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# Chemoselectivity on the synthesis of iridacycles: a theoretical and experimental study

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Dedicated to Dr. Maurizio Peruzzini in occasion of his 65<sup>th</sup> birthday.

## Abstract

The selective synthesis of a spirobifluorene-iridacyclopentadiene complex has been achieved through the corresponding methoxyalkenylcarbeneiridium complex. The chemoselectivity of the C–H bond activation over the precursor has been studied via DFT calculations on the relative energies of the *E* and *Z* isomers of several examples and compared with experimental results. The data suggest that the steric effect of the substituents has more influence than their electronic character on the structure of the resulting iridacycle compounds.

Keywords: metallacycles, spirobifluorene, iridium, stereoselectivity

## Introduction

Metallacyclic systems have been shown to greatly expand the properties of the purely organic counterpart.<sup>[1]</sup> Therefore several studies have been devoted to the development of new synthetic methodologies opening access to metallaromatic complexes<sup>[1a]</sup> as well as non-aromatic metallacycles.<sup>[2]</sup> In this regard, our research group has developed a synthetic methodology opening access to new metallaromatic compounds via the C–H bond activation of a methoxyalkenylcarbeneiridium and rhodium complexes.<sup>[3]</sup> We have earlier found experimental<sup>[3a, 3b, 3d]</sup> and theoretical<sup>[3b]</sup> evidence that the *E/Z* isomerism of this intermediate has a major role.

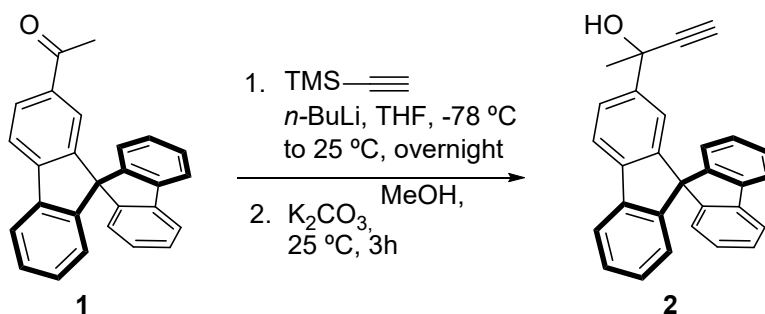
Spirobifluorene (SBF) is a polycyclic aromatic hydrocarbon formed by two fluorene units with perpendicular orientation with high rigidity and solubility.<sup>[4]</sup> Furthermore, SBFs may feature axial chirality by introducing substituents at specific positions.<sup>[5]</sup> Another very interesting property of SBFs is spiroconjugation, consisting of a delocalization of the charge on the carbons adjacent to the spiranic carbon, which implies characteristic absorption and emission bands.<sup>[6]</sup> On the contrary, there are also known examples of reactivity, where SBFs show an independent behaviour between the two fluorene units.<sup>[4]</sup> All these properties make SBF derivatives widely used in the field of materials.<sup>[7]</sup>

Extensive research has been performed in the synthesis and study of the properties of organic spirobifluorene derivatives by modulating the substitution pattern.<sup>[8]</sup> Although metal-containing compounds have shown an improvement of the optical properties when compared to their organic counterparts, the inclusion of the SBF moiety into organometallic complexes is still limited and under study.<sup>[9]</sup>

Recently, our group reported the synthesis of the first spirobifluorene metallaaromatic complex which shows distinct optical properties compared to free spirobifluorene.<sup>[3b]</sup> Our interest in the formation of spirobifluorene metallaromatics through our synthetic methodology leads in the present work to study the influence of the substituents in the structure of the resulting metallacycles.

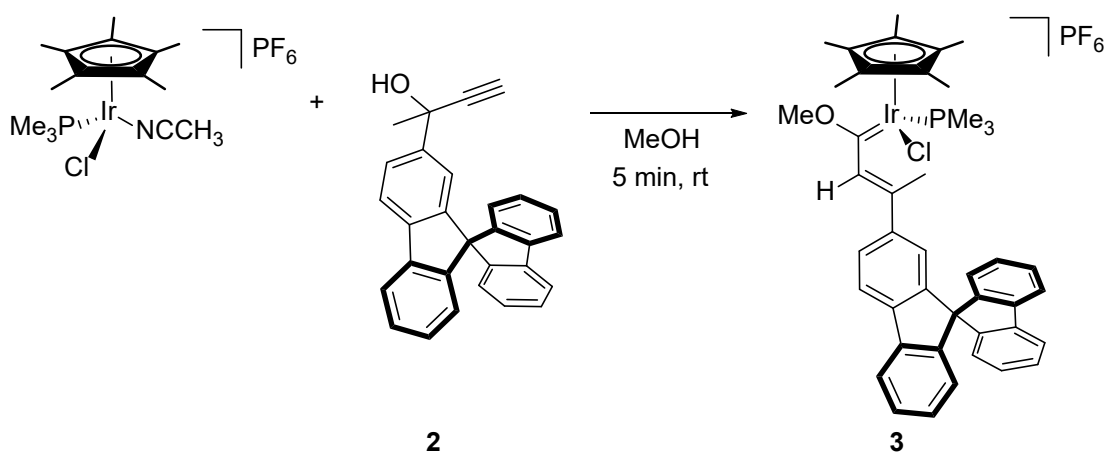
## Results and Discussion

Synthesis of the new propargylic alcohol 2-(2-SBF)-3-butyn-2-ol (**2**) was achieved by usual synthesis of the lithium acetylide which was reacted with the corresponding ketone 2-acetyl-SBF (**1**) (Scheme 1, see experimental section for characterization details).<sup>[10]</sup>



