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η^6-Hexahelicene Complexes of Iridium and Ruthenium: Running along the Helix

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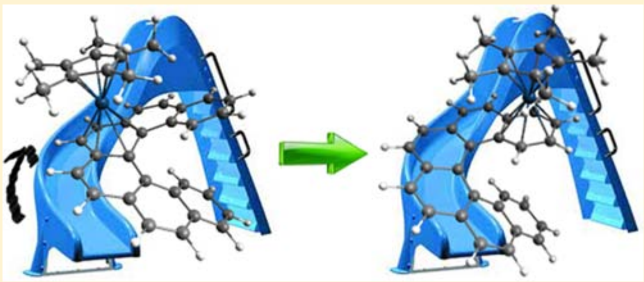
Ⓢ *Supporting Information*

ABSTRACT: The first η^6-complexes of iridium and ruthenium coordinated to helicenes have been obtained. Hexahelicene (**1**), 2,15-dimethylhexahelicene (**2**), and 2,15-dibromohexahelicene (**3**) react with $[Cp^*IrCl_2]_2$ and $AgBF_4$ in CD_3NO_2 to afford quantitatively the complexes $[Cp^*Ir(\eta^6\text{-}\mathbf{1})][BF_4]_2$ (**4A**), $[Cp^*Ir(\eta^6\text{-}\mathbf{2})][BF_4]_2$ (**5A**), and $[Cp^*Ir(\eta^6\text{-}\mathbf{3})][BF_4]_2$ (**6A**), respectively. In all cases, the final thermodynamic products are similar, and they exhibit coordination between the 12 e^- metal fragment $[IrCp^*]^{2+}$ and the terminal ring of the helicene. Monitoring the reaction by NMR shows formation of intermediates, some of which have been fully characterized in solution. These intermediates exhibit the metal fragment coordinated to the internal rings. We have also synthesized the bimetallic complex $[(Cp^*Ir)_2(\mu_2\text{-}\eta^6{:}\eta^6\text{-}\mathbf{2})][BF_4]_4$ (**7**), achieving coordination between two units $[IrCp^*]^{2+}$ and the helicene **2**. Following an analogous methodology, we have prepared the complex $[(\eta^6\text{-cymene})Ru(\eta^6\text{-}\mathbf{2})][BF_4]_2$ (**8**), which has been studied by X-ray diffraction, confirming the preferential binding to the terminal aromatic ring.



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 optical[2] and electronic[3] properties. Perhaps the most remarkable feature is their inherent chirality; therefore, they have raised attention over the years for their potential use as asymmetric catalysts.[4] This is due to the helicenes having a stereogenic axis that has a left- or right-handed chiral helical structure with M (−) or P (+) configuration, respectively.[5] Additionally, these nonplanar condensed aromatic compounds have been employed for molecular recognition,[6] self-assembly,[7] molecular machines synthesis,[8] biological applications[9] or in several other fields of materials science.[10] The hexahelicene (**1**) was obtained by Newman and Lednicer in 1956,[11] and other helicenes have been prepared by the oxidative photocyclization of bis(stilbene) derivatives[6a,12] or by other nonradiative methodologies.[13] In a recently published work, Shen and Chen[14] provide a comprehensive review of the synthesis and applications of these captivating molecules.

Coordination of the polycyclic aromatic molecules to metal atoms may alter the electronic density distribution and significantly change their properties. Therefore, it has been considered attractive to explore the chemistry of these kinds of complexes. The η^6-bis(arene) complexes of *p*-cymene with ruthenium or η^6-arene complexes of cyclopentadienyl with iridium have been widely studied,[15] and the coordination of the $[Ru(\eta^6\text{-cymene})]^{2+}$ fragment to coronene and other polyaromatic compounds has been described.[16] The preparation of η^6-polyaromatic complexes is simpler when the 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 exotic examples present this binding type in nonplanar polyaromatic compounds, especially buckybowl derivatives.[17] Particularly interesting are the works of Angelici and co-workers,[17e,g,h] which led to the preparation of η^6-corannulene complexes. In this study, they reported the synthesis and structure of a dimetalated buckybowl that presents the coordination of two 12 e^- metal fragments $[RuCp^*]^+$ to each side of corannulene, thereby increasing the flattening of the molecule. There are several structural differences between coronene, corannulene, and helicenes. 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 three-dimensional structures (Figure 1). The flattening in nonplanar polyaromatic compounds can be evaluated by the π-orbital axis vector (POAV) analysis,[18] and its value shows that corannulene has a more strained structure than helicenes. Therefore it is reasonable to anticipate that η^6-helicene complexes would be more stable and more robust than their corannulene analogues.

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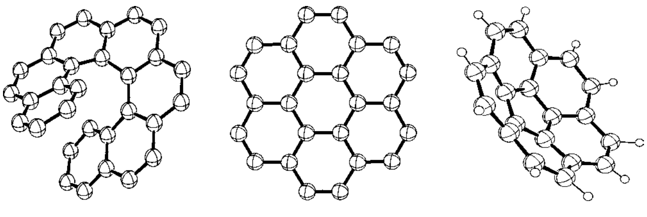


Figure 1. Structures of heptahelicene (left), coronene (middle), and corannulene (right).

However, there are no reported examples of complexes that contain η^6-coordinated helicenes. For all these reasons, we have considered it interesting to study the η^6-coordination between 12 e^- metal fragments $[IrCp^*]^{2+}$ or $[Ru(\eta^6\text{-cymene})]^{2+}$ and [6]helicene (**1**) or 2,15-disubstituted [6]helicenes such as 2,15-dimethylhexahelicene (**2**) and 2,15-dibromohexahelicene (**3**), as a starting point for exploration of the chemistry of η^6-hexahelicene complexes.[19]

EXPERIMENTAL SECTION

General Considerations. Synthetic procedures were carried out under an inert atmosphere of nitrogen, in solvents that had been dried by passage through alumina columns in an IT solvent purification system, and degassed with N_2. Standard Schlenk techniques were used unless otherwise noted. Solution NMR spectra were obtained on a Bruker AV-400 or a Varian MR 400 spectrometer, with CD_3NO_2 as the solvent, internal lock, and internal reference [δ 4.33 (^{1}H) and 62.8 (^{13}C)]. For a correct assignment of NMR signals, one should determine whether the metal fragment is bonded to A, B, or C ring as shown in Figure 2. Crystal evaluation and data collection of **8** were performed on an Oxford Diffraction Supernova diffractometer, equipped with an Atlas charge-coupled device (CCD) area detector and a four-circle κ 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-d_3 (CD_3NO_2) was purchased from Aldrich and subjected to three freeze−pump−thaw cycles before use. Hexahelicene (**1**),[20] 2,15-dimethylhexahelicene (**2**),[20a,21] and 2,15-dibromohexahelicene (**3**)[22] were prepared according to literature procedures, and their spectral data were in agreement with those in the literature.

