Dalton Transactions

Accepted Manuscript

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Electronic Effects of Substituents on the Stability of the Iridanaphthalene Compound [IrCp*{=C(OMe)CH=C(*o*–C$_6$H$_4$)(Ph)}(PMe$_3$)]PF$_6$

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Cite this: DOI: 10.1039/xoxxoooooox

Received ooth January 2012,
Accepted ooth January 2012

DOI: 10.1039/xoxxoooooox

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Iridanaphthalene complexes are synthesized from the corresponding methoxy(alkenyl)carbeneiridium compounds. The electronic character of the substituents on the 6-position of the metallanaphthalene ring is crucial from the point of view of the stability of the iridanaphthalene, [IrCp*{=C(OMe)CH=C(*o*–C$_6$H$_4$)(Ph)}(PMe$_3$)]PF$_6$, vs. its transformation to the corresponding indanone derivatives. Stability studies of the iridanaphthalene compounds revealed that strong donors substituents (-OMe) stabilize the iridanaphthalene, while weak electron donor (-Me) and electron withdrawing (-NO$_2$) groups favor the formation of indanone derivatives. Two possible indanone isomers can be obtained in the conversion of the unstable iridanaphthalene complexes and a mechanism for the formation of these isomers is proposed.

Introduction

Transition-metal cyclometalated complexes have increased their presence in organometallic chemistry. Much of the risen interest stems from a plethora of applications, for example, in organic transformations, catalysis, material science, and medicinal chemistry.[1] Within the large family of metallacycle compounds, the metallaaromatics have especially attracted attention since they can display both aromatic properties and organometallic reactivity.[2] The metal center, coligands, and substituents on the ring play an important role in the stabilization of these metallacycle compounds. *Xia et al*. have reported how phosphonium substituents on the aromatic ring are able to stabilize a great variety of osma-aromatic complexes.[1b] Understanding how substituents on the ring with different electronic properties affect the stability of these derivatives is crucial to optimize their synthesis, reactivity and applications. Metallanaphthalenes or superior analogs are practically unknown and very few examples have been isolated,[3] making their exploration of great interest to gain access to a promising rich chemistry.

We reported iridanaphthalene [IrCp*{=C(OMe)CH=C(*o*–C$_6$H$_4$)(Ph)}(PMe$_3$)]PF$_6$, which is unstable in solution and evolves into 3-phenyl-1-indanone.[3c] In order to exploit the full potential of iridanaphthalene complexes it is important to understand substituent effects on the metallanaphthalene ring. Herein, we report the synthesis of a series of new methoxy(alkenyl)carbeneiridium compounds bearing substituents of different electronic behavior and the corresponding iridanaphthalene complexes. In addition, we study how the substituents influence the conversion of the iridanaphthalene complexes to the corresponding indanone derivatives.

Results and discussion

Synthesis and Characterization.

The methoxy(alkenyl)carbeneiridium complexes **1–3** were prepared by a reaction of [IrCp*Cl(NCMe)(PMe$_3$)]PF$_6$ with the corresponding propargylic alcohol **I–III** (Scheme 1). The products **1–3** which contain a -NO$_2$, -OMe or -Me substituent, respectively, on one of the phenyl rings of the (alkenyl)carbene ligand were isolated as a mixture of cis/trans isomers respect to C$^{\beta}$–C$^{\gamma}$ double bond.

The corresponding mixture of two iridanaphthalene isomers **4(A,B)–6(A,B)** were obtained using our synthetic route:[3c] by treatment of **1–3** with AgPF$_6$ at room temperature, implying an intramolecular C–H bond activation of one phenyl ring of the (alkenyl)carbene ligand. It is a good general strategy for the preparation of a family of iridanaphthalene complexes from different aryl substituents of the (alkenyl)carbene ligand. Isomer **A** has a substituent on the 6-position of the iridanaphthalene skeleton, and the **B** isomer has a substituent on the *para*-position of the phenyl ring (Scheme 1).

Multidimensional and multinuclear NMR spectra, summarized in the Experimental Section, supported the proposed structure for all complexes and, in particular, the NOESY spectra confirm the cis/trans isomerism.

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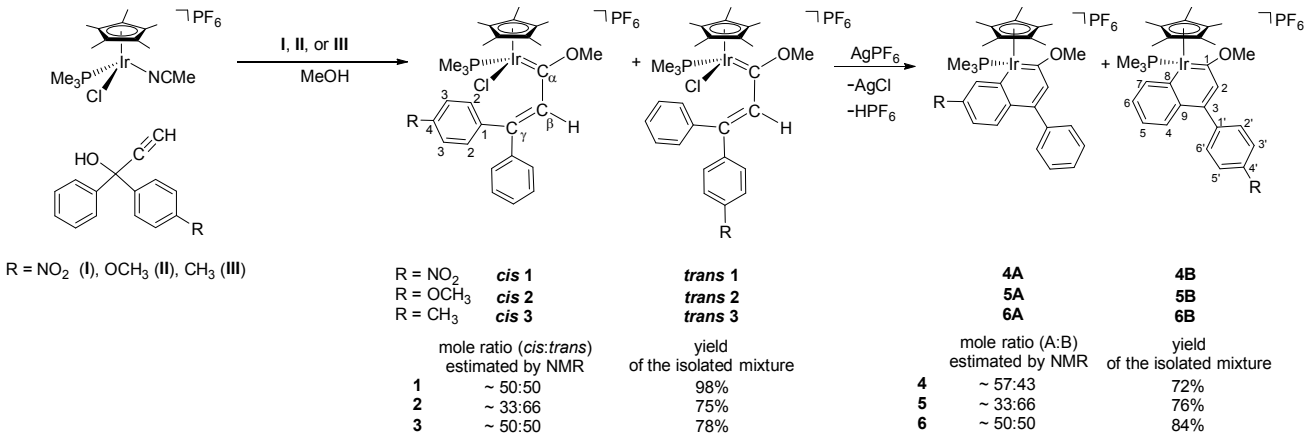

Scheme 1. Synthesis of methoxy(alkenyl)carbeneiridium complexes **1–3** and their conversion to the respective iridanaphthalene compounds **4–6**.

When the mixture **4(A,B)** was treated with a solution of $NaBPh_4$ in methanol, brown monocrystals of $[IrCp^*\{=C(OMe)CH=C(o\text{-}C_6H_4)(p\text{-}NO_2\text{-}C_6H_4)(PMe_3)]BPh_4$ (**4B**) were obtained. The structure of **4B** was confirmed by single-crystal X-ray diffraction analysis and the ORTEP representation of the complex cation **4B** accompanied by a selection of distances and angles is given in Figure 1. The asymmetric unit of complex **4B** contains an iridium cation complex, a BPh_4^- anion and a CH_2Cl_2 solvent molecule.

