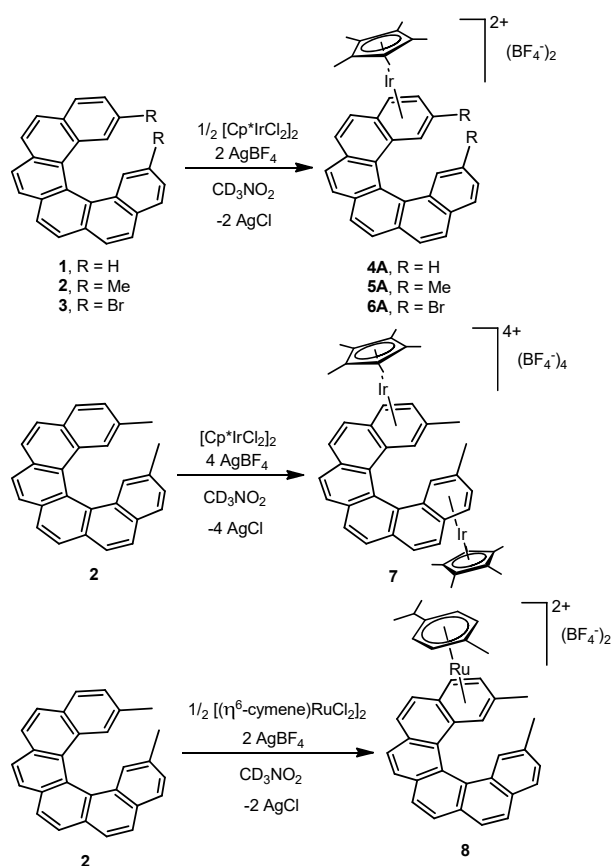
$[(\eta^6\text{-cymene})\text{Ru}(\eta^6\text{-2})][\text{BF}_4]_2$ (**8**). To a flask containing $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$ (4.3 mg, 0.007 mmol), **2** (5.0 mg, 0.014 mmol) and an excess of AgBF_4 (19.5 mg, 0.100 mmol) was added CD_3NO_2 (1 ml). The

solution was stirred for 1 hour at room temperature, and the AgCl precipitate was removed by filtration. The resulting solution was transferred by cannula to NMR tube for monitoring. The reaction was completed 15 days after and the solution formed was evaporated to dryness under vacuum obtained a red precipitate of **8**. This reaction is nearly quantitative by NMR spectroscopy. Red crystals of this complex suitable for an X-Ray diffraction study were obtained by layering a methylene chloride solution of the complex with hexane and stored at $-20\text{ }^{\circ}\text{C}$ for one week. ^1H NMR (400 MHz, CD_3NO_2 , 298 K): δ 8.630 (d, $^3J(\text{H,H}) = 8.2\text{ Hz}$, 1H, H8), 8.624 (d, $^3J(\text{H,H}) = 9.0\text{ Hz}$, 1H, H6), 8.320 (d(AB system), $^3J(\text{H,H}) = 8.4\text{ Hz}$, 1H, H9 or H10), 8.295 (d, $^3J(\text{H,H}) = 8.2\text{ Hz}$, 1H, H7), 8.292 (d(AB system), $^3J(\text{H,H}) = 8.4\text{ Hz}$, 1H, H10 or H9), 8.159 (d(AB system), $^3J(\text{H,H}) = 8.5\text{ Hz}$, 1H, H11 or H12), 8.118 (d(AB system), $^3J(\text{H,H}) = 8.5\text{ Hz}$, 1H, H12 or H11), 8.010 (d, $^3J(\text{H,H}) = 9.0\text{ Hz}$, 1H, H5), 7.981 (d, $^3J(\text{H,H}) = 8.2\text{ Hz}$, 1H, H13), 7.859 (d, $^3J(\text{H,H}) = 6.3\text{ Hz}$, 1H, H4), 7.355 (d, $^3J(\text{H,H}) = 8.2\text{ Hz}$, 1H, H14), 7.183 (s, 1H, H16), 7.140 (s, 1H, H1), 6.728 (d, $^3J(\text{H,H}) = 6.3\text{ Hz}$, 1H, H3), 6.293 (d, $^3J(\text{H,H}) = 6.6\text{ Hz}$, 1H, Hb), 6.228 (d, $^3J(\text{H,H}) = 6.6\text{ Hz}$, 1H, Hc), 5.822 (d, $^3J(\text{H,H}) = 6.6\text{ Hz}$, 1H, Hc), 5.781 (d, $^3J(\text{H,H}) = 6.6\text{ Hz}$, 1H, Hb), 1.871 (s, 3H, 15-Me), 1.854 (s, 3H, 2-Me), 1.832 (m, 1H, Hd), 1.645 (s, 3H, Ha), 0.902 (d, $^3J(\text{H,H}) = 7.0\text{ Hz}$, 3H, He), 0.622 (d, $^3J(\text{H,H}) = 7.0\text{ Hz}$, 3H, He). ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CD_3NO_2 , 298 K): δ 140.2 (C7), 138.5, 136.7, 136.3, 136.1 (C10), 135.0, 132.4, 131.5 (C12 or C13), 130.8 (C15 or C16), 130.1 (C19), 130.0 (C18), 129.8, 129.4 (C9), 128.8 (C12 or C13), 128.7 (C21), 126.8 (C15 or C16), 126.7 (C6), 126.1, 125.9, 122.6, 120.3, 112.0, 111.2, 110.1, 96.4 (Cc), 95.2 (C3), 95.1, 94.8 (Cc), 94.3 (Cd), 92.7 (C4), 91.7 (Cd), 88.1 (C1), 31.62 (Cf), 23.02 (Cg), 21.4 (15- CH_3), 20.8 (Cg), 19.3 (2- CH_3), 18.2 (Ca). Anal. Calcd for $\text{C}_{38}\text{H}_{34}\text{B}_2\text{F}_8\text{Ru}$: C, 59.63; H, 4.48. Found: 59.77; H 4.55.