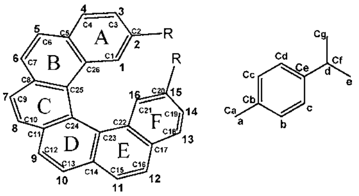


Figure 2. Atom labeling schemes for the cymene and hexahelicene ligands.

Synthesis. *[Cp*Ir(η^6-**1**)][BF$_4$]$_2$ (**4A**).* To a flask containing $[Cp^*IrCl_2]_2$ (6.1 mg, 0.008 mmol), **1** (5.0 mg, 0.015 mmol), an excess of $AgBF_4$ (19.5 mg, 0.100 mmol) was added CD_3NO_2 (1 mL). The solution was stirred for 1 h at room temperature, and the AgCl precipitate was removed by filtration. The resulting solution was transferred by cannula to an NMR tube for monitoring. The reaction was completed after 15 days, and the resulting solution was evaporated to dryness under vacuum to give an orange precipitate of **4A**, which was recrystallized from CH_2Cl_2/hexane. This reaction is nearly quantitative by NMR spectroscopy. ^{1}H NMR (400 MHz, CD_3NO_2, 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(H,H) = 8.6 Hz, 1H, H12 or H11], 8.11 [dd, ^3J(H,H) = 8.0 Hz and ^5J(H,H) = 1.0 Hz, 1H, H13], 7.97 [d, ^3J(H,H) = 9.0 Hz, 1H, H5], 7.96 [d, ^3J(H,H) = 6.1 Hz, 1H, H4], 7.75 [d, ^3J(H,H) = 8.5 Hz, 1H, H16], 7.51 (m, 1H, H14), 7.43 [d, ^3J(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}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$_5$*Me*$_5$). Anal. Calcd for $C_{36}H_{31}B_2F_8Ir$: C, 52.13; H, 3.77. Found: C, 52.17; H, 3.88.

*Low-Temperature Studies of the Reaction between [Cp*IrCl$_2$]$_2$, AgBF$_4$, and **1**.* Compound **1** (5.0 mg, 0.015 mmol), $[Cp^*IrCl_2]_2$ (6.1 mg, 0.008 mmol), and an excess of $AgBF_4$ (19.5 mg, 0.100 mmol) and CD_3NO_2 (1 mL) were introduced into an NMR tube in a bath at 195 K. The tube containing the frozen reagents and solvent was placed inside the NMR Bruker AV400 spectrometer and allowed to melt and warm to 253 K inside the instrument before measurement. NMR experiments showed the formation of three isomers, **4A**, **4B**, and **4C**. Isomer **4A**: ^{1}H NMR (400 MHz, CD_3NO_2, 253 K) δ 8.85 [d, ^3J(H,H) = 9.0 Hz, 1H, H6], 8.63 [d, ^3J(H,H) = 8.2 Hz, 1H, H8], 8.39 [d, ^3J(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(H,H) = 8.0 Hz, 1H, H13], 7.96 [d, ^3J(H,H) = 9.0 Hz, 1H, H5], 7.95 [d, ^3J(H,H) = 6.1 Hz, 1H, H4], 7.76 [d, ^3J(H,H) = 8.5 Hz, 1H, H16], 7.52 (m, 1H, H14), 7.44 [d, ^3J(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*). Isomer **4B**: ^{1}H NMR (400 MHz, CD_3NO_2, 253 K) δ 8.95 [d, ^3J(H,H) = 9.0 Hz, 1H, H6], 8.80 [d, ^3J(H,H) = 8.5 Hz, 1H, H8], 8.64 [d, ^3J(H,H) = 8.2 Hz, 1H, H7], 8.32 [d (AB system), ^3J(H,H) = 8.6 Hz, 1H, H12], 8.31 [d (AB system), ^3J(H,H) = 8.6 Hz, 1H, H9 or H10], 8.29 [d (AB system), ^3J(H,H) = 8.6 Hz, 1H, H10 or H9], 8.22 [d (AB system), ^3J(H,H) = 8.6 Hz, 1H, H11], 8.19 [d, ^3J(H,H) = 8.0 Hz, 1H, H13], 8.18 [d, ^3J(H,H) = 9.0 Hz, 1H, H5], 8.09 [d, ^3J(H,H) = 6.3 Hz, 1H, H4], 7.66 [d, ^3J(H,H) = 8.5 Hz, 1H, H16], 7.62 [d, ^3J(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*). Isomer **4C**: ^{1}H NMR (400 MHz, CD_3NO_2, 253 K) δ 8.72 [d, ^3J(H,H) = 8.8 Hz, 1H, H10], 8.59 [d, ^3J(H,H) = 8.2 Hz, 1H, H12], 8.57 [d, ^3J(H,H) = 8.5 Hz, 1H, H5], 8.25 [d, ^3J(H,H) = 8.2 Hz, 1H, H11], 8.17 [d, ^3J(H,H) = 8.5 Hz, 1H, H4], 8.16 [d, ^3J(H,H) = 8.8 Hz, 1H, H9], 8.15 [d, ^3J(H,H) = 8.0 Hz, 1H, H13], 8.04 [s (AB system), 2H, H7 and H8], 7.91 [d, ^3J(H,H) = 8.5 Hz, 1H, H6], 7.59 (m, 1H, H3), 7.54 (m, 1H, H14), 7.25 [d, ^3J(H,H) = 7.5 Hz, 1H, H1], 7.20 [d, ^3J(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}H} NMR (100 MHz, CD_3NO_2, 253 K): δ 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$_5$*Me*$_5$, **4B**), 7.4 (C$_5$*Me*$_5$, **4A**), 6.9 (C$_5$*Me*$_5$, **4C**). Some carbon atoms of isomer **4C** could not be detected.