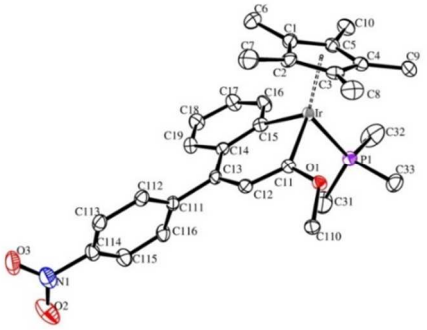

Figure 1. ORTEP view of the cation $[IrCp^*\{=C(OMe)CH=C(o\text{-}C_6H_4)(p\text{-}NO_2\text{-}C_6H_4)(PMe_3)\}]^+$ (**4B**) drawn at 50% probability level. Hydrogen atoms are not shown. Selected bond lengths (Å) and angles (deg): Ir–CT, 1.9167(3); Ir–C(11), 1.965(4); Ir–C(15), 2.037(4); Ir–P(1), 2.2754(11); C(11)–Ir–C(15), 89.47(16); CT–Ir–C(11), 125.49(11); CT–Ir–C(15), 123.26(12); C(15)–Ir–P(1), 89.46(12); C(11)–Ir–P(1), 87.43(12). CT refers to the centroid of the Cp* ligand.

The cation consists of a pentamethylcyclopentadienyl ligand (Cp*) η^5–coordinated to an iridium atom. The metal becomes part of the naphthalene moiety and the coordination sphere is completed by a phosphane ligand (PMe_3) with a "three-legged piano stool" structure in an octahedral arrangement. The iridanaphthalene shows Ir–C bond lengths of 1.965(4) and 2.037(4) Å. The distance between the iridium atom and the plane defined by the five carbon atoms of the ring is 0.425(5) Å, showing an envelope distortion. These data are similar to previously reported iridanaphthalene complexes.[3,4]

How the substituents influence on the stability of the iridanaphthalene $[IrCp^*\{=C(OMe)CH=C(o\text{-}C_6H_4)(Ph)\}(PMe_3)]PF_6$?

We studied the influence of the electronic character of the substituent on the 6-position of the naphthalene ring on the stability of the iridanaphthalene complex $[IrCp^*\{=C(OMe)CH=C(o\text{-}C_6H_4)(Ph)\}(PMe_3)]PF_6$, that is, the degree of conversion of the iridanaphthalene complex to the corresponding indanone derivatives, choosing -OMe, -Me, and $-NO_2$ as substituents due to their different electronic effects.

The nature of all indanone derivatives[5] (Chart 1) was confirmed by multidimensional and multinuclear NMR spectroscopy (Experimental Section).

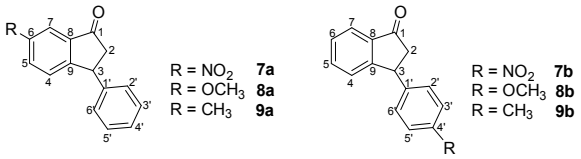

Chart 1. Indanone Derivatives.

When a solution of nitro-iridanaphthalene isomeric mixture **4(A,B)** (~57:43 mole ratio) in 1,2-dichloroethane was heated at 338 K for 24 hours, **7b** was isolated in 90% yield and **4A** was recovered unaltered. In an attempt to obtain the indanone derivative **7a** corresponding to **4A**, a solution of **4A** in 1,2-dichloroethane was heated at 368 K for 24 hours, resulting in a mixture of nitro-indanone derivatives **7a** and **7b** in ~30:70 mole

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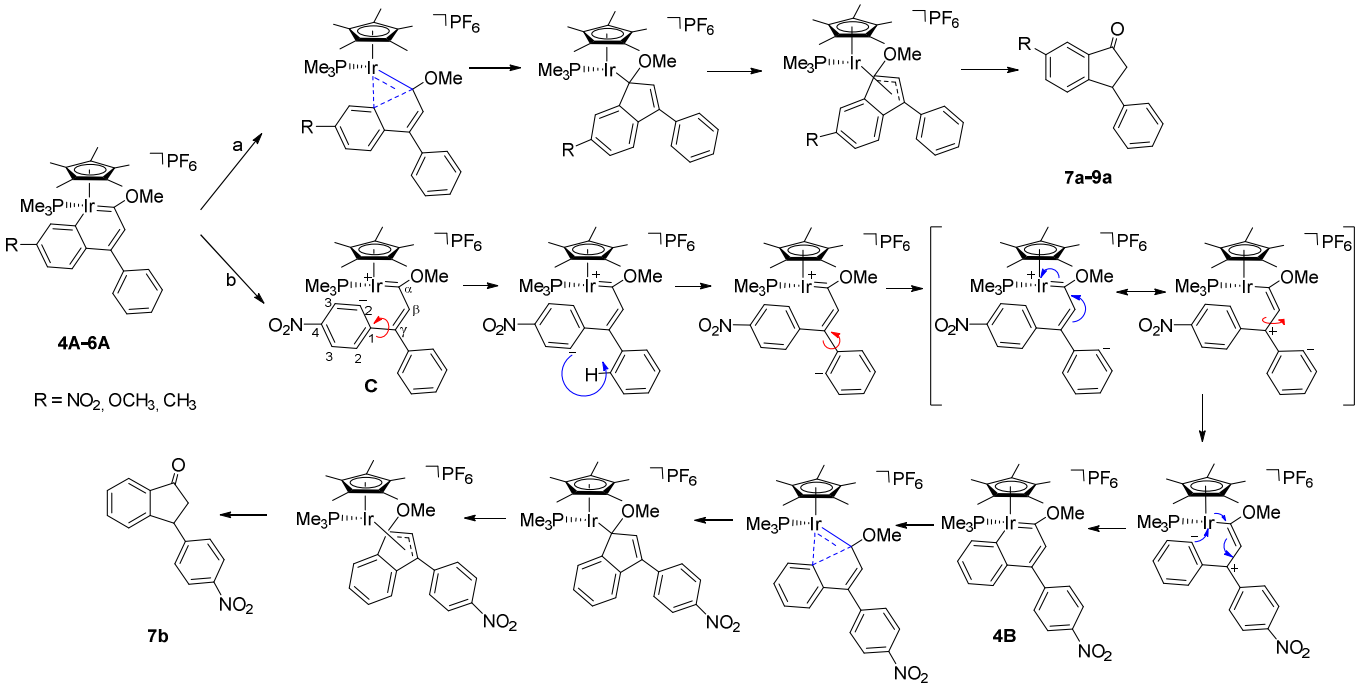


Scheme 2. Proposed mechanism for the formation of the indanone derivatives from the iridanaphthalene complex substituted on 6-position of the naphthalene ring.

ratio (estimated by NMR, 91% yield of the isolated mixture), respectively. This suggests that:

1) nitro-iridanaphthalene isomer **4A** is more stable than **4B** and requires harsher reaction conditions to convert it into the indanone derivatives.
2) nitro-iridanaphthalene isomer **4A** evolves into nitro-indanone derivatives **7a** and **7b**, with **7b** being the major product. This seems to indicate that during the conversion of **4A** in the corresponding indanone derivative **7a**, a transformation occurs giving **7b** as major product (path "b" Scheme 2). It has been tested that **7a** does not evolve to **7b** under the same conditions.