**Scheme 1.** Synthesis of 2-(2-SBF)-3-butyn-2-ol (**2**).

Once the spirobifluorene containing propargylic alcohol **2** was obtained, the first step was to synthesize the corresponding methoxyalkenylcarbene complex **3**. Therefore, treatment of **2** with  $[\text{IrCp}^*\text{Cl}(\text{NCMe})(\text{PMe}_3)]\text{PF}_6$  in methanol yielded the new iridium SBF containing methoxyalkenylcarbene  $[\text{IrCp}^*\text{Cl}\{\text{C}(\text{OMe})\text{CH}=\text{C}(2\text{-SBF})\text{Me}\}(\text{PMe}_3)]\text{PF}_6$  (**3**) (Scheme 2). The synthesis of **3** takes place through the formation of an allenylidene complex followed by the nucleophilic attack of the solvent to its *alpha* carbon atom.<sup>[11]</sup> Although a mixture of isomers can be expected due to the capability of the SBF ligand to be in the position close to the iridium metal<sup>[3b]</sup> and the previously observed mixture of isomers with substituted phenyl rings<sup>[3c]</sup> or bulky ligands,<sup>[3a]</sup> only the *E*-**3** isomer is obtained.

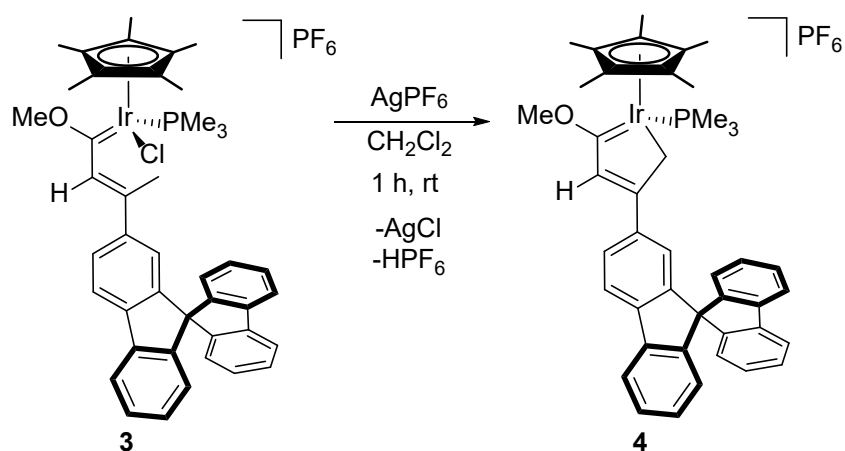


**Scheme 2.** Synthesis of complex **3**.

Apart from the typical resonances of the Cp\* and the phosphine ligands in **3**, the nature of the methoxyalkenylcarbene ligand is confirmed by the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra data. On the one hand, in the  $^1\text{H}$  NMR spectrum the methoxy ligand resonance appears at 4.73 ppm as a singlet while the one corresponding to the proton bonded to the beta carbon is observed at 6.95 ppm as a broad singlet. The resonances of the spirobifluorene moiety are similar to organic SBFs such as compound **2** while the signal of the methyl substituent at 2.26 ppm presents a small coupling to the proton of the *beta* carbon ( $^4J_{\text{HH}} = 0.5$  Hz). On the other hand, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum exhibits the usual signals of the alkenylcarbene ligand with the low field resonances at 262.5 and 154.5 ppm corresponding to the alpha and gamma carbon atoms, respectively. The  $\text{C}_\alpha$  signal could only be observed by its correlation with the methoxy ligand by a  $\{^1\text{H}, ^{13}\text{C}\}$  HMBC NMR spectrum. On the other hand, the  $\text{C}_\beta$  resonance at 141.4 ppm appears as a doublet of 6.1 Hz due to the carbon-phosphorus coupling confirming

the bound of the alkenyl ligand to the iridium centre. The rest of the signals, including the methoxy group (69.1 ppm), methyl substituent (20.9 ppm) and the spiranic carbon at 66.2 ppm, are in agreement to previously reported methoxy(alkenyl)carbene iridium complexes<sup>[3a-e, 11]</sup> and compound **2**. The stereoselective formation of *E* isomer is experimentally supported by the absence of correlation between the *beta* hydrogen and the methyl group at the *gamma* carbon by  $\{^1\text{H}, ^1\text{H}\}$  NOESY NMR.

In accordance with *E* isomerism in **3**, its treatment with silver hexafluorophosphate led to 1,3-iridacyclopentadiene complex,  $[\text{IrCp}^*\{\text{C}(\text{OMe})\text{CH}=\text{C}(2\text{-SBF})(\text{CH}_2)\}(\text{PMe}_3)]\text{PF}_6$  (**4**), in high yields by C–H bond activation of the methyl substituent in the alkenyl ligand (Scheme 3) instead of the spirobifluorene metallaromatic complex that would have been formed by activation of the SBF ligand in case of obtaining the *Z* isomer of the methoxyalkenylcarbene complex **3**.