*[Cp*Ir(η^6-**2**)][BF$_4$]$_2$ (**5A**).* To a flask containing $[Cp^*IrCl_2]_2$ (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 h at room temperature, and the AgCl precipitate was removed by filtration. The resulting solution was transferred by

cannula to an NMR tube for monitoring. The reaction was completed after 6 days. The solution formed was evaporated to dryness under vacuum to give an orange precipitate of **5A**, which was recrystallized from CH$_2$Cl$_2$/hexane. This reaction is nearly quantitative by NMR spectroscopy. ^{1}H NMR (400 MHz, CD$_3$NO$_2$, 298 K) δ 8.88 [d, ^3J(H,H) = 8.9 Hz, 1H, H6], 8.68 [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], 8.34 [d (AB system), ^3J(H,H) = 8.3 Hz, 1H, H10 or H9], 8.18 [d (AB system), ^3J(H,H) = 8.6 Hz, 1H, H11 or H12], 8.13 [d (AB system), ^3J(H,H) = 8.6 Hz, 1H, H12 or H11], 8.03 [d, ^3J(H,H) = 8.2 Hz, 1H, H13], 7.93 [d, ^3J(H,H) = 8.9 Hz, 1H, H5], 7.87 [d, ^3J(H,H) = 6.4 Hz, 1H, H4], 7.51 (s, 1H, H16), 7.43 [d, ^3J(H,H) = 8.2 Hz, 1H, H14], 7.31 (s, 1H, H1), 7.20 [d, ^3J(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 CD$_3$NO$_2$, we were unable to obtain satisfactory ^{13}C{^{1}H} NMR spectra. Anal. Calcd for C$_{38}$H$_{35}$B$_2$F$_8$Ir: C, 53.22; H, 4.11. Found: C, 53.05; H, 4.00.

[Cp*Ir(η^6-3)][BF$_4$]$_2$ (6A). To a flask containing [Cp*IrCl$_2$]$_2$ (4.1 mg, 0.005 mmol), **3** (5.0 mg, 0.010 mmol), and an excess of AgBF$_4$ (19.5 mg, 0.100 mmol) was added CD$_3$NO$_2$ (1 mL). The solution was stirred for 1 h at room temperature, and the AgCl precipitate was removed by filtration. The resulting solution was transferred by cannula to an NMR tube for monitoring. The reaction was completed after 14 days and the solution formed was evaporated to dryness under vacuum to afford an orange precipitate of **6A**, which was recrystallized from CH$_2$Cl$_2$/hexane. This reaction is nearly quantitative by NMR spectroscopy. ^{1}H NMR (400 MHz, CD$_3$NO$_2$, 298 K) δ 8.95 [d, ^3J(H,H) = 9.0 Hz, 1H, H6], 8.72 [d, ^3J(H,H) = 8.2 Hz, 1H, H8], 8.44 [d, ^3J(H,H) = 8.2 Hz, 1H, H7], 8.40 [d (AB system), ^3J(H,H) = 8.4 Hz, 1H, H9 or H10], 8.38 [d (AB system), ^3J(H,H) = 8.4 Hz, 1H, H10 or H9], 8.24 [s (AB system), 2H, H11 and H12], 8.09 [d, ^3J(H,H) = 8.6 Hz, 1H, H13], 8.06 [d, ^3J(H,H) = 6.6 Hz, 1H, H4], 8.04 [d, ^3J(H,H) = 9.0 Hz, 1H, H5], 7.80 [d, ^4J(H,H) = 1.8 Hz, 1H, H16], 7.72 [dd, ^3J(H,H) = 6.6 Hz and ^4J(H,H) = 1.8 Hz, 1H, H3], 7.71 [dd, ^3J(H,H) = 8.6 Hz and ^4J(H,H) = 1.5 Hz, 1H, H14], 7.64 [d, ^4J(H,H) = 1.5 Hz, 1H, H1], 1.54 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$NO$_2$, 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 (C$_5$Me$_5$), 101.6 (C3), 98.9, 97.2, 96.3 (C4), 92.8 (C1), 8.54 (C$_5$*Me*$_5$). Quaternary carbons of helicene could not be assigned. Anal. Calcd for C$_{36}$H$_{29}$B$_2$Br$_2$F$_8$Ir: C, 43.80; H, 2.96. Found: C, 43.62; H, 3.05.

Intermediate [Cp*Ir(η^6-3)][BF$_4$]$_2$ (6C). Compound **3** (5.0 mg, 0.010 mmol), [Cp*IrCl$_2$]$_2$ (4.1 mg, 0.005 mmol), and an excess of AgBF$_4$ (19.5 mg, 0.100 mmol) and CD$_3$NO$_2$ (1 mL) were introduced into an NMR tube in a bath at 195 K. The tube containing the frozen reagents and solvent was placed inside the NMR Bruker AV400 spectrometer and allowed to melt and warm to 253 K inside the instrument before measurement. Data for **6C**: ^{1}H NMR (400 MHz, CD$_3$NO$_2$, 253 K) δ 8.78 [d, ^3J(H,H) = 8.6 Hz, 1H, H10], 8.66 [d, ^3J(H,H) = 8.5 Hz, 1H, H12], 8.62 [d, ^3J(H,H) = 9.0 Hz, 1H, H5], 8.32 [d, ^3J(H,H) = 8.5 Hz, 1H, H11], 8.25 [d, ^3J(H,H) = 8.6 Hz, 1H, H9], 8.19 [d, ^3J(H,H) = 8.6 Hz, 1H, H4], 8.14 [d, ^3J(H,H) = 8.5 Hz, 1H, H13], 8.13 [d (AB system), ^3J(H,H) = 6.5 Hz 1H, H7 or H8], 8.10 [d (AB system), ^3J(H,H) = 6.5 Hz 1H, H8 or H7], 7.99 [d, ^3J(H,H) = 9.0 Hz, 1H, H6], 7.88 [dd, ^3J(H,H) = 8.6 Hz and ^4J(H,H) = 1.7 Hz, 1H, H3], 7.72 [dd, ^3J(H,H) = 8.5 Hz and ^4J(H,H) = 1.5 Hz, 1H, H14], 7.41 (br s, 1H, H16), 7.31 (br s, 1H, H1), 1.51 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$NO$_2$, 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$_5$Me$_5$), 97.5 (C9 or C10), 93.7 (C9 or C10), 93.1, 86.6, 8.2 (C$_5$*Me*$_5$). Quaternary carbons of helicene could not be assigned.