Results and Discussion

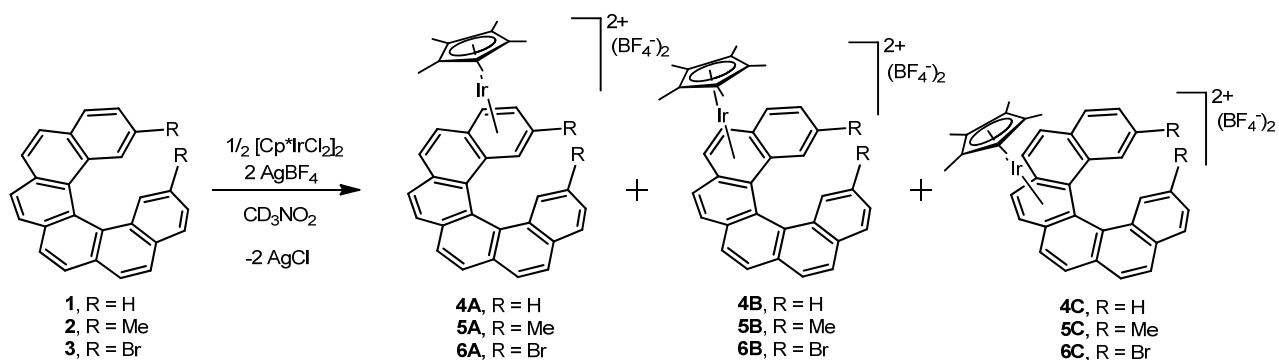
The cyclopentadienyl iridium (III) complexes presenting η^5 -coordination to hexahelicenes were obtained in nearly quantitative yield by reaction of $[\text{Cp}^*\text{IrCl}_2]_2$, AgBF_4 and one of hexahelicene ligands in CD_3NO_2 solvent at room temperature and under an inert nitrogen atmosphere. Thus, the reaction between hexahelicene (**1**), 2,15-dimethylhexahelicene (**2**) or 2,15-dibromohexahelicene (**3**), AgBF_4 and

$[\text{Cp}^*\text{IrCl}_2]_2$ led to formation of the complexes $[\text{Cp}^*\text{Ir}(\eta^6\text{-1})][\text{BF}_4]_2$ (**4A**), $[\text{Cp}^*\text{Ir}(\eta^6\text{-2})][\text{BF}_4]_2$ (**5A**) or $[\text{Cp}^*\text{Ir}(\eta^6\text{-3})][\text{BF}_4]_2$ (**6A**) respectively (Scheme 1).