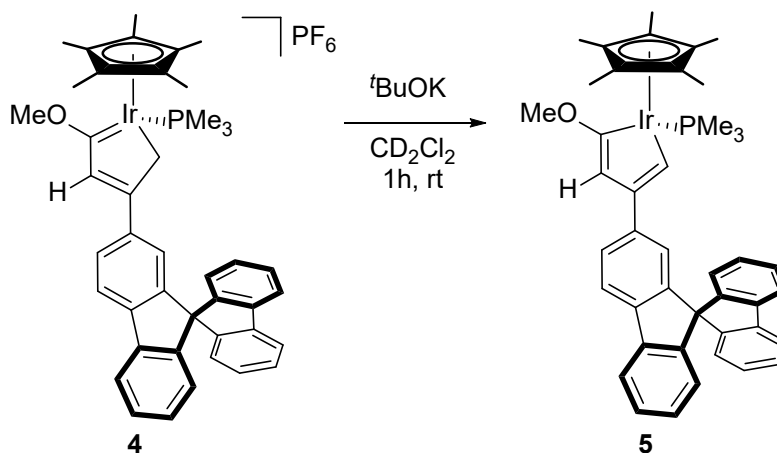


**Scheme 3.** Synthesis of complex **4**.

The C–H bond activation of the methyl group to form complex **4** is supported by the  $^1\text{H}$  NMR spectrum. Apart from the doublet of 1.3 Hz at 7.07 ppm corresponding to the proton bounded to the *beta* carbon coupled to the phosphorus atom, it exhibits a signal around 2.16 ppm as a multiplet which integrates by two protons instead of three which corresponds to the previous methyl substituent, now bonded to iridium as a  $\text{CH}_2$  group. Furthermore, the  $^{13}\text{C}\{^1\text{H}\}$  NMR resonance of the  $\text{CH}_2$  group appears as a doublet with a C–P coupling constant of 7.4 Hz, value in the range of the observed for the C–P coupling of the *alpha* carbon to the phosphine ligand ( $^2J_{\text{CP}} = 9.5$  Hz) at 249.4 ppm due to its carbene character. This fact confirms that both carbons are directly bonded to the iridium centre, and therefore, the iridacycle is formed.

Finally, the  $C_\beta$  and  $C_\gamma$  resonances at 135.7 and 196.6 ppm as singlets also endorse the arrangement proposed.

The 1,3-iridacyclopentadienes can be deprotonated using a base in order to obtain the neutral 2,4-iridacycle derivatives.<sup>[3d]</sup> Thus, complex **4** was reacted with  $K^tBuO$  for 1 h at room temperature to give  $[IrCp^*\{C(OMe)=CHC(2-SBF)=CH\}(PMe_3)]PF_6$  (**5**) quantitatively (Scheme 4).

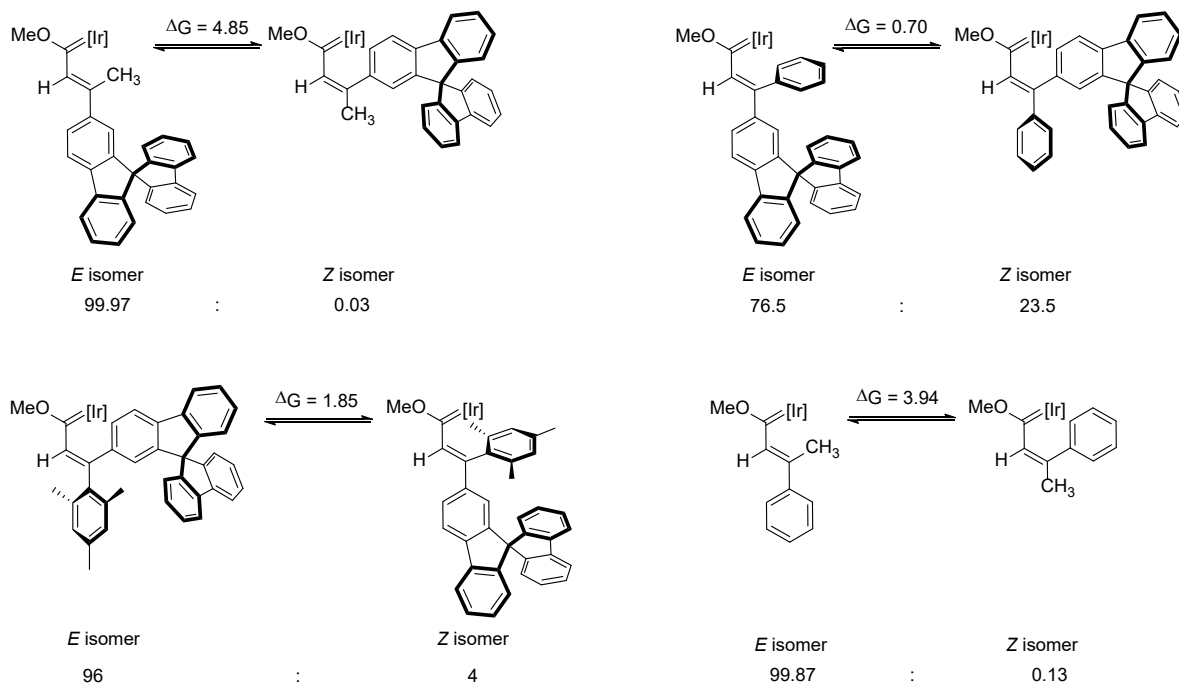


**Scheme 4.** Synthesis of complex **5**.

In contrast to complexes **3** and **4**, complex **5** does not exhibit the typical heptate at higher field in  $^3P\{^1H\}$  corresponding to the  $PF_6$  anion due to its neutral character. In  $^1H$  NMR spectrum, apart from the resonances of the  $Cp^*$ ,  $PMe_3$ ,  $OMe$  and  $SBF$  ligands, the double bonds rearrangement in the iridacycle may be confirmed. Therefore, no signal can be observed anymore at high field for the former  $CH_2$  group, instead, a new resonance, which integrates for one proton, appears at 7.49 ppm as a doublet of doublets corresponding to the proton bounded to the  $\delta$  carbon. The multiplicity exhibited is due to the coupling to the phosphorus atom ( $^3J_{HP} = 3.2$  Hz) and the proton in *beta* position ( $^4J_{HH} = 2.6$  Hz) which appears at 5.65 ppm with the same multiplicity and similar H–P coupling ( $^3J_{HP} = 2.1$  Hz). The shift and coupling of the  $C_\delta H$  moiety confirms not only the abstraction of a proton and the iridium-carbon bond but also the character change from  $C(sp^3)$  to  $C(sp^2)$ . The  $^{13}C\{^1H\}$  NMR spectrum also confirms the rearrangement of the iridacycle. Thus,  $C_\alpha$ ,  $C_\beta$  and  $C_\gamma$  resonances shifted to higher field compared to complex **4** (179.4, 105.9 and 142.4 ppm, respectively) and coupled to phosphorus atom with 13.7, 1.8 and 2.3 Hz, respectively. The

$\alpha$  carbon coupling is, again, similar to the one exhibit by the  $\delta$  carbon ( $^2J_{HP} = 13.3$  Hz) which appears at 133.8 ppm due to the double bond character.

