Supporting Information

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_2Me, PMe_3).

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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[1] and, prior to use, distilled under argon. The starting materials $[IrCp^*Cl_2(PPh_2Me)]$,[2] $[IrCp^*Cl_2(PMe_3)]$,[3] $[IrCp^*Cl(NCMe)(PPh_2Me)]PF_6$[4] and $[IrCp^*Cl(NCMe)(PMe_3)]PF_6$[5] 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[6] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[7] for integration of intensity of reflections and scaling, and SADABS[8] for empirical absorption correction.

The crystallographic treatment of the compounds was performed with the Oscail program.[9] The structure was solved by direct methods and refined by full–matrix least–squares based on F^2.[10] 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: 661.19681 $[M]^+$. IR (cm^{-1}): ν (PF$_6$) 838 (s). ^{1}H NMR (CD_2Cl_2): δ 1.53–1.54 (m, 3H, C(C*H*$_3$)$_2$); 1.57 (d, 15H, $^4J_{HP}$ = 2.2 Hz, C$_5$(C*H*$_3$)$_5$); 1.72–1.73 (m, 3H, C(C*H*$_3$)$_2$); 2.27 (d, 3H, $^2J_{HP}$ = 10.4 Hz, PPh$_2$C*H*$_3$); 4.40 (s, 3H, OC*H*$_3$); 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$_5$(CH$_3$)$_5$); 14.1 (d, $^1J_{CP}$ = 41.9 Hz, PPh$_2$CH$_3$); 23.2 (s, C(CH$_3$)$_2$); 27.1 (s, C(CH$_3$)$_2$) 69.3 (s, OCH$_3$); 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: 537.16546 $[M]^+$. 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(C*H*$_3$)$_3$); 1.75 (d, 15H, $^4J_{HP}$ = 2.4 Hz, C$_5$(C*H*$_3$)$_5$); 1.90–1.91 (m, 3H, C(C*H*$_3$)$_2$); 1.98–2.00 (m, 3H, C(C*H*$_3$)$_2$); 4.74 (s, 3H, OC*H*$_3$); 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$_5$(CH$_3$)$_5$); 14.3 (d, $^1J_{CP}$ = 40.8 Hz, P(CH$_3$)$_3$); 23.7 (s, C(CH$_3$)$_2$); 29.2 (s, C(CH$_3$)$_2$) 69.0 (s, OCH$_3$); 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: 625.21988 $[M]^+$. 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$_5$(C*H*$_3$)$_5$); 1.81–1.85 (m, 2H, C*H*$_2$); 1.87–1.90 (m, 3H, C*H*$_3$); 2.10 (d, 3H, $^2J_{HP}$ = 9.8 Hz, PPh$_2$C*H*$_3$); 4.17 (d, 3H, $^5J_{HP}$ = 0.5 Hz, OC*H*$_3$); 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$_5$(CH$_3$)$_5$); 14.6 (d, $^1J_{CP}$ = 41.0 Hz, PPh$_2$CH$_3$); 19.6 (d, $^2J_{CP}$ = 7.8 Hz, C^4); 24.6 (s, CH$_3$); 63.6 (s, OCH$_3$); 98.1 (d, $^2J_{CP}$ = 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(C*H*$_3$)$_3$); 1.65–1.72 (m, 1H, C*H*$_2$); 1.87 (d, 15H, $^4J_{HP}$ = 1.6 Hz, C$_5$(C*H*$_3$)$_5$); 1.88–1.94 (m, 1H, C*H*$_2$); 2.30–2.39 (m, 3H, C*H*$_3$); 4.24 (s, 3H, OC*H*$_3$); 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$_3$)$_5$); 15.5 (d, $^1J_{CP}$ = 40.2 Hz, P(CH$_3$)$_3$); 18.7 (d, $^2J_{CP}$ = 7.7 Hz, C^4); 24.3 (s, CH$_3$); 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$_6$* (***3a***). 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: 723.21154 $[M]^+$. 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$_5$(C*H*$_3$)$_5$); 1.84 (s, 3H, C*H*$_3$); 2.34 (d, 3H, $^2J_{HP}$ = 10.5 Hz, PPh$_2$C*H*$_3$); 4.47 (s, 3H, OC*H*$_3$); 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$_2$CH$_3$); 19.9 (s, CH$_3$); 69.8 (s, OCH$_3$); 100.4 (d, $^2J_{CP}$ = 2.0 Hz, C$_5$(CH$_3$)$_5$); 126.9 (s, 2C *Ph*); 129.1 (s, 2C *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, 1C *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_β); 139.7 (s, C_{ipso}–Ph); 143.6 (s, C_γ); 271.4 (d, $^2J_{CP}$ = 12.8 Hz, C_α) ppm.