The nitro group is an electron-withdrawing group through resonance and induction, and thus the *ortho*- and *para*-positions to the nitro group have a positive partial charge. We propose that the reaction follows a mechanism (Scheme 2), where the nitro group stabilizes the carbanion **C** and favors path "b" over path "a".[6]

Path "a": involves a carbene migratory insertion, leading to a η^1-indenyl intermediate followed by switching from η^1 to η^3 hapticity to give the η^3-indenyl complex, which detaches from the metallic center to form an indanone derivative.[3c]

Path "b": involves the initial formation of carbanion **C**, followed by a rotation over the C^{γ}–C^{1} σ bond and abstraction of a proton. Subsequent electronic rearrangements and rotations give an iridanaphthalene complex with the substituent in the *para*-position of the phenyl ring. This finally evolves into the corresponding indanone derivative.[7]

When a mixture of **5(A,B)** (~33:66 mole ratio) in 1,2-dichloroethane was heated at 338 K for 24 hours, methoxy-indanone derivatives **8a** and **8b** were obtained in a ~13:87 mole ratio (estimated by NMR) (50% yield of the isolated mixture), respectively, and **5A** was recovered in a minor proportion (80% regarding initial quantity). To confirm that **8a** is formed only from **5A** and **8b** only from **5B**, a solution of **5A** in 1,2-dichloroethane was heated at 368 K for 24 hours. **8a** together with 6-methoxy-3-phenylinden-1-one (~70:30 mole ratio estimated by NMR, respectively) were obtained and **5A** was recovered in a 78% regarding initial quantity. The formation of **8b** was not observed. This suggests that the conversion of iridanaphthalene **5A** to the respective methoxy-indanone derivative is less favored than that of **4A** into the corresponding nitro-indanone derivatives **7(a,b)**. In this example, methoxy group is an electron-withdrawing group and resonance donor but in alkoxy groups the resonance overrides induction. This means that *ortho*- and *para*-positions to the methoxy group have a negative partial charge. Thus, formation of carbanion **C** is not favored and path "b" is not followed. This significantly increases the stability of iridanaphthalene **5A** with respect to the formation of the methoxy-indanone derivatives and it is only converted in 14% yield through path "a" (Scheme 2).

The mixture methyl-iridanaphthalene isomers **6(A,B)** (~50:50 mole ratio) in 1,2-dichloroethane at 338 K for 24 hours gave the methyl-indanone derivatives, **9a** and **9b**, with a ~45:55

mole ratio (estimated by NMR) in 91% yield of the mixture isolated. In this case, isomer **6A** evolved to **9a** and **6B** to **9b**. Because the methyl group is a weak electron donor with no resonance effect, the carbanion is not favored and the stability of the iridanaphthalene decreases in favor of the methyl-indanone derivative formation following path "a" (Scheme 2).
Our results from solution stability studies of the iridanaphthalene compounds presented in this work demonstrate that donor substituents (-OMe) on the 6-position of the naphthalene skeleton stabilize the iridanaphthalene over the indanone derivative formation, whereas weak electron-donor (-Me) and electron-withdrawing (-NO_2) substituents on the 6-position favor the formation of indanone derivatives.

Conclusion

In conclusion, we presented the synthesis of new *cis*- and *trans*-isomers of methoxy(alkenyl)carbeneiridium complexes containing a nitro, methoxy or methyl substituent on one of the phenyl rings of the (alkenyl)carbene ligand. A mixture of two iridanaphthalene isomers were obtained from the methoxy(alkenyl)carbeneiridium complexes, one with the substituent on the 6-position of the iridanaphthalene skeleton and the other one on the *para*-position of the phenyl ring. Given the broad range of properties, reactivity, and applications related to metallaaromatic compounds and that the metallanaphthalene compounds are practically unknown,[3] it is important to understand how the substituents on the naphthalene skeleton affect their stability. Our studies indicate that the substituents have a significant effect on the stability of the iridanaphthalene complex [IrCp*{=C(OMe)CH=C(*o*–C_6H_4)(Ph)}(PMe_3)]PF_6 in the conversion to their corresponding indanone derivatives, with a π-donor substituent on the 6-position of the naphthalene skeleton stabilizing the iridanaphthalene. This information will be important for further exploration of different ways to create stable iridanaphthalene compounds to study their properties and future applications in material science.

Experimental section

Synthetic procedures, materials and methods.

All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by the usual procedures[8] and, prior to use, distilled under argon. The starting material [IrCp*Cl(NCMe)(PMe_3)]PF_6[3c] was prepared as described in the literature. All reagents were obtained from commercial sources except for propargylic alcohols (**I**,**II**,**III**), which were synthesized following the method described by Mantovani et al.[9] Unless stated, NMR spectra were recorded at room temperature on Bruker ARX–400 instrument, with resonating frequencies of 400 MHz (^{1}H), 161 MHz (^{31}P{^{1}H}), and 100 MHz (^{13}C{^{1}H}) using the solvent as the internal lock. ^{1}H and ^{13}C{^{1}H} signals are referred to internal TMS and those of ^{31}P{^{1}H} to 85% H_3PO_4; downfield shifts (expressed in ppm) are considered positive. ^{1}H and ^{13}C{1H} NMR (or JMOD) signal assignments were confirmed by {^{1}H, ^{1}H} COSY, {^{1}H, ^{1}H} NOESY, {^{1}H,^{13}C} HSQC, {^{1}H,^{13}C} HMBC and DEPT experiments. Coupling constants are given in hertz. The isomer ratios were determined using relaxation delays as longer as 30 s in order to collect reliable integral data of the ^{1}H NMR resonances. 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. Mass spectra are referred to the most abundant isotopes and they were acquired using an Apex–Qe spectrometer by high resolution electrospray technique for organometallic complexes and high and low resolution electron impact technique for organic compounds.