In an attempt to understand the iridamethoxyalkenylcarbene isomerism which is decisive in the reactivity of these complexes to obtain a particular metallacycle, free Gibbs energy calculations were carried out between the *E* and *Z* isomers and these values are compared with other examples using Gaussian 09 program package (Figure 1).<sup>[12]</sup>



**Figure 1.** Calculated *E/Z* ratios and  $\Delta G$  values (in kcal/mol) of the hypothetical equilibrium in different methoxyalkenylcarbeneiridium complexes (B3LYP/6-31G\*\*/lan12dz for Ir). [Ir] = [IrCp\*Cl(PMe<sub>3</sub>)].

For complex **3**, DFT calculations predict the higher stability of the *E* isomer with a difference of 4.85 kcal/mol over the *Z* complex, corresponding to a *E/Z* ratio of 99.97:0.03 in a hypothetical thermodynamic equilibrium. The formation of the metallacyclic complex **4** instead of a spirobifluorene metallaromatic complex resembles the reactivity observed for [IrCp\*Cl{=C(OMe)CH=C(Ph)(Me)}(PMe<sub>3</sub>)]PF<sub>6</sub> with a methyl and a phenyl substituents at  $\gamma$  carbon.<sup>[3d]</sup> However, when bearing spirobifluorene and mesityl groups as in [IrCp\*Cl{=C(OMe)CH=C(2-SBF)(Mes)}(PMe<sub>3</sub>)]PF<sub>6</sub>, a *E/Z* ratio of 96:4 with a  $\Delta G = 1.85$  kcal/mol was calculated, leading to obtaining the spirobifluorene metallaromatic complex.<sup>[3b]</sup> In order to gain further insight in the factors driving this behaviour, similar DFT

calculations were performed to study the hypothetical thermodynamic equilibrium in the conversion between the *E* and *Z* methoxyalkenylcarbene complexes (Figure 1).

Similarly to complex **3**,  $[\text{IrCp}^*\text{Cl}\{\text{C}(\text{OMe})\text{CH}=\text{C}(\text{Ph})(\text{Me})\}(\text{PMe}_3)]\text{PF}_6$  presents a *E/Z* ratio 99.87:0.13 with a  $\Delta G = 3.94$  kcal/mol, which supports the formation of the corresponding metallacycle by C–H bond activation of the methyl group. However, when a hypothetical complex bearing a benzene and a spirobifluorene substituents at *gamma* position was calculated, the *E/Z* ratio of 76.5:23.5 with a  $\Delta G = 0.70$  kcal/mol for the thermodynamic equilibrium was determined, which would lead to the formation of both isomers as observed in previously studied cases.<sup>[3a, 3c]</sup> All this seems to indicate that a bulky ligand and its spatial arrangement has a greater influence on the final product than its electronic properties.

## Conclusions

The synthesis with total chemoselectivity of iridacyclopentadiene **5** has been achieved. Mono and bidimensional NMR spectroscopy experiments were able to univocally confirm the structure of iridacycles **4** and **5** as well as the *E* isomer of the corresponding methoxyalkenylcarbeneiridium complex **3**. In order to get further insight on the effect of the substituents in the stability and reactivity towards the formation of metalacycles, DFT theoretical simulations on the methoxyalkenylcarbeneiridium intermediate of this and other structurally related examples have been performed. Comparison of the theoretically predicted relative energies of their *E/Z* isomers with the experimental results suggests that the steric effects of the substituents in the  $\gamma$  carbon of the methoxyalkenylcarbeneiridium intermediate are more important than their electronic character for the relative stability of the *E/Z* isomers, and therefore, also the reactivity of them in obtaining iridacycles. In this case, the iridacycles were obtained instead of the spirobifluorene metallaromatic.



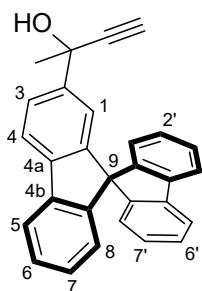
## Experimental Section

### General Procedures, Methods and Materials

All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by the usual procedures<sup>[13]</sup> and, prior to use, distilled under argon. The starting materials [IrCp\*Cl(NCMe)(PMe<sub>3</sub>)]PF<sub>6</sub><sup>[3e]</sup> and 2-acetyl-9,9'-spirobi[fluorene]<sup>[14]</sup> were prepared as described in the literature. All reagents were obtained from commercial sources. Unless stated, NMR spectra were recorded at room temperature on Bruker ARX-400 instrument, with resonating frequencies of 400 MHz (<sup>1</sup>H), 161 MHz (<sup>31</sup>P{<sup>1</sup>H}), and 100 MHz (<sup>13</sup>C{<sup>1</sup>H}) using the solvent as the internal lock. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} signals are referred to internal TMS and those of <sup>31</sup>P{<sup>1</sup>H} to 85% H<sub>3</sub>PO<sub>4</sub>; downfield shifts (expressed in ppm) are considered positive. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR (or JMOD) signal assignments were confirmed by {<sup>1</sup>H, <sup>1</sup>H} COSY, {<sup>1</sup>H, <sup>13</sup>C} HSQC, {<sup>1</sup>H, <sup>13</sup>C} HMBC and DEPT experiments. Coupling constants are given in hertz. High-resolution electrospray mass spectra were acquired using an apex-Qe spectrometer.

