Cyclometalated Iridium Complexes from an Intramolecular C–H Activation of [IrCp*Cl{=C(OMe)CH=C(CH$_3$)R}L] (R = CH$_3$, Ph; L = PPh$_2$Me, PMe$_3$).

M. Talavera†, S. Bolaño†*, J. Bravo†, J. Castro† and S. García–Fontán†.

†Departamento de Química Inorgánica, Universidad de Vigo. Campus Universitario, E–36310 Vigo (Spain).

KEYWORDS. Metallacycle · Alkenyl–carbene · C–H activation · Iridium

Supporting Information Placeholder

ABSTRACT: The (methoxy)alkenylcarbeneiridium complexes [IrCp*Cl{=C(OMe)CH=CR^{1}R^2}L]PF$_6$ (R^1 = CH$_3$, R^2= CH$_3$, Ph; R^1 = Ph, R^2= H; L = PPh$_2$Me, PMe$_3$) can suffer an intramolecular C–H activation of one of the substituents R of the alkenyl fragment to give new five–membered ring cyclometalated iridium complexes. In this work is shown that the arrangement of substituents in the alkenyl fragment determines the size of the ring in the iridacycle complexes. The iridacyclopenta–1,3–diene complexes [IrCp*{=C(OMe)CH=CRCH$_2$}L]PF$_6$ [L = PPh$_2$Me, R = CH$_3$ (**2a**) or Ph (**4a**); L = PMe$_3$, R = CH$_3$ (**2b**) or Ph (**4b**)] can be deprotonated to give the iridacyclopenta–2,4–diene complexes [IrCp*{C(OMe)=CHCR=CH}L] [L = PPh$_2$Me, R = CH$_3$ (**6a**) or Ph (**7a**); L = PMe$_3$, R = CH$_3$ (**6b**) or Ph(**7b**)].

Introduction

The cyclometalation reaction involving transition metals is based on activation of a strong C–R bond in mild conditions and it is a useful method for creating organometallic entities.[1] The product of this reaction, "a metallacycle", can also be obtained by other routes. In particular, some metallacycle compounds have been formed with pincer ligands,[2] by activation of the vinyl ethers,[3] and with free pyridyl–functionalized carbenes.[4]

Many C–C or C–heteroatom coupling reactions involving metallacycle complexes occur under relatively mild conditions than if they were carried out by conventional organic methods. Within the plentiful applications of metallacycle compounds organic transformations, catalysis, materials science and medicinal chemistry are included.[1,5]

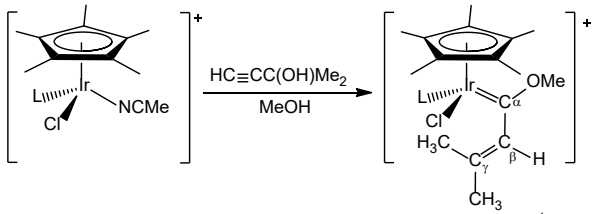
We have recently reported that the (methoxy)alkenylcarbeneiridium complexes [IrCp*Cl{=C(OMe)CH=CPh$_2$}L]PF$_6$ (L = PPh$_2$Me, PMe$_3$) suffer an intramolecular C–H activation of one of the phenyl rings of the alkenylcarbene ligand to give new cyclometalated iridium complexes.[6] Extension of these studies to other (methoxy)alkenylcarbeneiridium complexes with different substituents on the alkenyl fragment [IrCp*Cl{=C(OMe)CH=CR^{1}R^2}L]PF$_6$ (R^1 = CH$_3$, R^2= CH$_3$, Ph; R^1 = Ph, R^2= H) is relevant because five–, or six–membered cyclometalated rings can be obtained as a function of in which substituent the intramolecular C–H activation would take place.

In this paper, we report the formation of iridacyclopenta–1,3–diene complexes from [IrCp*Cl{=C(OMe)CH=C(CH$_3$)R}L]PF$_6$ (R = CH$_3$, Ph, L = PPh$_2$Me, PMe$_3$) and their conversion into iridacyclopentadiene–2,4–complexes.

Results and Discussion

Iridacyclopenta–1,3–diene Complexes

Treatment of [IrCp*Cl(NCMe)L]PF$_6$ (L = PPh$_2$Me, PMe$_3$) with 2–methyl–3–butyn–2–ol in methanol at room temperature gives the (methoxy)alkenylcarbeneiridium complexes [IrCp*Cl{=C(OMe)CH=CMe$_2$}L]PF$_6$ [L = PPh$_2$Me (**1a**), PMe$_3$ (**1b**)] in high yields (eq 1). Multidimensional and multinuclear NMR spectra supported the proposed formulation for both compounds. The ^{1}H NMR spectrum exhibits a broad singlet at 5.72 ppm for **1a** and at 6.77 ppm for **1b** corresponding to C$_\beta$–*H*. The α–carbon, β–carbon and γ–carbon resonances appear at 268.4 (d, $^2J_{CP}$ = 11.5 Hz), 138.0 (s) and 150.9 (s) ppm, respectively, for **1a** and at 264.5 (d, $^2J_{CP}$ = 11.2 Hz), 141.6 (d, $^3J_{CP}$ = 4.9 Hz) and 159.7 (s) ppm, respectively, for **1b** in their ^{13}C{^{1}H} NMR spectra.



L = PPh$_2$Me (**1a**), PMe$_3$ (**1b**) (1)

Single crystal X–ray structure of **1a** is obtained and the ORTEP representation is shown in Figure 1. The structure of the cation complex **1a** consists on a pentamethylcyclopentadienyl ligand (Cp*) η^5–coordinated to an iridium atom, which is also coordinated to other three donor atoms leading

to the formation of a "three-legged piano stool" structure with a pseudooctahedral geometry. These atoms belong to a Fisher–type carbene ligand [1-methoxy-3,3-dimethylprop-2-en-1-ylidene], a chlorine ligand and a diphenylmethylphosphane ligand.

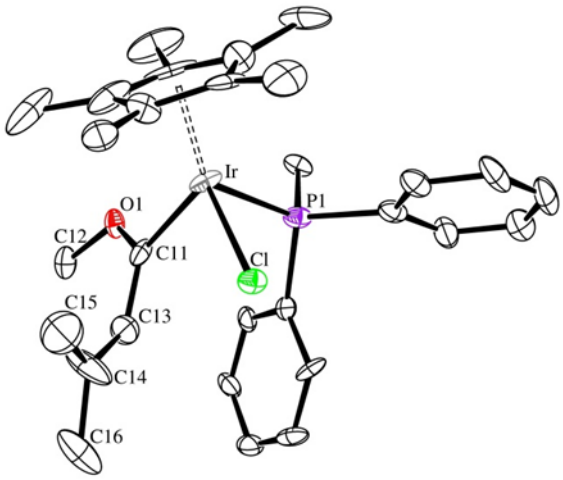
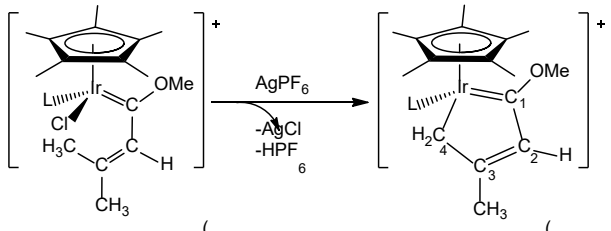


Figure 1. ORTEP view of the cation $[IrCp^*Cl\{=C(OMe)CH=CMe_2\}PPh_2Me]^+$ (**1a**) drawn at 50% probability level. The hydrogen atoms are not showed for clarity. Selected bond lengths [Å] and angles [deg]: Ir–CT, 1.8745(4); Ir–P(1), 2.320(3); Ir–Cl, 2.396(3); Ir–C(11), 2.000(11); CT–Ir–C(11), 126.0(3); CT–Ir–P(1), 130.04(7); CT–Ir–Cl, 122.17(7); C(11)–Ir–Cl, 92.7(3); C(11)–Ir–P(1), 86.7(3); P(1)–Ir–Cl, 87.28(10). CT refers to the centroid of the Cp* ligand.

The carbene Ir–C(11) bond length [2.000(11)] Å in complex **1a** is slightly longer than that found in the related cation $[IrCp^*Cl\{=C(OMe)CH=CPh_2\}(PPh_2Me)]^+$ [1.973(5) Å],[6] in the cation $[IrCp^*\{=C(OMe)CH_2Ph\}\{PPh_2(C_6H_3\text{-}2\text{-}(OMe)\text{-}6\text{-}O\}]^+$ [1.97(1) Å],[7] and in the complex $[IrTp^{Me_2}(H)_2(=C(H)OBu^n)]$ [1.859(2) Å].[8] This bond length is shorter than the Ir–C σ–bond length for other complexes,[7] showing the presence of some multiple character in the Ir–C carbene bond.

The addition of $AgPF_6$ to a solution of **1a** or **1b** in dichloromethane gives the cyclic carbene compounds **2a** and **2b**, respectively, through an intramolecular C–H activation of one of the methyl groups of the alkenyl fragment (eq 2). Complexes **2a** and **2b** are iridacyclopenta–1,3–dienes that are made up of a chelating organic ligand with alkyl and carbene termini, $[IrCp^*\{=C(OMe)CH=C(Me)CH_2\}L]PF_6$ [L = PPh_2Me (**2a**), PMe_3 (**2b**)].