[(Cp*Ir)$_2$(μ_2-η^6:η^6-2)][BF$_4$]$_4$ (7). To a flask containing [Cp*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$_3$NO$_2$ (1 mL). The solution was stirred for 1 h at room temperature, and the AgCl precipitate was removed by filtration. The resulting solution was transferred by cannula to an NMR tube for monitoring. The reaction was completed after 3 h and the solution formed was evaporated to dryness under vacuum to give an orange precipitate of **7**, which was recrystallized from CH$_2$Cl$_2$/hexane. This reaction is nearly quantitative by NMR spectroscopy. ^{1}H NMR (400 MHz, CD$_3$NO$_2$, 298 K) δ 8.91 [d, ^3J(H,H) = 9.1 Hz, 2H, H6 and H11], 8.78 [d, ^3J(H,H) = 8.3 Hz, 2H, H8 and H9], 8.60 [d, ^3J(H,H) = 8.3 Hz, 2H, H7 and H10], 8,12 [d, ^3J(H,H) = 9.1 Hz, 2H, H5 and H12], 8.04 [d, ^3J(H,H) = 6.8 Hz, 2H, H4 and H13], 7.38 (s, 2H, H1 and H16), 7.37 [d, ^3J(H,H) = 6.8 Hz, 2H, H3 and H14], 2.29 (s, 6H, Me), 1.50 (s, 30H, Cp*). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$NO$_2$, 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$_5$Me$_5$), 100.2 (C3 and C19), 99.2, 96.7 (C4 and C18), 89.9 (C1 and C21), 18.4 (Me), 8.6 (C$_5$*Me*$_5$). Quaternary carbons of helicene could not be assigned. Anal. Calcd for C$_{48}$H$_{50}$B$_4$F$_{16}$Ir$_2$: C, 42.44; H, 3.71. Found: C, 42.60; H, 3.82.

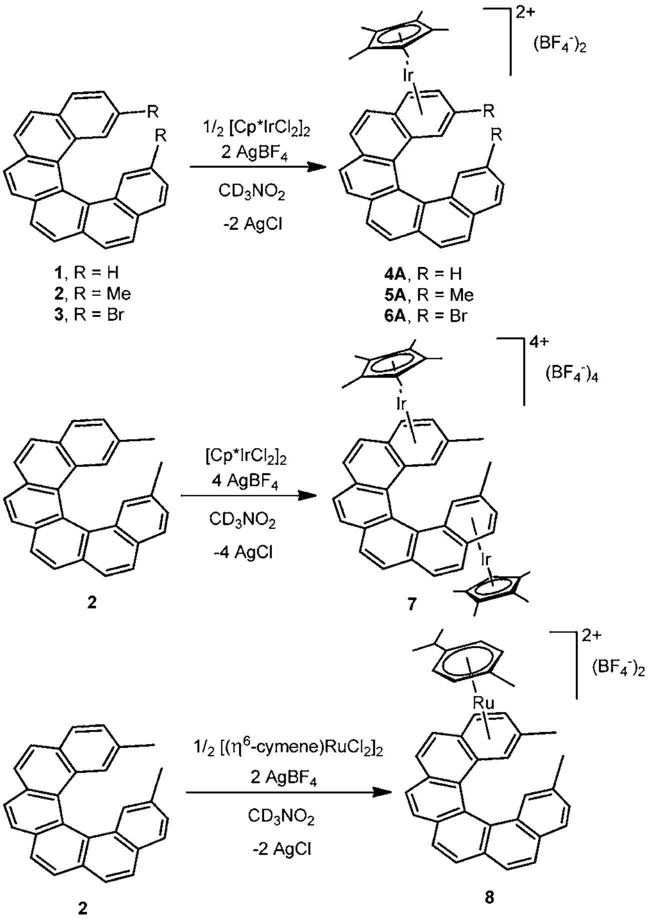
[(η^6-Cymene)Ru(η^6-2)][BF$_4$]$_2$ (8). To a flask containing [(η^6-cymene)RuCl$_2$]$_2$ (4.3 mg, 0.007 mmol), **2** (5.0 mg, 0.014 mmol), and an excess of AgBF$_4$ (19.5 mg, 0.100 mmol) was added CD$_3$NO$_2$ (1 mL). The solution was stirred for 1 h at room temperature, and the AgCl precipitate was removed by filtration. The resulting solution was transferred by cannula to an NMR tube for monitoring. The reaction was completed after 15 days and the solution formed was evaporated to dryness under vacuum to give a red precipitate of **8**, which was reprecipitated twice from CH$_2$Cl$_2$/hexane and vacuum-dried for 24 h. Anal. Calcd for C$_{38}$H$_{34}$B$_2$F$_8$Ru: C, 59.63; H, 4.48. Found: 59.77; H 4.55. 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 at −20 °C for 1 week. ^{1}H NMR (400 MHz, CD$_3$NO$_2$, 298 K) δ 8.630 [d, ^3J(H,H) = 8.2 Hz, 1H, H8], 8.624 [d, ^3J(H,H) = 9.0 Hz, 1H, H6], 8.320 [d (AB system), ^3J(H,H) = 8.4 Hz, 1H, H9 or H10], 8.295 [d, ^3J(H,H) = 8.2 Hz, 1H, H7], 8.292 [d (AB system), ^3J(H,H) = 8.4 Hz, 1H, H10 or H9], 8.159 [d (AB system), ^3J(H,H) = 8.5 Hz, 1H, H11 or H12], 8.118 [d (AB system), ^3J(H,H) = 8.5 Hz, 1H, H12 or H11], 8.010 [d, ^3J(H,H) = 9.0 Hz, 1H, H5], 7.981 [d, ^3J(H,H) = 8.2 Hz, 1H, H13], 7.859 [d, ^3J(H,H) = 6.3 Hz, 1H, H4], 7.355 [d, ^3J(H,H) = 8.2 Hz, 1H, H14], 7.183 (s, 1H, H16), 7.140 (s, 1H, H1), 6.728 [d, ^3J(H,H) = 6.3 Hz, 1H, H3], 6.293 [d, ^3J(H,H) = 6.6 Hz, 1H, Hb], 6.228 [d, ^3J(H,H) = 6.6 Hz, 1H, Hc], 5.822 [d, ^3J(H,H) = 6.6 Hz, 1H, Hc], 5.781 [d, ^3J(H,H) = 6.6 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(H,H) = 7.0 Hz, 3H, He], 0.622 [d, ^3J(H,H) = 7.0 Hz, 3H, He]). ^{13}C{^{1}H} NMR (100 MHz, CD$_3$NO$_2$, 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).