All DFT calculations were carried out with the Gaussian 09 program package.<sup>[12]</sup> Structures were optimized at the B3LYP level<sup>[15]</sup> employing the lanl2dz for the iridium atom and 6-31G\*\* basis set for the rest of the elements in gas phase.

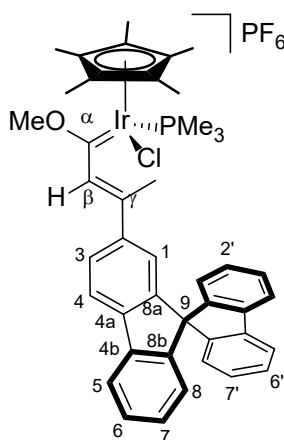
### Synthesis of HC≡C-C(OH)(2-SBF)CH<sub>3</sub> (2)



To a solution of trimethylsilylacetylene (2 mL, 13.95 mmol) in dry THF (50 mL) at around 203 K, *n*-butyllithium 1.6 M in hexanes (9 mL, 13.95 mmol) was added dropwise and the reaction mixture was stirred for one hour. After that, 2-acetyl-9,9'-spirobi[fluorene] (**1**) (0.5 g, 1.395 mmol) was added and the mixture was allowed to room temperature overnight. Then, methanol (50 mL) and K<sub>2</sub>CO<sub>3</sub> (1.9 g, 13.95 mmol) were added at room temperature and the mixture was stirred again for 3h. The mixture was filtrated through sort pad of SiO<sub>2</sub> and washed with ethyl acetate. Yield: 533 mg (99%). C<sub>29</sub>H<sub>20</sub>O: 384.5 g/mol. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 1.63 (s, 3H, CH<sub>3</sub>); 2.59 (s, 1H, ≡CH); 3.39 (s, 1H, OH); 6.68, 6.71 and 6.72 (all ddd, 1H, <sup>3</sup>J<sub>HH</sub>=7.6, <sup>4</sup>J<sub>HH</sub>=1.1, <sup>5</sup>J<sub>HH</sub>=0.7 Hz, H<sup>8</sup>, H<sup>1'</sup> and H<sup>8'</sup>); 7.00 (dd, 1H, <sup>4</sup>J<sub>HH</sub>=1.7, <sup>5</sup>J<sub>HH</sub>=0.6 Hz, H<sup>1</sup>); 7.12, 7.13 and 7.14 (all td, 1H, <sup>3</sup>J<sub>HH</sub>=7.5, <sup>4</sup>J<sub>HH</sub>=1.2 Hz, H<sup>7</sup>, H<sup>2'</sup> and

$H^{7'}$ ); 7.39, 7.398 and 7.403 (all td, 1H,  $^3J_{\text{HH}} = 7.5$ ,  $^4J_{\text{HH}} = 1.1$  Hz,  $H^6$ ,  $H^{3'}$  and  $H^6$ ); 7.69 (dd, 1H,  $^3J_{\text{HH}} = 8.0$ ,  $^4J_{\text{HH}} = 1.8$  Hz,  $H^3$ ); 7.88 (dd, 1H,  $^3J_{\text{HH}} = 8.1$ ,  $^5J_{\text{HH}} = 0.7$  Hz,  $H^4$ ); 7.89 (ddd, 1H,  $^3J_{\text{HH}} = 7.7$ ,  $^4J_{\text{HH}} = 1.1$ ,  $^5J_{\text{HH}} = 0.7$  Hz,  $H^5$ ); 7.90 (ddd, 2H,  $^3J_{\text{HH}} = 7.9$ ,  $^4J_{\text{HH}} = 1.1$ ,  $^5J_{\text{HH}} = 0.7$  Hz,  $H^4 + H^5$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  33.5 (s,  $\text{CH}_3$ ); 66.5 (s,  $\text{C}^9$ ), 70.0 (s,  $\text{C-OH}$ ); 73.1 (s,  $\text{C}\equiv\text{CH}$ ); 87.7 (s,  $\text{C}\equiv\text{CH}$ ); 120.3 (s,  $\text{C}^1$ ); 120.4 (s,  $\text{C}^4$ ) 120.59 (2C) and 120.61 (all s,  $\text{C}^5$ ,  $\text{C}^4'$  and  $\text{C}^5'$ ); 124.1 (s,  $\text{C}^8$ ); 124.2 (s, 2C,  $\text{C}^1'$  and  $\text{C}^8'$ ); 125.6 (s,  $\text{C}^3$ ); 128.20, 128.25 and 128.3 (all s, 2C,  $\text{C}^7$ ,  $\text{C}^2'$ ,  $\text{C}^7'$ ,  $\text{C}^6$ ,  $\text{C}^3'$  and  $\text{C}^6'$ ); 145.6 (s,  $\text{C}^2$ ); 141.6, 142.0 and 142.3 (all s,  $\text{C}^{4b}$ ,  $\text{C}^{4a'}$  and  $\text{C}^{4b'}$ ); 142.28 (s,  $\text{C}^{4a}$ ); 149.0, 149.1, 149.3 and 149.7 (all s,  $\text{C}^{8a}$ ,  $\text{C}^{8b}$ ,  $\text{C}^{8a'}$  and  $\text{C}^{8b'}$ ) ppm.