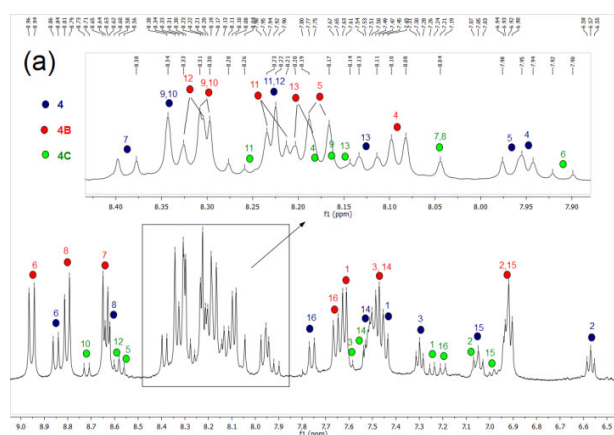
Scheme 1.

So far, the synthesis of $[\text{Cp}^*\text{Ir}(\eta^6\text{-arene})](\text{BF}_4)_2$ complexes had been described using the acetone solvent complex $[\text{Cp}^*\text{Ir}(\text{OCMe}_2)_3]$ as reagent.¹⁹ However η^6 -hexalicyclic complexes of cyclopentadienyl iridium were prepared in one pot reaction avoiding the synthesis of this precursor. Also, this reaction proceeded smoothly using a weakly coordinating solvent as nitromethane. Both facts promote a preferential binding between cyclopentadienyl iridium fragment and the aromatic compound reducing the problem of competitive reactions with other potential ligands.



Scheme 2.

The reaction between $[\text{Cp}^*\text{IrCl}_2]_2$, AgBF_4 and **1** at room temperature using the aforementioned conditions led to preparation of **4A**. In the course of the reaction three complexes (isomers) **4A**, **4B** and **4C** were observed by ^1H NMR (Scheme 2), two of which disappear over time evolving into the single thermodynamic product. After 15 min, the ratio between the isomers was 55:36:9 (**4A**:**4B**:**4C**). After 5 days at room temperature, the isomer **4C** had disappeared and the ratio between **4A** and **4B** was 80:20. This proportion was 93:7(**4A**:**4B**) within 10 days and the quantitative formation of **4A** was produced after 15 days. In order to characterize these intermediates we decided to carry out a low-temperature NMR experiments. Thus, $[\text{Cp}^*\text{IrCl}_2]_2$, AgBF_4 and **1** were mixed in CD_3NO_2 at 195 K and immediately transferred to a NMR tube for study at 253 K. In the ^1H NMR spectrum acquired at that temperature was again observed the presence of the three isomers in a ratio 27:64:9 (**4A**:**4B**:**4C**) (Figure 3).



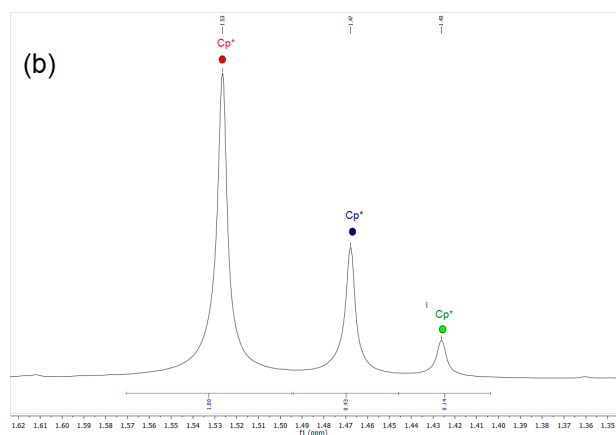


Figure 3. ^1H NMR spectrum at 253 K in the aromatic region (a) or in cyclopentadienyl region (b) of isomers **4A**, **4B** and **4C** formed in the reaction between $[\text{Cp}^*\text{IrCl}_2]_2$, AgBF_4 and **1** in CD_3NO_2 .