■ RESULTS AND DISCUSSION

The pentamethylcyclopentadienyl−iridium(III) complexes exhibiting η^6-coordination to hexahelicenes were obtained in nearly quantitative yield by reaction of [Cp*IrCl$_2$]$_2$, AgBF$_4$, and hexahelicene ligand in CD$_3$NO$_2$ solvent at room temperature and under an inert nitrogen atmosphere. Thus, the reaction of hexahelicene (**1**), 2,15-dimethylhexahelicene (**2**), or 2,15-dibromohexahelicene (**3**) with AgBF$_4$ and [Cp*IrCl$_2$]$_2$ led to formation of the complexes [Cp*Ir(η^6-**1**)][BF$_4$]$_2$ (**4A**), [Cp*Ir(η^6-**2**)][BF$_4$]$_2$ (**5A**), or [Cp*Ir(η^6-**3**)][BF$_4$]$_2$ (**6A**), respectively (Scheme 1). These new compounds can be stored in air for several months.

Previously, the synthesis of [Cp*Ir(η^6-arene)](BF$_4$)$_2$ complexes used the acetone solvent complex [Cp*Ir(OCMe$_2$)$_3$] as

Scheme 1



1, R = H
2, R = Me
3, R = Br

4A, R = H
5A, R = Me
6A, R = Br

2

7

2

8

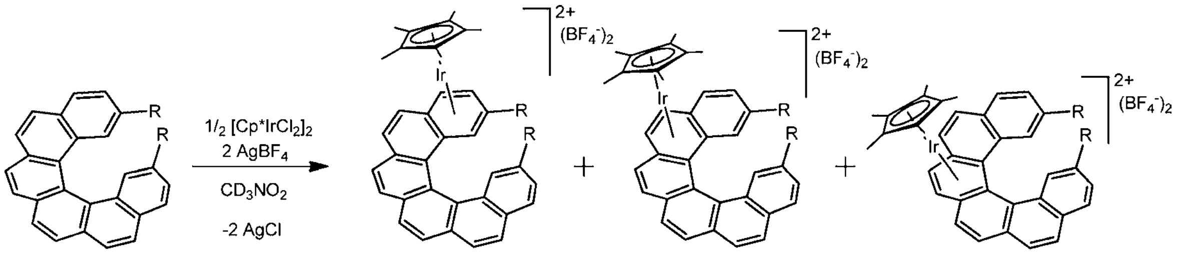
a reagent.[23] In the present work, η^6-hexalicene complexes of cyclopentadienyl−iridium have been prepared in a one-pot reaction starting from [Cp*IrCl$_2$]$_2$, removing the need for synthesis of the acetone precursor. Additionally, this reaction proceeded smoothly with a solvent as weakly coordinating as nitromethane. Both facts promote a preferential binding between the cyclopentadienyl−iridium fragment and the aromatic compound, reducing the problem of competitive reactions with other potential ligands.

The reaction between [Cp*IrCl$_2$]$_2$, AgBF$_4$, and **1** at room temperature under the aforementioned conditions led to preparation of **4A**. In the course of the reaction, three isomeric complexes **4A**, **4B**, and **4C** were observed by ^{1}H NMR (Scheme 2), two of which disappeared gradually, evolving into the single thermodynamic final product **4A**. 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 observed after 15 days. In order to characterize these intermediates, we decided to carry out low-temperature NMR experiments. Thus, [Cp*IrCl$_2$]$_2$, AgBF$_4$, and **1** were mixed in CD$_3$NO$_2$ directly into an NMR tube for study at 253 K. In the ^{1}H NMR spectrum acquired at that temperature, the presence of the three isomers in the ratio 27:64:9 (**4A**:**4B**:**4C**) was again observed (Figure 3).

Although none of the intermediates was isolated separately, the three isomers were characterized by NMR in CD$_3$NO$_2$ at low temperature [^{1}H, ^{13}C{^{1}H}, ^{1}H−^{1}H correlation spectroscopy (COSY), ^{1}H−^{1}H nuclear Overhauser effect spectroscopy (NOESY), and ^{1}H−^{13}C heteronuclear single-quantum coherence (HSQC) NMR spectra]. The biggest challenge was to establish in which ring of the hexahelicene the metal fragment was coordinated. In the ^{1}H−^{1}H NOESY NMR spectrum, several cross peaks were detected between the hydrogens of the Cp* and hexahelicene ligands (see Supporting Information, Figure S9). These data showed that the [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); and to H1, H5, H6, H7, H8, H9, and H10 in **4C** (bonded to C ring) (following the labeling of Figure 2). An inspection of Cp* chemical shifts in ^{1}H and ^{13}C spectra of complexes **4A**, **4B**, and **4C**, summarized in Table 1, revealed several general trends. The Cp* chemical shifts are upfield for isomer **4C**, showing that the C ring has more electron density than the other two (A and B rings). Therefore, if only electronic factors are considered, the C ring of hexahelicene should form the most stable compounds for metal coordination. However, the final product is not coordinated to the C ring. The reason for this behavior is not clear, but it is probably influenced by the increase of steric hindrance from H(C1) and R (see Figure 2) as we move from ring A to ring F (Figure 2). In fact, there is no NMR evidence for the formation of cyclopentadienyl−iridium complexes coordinated to the D, E, or F rings (same face of the hexahelicene as the final product), showing the importance of steric factors in the control of the reaction.