(2)

Comprehensive multidimensional and multinuclear NMR studies supported the proposed formulation for both compounds and the crystal structures confirm that this formulation is retained in the solid state with the iridium atom coordinated to a phosphane ligand (PPh_2Me for **2a** and PMe_3 for **2b**), to a η^5-pentamethylcyclopentadienyl ligand (Cp*) and to two carbon atoms of a chelating organic ligand which forms a five-membered cycle, (iridacyclopenta–1,3–diene). Note that **2a** presents two unit formulae in the asymmetric unit with small differences in the orientation of the iridacyclopentadiene cycle as it can be seen in Figure 2. The ORTEP representations for complexes **2a**,**b** are given in figures 2 and 3, and include a selection of distances and angles.

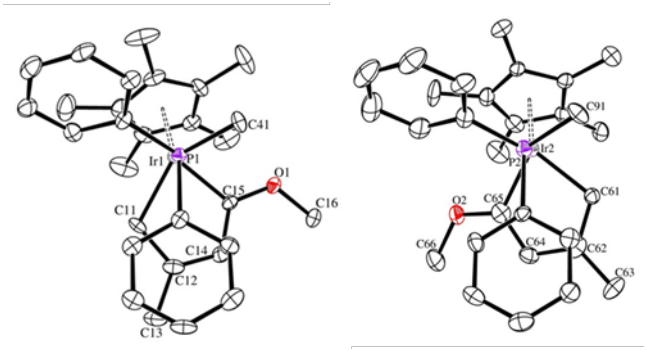


Figure 2. ORTEP view of the two cations found for $[IrCp^*\{=C(OMe)CH=CMeCH_2\}PPh_2Me]^+$ (**2a**) drawn at 50% probability level. The hydrogen atoms are not showed for clarity. Selected bond lengths [Å] and angles [deg]: Left molecule: Ir(1)–CT, 1.9025(4); Ir(1)–P(1), 2.2784(17); Ir(1)–C(11), 2.130(6), Ir(1)–C(15), 1.978(7); CT–Ir(1)–C(11), 127.1(2); CT–Ir(1)–C(15), 127.36(19); CT–Ir(1)–P(1), 128.56(4); C(11)–Ir(1)–C(15), 78.8(3); C(11)–Ir(1)–P(1), 90.2(2); C(15)–Ir(1)–P(1), 89.6(2). Right molecule: Ir(2)–CT, 1.9005(4); Ir(2)–P(2), 2.2740(18); Ir(2)–C(61), 2.117(7), Ir(2)–C(65), 1.981(8); CT–Ir(2)–C(61), 125.54(19); CT–Ir(2)–C(65), 129.3(2); CT–Ir(2)–P(2), 128.48(5); C(61)–Ir(2)–C(65), 78.3(3); C(61)–Ir(2)–P(2), 87.3(2); C(65)–Ir(2)–P(2), 92.1(2). CT refers to the centroid of the Cp* ligand.

The five atoms constituting the iridacyclopenta–1,3–diene ring are essentially coplanar, mean deviation of 0.0472 Å (figure 2, left) and 0.0382 Å (figure 2, right) for **2a** and 0.0113 Å for **2b**. The Ir–C double bond lengths in the iridacyclopenta–1,3–diene rings span from 1.978(7) to 1.984(9) Å. In the case of Ir–C single bond lengths these values vary from 2.117(7) to 2.130(6) Å. All these values are slightly longer to those found for the iridacyclopenta–1,3–dienes obtained by Paneque *et. al.*[3,5b]

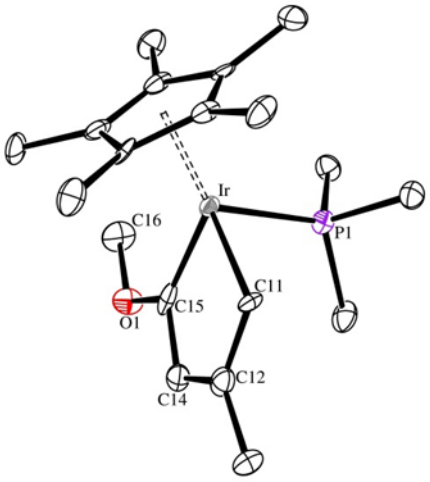
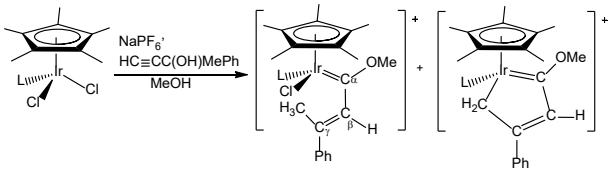


Figure 3. ORTEP view of the cation $[IrCp^*\{=C(OMe)CH=CPhCH_2\}(PMe_3)]^+$ (**2b**) drawn at 50% probability level. The hydrogen atoms are not showed for clarity. Selected bond lengths [Å] and angles [deg]: Ir–CT, 1.9207(12); Ir–P(1), 2.285(3); Ir–C(11), 2.121(7); Ir–C(15), 1.984(9) Å, CT–Ir–C(11), 121.4(2); CT–Ir–C(15), 133.3(2); CT–Ir–P(1), 129.12(7); C(11)–Ir–C(15), 79.2(3); C(11)–Ir–P(1), 87.0(2); C(15)–Ir–P(1), 89.8(2). CT refers to the centroid of the Cp* ligand.

The ^{1}H NMR spectrum in **2a** shows resonances at 1.81–1.85 (m, 2H, C^4H_2), at 1.87–1.90 (m, 3H, C^3CH_3) and at 6.25 (s br, 1H, C^2H) ppm (see eq 2 for labelling). Similar resonances are observed for complex **2b**: 1.65–1.72 (m, 1H, C^4H_2) and 1.88–1.94 (m, 1H, C^4H_2), 2.30–2.39 (m, 3H, C^3CH_3) and 6.68 (s br, 1H, C^2H) ppm. The corresponding $^{13}C\{^1H\}$ NMR resonances for **2a** appear at 19.6 (d, $^2J_{CP}$ = 7.8 Hz , C^4), at 137.3 (s, C^2), at 209.1 (s, C^3) and at 252.7 (d, $^2J_{CP}$ = 9.1 Hz, C^1) ppm. Resonances for **2b** are: 18.7 (d, $^2J_{CP}$ = 7.7 Hz , C^4), 139.7 (s, C^2), 206.2 (s, C^3) and 253.8 (s br, C^1) ppm.

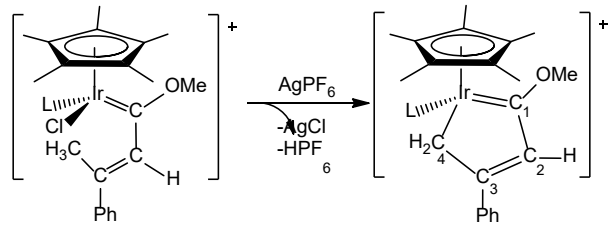
When 2-phenyl-3-butyn-2-ol is added to a solution of $[IrCp^*Cl_2L]$ (L = PPh_2Me) in methanol with sodium hexafluorophosphate at RT (eq 3) the compound $[IrCp^*Cl\{=C(OMe)CH=CPhMe\}(PPh_2Me)]PF_6$ (**3a**) is obtained. On the other hand, when L = PMe_3 the final product is a mixture of $[IrCp^*\{=C(OMe)CH=C(Ph)CH_2\}(PMe_3)]PF_6$ (**4b**) and $[IrCp^*Cl\{=C(OMe)CH=CPhMe\}(PMe_3)]PF_6$ (**3b**) (30:70 mol ratio approx., respectively).[9]



(3)

The NMR spectra supported the proposed formulation for **3a** and **3b**. The ^{1}H NMR spectrum exhibits a broad singlet at 5.69 ppm for **3a** and at 7.25 ppm for **3b** corresponding to C_β–*H*. The α–carbon, β–carbon and γ–carbon resonances in $^{13}C\{^1H\}$ NMR spectrum appear at 271.4 (d, $^2J_{CP}$ = 12.8 Hz), 136.7 (s) and 143.6 (s) ppm, respectively, for **3a** and at 266.1 (s br), 140.5 (s) and 153.3 (s) ppm, respectively, for **3b**.