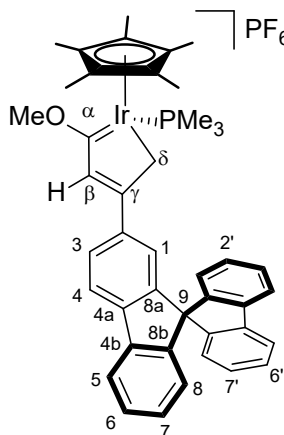
### Synthesis of $[\text{IrCp}^*\text{Cl}\{\text{C}(\text{OMe})\text{CH}=\text{C}(\text{2-SBF})\text{Me}\}(\text{PMe}_3)]\text{PF}_6$ (**3**)



To a yellow solution of  $[\text{IrCp}^*\text{Cl}(\text{NCMe})(\text{PMe}_3)]\text{PF}_6$  (240 mg, 0.28 mmol) in 20 ml of methanol,  $\text{HC}\equiv\text{C}-\text{C}(\text{OH})(\text{2-SBF})\text{CH}_3$  (**2**) (440 mg, 1.40 mmol) was added and the mixture was stirred for 5 min at room temperature. The brown suspension obtained was vacuum concentrated obtaining a brown solid which was washed with diethylether ( $3 \times 5$  mL) and dried in vacuum. Yield: 140 mg (63%). Anal. Calcd for  $\text{C}_{43}\text{H}_{46}\text{O}_6\text{ClIrP}_2$  (982.4 g/mol): C 52.57, H 4.72; found: C, 52.61; H, 4.75. **MS** ( $m/z$ , referred to the most abundant isotopes):  $m/z$ : 837.26  $[\text{M}]^+$ , 725.24  $[\text{M}-\text{PMe}_3]^+$ .  $^1\text{H}$  NMR:  $\delta$  1.43 (d, 9H,  $^2J_{\text{HP}} = 10.8$  Hz,  $\text{P}(\text{CH}_3)_3$ ); 1.62 (d, 15H,  $^4J_{\text{HP}} = 2.2$  Hz,  $\text{C}_5(\text{CH}_3)_5$ ); 2.26 (d, 3H,  $^4J_{\text{HH}} = 0.5$  Hz,  $\text{CH}_3$ ); 4.73 (s, 3H,  $\text{OCH}_3$ ); 6.72 (ddd, 2H,  $^3J_{\text{HH}} = 7.7$ ,  $^4J_{\text{HH}} = 1.8$ ,  $^5J_{\text{HH}} = 1.0$  Hz,  $H^{1'} + H^{8'}$ ); 6.81 (ddd, 1H,  $^3J_{\text{HH}} = 7.7$ ,  $^4J_{\text{HH}} = 1.0$ ,  $^5J_{\text{HH}} = 0.8$  Hz,  $H^8$ ); 6.83 (d br, 1H,  $^4J_{\text{HH}} = 1.8$  Hz,  $H^1$ ); 6.95 (s br, 1H,  $\text{C}_\beta\text{H}$ ); 7.15 and 7.17 (both td, 1H,  $^3J_{\text{HH}} = 7.5$ ,  $^4J_{\text{HH}} = 1.1$  Hz,  $H^{2'}$  and  $H^{7'}$ ); 7.24 (td, 1H,  $^3J_{\text{HH}} = 7.5$ ,  $^4J_{\text{HH}} = 1.1$  Hz,  $H^7$ ); 7.43 (td, 1H,  $^3J_{\text{HH}} = 7.5$ ,  $^4J_{\text{HH}} = 1.1$  Hz,  $H^6$ ); 7.46 (2 td, 2H,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.1$  Hz,  $H^{3'} + H^6$ ); 7.70 (dd, 1H,  $^3J_{\text{HH}} = 8.1$ ,  $^4J_{\text{HH}} = 1.9$  Hz,  $H^3$ ); 7.93 and 7.95 (both ddd, 1H,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.1$ ,  $^5J_{\text{HH}} = 0.7$  Hz,  $H^{4'}$  and  $H^5$ ); 7.96 (dd, 1H,  $^3J_{\text{HH}} = 8.1$ ,  $^5J_{\text{HH}} = 0.5$  Hz,  $H^4$ ); 7.97 (ddd, 1H,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.1$ ,  $^5J_{\text{HH}} = 0.8$  Hz,  $H^5$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  -144.11 (sept,  $^1J_{\text{PF}} = 709.1$  Hz,  $\text{PF}_6$ ); -30.15 (s,  $\text{P}(\text{CH}_3)_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  9.0 (d,  $^4J_{\text{CP}} = 0.95$ ,  $\text{C}_5(\text{CH}_3)_5$ ); 14.3 (d,  $^1J_{\text{CP}} = 40.7$  Hz,  $\text{P}(\text{CH}_3)_3$ ); 20.9 (s,  $\text{CH}_3$ ); 66.2 (s,  $\text{C}^9$ ), 69.1 (s,  $\text{OCH}_3$ ); 98.3 (d,  $^2J_{\text{CP}} = 2.5$  Hz,  $\text{C}_5(\text{CH}_3)_5$ ); 120.7 (both s, 2C  $\text{C}^4' + \text{C}^5'$ ); 121.4 (s,  $\text{C}^4$ ); 121.5 (s,  $\text{C}^5$ ); 122.1 (s,  $\text{C}^1$ ); 124.23 and 124.24 (both s,  $\text{C}^1'$  and  $\text{C}^8'$ ); 124.7 (s,  $\text{C}^8$ ); 128.4 (s,  $\text{C}^3$ );

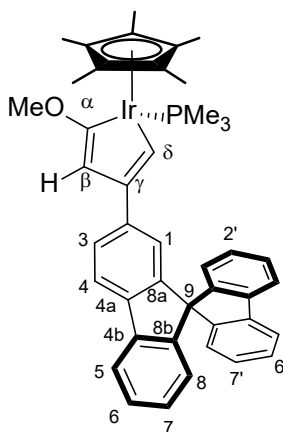
128.49, 128.51, 128.65 and 128.66 (all s,  $C^{2'}$ ,  $C^{7'}$ ,  $C^{3'}$  and  $C^{6'}$ ); 128.8 (s,  $C^6$ ); 129.7 (s,  $C^7$ ); 140.5 (s br,  $C^2$ ); 141.4 (d,  $^4J_{CP} = 6.1$  Hz,  $C_\beta$ ); 141.5, 141.6 (both s,  $C^{4a'}$  and  $C^{4b'}$ ); 145.4 (s br, 2C,  $C^{4a}$  and  $C^{4b}$ ); 148.3 and 148.5 (both s,  $C^{8a'}$  and  $C^{8b'}$ ); 149.5 (s,  $C^{8a}$ ); 150.8 (s,  $C^{8b}$ ); 154.5 (s,  $C_\gamma$ ); 262.5 (m, observed by  $^1H$ ,  $^{13}C$  HMBC experiment,  $C_\alpha$ ) ppm.