Complex **5A** was obtained by following the procedure used for **4A**. The reaction was completed after 6 days to form compound **5A** quantitatively (see Table 2). In this case, the reaction rate was significantly higher than in the preparation of **4A**. Perhaps this is partially due to the increased stability of

Scheme 2



1, R = H
2, R = Me
3, R = Br

4A, R = H
5A, R = Me
6A, R = Br

4B, R = H
5B, R = Me
6B, R = Br

4C, R = H
5C, R = Me
6C, R = Br

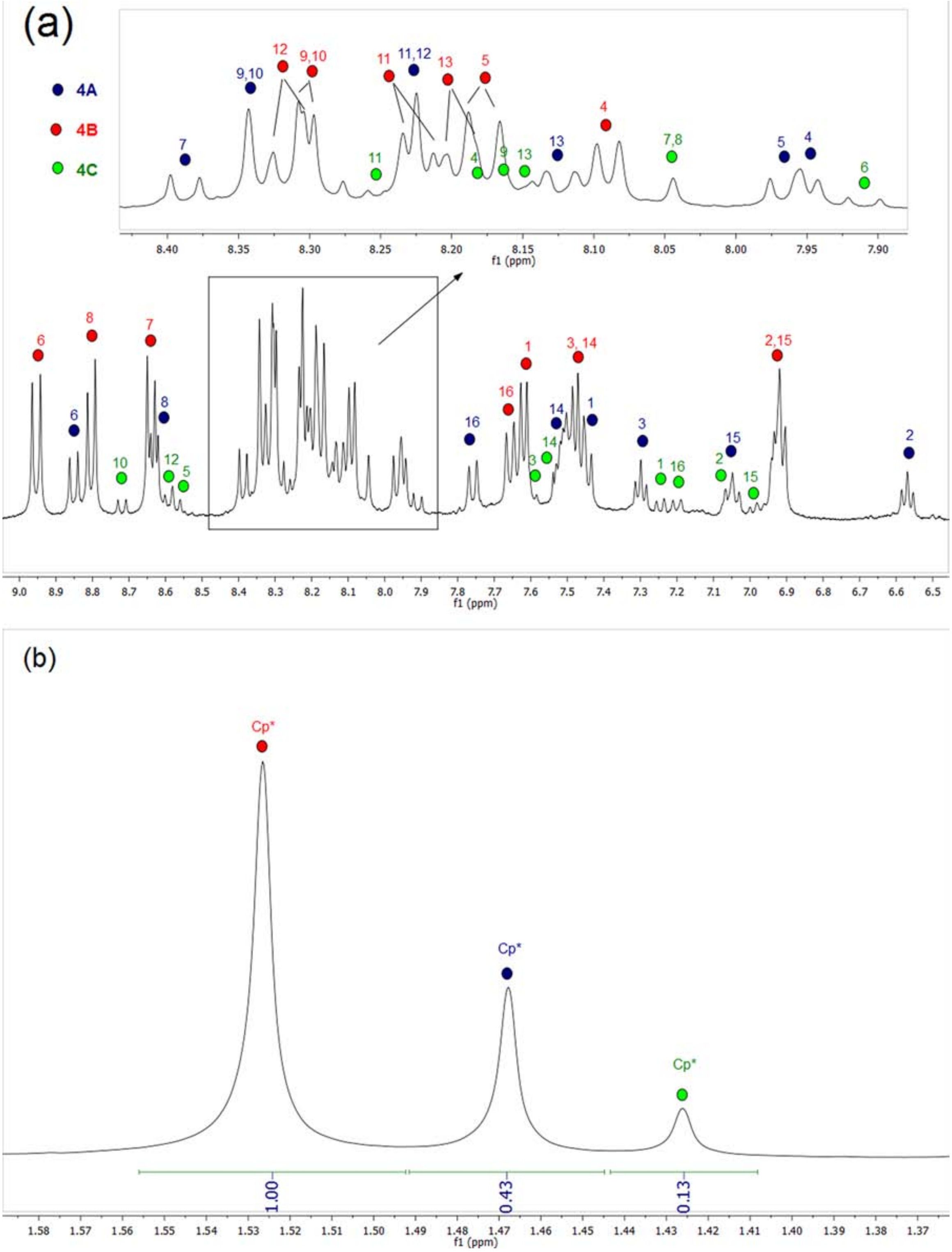


Figure 3. ^1H NMR spectrum at 253 K in (a) the aromatic region or (b) the cyclopentadienyl region of isomers **4A**, **4B**, and **4C** formed in the reaction between $[Cp^*IrCl_2]_2$, $AgBF_4$, and **1** in CD_3NO_2.

$[Cp^*Ir(\eta^6\text{-arene})](BF_4)_2$ complexes when the arenes are alkyl-substituted.[23] Monitoring the reaction by ^1H NMR spectroscopy showed the existence of two intermediates, as 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**, $[Cp^*IrCl_2]_2$, and $AgBF_4$ reacted at room temperature 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** (see Supporting Information). The ratio of the isomers **6A**:**6C** changed from 0:100 to 18:77 after 1 day at room temperature. The missing 5% was due to the presence of

Table 1. Chemical Shifts of the Cyclopentadienyl Ligand in Isomers 4A–C[a]

	chemical shift (ppm)		
	4A	4B	4C
	^{1}H NMR		
Cp*	1.47	1.53	1.43
	^{13}C{^{1}H} NMR		
C_5Me_5	103.6	104.5	102.5
$C_5\mathit{Me}_5$	8.7	8.8	8.1

[a] In CD_3NO_2 at 253 K.