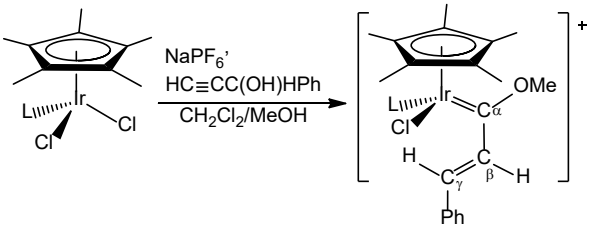
When **3a** or **3b** (in fact a mixture **3b**/**4b**) are treated with $AgPF_6$ the five-membered iridacycles $[IrCp^*\{=C(OMe)CH=C(Ph)CH_2\}(PPh_2Me)]PF_6$ (**4a**) or $[IrCp^*\{=C(OMe)CH=C(Ph)CH_2\}(PMe_3)]PF_6$ (**4b**) are isolated, respectively (eq 4). The formation of these compounds indicates that C(sp^3)–H activation of the methyl group takes place instead of the, "*a priori*" more favorable, C(sp^2)–H activation of the phenyl group. Obviously, there is a steric reason for this behavior, being the vicinity of methyl group to the iridium atom, in the (methoxy)alkenylcarbene compounds, what leads to the formation of a five-membered metallacycle. Of note, when both substituents of the alkenyl fragment are phenyl groups, a C(sp^2)–H activation was observed.[6]



(4)

The NMR data confirm the formulation of **4a** and **4b**. The ^{1}H NMR spectrum shows the resonances at 2.12–2.19 (m, 1H, C^4H_2) and 2.44–2.52 (m, 1H, C^4H_2) and at 6.88 (s br, 1H, C^2H) ppm for **4a**. Similar resonances are observed for the complex **4b**, at 2.27–2.29 (m, 2H, C^4H_2) and at 7.27 (s br, 1H, C^2H) ppm. The corresponding $^{13}C\{^1H\}$ NMR resonances for **4a** appear at 14.3 (d, $^2J_{CP}$ = 7.9 Hz, C^4), at 133.5 (s, C^2), at 198.4 (s, C^3) and at 249.4 (d, $^2J_{CP}$ = 9.1 Hz, C^1) ppm. The resonances for complex **4b** are: 13.9 (d, $^2J_{CP}$ = 7.4 Hz, C^4), 136.3 (s, C^2), 197.1 (s, C^3) and at 250.7 (d, $^2J_{CP}$ = 11.5 Hz, C^1) ppm.

In an attempt to get more information about the activation mechanism, new (methoxy)alkenylcarbeneiridium of formulae $[IrCp^*\{=C(OMe)CH=CHPh\}L]PF_6$ [L = PPh_2Me (**5a**), PMe_3 (**5b**)] are prepared. Complexes **5a** and **5b** are obtained by reaction of 1-phenyl-2-propyn-1-ol to a solution of $[IrCp^*Cl_2L]$ and sodium hexafluorophosphate in dichoromethane/methanol at RT (eq 5).



(5)

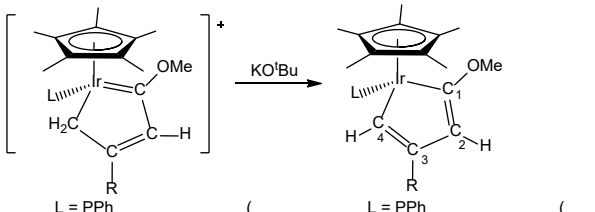
Multidimensional and multinuclear NMR spectra confirm the proposed structure for both complexes. Although in complexes **5a** and **5b** the resonance of C_β–*H* in ^{1}H NMR spectrum appears overlapped with other signals, {^{1}H, ^{1}H} COSY experiment help us to make the assignment. The resonance appears at 7.28 (d, $^3J_{HH}$=15.6 Hz, C_β–*H*) ppm for **5a** and 7.53 (d, $^3J_{HH}$=14.7 Hz, C_β–*H*) ppm for **5b**. The resonance at 8.66 (d, $^3J_{HH}$=15.1 Hz) ppm for **5a** and at 8.63 (d, $^3J_{HH}$=15.0 Hz) ppm for **5b** is assignable to C_γ–*H*. The H–H coupling constants are

typical for olefinic protons in *trans* position. In the $^{13}C\{^1H\}$ NMR spectrum for complex **5a** the resonances at 262.0 (d, $^2J_{CP}$ = 13.5 Hz), 129.6 (s) and 169.0 (s) ppm are assignable to α–carbon, β–carbon and γ–carbon, respectively, and, for complex **5b** these resonances appear at 262.1 (d, $^2J_{CP}$ = 14.0 Hz), at 126.9 (s) and at 170.0 (s) ppm, respectively.

When **5a** and **5b** are treated with $AgPF_6$ the formation of iridacycles is not observed and only a mixture of decomposition products is obtained. This result confirms that arrangement of substituents in the alkenyl fragment is important to obtain metallacycle complexes with different number of members in the ring.

Iridacyclopenta–2,4–diene Complexes

The metallacyclopenta–1,3–diene complexes are scarce[3,10] and, to the best of our knowledge, with iridium only the ones prepared by Paneque *et. al.*[3] have been reported. Besides, attempts to deprotonate the methylene group in these complexes[3] were fruitless. In contrast, when the iridacyclopenta–1,3–diene complexes (**2a**,**b**, **4a**,**b**) are treated with KO^tBu, the methylene group is deprotonated giving the new iridacyclopenta–2,4–diene complexes [IrCp*{C(OMe)=CHCR=CH}(L)] for L = PPh_2Me with R = CH_3 (**6a**) or R = Ph (**7a**) and for L = PMe_3 with R = CH_3 (**6b**) or R = Ph (**7b**) (eq 6). This type of metallacyclopentadiene complexes is interesting for its implication in the cyclooligomerization of alkynes.[11]



(6)

Multidimensional and multinuclear NMR experiments confirm the suggested formulation for **6a,b** and **7a**,**b**. The more relevant resonance in the ^1H NMR spectrum is C^4H which appears at 6.03–6.07 (m) (**6a**), at 7.31 (d, $^3J_{HP}$ = 8.3 Hz) (**7a**), at 6.06–6.11 (m) (**6b**) and at 7.42–7.46 (m) ppm (**7b**). In the $^{31}C\{^1H\}$ NMR spectrum the resonances corresponding to C^4 and C^1 appear between 120–132 ppm with C–P coupling constant in the order of 14 Hz and approximately at 180 ppm with C–P coupling constant nearly 14 Hz, respectively.

Conclusions

A family of (methoxy)alkenylcarbeneiridium complexes with different R substituents on the alkenyl fragment of the carbene ligands have been synthesized. These (methoxy)alkenylcarbeneiridium complexes are starting products in the cyclometalation reaction that we present here. When both R groups are different two possible products in the cyclometalation reaction may result, as a function of in which substituent intramolecular C–H activation occurs. With our (methoxy)alkenylcarbeneiridium complexes the final product could be iridacycle compounds with a five– or six–membered ring. We observed that, in all cases, only five–membered ring iridacyclopenta–1,3–dienes complexes have been obtained. The arrangement of the substituents on alkenyl fragment dictates the type of the final product.

Through a deprotonation reaction of the iridacyclopenta–1,3–dienes complexes, new iridacyclopenta–2,4–diene complexes are obtained. These compounds are important in the formation of different organic substrates.[5a–b,11,12]

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[13] and, prior to use, distilled under argon. The starting materials [IrCp*Cl_2(PPh_2Me)],[14] [IrCp*Cl_2(PMe_3)],[15] [IrCp*Cl(NCMe)(PPh_2Me)]PF_6[16] and [IrCp*Cl(NCMe)(PMe_3)]PF_6[6] 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 (^1H), 161 MHz ($^{31}P\{^1H\}$), and 100 MHz ($^{13}C\{^1H\}$) using the solvent as the internal lock. ^1H and $^{13}C\{^1H\}$ signals are referred to internal TMS and those of $^{31}P\{^1H\}$ to 85% H_3PO_4; downfield shifts (expressed in ppm) are considered positive. ^1H and $^{13}C\{^1H\}$ NMR (or JMOD) signal assignments were confirmed by $\{^1H, ^1H\}$ COSY, $\{^1H,^{13}C\}$ HSQC, $\{^1H,^{13}C\}$ HMBC and DEPT experiments. Coupling constants are given in hertz. Infrared spectra were run on a Jasco FT/IR–6100 spectrometer using KBr pellets. C, H, and N analyses were carried out with a Carlo Erba 1108 analyzer. High–resolution electrospray mass spectra were acquired using an apex–Qe spectrometer.

X–ray Diffraction Analysis.

Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) using graphite–monochromated Mo Kα radiation (λ = 0.71073 Å), and were corrected for Lorentz and polarisation effects. The software SMART[17] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[18] for integration of intensity of reflections and scaling, and SADABS[19] for empirical absorption correction.

The crystallographic treatment of the compounds was performed with the Oscail program.[20] The structure was solved by direct methods and refined by full–matrix least–squares based on F^2.[21] All non–hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters.

Details of crystal data and structural refinement for complex **1a** and **2a,b** are given in Table 1.

Table 1. Crystal Data and Structure Refinement Details for Complexes 1a, and 2a,b.