Although none of the intermediates was obtained separately, the three isomers were characterized by NMR in CD_3NO_2 at low temperature (^1H , $^{13}\text{C}\{^1\text{H}\}$, ^1H - ^1H COSY, ^1H - ^1H NOESY and ^1H - ^{13}C HSQC NMR spectra). The biggest challenge was to establish in which ring of the hexahelicene was coordinated the metal fragment. Taking into account the ^1H - ^1H NOESY NMR spectrum several cross peaks were detected between the hydrogens of the Cp^* and hexahelicene ligands (Figure S9). This data showed that the $[\text{IrCp}^*]^{2+}$ metal fragment was in spatial proximity to H1, H2, H3, H4, H5 and H6 in **4A** (bonded to A ring), to H1, H2, H3, H4, H5, H6, H7 and H8 in **4B** (bonded to B ring), to H1, H5, H6, H7, H8, H9 and H10 in **4C** (bonded to C ring) (following the assignment of figure 2). An inspection of Cp^* chemical shifts in ^1H and ^{13}C spectra of complexes **4A**, **4B** and **4C** revealed several general trends. These data have been summarized at table 1. As can be seen these chemical shifts are upfield for isomer **4C**, showing that C ring has more electron density than the other two (A and B rings). In this regard, considering only electronic factors, C ring of hexahelicene should form the most stable compounds for metal coordination. However, the final product is not coordinated to C ring. The reason for this behavior is not clear, but is probably influenced by the steric hindrance, as we move from ring A to ring F (Figure 2), the steric hindrance is increased. In fact, there is no NMR evidence of formation of cyclopentadienyl iridium complexes coordinated to the D, E or F rings (same face of the hexahelicene), showing the

importance of steric factor in the control of the reaction. DFT calculations were performed to gain additional information into the experimental findings. The potential energy surfaces (PES) are simulated in nitromethane as the solvent for the systems with cyclopentadienyl iridium coordinated to A, B and C rings of hexahelicene (complexes **4A**, **4B** and **4C**, respectively). Choosing the structure of **4B** as the zero-energy reference point, the final product **4A** is lower in energy by $\Delta G_{298K} = -7.7$ kcal/mol, while the complex **4C** has a $\Delta G_{298K} = -2.3$ kcal/mol. As expected, these energies are in good agreement with the empirical data.

		4A	4B	4C
¹ H NMR	Cp*	1.47	1.53	1.43
¹³ C { ¹ H} NMR	C ₅ Me ₅	103.6	104.5	102.5
	C ₅ Me ₅	8.7	8.8	8.1

Table 1. Chemical shift (ppm) of the cyclopentadienyl ligand for **4A**, **4B** and **4C** in CD₃NO₂ at 253K.

The complex **5A** was obtained following the procedure used for **4A**. The reaction was completed after 6 days to form the compound **5A** quantitatively. In this case, the reaction rate was significantly higher than in the preparation of **4A**. Perhaps this is partially due to the [Cp*Ir(η^6 -arene)](BF₄)₂ complexes are more stable when the arenes are alkyl-substituted.¹⁹ Monitoring the reaction by ¹H NMR spectroscopy showed the existence of two intermediates as it was observed in the case of **4A**. Although, unfortunately, none of them could be fully characterized, their spectroscopic similarities with the isomers **4B** and **4C** suggest their identification as the complexes **5B** and **5C**.

Under the same conditions, helicene **3**, [Cp*IrCl₂]₂ and AgBF₄ reacted to afford the complex **6A**. In the course of the reaction two intermediates were detected. One of them was isolated and fully characterized at 253 K as complex **6C**. The ratio between the isomers **6A**:**6C** changed from 0:100 to 18:77 after 1 day at room temperature. The remaining 5% was due to the presence of the other isomer that cannot be identified. The compound **6A** is the only product of the reaction mixture after 14 days. The isomer **6C**

could be fully characterized by spectroscopic methods. The ^1H NMR spectra at 253 K of complexes **4C** and **6C** display similar pattern. The hydrogen signal for H10, H12 and H5 appear as doublet at 8.72, 8.59 and 8.57 ppm in **4C** and at 8.78, 8.65 and 8.62 ppm in **6C**. The next four signals between 8.3 and 8.1 ppm are assigned to H11, H4, H9 and H13 showing all appearance of doublet. Two signals of the C ring, H7 and H8, arise from second order AB coupling at 8.04 ppm in **4C** and between 8.15 and 8.10 ppm in **6C**. At 7.91 in **4C** and at 7.99 in **6C** appear as doublet the signal for H6. Upfield signals corresponding to terminal rings of hexahelicenes could not be compared due to different substituents in 2 and 15 positions.