Table 2. Selected Chemical Shifts for Compounds 4A, 5A, and 6A[a]

	chemical shift (ppm)		
	4A	5A	6A
	^{1}H 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}H} NMR		
C_5Me_5	105.3	104.7	106.4
$C_5\mathit{Me}_5$	8.9	8.6	8.5
C1	128.37		92.8
C2	128.43		
C3	98.14		101.6
C4	96.50		96.3

[a] In CD_3NO_2 at room temperature.

another isomer that could not be identified. Compound **6A** is the only product of the reaction mixture after 14 days. Isomer **6C** could be fully characterized by spectroscopic methods, since the ^{1}H NMR spectra at 253 K of complexes **4C** and **6C** display a similar pattern. The hydrogen signals for H10, H12, and H5 appear as doublets 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, all showing a doublet appearance. 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**. The signal for H6 appears as a doublet at 7.91 in **4C** and at 7.99 in **6C**. Upfield signals corresponding to terminal rings of hexahelicenes could not be compared due to different substituents in 2 and 15 positions.

The availability 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 the terminal ring of the helicene. In addition, we found a clear preference for coordination to the C ring at the beginning of the reaction. This coordination is fast (less than 30 s), because free hexahelicene ligand was never observed. However, formation of the thermodynamic product occurs after several days at room temperature, which evidences a slow isomerization. This movement can occur by two ways: through a migration of metal cationic units walking over the surface or through an intermolecular dissociation/association mechanism. Recently, this migration has been observed in another nonplanar polyaromatic compound containing corannulene, $[(COE)_2Rh(\eta^6\text{-}C_{20}H_{10})]PF_6$, for which both NMR and computational data seem to demonstrate the slide as the most feasible mechanism.[17d]

The reaction between equivalent amounts of $[Cp^*IrCl_2]_2$ and **2** with an excess of $AgBF_4$ at room temperature in CD_3NO_2 solvent and under an nitrogen inert atmosphere led to formation of the homobimetallic complex $[(Cp^*Ir)_2(\mu_2\text{-}\eta^6{:}\eta^6\text{-}\mathbf{2})][BF_4]_4$ (**7**) (Scheme 1). The reaction was completed after 3 h to form the final compound quantitatively. This thermodynamic product **7** was isolated and fully characterized by ^{1}H, ^{13}C{^{1}H}, ^{1}H–^{1}H COSY, and ^{1}H–^{1}H NOESY NMR spectra in CD_3NO_2 (see Supporting Information). The reduced number of signals in the final ^{1}H NMR spectrum evidences the higher symmetry of this dimer, which presents the coordination of two metal fragments $[IrCp^*]^{2+}$ on the hexahelicene terminal rings. We assume that the coordination is on the exo side, since the geometry of the helicene does not permit the coordination on the endo side due to steric hindrance. The reaction rate is much higher than in the synthesis of the above monometallic complexes and 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 when electronic and steric factors are considered. In addition, as already mentioned, the methyl group in the hexahelicene terminal rings favors the binding in this position. Both facts could help to promote this unusual and rapid evolution of the intermediates to afford the thermodynamic product **7**.

In an attempt to determine how many $[IrCp^*]^{2+}$ metal fragments can coordinate to 2,15-dimethylhexahelicene, an experiment was carried out in which 1 equiv of **2** and 3 equiv of $[IrCp^*]^{2+}$ were reacted under the same conditions. This reaction was monitored by ^{1}H NMR periodically over several weeks. No products with three $[IrCp^*]^{2+}$ units coordinated to **2** were observed, and the complex **7** was identified as the unique coordination product to the helicene. This reaction shows that only one $[IrCp^*]^{2+}$ 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, $[(\eta^6\text{-cymene})Ru]^{2+}$. Thus, 1 equiv of $[(\eta^6\text{-cymene})RuCl_2]_2$ dimer, 2 equiv of helicene **2**, and 2 equiv of $AgBF_4$ in CD_3NO_2 solvent were reacted at room temperature to afford $[(\eta^6\text{-cymene})Ru(\eta^6\text{-}\mathbf{2})][BF_4]_2$ (**8**) in quantitative yield after 15 days (Scheme 1). During the reaction several intermediates were observed, but none could be fully characterized. The ^{1}H and ^{13}C NMR spectra of complex **8** (see Supporting Information) display a pattern similar to those observed in cymene–ruthenium compounds containing other arene ligands. For example, the proton signals for hydrogens attached to the coordinated rings are upfield relative to the free ligand, as reported for $[(\eta^6\text{-cymene})Ru(\eta^6\text{-coronene})][BF_4]_2$.[16c] The observed ^{13}C and ^{1}H chemical shifts for the *p*-cymene ligand in **8** are in agreement with those found in other Ru(II) sandwich complexes. The methyls of the isopropyl group in **8** are diasterotopic and appear as a pair of doublets. The same behavior has been found in $[(\eta^6\text{-cymene})Ru(\eta^6\text{-}L)][BF_4]_2$, where L = triphenylene, 4*H*-cyclopentaphenanthrene, pyrene, 4,5-benzopyrene, 1,2:5,6-dibenzanthracene, naphthalene, phenanthrene, anthracene, fluorene, 9,10-dihydroanthracene, *trans*-stilbene, *cis*-stilbene, coronene, chrysene, and perylene.[16]

Red crystals of 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 **8** the transition metal is 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 4).

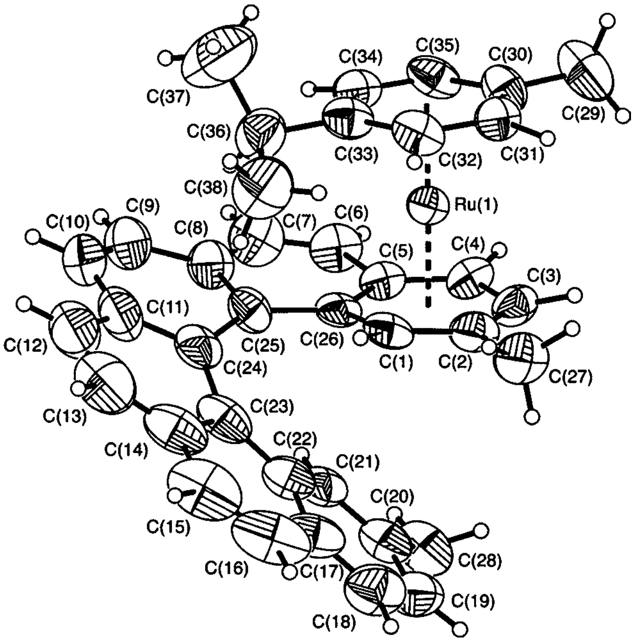


Figure 4. View of the $[(\eta^6\text{-cymene})\text{Ru}(\eta^6\text{-}\mathbf{2})][\text{BF}_4]_2$ (**8**) structure illustrating the atomic numbering scheme. Only one of the stereo isomers is represented for clarity. Thermal ellipsoids have been drawn at the 30% probability level. The two BF_4^- counterions are not shown.