	1a	**2a**	**2b**
empirical formula	$C_{29}H_{38}ClF_6IrOP_2$	$C_{58}H_{74}F_{12}O_2P_4Ir_2$	$C_{19}H_{33}F_6OP_2Ir$
formula wt	806.18	1539.45	645.59
temp (K)	100(2)	100(2)	100(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	Orthorhombic	Monoclinic	Monoclinic

space group	*Pbca*	$P2_1/c$	$P2_1/n$
a(Å)	19.682(2)	16.486(3)	13.185(11)
b(Å)	14.4566(17)	18.667(4)	12.282(11)
c(Å)	20.905(3)	19.250(4)	14.850(13)
β(deg)	90	93.303(4)	103.214(15)
V (Å^3)	5948.3(12) Å^3	5914(2) Å^3	2341(3) Å^3
Z	8	4	4
density (Mg/m^3)	1.800	1.729	1.832
abs coeff (mm^{-1})	4.747	4.683	5.895
F(000)	3184	3040	1264
cryst size (mm)	0.32 × 0.20 × 0.10	0.48 × 0.23 × 0.19	0.37 × 0.19 × 0.14
θ range for data collection (deg)	1.95 to 28.03.	1.52 to 28.04.	1.87 to 25.22
Index ranges	−25≤h≤25	−21≤h≤21	−15≤h≤15
	−19≤k≤19	−24≤k≤24	−14≤k≤14
	−27≤l≤27	−25≤l≤24	−17≤l≤17
no. of rflns collected	52831	52415	16536
no. of indep rflns	7173 [R(int) = 0.1038]	14190 [R(int) = 0.0609]	4148 [R(int) = 0.0754]
no. of rflns obsd (>2σ)	3366	11230	3287
data completeness	0.997	0.989	0.979
abs cor	Semi-empirical from equivalents		
max. and min. transmission	0.5318 and 0.7456	0.7456 and 0.5619	0.7456 and 0.2633
refinement method	Full-matrix least-squares on F^2		
no. of data/restraints/params	7173/0/420	14190/0/719	4148/0/251
Goodness-of-fit on F^2	1.027	1.051	1.059
R indices (I>2σ(I))	R_1 = 0.0537	R_1 = 0.0459	R_1 = 0.0394
	wR_2 = 0.1040	wR_2 = 0.1279	wR_2 = 0.0931
R indices (all data)	R_1 = 0.1442	R_1 = 0.0633	R_1 = 0.0583
	wR_2 = 0.1515	wR_2 = 0.1372	wR_2 = 0.1060
Largest diff. peak and hole (e. Å^{-3})	2.485 and −3.069	2.615 and −1.572	3.322 and −2.846

Synthesis and Characterization of New Complexes. *Preparation of [IrCp*Cl{=C(OMe)CH=CMe$_2$}(PPh$_2$Me)]PF$_6$* (***1a***).To a yellow solution of [IrCp*Cl(NCMe)(PPh$_2$Me)]PF$_6$ (230 mg, 0.31 mmol) in 25 ml of methanol, 2–methyl–3–butyn–2–ol (45 μl, 0.46 mmol) was added and the mixture was stirred for 90 min at room temperature. The green suspension obtained was vacuum concentrated obtaining a brown solid which was washed with pentane (3 × 5 mL) and dried in vacuum. Yield: 240 mg (96%). Anal. Calcd for $C_{29}H_{38}OClF_6IrP_2$ (806 g/mol): C 43.20, H 4.75; found: C, 43.36; H, 4.77. MS (m/z, referred to the most abundant isotopes): m/z: 661.2 [M]$^+$. IR (cm^{-1}): ν (PF$_6$) 838 (s). ^{1}H NMR (CD_2Cl_2): δ 1.53–1.54 (m, 3H, C(CH_3)$_2$); 1.57 (d, 15H, $^4J_{HP}$ =2.2 Hz, C$_5$(CH_3)$_5$); 1.72–1.73 (m, 3H, C(CH_3)$_2$); 2.27 (d, 3H, $^2J_{HP}$ = 10.4 Hz, PPh$_2$CH_3); 4.40 (s, 3H, OCH_3); 5.72 (s br, 1H, C$_\beta$*H*); 7.46–7.56 (m, 10H, P*Ph*$_2$CH$_3$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –144.14 (hept, $^1J_{PF}$ = 710.5 Hz, *P*F$_6$); –14.95 (s, *P*Ph$_2$CH$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 8.9 (s, C$_5$(*C*H$_3$)$_5$); 14.1 (d, $^1J_{CP}$ = 41.9 Hz, PPh$_2$*C*H$_3$); 23.2 (s, C(*C*H$_3$)$_2$); 27.1 (s, C(*C*H$_3$)$_2$) 69.3 (s, O*C*H$_3$); 100.0 (d, $^2J_{CP}$ = 2.1 Hz, C$_5$(CH$_3$)$_5$); 129.1 (d, $^3J_{CP}$ = 4.7 Hz, P*Ph*$_2$Me); 129.2 (d, $^3J_{CP}$ = 4.8 Hz, P*Ph*$_2$Me); 131.0 (d, $^1J_{CP}$ = 57.5 Hz, P*Ph*$_2$Me); 131.3 (d, $^1J_{CP}$ = 57.6 Hz, P*Ph*$_2$Me); 132.0 (d, $^4J_{CP}$ = 2.8 Hz, P*Ph*$_2$Me); 132.1 (d, $^4J_{CP}$ = 2.7 Hz, P*Ph*$_2$Me); 132.7 (d, $^2J_{CP}$ = 9.4 Hz, P*Ph*$_2$Me); 133.1 (d, $^2J_{CP}$ = 9.9 Hz, P*Ph*$_2$Me); 138.0 (s, *C*$_\beta$); 150.9 (s, *C*$_\gamma$); 268.4 (d, $^2J_{CP}$ = 11.5 Hz, *C*$_\alpha$) ppm.

*Preparation of [IrCp*Cl{=C(OMe)CH=CMe$_2$}(PMe$_3$)]PF$_6$* (***1b***). 200 mg (0.32 mmol) of [IrCp*Cl(NCMe)(PMe$_3$)]PF$_6$ in methanol (15 mL), were treated with 2–methyl–3–butyn–2–ol (70 μl, 0.704 mmol). The yellow solution turned orange and the mixture was stirred for 90 min at room temperature. The solution, which finally turned brown, was vacuum concentrated obtaining a brown solid that was washed with pentane (3 × 8 mL) and dried in vacuum. Yield: 204 mg (85%). Anal. Calcd for $C_{19}H_{34}OClF_6IrP_2$ (682.1 g/mol): C 33.46, H 5.02; found: C, 33.39; H, 5.07. MS (m/z, referred to the most abundant isotopes): m/z: 537 [M]$^+$. IR (cm^{-1}): ν (PF$_6$) 839 (s). ^{1}H NMR (CD_2Cl_2): δ 1.65 (d, 9H, $^2J_{HP}$ = 10.9 Hz, P(CH_3)$_3$); 1.75 (d, 15H, $^4J_{HP}$ = 2.4 Hz, C$_5$(CH_3)$_5$); 1.90–1.91 (m, 3H, C(CH_3)$_2$); 1.98–2.00 (m, 3H, C(CH_3)$_2$); 4.74 (s, 3H, OCH_3); 6.77 (s br, 1H, C$_\beta$*H*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –144.15 (hept, $^1J_{PF}$ = 710.6 Hz, *P*F$_6$); –29.90 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 9.0 (s, C$_5$(*C*H$_3$)$_5$); 14.3 (d, $^1J_{CP}$ = 40.8 Hz, P(*C*H$_3$)$_3$); 23.7 (s, C(*C*H$_3$)$_2$); 29.2 (s, C(*C*H$_3$)$_2$) 69.0 (s, O*C*H$_3$); 98.3 (d, $^2J_{CP}$ = 2.2 Hz, *C*$_5$(CH$_3$)$_5$); 141.6 (d, $^3J_{CP}$ = 4.9 Hz, *C*$_\beta$); 159.7 (s, *C*$_\gamma$); 264.5 (d, $^2J_{CP}$ = 11.2 Hz, C$_\alpha$) ppm.

Preparation of [IrCp{=C(OMe)CH=C(Me)(CH$_2$)}(PPh$_2$Me)]PF$_6$* (***2a***). A brown solution of **1a** (300 mg, 0.37 mmol) in 15 mL of dichloromethane was treated with AgPF$_6$ (105 mg, 0.41 mmol). The solution was stirred for 5 min at room temperature. Then, the solution was filtered and vacuum concentrated, obtaining a brown solid that was washed with pentane (3 × 5 mL). Finally, the solid obtained was dried in vacuum. Yield: 255 mg (81 %). Anal. Calcd for $C_{29}H_{37}OF_6IrP_2$ (769.8 g/mol): C 45.25, H 4.84; found: C 45.32, H 4.87. MS (m/z, referred to the most abundant isotopes): m/z: 625 [M]$^+$. IR (cm^{-1}): ν (PF$_6$) 837 (s). ^{1}H NMR (CD_2Cl_2): δ 1.72 (d, 15H, $^4J_{HP}$ = 1.8 Hz, C$_5$(CH_3)$_5$); 1.81–1.85 (m, 2H, CH_2); 1.87–1.90 (m, 3H, CH_3); 2.10 (d, 3H, $^2J_{HP}$ = 9.8 Hz, PPh$_2$CH_3); 4.17 (d, 3H, $^5J_{HP}$ = 0.5 Hz, OCH_3); 6.25 (s br, 1H, C*H*); 7.17–7.29 (m, 4H, P*Ph*$_2$CH$_3$); 7.39–7.48 (m, 6H, P*Ph*$_2$CH$_3$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –144.13 (hept, $^1J_{PF}$ = 710.6 Hz, *P*F$_6$); –8.81 (s, *P*Ph$_2$CH$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 9.2 (s, C$_5$(*C*H$_3$)$_5$); 14.6 (d, $^1J_{CP}$ = 41.0 Hz, PPh$_2$*C*H$_3$); 19.6 (d, $^2J_{CP}$ = 7.8 Hz, *C*^{4}); 24.6 (s, *C*H$_3$); 63.6 (s, O*C*H$_3$); 98.1 (d, $^2J_{C-P}$ = 2.1 Hz, *C*$_5$(CH$_3$)$_5$); 129.0 (d, $^3J_{CP}$ = 2.7 Hz, P*Ph*$_2$Me); 129.1 (d, $^3J_{CP}$ = 2.6 Hz, P*Ph*$_2$Me); 130.6 (d, $^1J_{CP}$ = 57.2 Hz, P*Ph*$_2$Me); 131.5 (d, $^4J_{CP}$ = 2.6 Hz, P*Ph*$_2$Me); 131.6 (d, $^4J_{CP}$ = 2.6 Hz, P*Ph*$_2$Me); 131.8 (d, $^1J_{CP}$ = 57.9 Hz, P*Ph*$_2$Me); 132.3 (d, $^2J_{CP}$ = 10.2 Hz, P*Ph*$_2$Me); 132.6 (d, $^2J_{CP}$ = 10.0 Hz, P*Ph*$_2$Me); 137.3 (s, *C*^{2}); 209.1 (s, *C*^{3}); 252.7 (d, $^2J_{CP}$= 9.1 Hz, *C*^{1}) ppm.