All new complexes **4A**, **5A** and **6A** were characterized by analytical and spectroscopic methods. Analysis of the NMR spectroscopic data of cyclopentadienyl ligand of these three thermodynamic products appears to indicate that complex **5A** is more stable than **4A** and this in turn more than **6A** (Table 2). These data can be interpreted easily considering the electronic influence of the substituent in position 2 of the hexahelicene. In this way, while the methyl group in **5A** donates electron density to the terminal ring of the helicene ligand, the bromo in **6A** withdraws electron density. This three complexes display similar ^1H NMR spectra where the resonance of H atoms of the ring involved in coordination to transition metal was shifted upfield than the other hydrogens. A similar behavior was observed for the carbons chemical shifts.

		4A	5A	6A
^1H NMR	Cp*	1.51	1.50	1.54
	H1	7.43	7.31	7.64
	H3	7.32	7.20	7.72
	H4	7.96	7.87	8.06
^{13}C $\{^1\text{H}\}$ NMR	C_5Me_5	105.3	104.7	106.4
	C_5Me_5	8.9	8.6	8.5
	C1	128.37	-	92.8
	C2	128.43	-	-
	C3	98.14	-	101.6
	C4	96.50	-	96.3

Table 2. Selected shifts (ppm) for **4A**, **5A** and **6A** in CD₃NO₂ at room temperature.

The presence of six rings in these systems permits the transition metal an opportunity to coordinate at more than one position. In all cases, the final products show coordination of the metal fragment to terminal ring of the helicene. In addition, we found a clear preference for coordination to the ring C at the beginning of the reaction. This coordination is extremely fast because free hexahelicene ligand was never observed. However, the formation of the thermodynamic product occurs after several days at room temperature, which evidence a slow isomerization. This movement can occur by two ways: migration of metal cationic units walking over the surface or through an intermolecular dissociation/association mechanism. Recently, in other nonplanar polyaromatic compound as corannulene have been observed this migration and NMR and calculation data seem to demonstrate the slide as the most feasible mechanism.^{14d} DFT calculations were again performed to determine the transition states and the barriers connecting complex **4A**, **4B** and **4C** (Figure 4). Two new local minima (**4AB** and **4BC**) were located in the potential energy surfaces (PES), which correspond to η^3 -C=C-C coordination of the metal between two adjacent rings. Also, four transition states were observed, all of them present η^2 -C=C coordination. The movement of the metal center from **4C** to **4B** involves a haptotropic rearrangement from η^6 -arene to η^3 -C=C-C (**4C**→**4BC**) via **TS(4BC-4C)**, followed by a new haptotropic migration from η^3 -C=C-C to η^6 -arene (**4BC**→**4B**) via **TS(4AB-4B)**. A similar reorganization was observed to pass from **4B** to **4A**. These computational results seem to suggest that a ring walking process through a haptotropic rearrangement is a plausible movement for this system although dissociation could not be ruled out.