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[10] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[11] for integration of intensity of reflections and scaling, and SADABS[12] for empirical absorption correction.
The crystallographic treatment of the compound was performed with the Oscail program.[13] The structure was solved by direct methods and refined by full–matrix least–squares based on F2.[14] All non–hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealized positions and refined with isotropic displacement parameters.
Crystal data and structural refinement details for complex **4B** are given in Table 1.

Table 1. Crystal Data and Structure Refinement for **4B.**

Empirical formula	$C_{54}H_{58}BCl_2NO_3PIr$
Formula wt	1073.89
Temp (K)	100(2)
Wavelength (Å)	0.71073
Cryst syst	Monoclinic
Space group	$P2_1/n$
a (Å)	18.696(2)
b (Å)	11.6073(14)
c (Å)	24.032(3)
α (deg)	90
β (deg)	112.526(2)
γ (deg)	90
V (Å^3)	4817.2(10)
Z	4
Density (Mg/m^3)	1.481
Abs coeff (mm^{-1})	2.960
F(000)	2176
Cryst size (mm)	0.29 × 0.24 × 0.19
θ range for data collection (deg)	2.36–28.09
Index ranges	$-24 \le h \le 24$ $-15 \le k \le 15$ $-31 \le l \le 31$
No. of rflns collected	82883
No. of indep rflns	11700 [R(int)=0.0593]
No. of rflns obsd (>2σ)	9026
Data Completeness	0.997
Abs cor	Semi–empirical from equivalents
Max. and min. transmission	0.4309 and 0.3395
Refinement method	Full–matrix least-squares on F^2
No. of data / restraints / params	11700/0/577

Goodness of fit on F^2	1.084
R indices [$I > 2\sigma(I)$]	R_1=0.0347, wR_2=0.0668
R indices (all data)	R_1=0.0599, wR_2=0.0784
Largest diff. peak and hole (e.Å^{-3})	5.259 and –3.510

Preparation of *cis*- and *trans*-[IrCp*Cl{=C(OMe)–CH=C(*p*–NO$_2$–C$_6$H$_4$)(Ph)}(PMe$_3$)]PF$_6$ (1)

To a yellow solution of [IrCp*Cl(NCMe)(PMe$_3$)]PF$_6$ (300 mg, 0.48 mmol) in methanol (20 mL), 1-(4-nitrophenyl)-1-phenyl-2-propyn-1-ol (159 mg, 0.62 mmol) was added and the mixture was stirred for 20 min. The dark red solution obtained was concentrated under vacuum yielding a dark red solid that was washed with pentane (3 × 5 mL) and diethylether (2 × 5 mL). Finally, it was dried under vacuum giving a mixture of ***cis*-, *trans*-1** isomers in a ~50:50 mole ratio (estimated by NMR), respectively. Yield (isolated mixture): 400 mg (98%).
Anal. Calcd for $C_{29}H_{37}O_3NClF_6IrP_2$ (851.23 g/mol): C 40.92, H 4.38, N 1.65; found: C 41.05, H 4.45, N 1.71. MS (m/z): 706.18114 $[M]^+$. IR (cm^{-1}): *ν* (NO_2) 1519 (m), 1346 (m); (PF_6) 840 (s). ***cis*-1:** ^{1}H NMR: *δ* 1.69 (d, 9H, $^2J_{HP}$ = 11.0 Hz, P(C*H*$_3$)$_3$); 1.79 (d, 15H, $^4J_{HP}$ = 2.2 Hz, C$_5$(C*H*$_3$)$_5$); 4.20 (s, 3H, OC*H*$_3$); 7.34 (d, 2H, $^3J_{HH}$ = 8.9 Hz, C^2*H*); 7.37–7.39 (m, 2H, *Ph*); 7.40–7.60 (m, 3H, *Ph*); 7.64 (s br, 1H, C$_\beta$*H*); 8.30 (d, 2H, $^3J_{HH}$ = 8.9 Hz, C^3*H*) ppm. ^{31}P{^{1}H} NMR: *δ* –144.14 (sept, $^1J_{PF}$ = 710.9 Hz, *P*F$_6$); –30.93 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR: *δ* 9.2 (s, C$_5$(*C*H$_3$)$_5$); 15.2 (d, $^1J_{CP}$ = 40.9 Hz, P(*C*H$_3$)$_3$); 68.9 (s, OCH$_3$); 99.2 (d, $^2J_{CP}$ = 2.2 Hz, *C*$_5$(CH$_3$)$_5$); 124.0 (s, 2C *C*^{3}); 129.2 (s, 2C *C*^{2}); 129.7 (s, 2C *Ph*); 129.8 (s, 2C *Ph*); 132.3 (s, 1C *Ph*); 138.9 (s, *C*$_{ipso}$); 139.5 (s, *C*$_\beta$); 146.1 (s, *C*^{1}); 148.2 (s, *C*^{4}); 150.7 (s br, *C*$_\gamma$); 264.0 (s br, *C*$_\alpha$) ppm. ***trans*-1:** ^{1}H NMR: *δ* 1.70 (d, 9H, $^2J_{HP}$ = 11.0 Hz, P(C*H*$_3$)$_3$); 1.74 (d, 15H, $^4J_{HP}$ = 2.1 Hz, C$_5$(C*H*$_3$)$_5$); 4.17 (s, 3H, OC*H*$_3$); 6.97 (s br, 1H, C$_\beta$*H*); 7.12–7.15 (m, 2H, *Ph*); 7.40–7.60 (m, 3H, *Ph*); 7.59 (d, 2H, $^3J_{HH}$ = 8.9 Hz, C^2*H*); 8.22 (d, 2H, $^3J_{HH}$ = 8.9 Hz, C^3*H*) ppm. ^{31}P{^{1}H} NMR: *δ* –144.14 (sept, $^1J_{PF}$ = 710.9 Hz, *P*F$_6$); –29.41 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR: *δ* 9.2 (s, C$_5$(*C*H$_3$)$_5$); 15.2 (d, $^1J_{CP}$ = 40.9 Hz, P(*C*H$_3$)$_3$); 69.0 (s, OCH$_3$); 100.2 (s br, *C*$_5$(CH$_3$)$_5$); 124.3 (s, 2C *C*^{3}); 130.6 (s, 2C *C*^{2}); 129.4 (s, 2C *Ph*); 129.7 (s, 2C *Ph*); 129.8 (s, 1C *Ph*); 137.9 (s, *C*$_{ipso}$); 139.8 (s, *C*$_\beta$); 146.8 (s, *C*^{1}); 149.0 (s, *C*^{4}); 150.7 (s br, *C*$_\gamma$); 264.0 (s br, *C*$_\alpha$) ppm.