Preparation of [IrCp{=C(OMe)CH=C(Me)(CH$_2$)}(PMe$_3$)]PF$_6$* (***2b***). A dark brown solution of **1b** (200 mg, 0.3 mmol) in 10 mL of dichloromethane was treated with AgPF$_6$ (85 mg, 0.33 mmol). The solution was stirred for 5 min at room temperature, filtered and vacuum concentrated, obtaining a brown solid that was washed with pentane (3 x 4 mL) and dried in vacuum. Yield: 139 mg (72 %). Anal. Calcd for $C_{19}H_{33}OF_6IrP_2$ (645.6 g/mol): C 35.35, H 5.15; found: C 35.42, H 5.17. MS (m/z, referred to the most abundant isotopes): m/z: 501 [M]$^+$. IR (cm^{-1}): ν (PF$_6$) 837 (s). ^{1}H NMR (CD_2Cl_2): δ 1.35 (d, 9H, $^2J_{HP}$

= 10.4 Hz, P(CH_3)$_3$); 1.65–1.72 (m, 1H, CH_2); 1.87 (d, 15H, $^4J_{HP}$ = 1.6 Hz, C$_5$(CH_3)$_5$); 1.88–1.94 (m, 1H, CH_2); 2.30–2.39 (m, 3H, CH_3); 4.24 (s, 3H, OCH_3); 6.68 (s br, 1H, C*H*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –144.17 (hept, $^1J_{PF}$ = 710.5 Hz, *P*F$_6$); –36.79 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 9.4 (s, C$_5$(CH$_3$)$_5$); 14.5 (d, $^1J_{CP}$ = 40.21 Hz, P(CH$_3$)$_3$); 18.7 (d, $^2J_{CP}$ = 7.7 Hz, *C*^{4}); 24.3 (s, *C*H$_3$); 64.4 (s, OCH$_3$); 97.7 (d, $^2J_{CP}$ = 2.1 Hz, *C*$_5$(CH$_3$)$_5$); 139.7 (s, *C*^{2}); 206.2 (s, *C*^{3}); 253.8 (s br, *C*^{1}) ppm.

*Preparation of [IrCp*Cl{=C(OMe)CH=CPhMe}(PPh$_2$Me)]PF$_6$* (**3*a***). An orange solution of [IrCp*Cl$_2$(PPh$_2$Me)] (500 mg, 0.84 mmol) and sodium hexafluorophosphate (172 mg, 1.0 mmol) in methanol (40 mL) was prepared. After that, 2–phenyl–3–butyn–2–ol (402 mg, 2.76 mmol) was added and the mixture was stirred for 5 h at room temperature. The resulting brown solution was filtrated and vacuum concentrated obtaining a brown solid that was redissolved in dichloromethane (15 mL), filtered and vacuum concentrated. The brown solid obtained was washed with pentane (3 × 8 mL) and dried in vacuum. Yield: 650 mg (89%). When [IrCp*Cl(NCMe)(PPh$_2$Me)]PF$_6$ reacts with 1.2 equivalents of 2–phenyl–3–butyn–2–ol in methanol for 1h at room temperature, the methoxycarbene **3a,** accompanied with other not identified products, is obtained. Anal. Calcd for $C_{34}H_{40}OClF_6IrP_2$ (868.3 g/mol): C 47.03, H 4.64; found: C, 47.15; H, 4.62. MS (m/z, referred to the most abundant isotopes): m/z: 723 [M]$^+$. IR (cm^{-1}): ν (PF$_6$) 839 (s). ^{1}H NMR (CD_2Cl_2): δ 1.62 (d, 15H, $^4J_{HP}$ = 1.8 Hz, C$_5$(CH_3)$_5$); 1.84 (s, 3H, CH_3); 2.34 (d, 3H, $^2J_{HP}$ = 10.5 Hz, PPh$_2$CH_3); 4.47 (s, 3H, OCH_3); 5.69 (s br, 1H, C$_\beta$*H*); 7.24–7.28 (m, 2H, *Ph*); 7.32–7.40 (m, 3H, *Ph*); 7.42–7.63 (m, 10H, P*Ph*$_2$CH$_3$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –144.11 (hept, $^1J_{PF}$ = 710.6 Hz, *P*F$_6$); –16.03 (s, *P*Ph$_2$CH$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 9.0 (s, C$_5$(CH$_3$)$_5$); 13.5 (d, $^1J_{CP}$ = 42.4 Hz, PPh$_2$*C*H$_3$); 19.9 (s, *C*H$_3$); 69.8 (s, OCH$_3$); 100.4 (d, $^2J_{CP}$ = 2.0 Hz, *C*$_5$(CH$_3$)$_5$); 126.9 (s, 2*C Ph*); 129.1 (s, 2*C Ph*); 129.2 (d, $^4J_{CP}$ = 1.7 Hz, P*Ph*$_2$Me); 129.3 (d, $^4J_{CP}$ = 1.5 Hz, P*Ph*$_2$Me); 130.3 (s, 1*C Ph*); 130.9 (d, $^1J_{CP}$ = 57.9 Hz, P*Ph*$_2$Me); 131.4 (d, $^1J_{CP}$ = 57.9 Hz, P*Ph*$_2$Me); 132.1 (d, $^3J_{CP}$ = 2.8 Hz, P*Ph*$_2$Me); 132.2 (d, $^3J_{CP}$ = 2.6 Hz, P*Ph*$_2$Me); 132.6 (d, $^2J_{CP}$ = 9.4 Hz, P*Ph*$_2$Me); 133.1 (d, $^2J_{CP}$ = 9.9 Hz, P*Ph*$_2$Me); 136.7 (s, *C*$_\beta$); 139.7 (s, *C*$_{ipso}$–Ph); 143.6 (s, *C*$_\gamma$); 271.4 (d, $^2J_{CP}$ = 12.8 Hz, *C*$_\alpha$) ppm.

*Preparation of [IrCp*Cl{=C(OMe)CH=CPhMe}(PMe$_3$)]PF$_6$* (**3*b***). An orange solution of [IrCp*Cl$_2$(PMe$_3$)] (100 mg, 0.21 mmol) and sodium hexafluorophosphate (36.4 mg, 0.21 mmol) in methanol (10 mL) was prepared. After that, 2–phenyl–3–butyn–2–ol (101 mg, 0.69 mmol) was added and the mixture was stirred for 7 h 30' at room temperature. The resulting brown solution was vacuum concentrated and the brown solid obtained was redissolved in CH_2Cl_2 (5 mL), filtered and vacuum concentrated. The solid was washed with pentane (3 × 8 mL) obtaining a mixture of the **3b** and **4b** in a 70:30 ratio. Yield: 114 mg (53% for **3b**, approx.) Alternatively, **3b** (with the corresponding metallacycle **4b** in a 85:15 ratio) can be synthesized by reacting [IrCp*Cl(NCMe)(PMe$_3$)]PF$_6$ and 1.3 equivalents of 2–phenyl–3–butyn–2–ol in methanol for 30 minutes at room temperature. Yield: 100 mg (71% for **3b**, approx.) $C_{24}H_{36}OClF_6IrP_2$ (743.6g/mol). ^{1}H NMR (CD_2Cl_2): δ 1.67 (d, 9H, $^2J_{HP}$ = 10.9 Hz, P(CH_3)$_3$); 1.79 (d, 15H, $^4J_{HP}$ = 2.2 Hz, C$_5$(CH_3)$_5$); 2.34 (d, 3H, $^4J_{HH}$ = 0.9 Hz, CH_3); 4.77 (s, 3H, OCH_3); 7.25 (s br, 1H, C$_\beta$*H*); 7.44–7.50 (m, 3H, *Ph*); 7.58–7.62 (m, 2H, *Ph*) ppm. ^{31}P{^{1}H}–NMR (CD_2Cl_2): δ –144.15 (hept, $^1J_{PF}$ = 710.5 Hz, *P*F$_6$); –30.23 (s, *P*(CH$_3$)$_3$) ppm.^{13}C{^{1}H} NMR (CD_2Cl_2): δ 9.2 (s, C$_5$(*C*H$_3$)$_5$); 14.8 (d, $^1J_{CP}$ = 40.7 Hz, P(*C*H$_3$)$_3$); 21.4 (s, *C*H$_3$); 69.4 (s, OCH$_3$); 98.6 (d, $^2J_{CP}$ = 2.3 Hz, *C*$_5$(CH$_3$)$_5$); 127.4 (s, 2*C Ph*); 129.6 (s, 2*C Ph*); 131.3 (s, 1*C Ph*); 140.5 (s, *C*$_\beta$); 141.4 (s, *C*$_{ipso}$); 153.3 (s, *C*$_\gamma$); 266.1 (s br, *C*$_\alpha$) ppm.