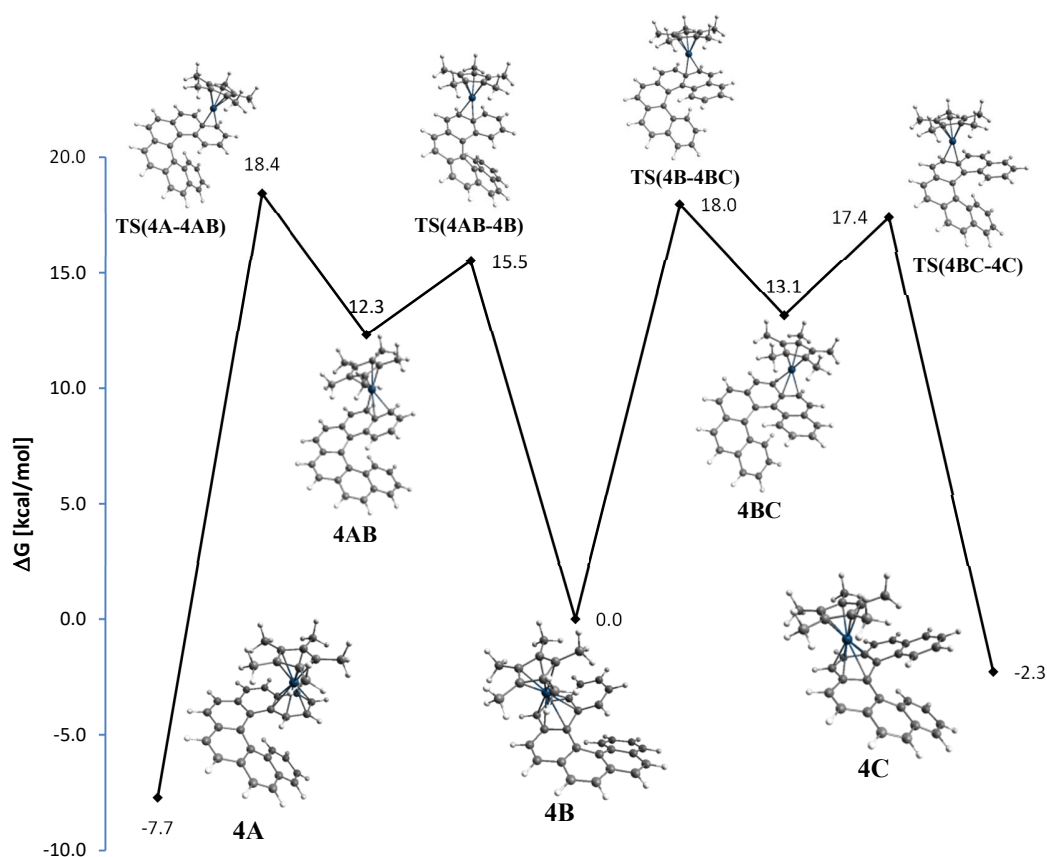


Figure 4. Reaction profile (kcal/mol, B3LYP/SVP (SDD for Ir)) for the ring-walking and the structures of the various complexes. (Atomic color scheme: C-grey, H-white, Iridium-blue).

The reaction between equivalent amounts of $[\text{Cp}^*\text{IrCl}_2]_2$ and **2** with excess of AgBF_4 at room temperature in CD_3NO_2 solvent and under a nitrogen inert atmosphere led to formation of the homobimetallic complex $[(\text{Cp}^*\text{Ir})_2(\mu_2-\eta^6:\eta^6\text{-2})][\text{BF}_4]_4$ (**7**) (Scheme 1). The reaction was completed after 3 hours to form the final compound quantitatively. This thermodynamic product **7** was isolated and fully characterized by their ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^1H - ^1H COSY and ^1H - ^1H NOESY NMR spectra in CD_3NO_2 . The reduced number of signals in the final ^1H NMR spectrum evidences the higher symmetry of this dimer that presents the coordination of two metal fragments $[\text{IrCp}^*]^{2+}$ on the exo side of terminal ring of the hexahelicene. The reaction rate is much higher than in the synthesis of the above monometallic complexes. This could be explained by the formation of less stable intermediates. These plausible intermediates would have at least one of the two metal fragments coordinated to the internal rings. The proximity of the two rings coordinated to the metals would be disadvantageous considering electronic and steric factors. In addition, as already mentioned, the methyl group in the terminal rings of

hexahelicene favors the binding in this position. Both facts could promote this unusual and rapid evolution of the intermediates reaction to thermodynamic product **7**.

In an attempt to determinate how many $[\text{IrCp}^*]^{2+}$ metal fragment can coordinate to 2,15-dimethylhexahelicene, an experiment in which 1 equiv of **2** and 3 equiv of $[\text{IrCp}^*]^{2+}$ were reacted under the same conditions. This reaction was monitored by ^1H NMR periodically over several weeks. No products with three $[\text{IrCp}^*]^{2+}$ units coordinates to **2** was observed identifying the complex **7** as the unique coordination product to the helicene. This reaction shows that only one $[\text{IrCp}^*]^{2+}$ metal fragment can be coordinated to each side of hexahelicene.