Preparation of *cis*- and *trans*-[IrCp*Cl{=C(OMe)–CH=C(*p*–OCH$_3$–C$_6$H$_4$)(Ph)}(PMe$_3$)]PF$_6$ (2)

To a yellow solution of [IrCp*Cl(NCMe)(PMe$_3$)]PF$_6$ (150 mg, 0.24 mmol) in methanol (10 mL), 1-(4-methoxyphenyl)-1-phenyl-2-propyn-1-ol (74 mg, 0.31 mmol) was added and the mixture was stirred for 15 min. The dark solution obtained was vacuum-concentrated yielding a dark red solid that was washed with pentane (2 × 5 mL) and diethylether (2 × 5 mL). Finally, it was dried under vacuum giving ***cis*-, *trans*-2** isomers in a ~33:66 mole ratio (estimated by NMR), respectively. Yield (isolated mixture): 150 mg (75%).
Anal. Calcd for $C_{30}H_{40}O_2ClF_6IrP_2$ (836.26 g/mol): C 43.09, H 4.82; found: C 43.36, H 4.77. MS (m/z): 691.20651 $[M]^+$; 655.22979 $[M–HCl]^+$. IR (cm^{-1}): *ν* (PF_6) 840 (s). ***cis*-2:** ^{1}H NMR: *δ* 1.70 (d, 9H, $^2J_{HP}$ = 11.0 Hz, P(C*H*$_3$)$_3$); 1.77 (d, 15H, $^4J_{HP}$ = 2.3 Hz, C$_5$(C*H*$_3$)$_5$); 3.87 (s, 3H, C^4–OC*H*$_3$); 4.11 (s, 3H, C$_\alpha$–OC*H*$_3$); 6.94 (d, 2H, $^3J_{HH}$ = 9.0 Hz, C^3*H*); 7.01 (s br, 1H, C$_\beta$*H*); 7.09 (d, 2H, $^3J_{HH}$ = 9.0 Hz, C^2*H*); 7.37–7.40 (m, 2H, *Ph*); 7.40–7.43 (m, 3H, *Ph*) ppm. ^{31}P{^{1}H} NMR: *δ* –144.17 (sept, $^1J_{PF}$ = 710.5 Hz, *P*F$_6$); –29.59 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR: *δ* 9.3 (s, C$_5$(*C*H$_3$)$_5$); 15.0 (d, $^1J_{CP}$ = 40.5 Hz, P(*C*H$_3$)$_3$); 55.9 (s, C^4–O*C*H$_3$); 68.4 (s, C$_\alpha$–O*C*H$_3$); 99.4 (d, $^2J_{CP}$ = 2.2 Hz, *C*$_5$(CH$_3$)$_5$); 114.4 (s, 2C *C*^{3}); 129.5 (s, 3C *Ph*); 130.2 (s, 2C *Ph*); 131.2 (s, *C*^{1}); 131.7 (s, 2C *C*^{2}); 137.4 (s br, *C*$_\beta$); 141.1 (s, *C*$_{ipso}$); 161.9 (s, *C*^{4}); 154.1 (s br, *C*$_\gamma$); 260.6 (d, $^2J_{CP}$ = 11.9 Hz, *C*$_\alpha$) ppm. ***trans*-2:** ^{1}H NMR: *δ* 1.70 (d, 9H, $^2J_{HP}$ = 10.8 Hz, P(C*H*$_3$)$_3$); 1.78 (d, 15H, $^4J_{HP}$ = 2.2 Hz, C$_5$(C*H*$_3$)$_5$); 3.85 (s, 3H, C^4–OC*H*$_3$); 4.05 (s, 3H, C$_\alpha$–OC*H*$_3$); 6.93 (d, 2H, $^3J_{HH}$ = 9.1 Hz, C^3*H*); 7.09–7.12 (m, 2H, *Ph*); 7.37 (d, 2H, $^3J_{HH}$ = 9.1 Hz, C^2*H*); 7.43–7.47 (m, 3H, *Ph*); 7.49 (s br, 1H, C$_\beta$*H*) ppm. ^{31}P{^{1}H} NMR: *δ* –144.17 (sept, $^1J_{PF}$ = 710.5 Hz, *P*F$_6$); –31.05 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR: *δ* 9.2 (s, C$_5$(*C*H$_3$)$_5$); 15.0 (d, $^1J_{CP}$ = 40.5 Hz, P(*C*H$_3$)$_3$); 56.1 (s, C^4–O*C*H$_3$); 68.0 (s, C$_\alpha$–O*C*H$_3$); 98.6 (d, $^2J_{CP}$ = 2.6 Hz, *C*$_5$(CH$_3$)$_5$); 115.1 (s, 2C *C*^{3}); 128.7 (s, 2C *Ph*); 128.7 (s, 2C *Ph*); 129.4 (s, 1C *Ph*); 132.1 (s, *C*^{1}); 132.3 (s, 2C *C*^{2}); 136.7 (d, $^3J_{CP}$ = 3.1 Hz, *C*$_\beta$); 139.7 (s, *C*$_{ipso}$); 163.5 (s, *C*^{4}); 155.6 (s br, *C*$_\gamma$); 259.4 (d, $^2J_{CP}$ = 11.5 Hz, *C*$_\alpha$) ppm.