Preparation of [IrCp{=C(OMe)CH=C(Ph)(CH$_2$)}(PPh$_2$Me)]PF$_6$* (**4*a***). 600 mg (0.75 mmol) of **3a** were dissolved in 35 mL of dichloromethane and then, treated with $AgPF_6$ (213 mg, 0.82 mmol). The brown solution obtained was stirred for 5 min at room temperature. After that, the solution was filtered and vacuum concentrated. A dark brown solid was obtained. The solid was washed with pentane (3 × 10 mL) and dried in vacuum. Yield: 575 mg (92 %). Anal. Calcd for $C_{34}H_{39}OF_6IrP_2$ (831.8 g/mol): C 49.09, H 4.73; found: C 49.23, H 4.78. MS (m/z, referred to the most abundant isotopes): m/z: 687 [M]$^+$. IR (cm^{-1}): ν (PF$_6$) 839 (s). ^{1}H NMR (CD_2Cl_2): δ 1.77 (d, 15H, $^4J_{HP}$ = 1.5 Hz, C$_5$(CH_3)$_5$); 2.10 (d, 3H, $^2J_{HP}$ = 10.0 Hz, PPh$_2$CH_3); 2.12–2.19 (m, 1H, CH_2); 2.44–2.52 (m, 1H, CH_2); 4.27 (s, 3H, OCH_3); 6.88 (s, 1H, C*H*); 7.08–7.56 (m, 15H, *Ph* + P*Ph*$_2$CH$_3$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –144.16 (hept, $^1J_{PF}$ = 710.5 Hz, *P*F$_6$); –8.45 (s, *P*Ph$_2$CH$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 9.3 (s, C$_5$(*C*H$_3$)$_5$); 14.3 (d, $^2J_{CP}$= 7.8 Hz, *C*^{4}); 14.7 (d, $^1J_{CP}$ = 41.1 Hz, PPh$_2$*C*H$_3$); 63.5 (s, OCH$_3$); 98.5 (d, $^2J_{CP}$ = 2.1 Hz, *C*$_5$(CH$_3$)$_5$); 128.7 (s, 2*C Ph*); 128.9 (s, 2*C Ph*); 129.0 (d, $^3J_{CP}$ = 8.2 Hz, P*Ph*$_2$Me); 129.1 d, $^3J_{CP}$ = 8.2 Hz, P*Ph*$_2$Me); 130.2 (d, $^1J_{CP}$ = 57.5 Hz, P*Ph*$_2$Me); 131.4 (d, $^4J_{CP}$ = 2.6 Hz, P*Ph*$_2$Me); 131.6 (d, $^4J_{CP}$ = 2.5 Hz, P*Ph*$_2$Me); 131.6 (d, $^1J_{CP}$ = 58.4 Hz, P*Ph*$_2$Me); 132.2 (d, $^2J_{CP}$ = 10.3 Hz, P*Ph*$_2$Me); 132.5 (d, $^2J_{CP}$ = 10.0 Hz, P*Ph*$_2$Me); 132.6 (s, 1*C Ph*); 133.5 (s, *C*^{2}); 137.1 (d, $^4J_{CP}$= 1.1 Hz, *C*$_{ipso}$–Ph); 198.4 (s, *C*^{3}); 249.4 (d, $^2J_{CP}$ = 9.1 Hz, *C*^{1}) ppm.

Preparation of [IrCp{=C(OMe)CH=C(Ph)(CH$_2$)}(PMe$_3$)]PF$_6$* (**4*b***). A mixture of **3b** and **4b** in a 85:15 ratio (235 mg, 0.27 mmol of methoxycarbene, approx.) was dissolved in 10 mL of dichloromethane. After that, the solution was treated with $AgPF_6$ (80 mg, 0.32 mmol) and stirred for 5 min at room temperature. Then, the brown solution was filtered and vacuum concentrated, obtaining a dark brown solid that was washed with pentane (3 × 8 mL). Finally, it was dried in vacuum. Yield: 180 mg (94%). Anal. Calcd for $C_{24}H_{35}OF_6IrP_2$ (707.7 g/mol): C 40.73, H 4.98; found: C 40.81, H 5.01. MS (m/z, referred to the most abundant isotopes): m/z: 563 [M]$^+$. IR (cm^{-1}): ν (PF$_6$) 838 (s). ^{1}H NMR (CD_2Cl_2): δ 1.35 (d, 9H, $^2J_{HP}$ = 10.4 Hz, P(CH_3)$_3$); 1.93 (d, 15H, $^4J_{HP}$ = 1.6 Hz, C$_5$(CH_3)$_5$); 2.27–2.29 (m, 2H, CH_2); 4.34 (d, $^5J_{HP}$ = 0.4 Hz, 3H, OCH_3); 7.27 (s br, 1H, C*H*); 7.46–7.59 (m, 3H, *Ph*); 7.87–7.92 (m, 2H, *Ph*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –144.15 (hept, $^1J_{PF}$ = 710.5 Hz, *P*F$_6$); –35.37 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 9.6 (s, C$_5$(*C*H$_3$)$_5$); 13.9 (d, $^2J_{CP}$ = 7.4 Hz, *C*^{4}); 15.8 (d, $^1J_{CP}$ = 40.1 Hz, P(*C*H$_3$)$_3$); 64.3 (s, OCH$_3$); 98.2 (d, $^2J_{CP}$ = 2.0 Hz, *C*$_5$(CH$_3$)$_5$); 128.7 (s, 2*C Ph*); 129.5 (s, 2*C Ph*); 132.6 (s, 1*C Ph*); 136.3 (s br, *C*^{2}); 137.3 (d, $^4J_{HP}$ = 1.39 Hz, *C*$_{ipso}$); 197.1 (s, *C*^{3}); 250.7 (d, $^2J_{CP}$ = 11.5 Hz, *C*^{1}) ppm.

*Preparation of [IrCp*Cl{=C(OMe)CH=CHPh}(PPh$_2$Me)]PF$_6$* (**5*a***). An orange solution of [IrCp*Cl$_2$(PPh$_2$Me)] (100 mg, 0.17 mmol) and sodium hexafluorophosphate (29 mg, 0.17 mmol) in dichloromethane/methanol 5:1 (12 mL) was prepared. After that, 1–phenyl–2–propyn–1–ol (70 µl, 0.55 mmol) was added and the mixture was stirred for 20 h at room temperature.

The resulting dark red solution was concentrated and the red oil obtained was redissolved in CH_2Cl_2 (5 ml). The red solution was filtered and vacuum concentrated obtaining a red oil. The oil was triturated and washed with pentane (2 × 5 mL) and diethylether (5 ml). Finally, the red solid obtained was dried in vacuum. Yield: 102 mg (70%). Anal. Calcd for $C_{33}H_{38}OClF_6IrP_2$ (854.3 g/mol): C 46.40, H 4.48; found: C, 46.54; H, 4.53. MS (m/z, referred to the most abundant isotopes): m/z: 709 $[M]^+$. IR (cm^{-1}): ν (PF_6) 839 (s). ^1H NMR (CD_2Cl_2): δ 1.55 (d, 15H, $^4J_{HP}$ = 2.3 Hz, $C_5(CH_3)_5$); 2.26 (d, 3H, $^2J_{HP}$ = 10.6 Hz, PPh_2CH_3); 4.16 (s, 3H, OCH_3); 7.23–7.89 (m, 15H, *Ph* + PPh_2CH_3); 7.28 (d, 1H, $^3J_{HH}$ = 15.6 Hz, $C_\beta H$); 8.66 (d, 1H, $^3J_{HH}$ = 15.1 Hz, $C_\gamma H$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ –144.11 (hept, $^1J_{PF}$ = 710.6 Hz, PF_6); –13.28 (s br, PPh_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 9.0 (s, $C_5(CH_3)_5$); 14.5 (d, $^1J_{CP}$ = 41.0 Hz, PPh_2CH_3); 65.5 (s, OCH_3); 99.0 (d, $^2J_{CP}$ = 2.4 Hz, $C_5(CH_3)_5$); 125.3–135.0 (PPh_2Me + *Ph*) 129.6 (s, C_β); 134.5 (s, C_{ipso}–Ph); 169.0 (s, C_γ); 262.0 (d, $^2J_{CP}$ = 13.5 Hz, C_α) ppm.