In order to explore the η^6 -coordination of other metal fragments to hexahelicenes we decided to study the coordination between 2,15-dimethylhexahelicene and another 12 e⁻ metal fragment such as $[(\eta^6\text{-cymene})\text{Ru}]^{2+}$. Thus, 1 equiv of $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$ dimer, 2 equiv of helicene **2**, and 2 equiv of AgBF_4 in CD_3NO_2 solvent reacted at room temperature to afford $[(\eta^6\text{-cymene})\text{Ru}(\eta^6\text{-2})][\text{BF}_4]_2$ (**8**) in quantitative yield after 15 days (Scheme 1). Along the reaction several intermediates has been observed but no one has been fully characterized. The ^1H and ^{13}C NMR spectra of the complex **8** display trend similar to those observed in other ruthenium cymene compounds containing other arene ligands. For example the proton signals for hydrogens attached to the coordinated rings are upfield relative to the free ligand. The observed ^{13}C and ^1H chemical shifts for the p-cymene ligand are in agreement with other Ru(II) sandwich complexes, therefore in this complexes the methyls of the isopropyl group are diastereotopics and appear as a pair of doublets.

Red crystals of the complex **8** suitable for an X-ray diffraction study were obtained by layering a methylene chloride solution of the compound with diethyl ether and storing it at -20°C overnight. In the structure of the complex we find the transition metal η^6 -coordinated to p-cymene ligand and η^6 -coordinated to the terminal ring of hexahelicene. The distances between the ruthenium atom and the rings centroid are 1.710 Å (p-cymene ligand) and 1.735 Å (terminal ring of hexahelicene) (Figure 5).

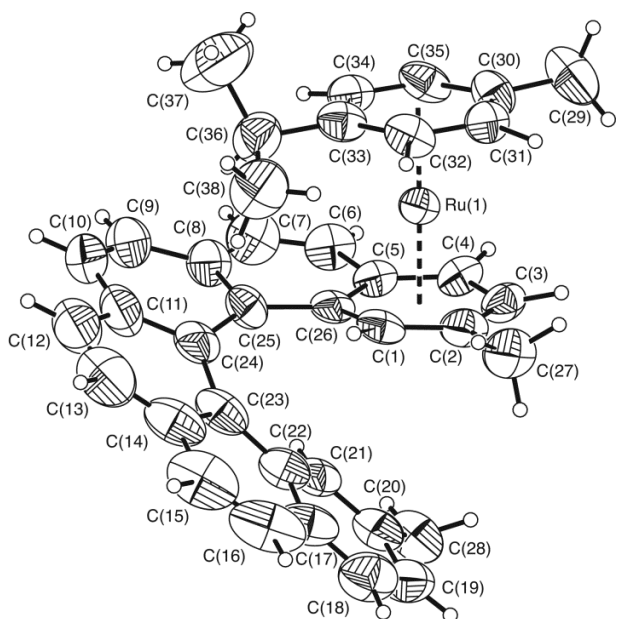


Figure 5. View of the $[(\eta^6\text{-cymene})\text{Ru}(\eta^6\text{-2})][\text{BF}_4]_2$ (**8**) structure illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 30% probability level. The two BF_4^- counterions are not shown.

One of the parameter that can be used to describe the change of the helical structure as consequence of metal fragment coordination is the helical pitch; this could be defined as the distance along the helical axis that results in one full turn of the helix. Thus, in this structure, the helical pitch between C2 and C20 is 3.828 Å, while in hexahelicene free is 4.576 Å.²⁰ This data evidence the influence that the coordination of the metal fragment has on the flattening of the ligand hexahelicene.

Conclusions

In summary, the first η^6 -complexes of Iridium and Ruthenium coordinated to helicenes have been obtained. All of them show the η^6 -coordination of the metal fragment to terminal ring of the helicene, as it is manifested in the X-Ray structure of the complex **8**. We have also identified and fully characterized some of the intermediates that present the coordination of metal fragments to the internal rings of helicene. The first detected intermediates show the metal unit η^6 -coordinated to ring C. The followed migration from ring C to ring A (final products) is a slow isomerization of several days. DFT calculations were performed to support a plausible profile reaction of this isomerization. In this studies

news local minima and some transition states were located and a haptotropic rearrangement seem to be the most feasible movement. In order to coordinate the maximum metal fragments to hexahelicene, we synthesized the complex **7**. This dimer present the coordination of two metal fragments $[\text{IrCp}^*]^{2+}$ on the exo side of terminals ring of the hexahelicene, being the maximum number of metal units that can be bonded.

Acknowledgment. Research was supported by

Supporting Information Available: NMR spectra for all compounds (^1H , $^{13}\text{C}\{^1\text{H}\}$, COSY, NOESY, HSQC), computational details, crystallographic data for complex **8** This material is available free of charge via the Internet at <http://pubs.acs.org>.

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