Preparation of *cis*- and *trans*-[IrCp*Cl{=C(OMe)–CH=C(*p*–CH$_3$–C$_6$H$_4$)(Ph)}(PMe$_3$)]PF$_6$ (3)

To a yellow solution of [IrCp*Cl(NCMe)(PMe$_3$)]PF$_6$ (150 mg, 0.24 mmol) in methanol (10 mL), 1-(4-methylphenyl)-1-phenyl-2-propyn-1-ol (70 mg, 0.31 mmol) was added and the mixture was stirred for 15 min. The dark solution obtained was vacuum-concentrated yielding a dark green solid that was washed with pentane (2 × 5 mL) and diethylether (2 × 5 mL). Finally, it was dried under vacuum giving a mixture of ***cis*-, *trans*-3** isomers in a ~50:50 mole ratio (estimated by NMR), respectively. Yield (isolated mixture): 153 mg (78%).
Anal. Calcd for $C_{30}H_{40}OClF_6IrP_2$ (820.26 g/mol): C 43.93, H 4.92; found: C 44.06, H 4.96. MS (m/z): 675.21166 $[M]^+$.IR (cm^{-1}): ν (PF_6) 839 (s). ***cis*-3:** ^{1}H NMR: *δ* 1.70 (d, 9H, $^2J_{HP}$ = 11.0 Hz, P(C*H*$_3$)$_3$); 1.77 (d, 15H, $^4J_{HP}$ = 2.2 Hz, C$_5$(C*H*$_3$)$_5$); 2.42 (s, 3H, C*H*$_3$); 4.10 (s, 3H, OC*H*$_3$); 7.01 (d, 2H, $^3J_{HH}$ = 8.1 Hz, C^3*H*); 7.13 (s br, 1H, C$_\beta$*H*); 7.18–7.33 (m, 2H, C^2*H*); 7.36–7.55 (m, 5H, *Ph*) ppm. ^{31}P{^{1}H} NMR: *δ* –144.17 (sept, $^1J_{PF}$ = 710.6 Hz, *P*F$_6$); –29.80 (s, *P*(CH$_3$)$_3$) ppm.^{13}C{^{1}H} NMR: *δ* 9.3 (s, C$_5$(*C*H$_3$)$_5$); 15.1 (d, $^1J_{CP}$ = 40.4 Hz, P(*C*H$_3$)$_3$); 21.5 (s, *C*H$_3$); 68.5 (s, OC*H*$_3$); 99.4 (d, $^2J_{CP}$ = 2.17 Hz, *C*$_5$(CH$_3$)$_5$); 128.7–130.3 (all s, 5C *Ph* + 4C *C*$_6$H$_4$CH$_3$); 137.9 (s br, *C*$_\beta$); 139.5 (s, *C*$_{ipso}$); 140.7 (s, *C*^{1}); 140.8 (s, *C*^{4}); 154.3 (s br, *C*$_\gamma$); 261.6 (d, $^2J_{CP}$ = 11.1 Hz, *C*$_\alpha$) ppm. ***trans*-3:** ^{1}H NMR: *δ* 1.70 (d, 9H, $^2J_{HP}$ = 10.9 Hz, P(C*H*$_3$)$_3$); 1.78 (d, 15H, $^4J_{HP}$ = 2.3 Hz, C$_5$(C*H*$_3$)$_5$); 2.37 (s, 3H, C*H*$_3$); 4.08 (s, 3H, OC*H*$_3$); 7.08–7.12 (m, 2H, *Ph*); 7.18–7.33 (m, 4H, C^3*H* + C^2*H*); 7.36–7.55 (m, 4H, C$_\beta$*H* + *Ph*) ppm. ^{31}P{^{1}H} NMR: *δ* –144.17 (sept, $^1J_{PF}$ = 710.6 Hz, *P*F$_6$); –30.56 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR: *δ* 9.2 (s, C$_5$(*C*H$_3$)$_5$); 15.0 (d, $^1J_{CP}$ = 40.6 Hz, P(*C*H$_3$)$_3$); 21.7 (s, *C*H$_3$); 68.3 (s, OCH$_3$); 98.9 (d, $^2J_{CP}$ = 2.3 Hz, *C*$_5$(CH$_3$)$_5$); 128.7–130.3 (all s, 5C *Ph* + 4C *C*$_6$H$_4$CH$_3$); 136.2 (s, *C*^{1}); 137.3 (s, *C*$_{ipso}$); 137.7 (d, $^3J_{CP}$ = 2.3 Hz, *C*$_\beta$); 143.2 (s, *C*^{4}); 154.7 (s br, *C*$_\gamma$); 261.2 (d, $^2J_{CP}$ = 10.3 Hz, *C*$_\alpha$) ppm.

The synthesis of the **1-3** complexes was done with different experimental conditions trying to direct the synthesis towards one isomer but a mixture of cis/trans isomers was always obtained. Different attempts to separate them by a silica column were unsuccessful. Using this mixture have not any influence in the cyclometallation reaction since each isomer gives the corresponding isomer of iridanaphthalene as it is observed in the isomers ratio.

Preparation of [IrCp*{=C(OMe)–CH=C(*o*–C$_6$H$_3$–*p*–NO$_2$)(Ph)}(PMe$_3$)]PF$_6$ (4A) and [IrCp*{=C(OMe)–CH=C(*o*–C$_6$H$_4$)(*p*–NO$_2$–C$_6$H$_4$)}(PMe$_3$)]PF$_6$ (4B)

A dark red solution of the mixture ***cis-, trans*-1** (~50:50 mole ratio, 350 mg, 0.41 mmol) in 30 mL of dichloromethane was treated with $AgPF_6$ (117 mg, 0.45 mmol). The brown solution was stirred 5 min at room temperature, and then, it was filtered obtaining a brown oil that was treated and washed with pentane (3 × 5 mL). Finally, the brown solid was dried under vacuum obtaining a mixture of isomers **4(A,B)** (~57:43 mole ratio estimated by NMR, respectively). Yield (mixture isolated): 240 mg (72%).This solid was dissolved in dichloromethane and a solution of $NaBPh_4$ in methanol was added dropwise yielding brown monocrystals of complex **4B** adequate for X–ray diffraction analysis.

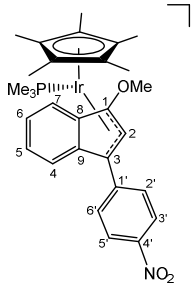
Anal. Calcd for $C_{29}H_{36}O_3NF_6IrP_2$ (814.77 g/mol): C 42.75, H 4.45, N 1.72; found: C 42.88, H 4.48, N 1.76. MS (m/z): 670.20487 $[M]^+$. IR (cm^{-1}): ν (NO_2) 1519 (m) and 1345 (m); (PF_6) 839 (s).