One of the parameters that can be used to describe the change of the helical structure as a consequence of the metal fragment coordination is the helical pitch, defined as the distance along the helical axis that results in one full turn of the helix. In this structure, the helical pitch measured between C2 and C20 is 3.828 Å, while in free hexahelicene the pitch is 4.576 Å.[24] These data show that the coordination of the (η^6-cymene)Ru^+ unit flattens the hexahelicene ligand.

DFT calculations were performed to gain additional information into the experimental findings. Complex **8** was examined computationally at the B3LYP/SVP (SDD for Ru) level of theory in nitromethane as solvent. The calculated structure of **8** is in reasonable agreement with the obtained X-ray crystallography structure. All bond distances in the minimized structure compare well with the experimental ones (see Supporting Information, Table S1). For example, the calculated helical pitch distance of 4.152 Å is close to the experimentally observed value of 3.828 Å, when it is taken into account that packing forces in the solid state can affect to some extent the helical pitch.

The potential energy surfaces (PES) were also simulated for the systems with cyclopentadienyl iridium coordinated to A, B, and C rings of hexahelicene (complexes **4A**, **4B**, and **4C**, respectively). If the structure of **4B** is chosen as the zero-energy reference point, the final product **4A** is lower in energy by $\Delta G_{298\text{K}} = -7.7$ kcal/mol, while the complex **4C** has $\Delta G_{298\text{K}} = -2.3$ kcal/mol. As expected, these energies are in good agreement with the formation of the observed structures.

DFT calculations were again performed to determine the transition states and the barriers connecting complexes **4A**, **4B**, and **4C** (Figure 5). Two new local minima (**4AB** and **4BC**) were located in the potential energy surface (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 presenting 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(**4C**−**4BC**), followed by a new haptotropic migration from

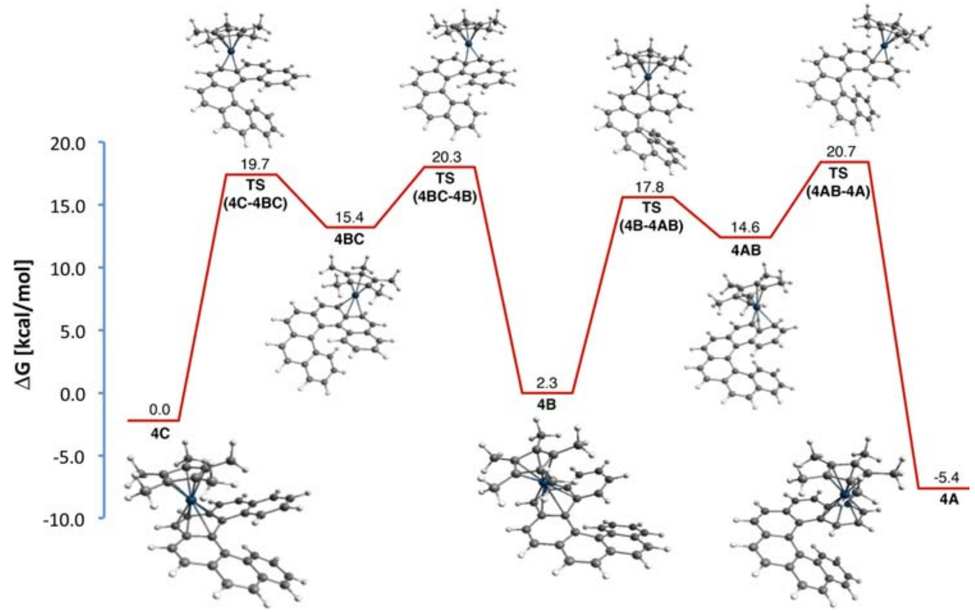


Figure 5. Reaction profile [kilocalories per mole, B3LYP/SVP (SDD for Ir)] for the ring-walking and the structures of the various complexes. (Atomic color scheme: C, gray; H, white; iridium, blue.)

η^3-C═C−C to η^6-arene (**4BC** → **4B**) via TS(**4BC**−**4B**). A similar reorganization was observed to pass from **4B** to **4A**. Related findings have been observed by Solà and co-workers[25] in a previous work, where the metal fragment is tricarbonylchromium. These computational results suggest that a ring walking process through a haptotropic rearrangement is a plausible movement for this system, although dissociation could not be completely ruled out.

■ CONCLUSIONS

In summary, the first η^6-complexes of iridium and ruthenium coordinated to helicenes have been obtained. All of them show η^6-coordination of the metal fragment to the helicene terminal ring as manifested in the X-ray structure of complex **8**. We have also identified and fully characterized some of the intermediates in which the metal fragment is coordinated to the helicene internal rings. The first detected intermediates show the metal unit η^6-coordinated to the C ring. The subsequent migration from the C ring to the A ring (final product) is a slow process that occurs over several days. DFT calculations were performed to support a plausible reaction profile of this isomerization. In these studies, new local minima and some transition states were located and a haptotropic rearrangement seems to be the most feasible movement. In search of the maximum number of metal fragments that can be coordinated to hexahelicene, we synthesized complex **7**. This dimer involves coordination of two metal fragments $[IrCp^*]^{2+}$ on the exo side of the hexahelicene terminal rings, which is the maximum number of metal units that can be bonded.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional text, 31 figures, and additional tables giving full characterization, NMR spectra (^{1}H, ^{13}C{^{1}H}, COSY, NOESY, and HSQC) for compounds **4A**, **4A**/**4B**/**4C** mixture, **5A**, **6A**, **6C**, **7**, and **8**; computational details; and crystallographic data for complex **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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