**Synthesis of  $[\text{IrCp}^*\{\text{C}(\text{OMe})\text{CH}=\text{C}(2\text{-SBF})(\text{CH}_2)\}_2(\text{PMe}_3)]\text{PF}_6$  (**4**)**



A dark brown solution of **3** (150 mg, 0.153 mmol) in 10 mL of dichloromethane was treated with  $\text{AgPF}_6$  (50 mg, 0.198 mmol). The solution was stirred for 1 h at room temperature, filtered and vacuum concentrated, obtaining a brown solid that was washed with diethylether (3 x 4 mL) and dried in vacuum. Yield: 90 mg (62 %). Anal. Calcd for  $\text{C}_{43}\text{H}_{45}\text{O}_6\text{IrP}_2$  (946.0 g/mol): C 54.60, H 4.79; found: C 54.70, H 4.83. **MS** (m/z, referred to the most abundant isotopes): m/z: 801.28  $[\text{M}]^+$ .  **$^1\text{H NMR}$** :  $\delta$  1.28 (d, 9H,  $^2J_{HP} = 10.4$  Hz,  $\text{P}(\text{CH}_3)_3$ ); 1.86 (d, 15H,  $^4J_{HP} = 1.6$  Hz,  $\text{C}_5(\text{CH}_3)_5$ ); 2.14–2.19 (m, 2H,  $\text{C}_8\text{H}_2$ ); 4.21 (s br, 3H,  $\text{OCH}_3$ ); 6.64 (ddd, 1H,  $^3J_{HH} = 7.6$ ,  $^4J_{HH} = 1.0$ ,  $^5J_{HH} = 0.7$  Hz,  $H^8$ ); 6.71 and 6.74 (both ddd, 1H,  $^3J_{HH} = 7.7$ ,  $^4J_{HH} = 1.1$ ,  $^5J_{HH} = 0.8$  Hz,  $H^{1'}$  and  $H^{8'}$ ); 7.07 (d, 1H,  $^4J_{HP} = 1.3$  Hz,  $C_\beta H$ ); 7.13 and 7.15 (both td, 1H,  $^3J_{HH} = 7.4$ ,  $^4J_{HH} = 1.2$  Hz,  $H^{2'}$  and  $H^{7'}$ ); 7.18 (td, 1H,  $^3J_{HH} = 7.5$ ,  $^4J_{HH} = 1.1$  Hz,  $H^7$ ); 7.22 (dm, 1H,  $^4J_{HH} = 1.5$  Hz,  $H^1$ ); 7.42 (2 td, 2H,  $^3J_{HH} = 7.6$ ,  $^4J_{HH} = 1.1$  Hz,  $H^{3'} + H^{6'}$ ); 7.43 (td, 1H,  $^3J_{HH} = 7.5$ ,  $^4J_{HH} = 1.1$  Hz,  $H^6$ ); 7.8–7.9 (m, 2H,  $H^{4'}$  and  $H^5$ ); 7.97 (ddd, 1H,  $^3J_{HH} = 7.7$ ,  $^4J_{HH} = 1.0$ ,  $^5J_{HH} = 0.7$  Hz,  $H^5$ ); 8.00 (dd, 1H,  $^3J_{HH} = 8.1$ ,  $^5J_{HH} = 0.6$  Hz,  $H^4$ ); 8.04 (dd, 1H,  $^3J_{HH} = 8.1$ ,  $^4J_{HH} = 1.6$  Hz,  $H^3$ ) ppm.  **$^{31}\text{P}\{^1\text{H}\}$  NMR**:  $\delta$  –144.06 (sept,  $^1J_{PF} = 710.2$  Hz,  $\text{PF}_6$ ); –35.20 (s,  $\text{P}(\text{CH}_3)_3$ ) ppm.  **$^{13}\text{C}\{^1\text{H}\}$  NMR**:  $\delta$  9.5 (s,  $\text{C}_5(\text{CH}_3)_5$ ); 13.6 (d,  $^2J_{CP} = 7.4$  Hz,  $C_\delta$ ); 15.7 (d,  $^1J_{CP} = 40.1$  Hz,  $\text{P}(\text{CH}_3)_3$ ); 66.4 (s,  $C^9$ ), 64.2 (s,  $\text{OCH}_3$ ); 98.1 (d,  $^2J_{CP} = 1.9$  Hz,  $\text{C}_5(\text{CH}_3)_5$ ); 120.7 (s, 2C,  $C^{4'} + C^5$ ); 121.1 (s,  $C^4$ ); 121.5 (s,  $C^5$ ); 123.8 (s,  $C^1$ ); 124.1, 124.2 and 124.3 (s,  $C^8$ ,  $C^{1'}$  and  $C^{8'}$ ); 128.31 and 128.33, (s,  $C^{2'}$  and  $C^{7'}$ ); 128.4 (s, 2C,  $C^{3'} + C^{6'}$ ); 128.5 (s,  $C^6$ ); 129.6 (s,  $C^3$ ); 129.7 (s,  $C^7$ ); 135.7 (s br,  $C_\beta$ ); 137.0 (s,  $C^2$ ); 140.6 (s,  $C^{4b}$ ); 142.3 and 142.4 (s,  $C^{4a'}$  and  $C^{4b'}$ ); 146.7 (s,  $C^{4a}$ ); 148.3 (s, 2C  $C^{8a'} + C^{8b'}$ ); 149.8 (s,  $C^{8b}$ ); 150.7 (s,  $C^{8a}$ ); 196.6 (s,  $C_\gamma$ ); 249.4 (d,  $^2J_{CP} = 9.5$  Hz,  $C_\alpha$ ) ppm.