4A: ^{1}H NMR: δ 1.30 (d, 9H, $^2J_{HP}$ = 10.9 Hz, P(CH_3)$_3$); 1.84 (d, 15H, $^4J_{HP}$ = 1.7 Hz, C$_5$(CH_3)$_5$); 4.50 (d, 3H, $^5J_{HP}$ = 0.8 Hz, OCH_3); 6.80 (d, 1H, $^4J_{HP}$ = 1.0 Hz, C^2*H*); 7.42–7.47 (m, 2H, *Ph*); 7.56–7.60 (m, 3H, *Ph*); 7.79–7.83 (m, 1H, C^4*H*); 7.85–7.90 (m, 1H,C^5*H*); 8.63 (d, 1H, $^4J_{HP}$ = 2.4 Hz, C^7*H*) ppm. ^{31}P{^{1}H} NMR: δ –144.14 (sept, $^1J_{PF}$ = 711.3 Hz, *P*F$_6$); –34.43 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR: δ 9.6 (s, C$_5$(CH_3)$_5$); 14.2 (d, $^1J_{CP}$ = 41.1 Hz, P(CH_3)$_3$); 64.9 (s, OCH_3); 100.9 (d, $^2J_{CP}$ = 1.8 Hz, *C*$_5$(CH$_3$)$_5$); 118.0 (s, *C*^{5}); 121.8 (d, $^3J_{CP}$ = 1.9 Hz, *C*^{2}); 129.0 (s, 1C *Ph*); 129.1 (s, 2C *Ph*); 129.3 (s, 2C *Ph*); 136.2 (d, $^3J_{CP}$ = 4.7 Hz, *C*^{7}); 137.2 (s, *C*^{4}); 140.6 (s, *C*^{9}); 140.9 (s, *C*$_{ipso}$); 146.8 (s, *C*^{6}); 154.2 (d, $^2J_{CP}$ = 10.3 Hz, *C*^{8}); 175.1 (s, *C*^{3}); 251.2 (d, $^2J_{CP}$ = 9.7 Hz, *C*^{1}) ppm. **4B:** ^{1}H NMR: δ 1.27 (d, 9H, $^2J_{HP}$ = 11.0 Hz, P(CH_3)$_3$); 1.81 (d, 15H, $^4J_{HP}$ = 1.7 Hz, C$_5$(CH_3)$_5$); 4.43 (d, 3H, $^5J_{HP}$ = 0.7 Hz, OCH_3); 6.59 (d, 1H, $^4J_{HP}$ = 1.0 Hz, C^2*H*); 7.14–7.17 (m, 2H, C^4*H* + C^5*H*); 7.48–7.51 (m, 1H, C^6*H*); 7.61–7.64 (m, 2H, C$^{2'}$*H* + C$^{6'}$*H*); 7.87–7.88 (m, 1H, C^7*H*); 8.33–8.37 (m, 2H, C$^{3'}$*H* + C$^{5'}$*H*) ppm. ^{31}P{^{1}H} NMR: δ –144.14 (sept, $^1J_{PF}$ = 710.7 Hz, *P*F$_6$); –34.80 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR: δ 9.7 (s, C$_5$(CH_3)$_5$); 14.1 (d, $^1J_{CP}$ = 41.0 Hz, P(CH_3)$_3$); 64.1 (s, OCH$_3$); 100.5 (d, $^2J_{CP}$ = 1.9 Hz, *C*$_5$(CH$_3$)$_5$); 118.5 (d, $^3J_{CP}$ = 2.1 Hz, *C*^{2}); 123.8 (s, *C*^{5}); 124.0 (s, *C*$^{3'}$ + *C*$^{5'}$); 130.6 (s, *C*$^{2'}$ + *C*$^{6'}$); 132.1 (s, *C*^{4}); 133.1 (s, *C*^{9}); 137.2 (s, *C*^{6}); 143.2 (d, $^3J_{CP}$ = 4.7 Hz, *C*^{7}); 148.1 (s, *C*$^{4'}$ + *C*$^{1'}$); 156.5 (d, $^2J_{CP}$ = 10.3 Hz, *C*^{8}); 175.1 (s, *C*^{3}); 249.5 (d, $^2J_{CP}$ = 9.9 Hz, *C*^{1}) ppm.

Note: During NMR characterization the formation of **7b** was observed.

Preparation of [IrCp*{η^3–(C$_9$H$_5$)(OMe)(*p*–NO$_2$–C$_6$H$_4$)}(PMe$_3$)]PF$_6$ (D)

In a NMR tube, a mixture of **4(A,B)** (57:43 mole ratio, 10 mg, 0.012 mmol) was dissolved in 500 µL of dichloromethane-*d*^{2} and heated at 308 K for 7 days. After that, complex **4A** remained unaltered and **4B** has almost completely evolved to a new complex [IrCp*{η^3–(C$_9$H$_5$)(OMe)(*p*–NO$_2$–C$_6$H$_4$)}(PMe$_3$)]PF$_6$ (~10:90 mole ratio estimated by NMR, respectively).



^{1}H NMR: δ 1.31 (d, 9H, $^2J_{HP}$ = 9.8 Hz, P(CH_3)$_3$); 1.45 (d, 15H, $^4J_{HP}$ = 2.0 Hz, C$_5$(CH_3)$_5$); 3.86 (s, 3H, OCH_3); 5.98 (d, 1H, $^3J_{HP}$ = 10.6 Hz, C^2*H*); 6.57 (d, 1H, $^3J_{HH}$ = 7.6 Hz, C$_6$*H*$_4$); 6.84 (d, 1H, $^3J_{HH}$ = 7.6 Hz, C$_6$*H*$_4$); 7.41–7.46 (m, 3H, C$_6$*H*$_4$ + C$^{2'}$*H* + C$^{6'}$*H*); 7.79–7.84 (m, 1H, C$_6$*H*$_4$); 8.17–8.22 (m, 2H, C$^{3'}$*H* + C$^{5'}$*H*) ppm. ^{31}P{^{1}H} NMR: δ –144.16 (sept, $^1J_{PF}$ = 710.6 Hz, *P*F$_6$); –38.92 (s, *P*(CH$_3$)$_3$)ppm. ^{13}C{^{1}H} NMR: δ 8.9 (s, C$_5$(*C*H$_3$)$_5$); 18.2 (d, $^1J_{CP}$ = 38.5 Hz, P(*C*H$_3$)$_3$); 62.0 (s, O*C*H$_3$); 96.4 (d, $^2J_{CP}$ = 2.6 Hz, *C*$_5$(CH$_3$)$_5$); 187.0 (*C*^{1}, observed by {^{1}H, ^{13}C} HMBC correlations) ppm.

Preparation of [IrCp*{=C(OMe)–CH=C(*o*–C$_6$H$_3$–*p*–OCH$_3$)(Ph)}(PMe$_3$)]PF$_6$ (5A) and [IrCp*{=C(OMe)–CH=C(*o*–C$_6$H$_4$)(*p*–OCH$_3$–C$_6$H$_4$)}(PMe$_3$)]PF$_6$ (5B)

A dark red solution of the mixture ***cis-, trans*-2** (~33:66 mole ratio, 150 mg, 0.18 mmol) in 10 mL of dichloromethane was treated with $AgPF_6$ (50 mg, 0.20 mmol). The brown solution was stirred 5 min at room temperature, and then, it was filtered and vacuum-concentrated giving a dark green oil that was treated and washed with pentane (3 × 5 mL). Finally, the dark green solid was dried under vacuum obtaining a mixture of isomers **5(A,B)** (~33:66 mole ratio estimated by NMR, respectively). Yield (isolated mixture): 110 mg (76%).