*Preparation of [IrCp*Cl{=C(OMe)CH=CHPh}(PMe$_3$)]PF$_6$* (***5b***). An orange solution of [$IrCp^*Cl_2(PMe_3)$] (300 mg, 0.63 mmol) and sodium hexafluorophosphate (130 mg, 0.76 mmol) in dichloromethane/methanol 2:1 (30 mL) was prepared. After that, 1–phenyl–2–propyn–1–ol (263 µl, 2.08 mmol) was added and the mixture was stirred for 6 h at room temperature. The resulting dark red solution was concentrated and the red oil obtained was redissolved in dichloromethane (10 mL). The solution was filtered and vacuum concentrated obtaining a red oil that was washed with pentane (3 × 8 mL) and diethylether (2 × 8 ml), and dried in vacuum. Yield: 305 mg (66%). Anal. Calcd for $C_{23}H_{34}OClF_6IrP_2$ (730.1 g/mol): C 37.84, H 4.69; found: C, 37.91; H, 4.73. MS (m/z, referred to the most abundant isotopes): m/z: 585 $[M]^+$. IR (cm^{-1}): ν (PF_6) 840 (s). ^1H NMR (CD_2Cl_2): δ 1.65 (d, 9H, $^2J_{HP}$ = 11.2 Hz, $P(CH_3)_3$); 1.74 (d, 15H, $^4J_{HP}$ = 2.3 Hz, $C_5(CH_3)_5$); 4.53 (s, 3H, OCH_3); 7.52–7.57 (m, 2H, *Ph*); 7.53 (d, $^3J_{HH}$ = 14.7 Hz, $C_\beta H$); 7.65–7.71 (m, 1H, *Ph*); 7.85–7.90 (m, 2H, *Ph*); 8.63 (d, $^3J_{HH}$ = 14.9 Hz, $C_\gamma H$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ –144.10 (hept, $^1J_{PF}$ = 710.6 Hz, PF_6); –24.93 (s, $P(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 9.2 (d, $^3J_{CP}$ = 0.7 Hz, $C_5(CH_3)_5$); 14.5 (d, $^1J_{CP}$ = 40.7 Hz, $P(CH_3)_3$); 65.6 (s, OCH_3); 98.3 (d, $^2J_{CP}$ = 2.5 Hz, $C_5(CH_3)_5$); 126.9 (s, C_β); 130.2 (s, 2*C Ph*); 131.3 (s, 2*C Ph*); 134.6 (s, C_{ipso}); 134.9 (s, 1*C Ph*); 170.0 (s, C_γ); 262.1 (d, $^2J_{CP}$ = 14.0 Hz, C_α) ppm.

Preparation of [IrCp{C(OMe)=CHC(Me)=CH}(PPh$_2$Me)]* (***6a***). A dark brown solution of **2a** (100 mg, 0.013 mmol) in 13 mL of dichloromethane was treated with KO^{t}Bu (80 mg, 0.71 mmol). The solution was stirred for 2 hours at room temperature. After that, the brown solution was filtered and vacuum concentrated obtaining dark green oil that was triturated with pentane (4 mL). Finally, the resulting brown solid was dried in vacuum. Yield: 72 mg (89%). Anal. Calcd for $C_{29}H_{36}OIrP$ (623.8 g/mol): C 55.84, H 5.82; found: C 65.03, H 5.88. MS (m/z, referred to the most abundant isotopes): m/z: 625 [M+1]. ^1H NMR (CD_2Cl_2): δ 1.56 (d, 15H, $^4J_{HP}$ = 1.8 Hz, $C_5(CH_3)_5$); 1.67 (d, 3H, $^2J_{HP}$ = 10.2 Hz, PPh_2CH_3); 1.78–1.79 (m, 3H, CH_3); 3.64 (s, 3H, OCH_3); 5.20–5.22 (m, 1H, C^2H); 6.03–6.07 (m, 1H, C^4H); 7.23–7.41 (m, 8H, PPh_2CH_3); 7.47–7.54 (m, 2H, PPh_2CH_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ –6.59 (s, PPh_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 9.0 (s, $C_5(CH_3)_5$); 12.4 (d, $^1J_{CP}$ = 42.9 Hz, PPh_2CH_3); 21.7 (d, $^4J_{CP}$ = 1.9 Hz, CH_3) 56.4 (s, OCH_3); 93.9 (d, $^2J_{CP}$ = 2.9 Hz, $C_5(CH_3)_5$); 110.1 (d, $^3J_{CP}$ = 2.3 Hz, C^2); 122.9 (d, $^2J_{CP}$ = 14.6 Hz, C^4); 127.5 (d, $^3J_{CP}$ = 9.9 Hz, PPh_2Me); 127.8 (d, $^3J_{CP}$ = 10.2 Hz, PPh_2Me); 129.0 (d, $^4J_{CP}$ = 2.4 Hz, PPh_2Me); 129.9 (d, $^4J_{CP}$ = 2.3 Hz, PPh_2Me); 132.2 (d, $^2J_{CP}$ = 10.2 Hz, PPh_2Me); 133.9 (d, $^2J_{CP}$ = 11.1 Hz, PPh_2Me); 134.0 (d, $^1J_{CP}$ = 53.3 Hz, PPh_2Me); 137.5 (d, $^1J_{CP}$ = 50.9 Hz, PPh_2Me); 145.6 (d, $^3J_{CP}$ = 0.8 Hz, C^3); 180.4 (d, $^2J_{CP}$= 13.4 Hz, C^1) ppm.

Preparation of [IrCp{C(OMe)=CHC(Me)=CH}(PMe$_3$)]* (***6b***). The complex **2b** (118 mg, 0.18 mmol) was dissolved in 10 mL of dichloromethane and then, KO^{t}Bu (102 mg, 0.91 mmol) was added. The brown solution was stirred for three hours at room temperature. After that, the clear brown solution obtained was filtered and vacuum concentrated. The dark brown oil obtained was treated with pentane (4 mL) giving a dark brown solid that was dried in vacuum. Yield: 70 mg (78%). Anal. Calcd for $C_{19}H_{32}OIrP$ (499.7 g/mol): C 45.67, H 6.46; found: C 45.74, H 6.50. MS (m/z, referred to the most abundant isotopes): m/z: 501 [M+1]. ^1H NMR (CD_2Cl_2): δ 1.26 (d, 9H, $^2J_{HP}$ = 10.3 Hz, $P(CH_3)_3$); 1.82 (d, 15H, $^4J_{HP}$ = 1.6 Hz, $C_5(CH_3)_5$); 1.89 (dd, 3H, $^4J_{HH}$ = 2.2 Hz and $^4J_{HH}$ =1.4 Hz, CH_3); 3.57 (s, 3H, OCH_3); 5.30–5.33 (overlapped with solvent signal, 1H, C^2H); 6.07–6.11 (m, 1H, C^4H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ –40.76 (s, $P(CH_3)_3$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 9.7 (s, $C_5(CH_3)_5$); 15.3 (d, $^1J_{CP}$ = 38.9 Hz, $P(CH_3)_3$); 21.5 (d, $^4J_{CP}$ = 2.0 Hz, CH_3); 56.1 (s, OCH_3); 93.3 (d, $^2J_{CP}$ = 2.8 Hz, $C_5(CH_3)_5$); 109.9 (d, $^3J_{CP}$ = 2.0 Hz, C^2); 123.4 (d, $^2J_{CP}$ = 14.2 Hz, C^4); 145.2 (d, $^3J_{CP}$ = 1.4 Hz, C^3); 180.0 (d, $^2J_{CP}$ = 13.7 Hz. C^1) ppm.

Preparation of [IrCp{C(OMe)=CHC(Ph)=CH}(PPh$_2$Me)]* (***7a***). A dark brown solution of **4a** (600 mg, 0.72 mmol) in 40 mL of dichloromethane was treated with KO^{t}Bu (445 mg, 3.97 mmol). The solution was stirred for 150 min at room temperature. After that, the brown solution was filtered and vacuum concentrated, obtaining a brown oil that was treated with pentane (2 × 6 mL), giving a brown solid obtained that was dried in vacuum. Yield: 416 mg (70%). Anal. Calcd for $C_{34}H_{38}OIrP$ (685.9 g/mol): C 59.54, H 5.58; found: C 59.73, H 5.62. MS (m/z, referred to the most abundant isotopes): m/z: 687 [M+1]. ^1H NMR (CD_2Cl_2): δ 1.59 (d, 15H, $^4J_{HP}$ = 1.7 Hz, $C_5(CH_3)_5$); 1.66 (d, 3H, $^2J_{HP}$ = 10.2 Hz, PPh_2CH_3); 3.75 (s, 3H, OCH_3); 5.82 (s br, 1H, C^2H); 6.95–7.00 (m, 1H, *Ph*); 7.11–7.17 (m, 2H, *Ph*); 7.28–7.54 (m, 12H, PPh_2CH_3 + *Ph*); 7.31 (d, 1H, $^3J_{HP}$ = 8.3 Hz, C^4H) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ –7.19 (s, PPh_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 9.0 (s, $C_5(CH_3)_5$); 12.6 (d, $^1J_{CP}$ = 43.1 Hz, PPh_2CH_3); 56.6 (s, OCH_3); 94.5 (d, $^2J_{CP}$ = 2.8 Hz, $C_5(CH_3)_5$); 107.3 (d, $^3J_{CP}$ = 2.2 Hz, C^2); 124.1 (s, 1*C Ph*); 125.2 (s, 2*C Ph*); 127.7 (d, $^3J_{CP}$ = 10.0 Hz, PPh_2Me); 127.9 (d, $^3J_{CP}$ = 10.2 Hz, PPh_2Me); 128.1 (s, 2*C Ph*); 129.3 (d, $^4J_{CP}$ = 2.3 Hz, PPh_2Me); 129.9 (d, $^4J_{CP}$ = 2.4 Hz, PPh_2Me); 131.4 (d, $^2J_{CP}$ = 14.1 Hz, C^4); 132.4 (d, $^2J_{CP}$ = 10.4 Hz, PPh_2Me); 133.5 (d, $^2J_{CP}$ = 11.0 Hz, PPh_2Me); 134.0 (d, $^1J_{CP}$ = 53.9 Hz, PPh_2Me); 136.7 (d, $^1J_{CP}$ = 51.2 Hz, PPh_2Me); 143.1 (d, $^3J_{CP}$ = 2.1 Hz, C^3); 151.4 (d, $^4J_{CP}$ = 0.7 Hz, C_{ipso}–Ph); 180.5 (d, $^2J_{CP}$ = 13.1 Hz, C^1) ppm.