## Formation of $[\text{IrCp}^*\{\text{C}(\text{OMe})=\text{CHC}(\text{2-SBF})=\text{CH}\}(\text{PMe}_3)]$ (**5**)



In a NMR tube, complex **4** (20 mg, 0.020 mmol) was dissolved in 0.5 mL of dichloromethane- $d_2$  and then,  $\text{KO}^t\text{Bu}$  (12 mg, 0.11 mmol) was added. After 1 h, NMR spectroscopic data of the brown solution confirmed the fully conversion of complex **4** into complex **5**.  $^1\text{H}$  NMR:  $\delta$  1.22 (d, 9H,  $^2J_{\text{HP}} = 10.5$  Hz,  $\text{P}(\text{CH}_3)_3$ ); 1.81 (d, 15H,  $^4J_{\text{HP}} = 1.6$  Hz,  $\text{C}_5(\text{CH}_3)_5$ ); 3.56 (s, 3H,  $\text{OCH}_3$ ); 5.65 (dd, 1H,  $^4J_{\text{HH}} = 2.6$ ,  $^4J_{\text{HP}} = 2.1$  Hz,  $\text{C}_\beta\text{H}$ ); 6.56 (ddd, 1H,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.1$ ,  $^5J_{\text{HH}} = 0.7$  Hz,  $H^8$ ); 6.71 (dm, 1H,  $^4J_{\text{HH}} = 1.4$  Hz,  $H^1$ ); 6.74 and 6.76 (both ddd, 1H,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.1$ ,  $^5J_{\text{HH}} = 0.7$  Hz,  $H^{1'}$  and  $H^8$ ); 7.01 (td, 1H,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.1$  Hz,  $H^7$ ); 7.13 (td, 2H,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.1$  Hz,  $H^{2'}$  and  $H^{7'}$ ); 7.31 (td, 1H,  $^3J_{\text{HH}} = 7.5$ ,  $^4J_{\text{HH}} = 1.1$  Hz,  $H^6$ ); 7.380 and 7.381 (td, 2H,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.1$  Hz,  $H^{3'}$  and  $H^{6'}$ ); 7.49 (dd, 1H,  $^4J_{\text{HH}} = 2.6$ ,  $^3J_{\text{HP}} = 3.4$  Hz,  $\text{C}_\delta\text{H}$ ); 7.59 (dd, 1H,  $^3J_{\text{HH}} = 8.1$ ,  $^4J_{\text{HH}} = 1.7$  Hz,  $H^3$ ); 7.71 (dd, 1H,  $^3J_{\text{HH}} = 8.1$ ,  $^5J_{\text{HH}} = 0.6$  Hz,  $H^4$ ); 7.78 (ddd, 1H,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.2$ ,  $^5J_{\text{HH}} = 0.7$  Hz,  $H^5$ ); 7.89 (ddd, 2H,  $^3J_{\text{HH}} = 7.6$ ,  $^4J_{\text{HH}} = 1.1$ ,  $^5J_{\text{HH}} = 0.8$  Hz,  $H^{4'}$  and  $H^{5'}$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  -40.74 (s,  $\text{P}(\text{CH}_3)_3$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  9.2 (s,  $\text{C}_5(\text{CH}_3)_5$ ); 15.0 (d,  $^1J_{\text{CP}} = 39.1$  Hz,  $\text{P}(\text{CH}_3)_3$ ); 55.9 (s,  $\text{OCH}_3$ ); 65.6 (s,  $\text{C}^9$ ); 93.6 (d,  $^2J_{\text{CP}} = 2.6$  Hz,  $\text{C}_5(\text{CH}_3)_5$ ); 105.9 (d,  $^3J_{\text{CP}} = 1.8$  Hz,  $\text{C}_\beta$ ); 119.1 (s,  $\text{C}^1$ ); 119.2 (s,  $\text{C}^5$ ); 119.4 (s,  $\text{C}^4$ ); 119.9 and 120.0 (both s,  $\text{C}^{4'}$  and  $\text{C}^{5'}$ ); 123.3 (s,  $\text{C}^8$ ); 123.8 and 123.84 (s,  $\text{C}^{1'}$  and  $\text{C}^8$ ); 124.5 (s,  $\text{C}^3$ ); 126.4 (s,  $\text{C}^7$ ); 127.43 and 127.45, (s,  $\text{C}^{2'}$  and  $\text{C}^{7'}$ ); 127.5 (s,  $\text{C}^6$ ), 127.6 and 127.7 (both s,  $\text{C}^{3'} + \text{C}^{6'}$ ); 133.8 (d,  $^2J_{\text{CP}} = 13.3$  Hz,  $\text{C}_\delta$ ); 137.5 (s,  $\text{C}^{4a}$ ); 141.7 and 141.8 (s,  $\text{C}^{4a'}$  and  $\text{C}^{4b'}$ ); 142.3 (s,  $\text{C}^{4b}$ ); 142.4 (d,  $^3J_{\text{CP}} = 2.3$  Hz,  $\text{C}_\gamma$ ); 148.4 (s,  $\text{C}^{8a}$ ); 149.0 (s,  $\text{C}^{8b}$ ); 149.3 and 149.4 (s, 2C  $\text{C}^{8a'}$  and  $\text{C}^{8b'}$ ); 150.3 (d,  $^4J_{\text{CP}} = 1.2$  Hz,  $\text{C}^2$ ); 179.4 (d,  $^2J_{\text{CP}} = 13.7$  Hz,  $\text{C}_a$ ) ppm.

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