*Preparation of [IrCp*Cl{=C(OMe)CH=CPhMe}(PMe$_3$)]PF$_6$* (***3b***). 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: 118 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.) $C_{24}H_{36}OClF_6IrP_2$ (744.2g/mol). ^{1}H NMR (CD_2Cl_2): δ 1.67 (d, 9H, $^2J_{HP}$ = 10.9 Hz, P(C*H*$_3$)$_3$); 1.79 (d, 15H, $^4J_{HP}$ = 2.2 Hz, C_5(C*H*$_3$)$_5$); 2.34 (d, 3H, $^4J_{HH}$ = 0.9 Hz, C*H*$_3$); 4.77 (s, 3H, OC*H*$_3$); 7.25 (s br, 1H, C_β*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(CH$_3$)$_5$); 14.8 (d, $^1J_{CP}$ = 40.7 Hz, P(CH$_3$)$_3$); 21.4 (s, CH$_3$); 69.4 (s, OCH$_3$); 98.6 (d, $^2J_{CP}$ = 2.3 Hz, C_5(CH$_3$)$_5$); 127.4 (s, 2C *Ph*); 129.6 (s, 2C *Ph*); 131.3 (s, 1C *Ph*); 140.5 (s, C_β); 141.4 (s, C_{ipso}); 153.3 (s, C_γ); 266.1 (s br, C_α) ppm.

Preparation of [IrCp{=C(OMe)CH=C(Ph)(CH$_2$)}(PPh$_2$Me)]PF$_6$* (***4a***). 650 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: 687.23380 $[M]^+$. 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(C*H*$_3$)$_5$); 2.10 (d, 3H, $^2J_{HP}$ = 10.0 Hz, PPh$_2$C*H*$_3$); 2.12–2.19 (m, 1H, C*H*$_2$); 2.44–2.52 (m, 1H, C*H*$_2$); 4.27 (s, 3H, OC*H*$_3$); 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(CH$_3$)$_5$); 14.3 (d, $^2J_{CP}$= 7.8 Hz, C^4); 14.7 (d, $^1J_{CP}$ = 41.1 Hz, PPh$_2$CH$_3$); 63.5 (s, OCH$_3$); 98.5 (d, $^2J_{CP}$ = 2.1 Hz, C_5(CH$_3$)$_5$); 128.7 (s, 2C *Ph*); 128.9 (s, 2C *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, 1C *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$_6$* (***4b***). 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: 563.20465 $[M]^+$. 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(C*H*$_3$)$_3$); 1.93 (d, 15H, $^4J_{HP}$ = 1.6 Hz, C_5(C*H*$_3$)$_5$); 2.27–2.29 (m, 2H, C*H*$_2$); 4.34 (d, $^5J_{HP}$ = 0.4 Hz, 3H, OC*H*$_3$); 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(CH$_3$)$_5$); 13.9 (d, $^2J_{CP}$ = 7.4 Hz, C^4); 15.8 (d, $^1J_{CP}$ = 40.1 Hz, P(CH$_3$)$_3$); 64.3 (s, OCH$_3$); 98.2 (d, $^2J_{CP}$ = 2.0 Hz, C_5(CH$_3$)$_5$); 128.7 (s, 2C *Ph*); 129.5 (s, 2C *Ph*); 132.6 (s, 1C *Ph*); 136.3 (s br, C^2); 137.3 (d, $^4J_{HP}$ = 1.4 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$_6$* (***5a***). 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%). When [IrCp*Cl(NCMe)(PMe$_3$)]PF$_6$ was used as starting material the reaction gave unidentified decomposition products. 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: 709.19722 $[M]^+$. IR (cm^{-1}): ν (PF_6) 839 (s). ^{1}H NMR (CD_2Cl_2): δ 1.55 (d, 15H, $^4J_{HP}$ = 2.3 Hz, C_5(C*H*$_3$)$_5$); 2.26 (d, 3H, $^2J_{HP}$ = 10.6 Hz, PPh$_2$C*H*$_3$); 4.16 (s, 3H, OC*H*$_3$); 7.23–7.89 (m, 15H, *Ph* + P*Ph*$_2$CH$_3$); 7.28 (d, 1H, $^3J_{HH}$ = 15.6 Hz, C_β*H*); 8.66 (d, 1H, $^3J_{HH}$ = 15.1 Hz, C_γ*H*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –144.11 (hept, $^1J_{PF}$ = 710.6 Hz, *P*F$_6$); –13.28 (s br, *P*Ph$_2$CH$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 9.0 (s, C_5(CH$_3$)$_5$); 14.5 (d, $^1J_{CP}$ = 41.0 Hz, PPh$_2$CH$_3$); 65.5 (s, OCH$_3$); 99.0 (d, $^2J_{CP}$ = 2.4 Hz, C_5(CH$_3$)$_5$); 125.3–135.0 (P*Ph*$_2$Me + *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%). When [IrCp*Cl(NCMe)(PMe$_3$)]PF$_6$ was used as starting material the reaction gave unidentified decomposition products. 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: 585.16492 [M]$^+$. IR (cm^{-1}): ν (PF_6) 840 (s). ^{1}H 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{^{1}H} NMR (CD_2Cl_2): δ –144.10 (hept, $^1J_{PF}$ = 710.6 Hz, *P*F_6); –24.93 (s, *P*(CH_3)$_3$) ppm. ^{13}C{^{1}H} 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$_\beta$); 130.2 (s, 2C *Ph*); 131.3 (s, 2C *Ph*); 134.6 (s, C$_{ipso}$); 134.9 (s, 1C *Ph*); 170.0 (s, C$_\gamma$); 262.1 (d, $^2J_{CP}$ = 14.0 Hz, C$_\alpha$) ppm.