Preparation of [IrCp{C(OMe)=CHC(Ph)=CH}(PMe$_3$)]* (***7b***). The complex **4b** (115 mg, 0.16 mmol) was dissolved in 10 mL of dichloromethane and then, KO^{t}Bu (100 mg, 0.89 mmol) was added. The brown suspension was stirred for three hours at room temperature. After that, the resulting clear brown suspension was filtered and vacuum concentrated. The dark brown oil obtained was treated with pentane (4 mL) giving a dark brown solid that was dried in vacuum. Yield: 74 mg

(82%). Anal. Calcd for $C_{24}H_{34}OIrP$ (561.7 g/mol): C 51.32, H 6.10; found: C 51.46, H 6.15. MS (m/z, referred to the most abundant isotopes): m/z: 563 [M+1]. ^{1}H NMR (CD_2Cl_2): δ 1.29 (d, 9H, $^2J_{HP}$ = 10.4 Hz, P(CH_3)$_3$); 1.87 (d, 15H, $^4J_{HP}$ = 1.6 Hz, C_5(CH_3)$_5$); 3.70 (s, 3H, OCH_3); 5.92–5.94 (m, 1H, C^2*H*); 6.98–7.03 (m, 1H, *Ph*); 7.15–7.21 (m, 2H, *Ph*); 7.42–7.46 (m, 3H, *Ph* + C^4*H*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –40.72 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 9.7 (s, C_5(*C*H$_3$)$_5$); 15.4 (d, $^1J_{CP}$ = 39.0 Hz, P(*C*H$_3$)$_3$); 56.3 (s, O*C*H$_3$); 94.0 (d, $^2J_{CP}$ = 2.9 Hz, C_5(CH$_3$)$_5$); 106.8 (d, $^3J_{CP}$= 2.0 Hz, *C*^{2}); 124.0 (s, 1*C Ph*); 124.9 (s, 2*C Ph*); 128.3 (s, 2*C Ph*);132.5 (d, $^2J_{CP}$ = 13.6 Hz, *C*^{4}); 143.1 (d, $^3J_{CP}$ = 2.3 Hz, *C*^{3}); 151.0 (d, $^4J_{CP}$ = 1.2 Hz, C_{ipso}); 180.0 (d, $^2J_{CP}$= 13.7 Hz, *C*^{1}) ppm.

ASSOCIATED CONTENT

Supporting Information

CIF files giving Crystallographic data for compounds **1a, 2a** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail for S.B.: bgs@uvigo.es

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

We thank the University of Vigo CACTI services for collecting X–ray data.

REFERENCES

(1) (a) Albrecht, M. *Chem. Rev*. **2010**, *110*, 576–623 and its references. (b) Campos, J.; Espada, M. F.; López–Serrano, J.; Carmona, E. *Inorg. Chem*. **2013**, *52*, 6694–6704 and its references.

(2) Morales–Morales, D.; Jensen, C. M. *The Chemistry of Pincer Compounds*; Elsevier: Amsterdam, 2007.

(3) Paneque, M.; Poveda, M. L.; Santos, L. L.; Carmona, E.; Mereiter, K. *Organometallics* **2008**, *27*, 6353–6359.

(4) Danapoulos, A. A.; Winston, S.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans*. **2002**, 3090–3091.

(5) (a) Paneque, M.; Poveda, M. L.; Rendón, N.; Mereiter, K. *J. Am. Chem. Soc.* **2004**, *126*, 1610–1611. (b) Paneque, M.; Poveda, M. L.; Rendón, N.; Mereiter, K. *Organometallics* **2009**, *28*, 172–180. (c) Li, L.; Brennessel, W. W.; Jones, W. D. *Organometallics* **2009**, *28*, 3492–3500.

(6) Talavera, M.; Bolaño, S.; Bravo, J.; Castro, J.; García–Fontán, S.; Hermida–Ramón, J. M. *Organometallics*, dx.doi.org/10.1021/om400702b.

(7) Yamamoto, Y.; Sugawara, K.; Han, X–H. *J. Chem. Soc., Dalton Trans*. **2002**, 195–211.

(8) Álvarez, E.; Paneque, M.; Petronilho, A. G.; Poveda, M. L.; Santos, L. L.; Carmona, E.; Mereiter, K. *Organometallics* **2007**, *26*, 1231–1240.

(9) When [IrCp*Cl(NCMe)L]PF_6 [L = PPh_2Me] is used as starting material the compound **3a** appears accompanied with other not identified products. When L = PMe_3 the final product is a mixture of **4b** and **3b**.

(10) (a) Morrow, J. R.; Tonker, T. L.; Templeton J. L. *J. Am. Chem. Soc.* **1985**, *107*, 5004–5005. (b) Carlton, L.; Davidson, J. L.; Ewing, P.; Manojlovic–Muir, L.; Muir, K. W. *Chem. Commun.* **1985**, 1474–1476. (c) Busetto, L.; Mazzoni, R.; Salmi, M.; Zacchini, S.; Zanotti, V. *J. Organomet. Chem.* **2010**, *695*, 2519–2525. (d) Busetto, L.; Marchetti, F.; Zacchini, S.; Zanotti, V. *Organometallics* **2005**, *24*, 2297–2306. (e) Cabrera, E.; Daran, J.C.; Jeannin, Y. *Organometallics* **1989**, *8*, 1811–1819. (f) Herberich, G. E.; Mayer, H. *Organometallics* **1990**, *9*, 2655–2661. (g) Kriley, C. E.; Kerschner, J. L.; Fanwick, P. E.; Rothwell, P. I. *Organometallics* **1993**, *12*, 2051–2058. (h) Agh–Atabay, N. M.; Davidson, J. L.; Douglas, G.; Muir, K. W. *Chem. Commun*. **1989**, 549–551. (i) Agh–Atabay, N. M.; Davidson, J. L.; Muir, K. W. *Chem. Commun.* **1990**, 1399–1401. (j) Yeh, W–Y.; Peng, S–M.; Liu, L–K. *Inorg. Chem.* ,**1993**, *32*, 2965–2967. (k) Biasotto, F.; Etienne, M.; Dahan, F. *Organometallics* **1995**, *14*, 1870–1874.

(11) (a) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Alvarez, E.; Mereiter, K. *Chem. Eur. J.* **2007**, *13*, 5160.**7b** (b) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Mereiter, K. *Organometallics* **2007**, *26*, 3120–3129. (c) Gandon, V.; Agenet, N.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C. *J. Am. Chem. Soc.* **2006**, *128*, 8509–8520. (d) Nishiyama, H.; Niwa, E.; Inoue, T.; Ishima, Y.; Aoki, K. *Organometallics* **2002**, *21*, 2572–2574.

(12) (a) Kirchner, K.; Calhorda, M. J.; Schmid, R.; Veiros, L. F. *J. Am.Chem. Soc.* **2003**, *125*, 11721–11729. (b) Yamamoto, Y.; Arakawa, T.; Ogawa, R.; Itoh, K. *J. Am. Chem. Soc.* **2003**, *125*, 12143–12160.

(13) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Butterworth/Heinemann: London/Oxford, 1988.

(14) Glueck, D. S.; Bergman, R. G. *Organometallics*, **1991**, *10*, 1479.

(15) Paz–Michel, B.; Cervantes–Vázquez, M.; Paz–Sandoval, M. A. *Inorganica Chimica Acta*, **2008**, *361*, 3094–3102.

(16) Talavera, M.; Bolaño, S.; Bravo, J.; Castro, J.; García–Fontán, S.; Hermida–Ramón, J. M. *Organometallics*, dx.doi.org/10.1021/om400565c.

(17) SMART *Version 5.054, Instrument control and data collection software*; Bruker Analytical X–ray Systems: Madison, WI, 1997.

(18) SAINT *Version 6.01, Data Integration software package*; Bruker Analytical X–ray Systems: Madison, WI, 1997.

(19) Sheldrick, G. M., *SADABS. A Computer Program for Absorption Corrections*; University of Göttingen, Germany, 1996.

(20) McArdle, P. *J. Appl. Cryst*. **1995**, *28,* 65.

(21) Sheldrick, G. M. *Acta Cryst*. **2008,** *A64*, 112–122.

Cyclometalated Iridium Complexes from an Intramolecular C–H Activation of [IrCp*Cl{=C(OMe)CH=C(CH$_3$)R}L] (R = CH$_3$, Ph; L = PPh$_2$Me, PMe$_3$).

M. Talavera, S. Bolaño,* J. Bravo, J. Castro and S. García–Fontán.