Preparation of [Ir(Cp{C(OMe)=CHC(Me)=CH}(PPh$_2$Me)]* (***6a***). A dark brown solution of **2a** (100 mg, 0.13 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: 625.22056 [M+1]. ^{1}H 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$_2$CH_3); 1.78–1.79 (m, 3H, CH_3); 3.64 (s, 3H, OCH_3); 5.20–5.22 (m, 1H, C^2*H*); 6.03–6.07 (m, 1H, C^4*H*); 7.23–7.41 (m, 8H, P*Ph*$_2$CH$_3$); 7.47–7.54 (m, 2H, P*Ph*$_2$CH$_3$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –6.59 (s, *P*Ph$_2$CH$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 9.0 (s, C_5(CH$_3$)$_5$); 12.4 (d, $^1J_{CP}$ = 42.9 Hz, PPh$_2$CH$_3$); 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, P*Ph*$_2$Me); 127.8 (d, $^3J_{CP}$ = 10.2 Hz, P*Ph*$_2$Me); 129.0 (d, $^4J_{CP}$ = 2.4 Hz, P*Ph*$_2$Me); 129.9 (d, $^4J_{CP}$ = 2.3 Hz, P*Ph*$_2$Me); 132.2 (d, $^2J_{CP}$ = 10.2 Hz, P*Ph*$_2$Me); 133.9 (d, $^2J_{CP}$ = 11.1 Hz, P*Ph*$_2$Me); 134.0 (d, $^1J_{CP}$ = 53.3 Hz, P*Ph*$_2$Me); 137.5 (d, $^1J_{CP}$ = 50.9 Hz, P*Ph*$_2$Me); 145.6 (d, $^3J_{CP}$ = 0.8 Hz, C^3); 180.4 (d, $^2J_{CP}$= 13.4 Hz, C^1) ppm.

Preparation of [Ir(Cp{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: 501.18899 [M+1]. ^{1}H 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^2*H*); 6.07–6.11 (m, 1H, C^4*H*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –40.76 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} 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 [Ir(Cp{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: 687.23643 [M+1]. ^{1}H 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$_2$CH_3); 3.75 (s, 3H, OCH_3); 5.82 (s br, 1H, C^2*H*); 6.95–7.00 (m, 1H, *Ph*); 7.11–7.17 (m, 2H, *Ph*); 7.28–7.54 (m, 12H, P*Ph*$_2$CH$_3$ + *Ph*); 7.31 (d, 1H, $^3J_{HP}$ = 8.3 Hz, C^4*H*) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –7.19 (s, *P*Ph$_2$CH$_3$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 9.0 (s, C_5(CH$_3$)$_5$); 12.6 (d, $^1J_{CP}$ = 43.1 Hz, PPh$_2$CH$_3$); 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, 1C *Ph*); 125.2 (s, 2C *Ph*); 127.7 (d, $^3J_{CP}$ = 10.0 Hz, P*Ph*$_2$Me); 127.9 (d, $^3J_{CP}$ = 10.2 Hz, P*Ph*$_2$Me); 128.1 (s, 2C *Ph*); 129.3 (d, $^4J_{CP}$ = 2.3 Hz, P*Ph*$_2$Me); 129.9 (d, $^4J_{CP}$ = 2.4 Hz, P*Ph*$_2$Me); 131.4 (d, $^2J_{CP}$ = 14.1 Hz, C^4); 132.4 (d, $^2J_{CP}$ = 10.4 Hz, P*Ph*$_2$Me); 133.5 (d, $^2J_{CP}$ = 11.0 Hz, P*Ph*$_2$Me); 134.0 (d, $^1J_{CP}$ = 53.9 Hz, P*Ph*$_2$Me); 136.7 (d, $^1J_{CP}$ = 51.2 Hz, P*Ph*$_2$Me); 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 [Ir(Cp{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: 563.20465 [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(CH$_3$)$_5$); 15.4 (d, $^1J_{CP}$ = 39.0 Hz, P(CH$_3$)$_3$); 56.3 (s, OCH$_3$); 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, 1C *Ph*); 124.9 (s, 2C *Ph*); 128.3 (s, 2C *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.

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