Anal. Calcd for $C_{30}H_{39}O_2F_6IrP_2$ (799.80 g/mol): C 45.05, H 4.91; found: C 45.23, H 4.96. MS (m/z): 655.23038 $[M]^+$. IR (cm^{-1}): ν (PF_6) 839 (s).

5A: ^{1}H NMR: δ 1.27 (d, 9H, $^2J_{HP}$ = 10.8 Hz, P(CH_3)$_3$); 1.80 (d, 15H, $^4J_{HP}$ = 1.6 Hz, C$_5$(CH_3)$_5$); 3.91 (s, 3H, C^6–OCH_3); 4.31 (s, 3H, C^1–OCH_3); 6.54 (s, 1H, C^2*H*); 6.74 (dd, 1H, $^3J_{HH}$ = 9.2 Hz, $^4J_{HH}$ = 2.7 Hz, C^5*H*); 7.37–7.40 (m, 3H, *Ph* + C^7*H*); 7.50–7.54 (m, 3H, *Ph*); 7.62 (d, 1H, $^3J_{HH}$ = 8.9 Hz, C^4*H*) ppm. ^{31}P{^{1}H} NMR: δ –144.17 (sept, $^1J_{PF}$ = 710.4 Hz, *P*F$_6$); –34.99 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR: δ 9.7 (s, C$_5$(CH_3)$_5$); 14.1 (d, $^1J_{CP}$ = 40.9 Hz, P(CH_3)$_3$); 55.8 (s, C^6–OCH_3); 63.0 (s, C^1–OCH_3); 100.0 (d, $^2J_{CP}$ = 2.0 Hz, *C*$_5$(CH$_3$)$_5$); 110.4 (s, *C*^{5}); 116.1 (d, $^3J_{CP}$ = 2.0 Hz, *C*^{2}); 126.9 (s, *C*$_{ipso}$); 127.9 (d, $^3J_{CP}$ = 5.2 Hz, *C*^{7}); 128.8–129.7 (all s, *Ph*); 140.5 (s, *C*^{4}); 142.4 (s, *C*^{9}); 160.1 (d, $^2J_{CP}$ =10.1 Hz, *C*^{8}); 162.0 (s, *C*^{6}); 178.7 (s, *C*^{3}); 241.7 (d, $^2J_{CP}$ = 10.6 Hz, *C*^{1}) ppm. **5B:** ^{1}H NMR: δ 1.24 (d, 9H, $^2J_{HP}$ = 10.8 Hz, P(CH_3)$_3$); 1.77 (d, 15H, $^4J_{HP}$ = 1.6 Hz, C$_5$(CH_3)$_5$); 3.90 (s, 3H, C^6–OCH_3); 4.38 (s, 3H, C^1–OCH_3); 6.64 (s, 1H, C^2*H*); 7.05 (d, 2H, $^3J_{HH}$ = 8.8 Hz, C$^{3'}$*H* + C$^{5'}$*H*); 7.09–7.14 (m, 1H, C^6*H*); 7.14–7.19 (m, 1H, C^5*H*); 7.41 (d, 2H, $^3J_{HH}$ = 7.13 Hz, C$^{2'}$*H* + C$^{6'}$*H*); 7.71 (dd, 1H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz, C^4*H*); 7.80–7.84 (m, 1H, C^7*H*) ppm. ^{31}P{^{1}H} NMR: δ –144.17 (sept, $^1J_{PF}$ = 710.4 Hz, *P*F$_6$); –34.83 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR: δ 9.7 (s, C$_5$(*C*H$_3$)$_5$); 14.3 (d, $^1J_{CP}$ = 40.8 Hz, P(*C*H$_3$)$_3$); 56.0 (s, C^6–O*C*H$_3$); 63.6 (s, C^1–O*C*H$_3$); 99.8 (d, $^2J_{CP}$ = 2.0 Hz, *C*$_5$(CH$_3$)$_5$); 114.4 (s, *C*$^{3'}$ + *C*$^{5'}$); 118.7 (d, $^3J_{CP}$ = 2.0 Hz, *C*^{2}); 123.6 (s, *C*^{5}); 131.2 (s, *C*$^{2'}$ + *C*$^{6'}$); 131.6 (s, *C*^{6}); 134.2 (s, *C*$^{1'}$); 134.5 (s, *C*^{9}); 137.7 (s, *C*^{4}); 143.1 (d, $^3J_{CP}$ = 5.1 Hz, *C*^{7}); 156.0 (d, $^2J_{CP}$ = 9.9 Hz, *C*^{8}); 161.8 (s, *C*$^{4'}$); 178.9 (s, *C*^{3}); 246.7 (d, $^2J_{CP}$ = 10.4 Hz, *C*^{1}) ppm.

Preparation of [IrCp*{=C(OMe)–CH=C(*o*–C$_6$H$_3$–*p*–CH$_3$)(Ph)}(PMe$_3$)]PF$_6$ (6A) and [IrCp*{=C(OMe)–CH=C(*o*–C$_6$H$_4$)(*p*–CH$_3$–C$_6$H$_4$)}(PMe$_3$)]PF$_6$ (6B)

A green solution of the mixture ***cis-, trans*-3** (~50:50 mole ratio, 130 mg, 0.16 mmol) in 10 mL of dichloromethane was treated with $AgPF_6$ (45 mg, 0.17 mmol). The brown solution was stirred 5 min at room temperature, and then, it was filtered and vacuum-concentrated giving a dark green oil that was treated and washed with pentane (3 × 5 mL). The dark green solid obtained was dried under vacuum yielding a mixture of the isomers **6(A,B)** (~50:50 mole ratio estimated by NMR, respectively). Yield (isolated mixture): 105 mg (84%).

Anal. Calcd for $C_{30}H_{39}OF_6IrP_2$ (783.80 g/mol): C 45.97, H 5.02; found: C 45.19, H 5.07. MS (m/z): 639.22447 $[M]^+$. IR (cm^{-1}): ν (PF_6) 840 (s).

6A: ^{1}H NMR: δ 1.25 (d, 9H, $^{2}J_{HP}$ = 10.9 Hz, P(CH_3)$_3$); 1.78 (d, 15H, $^{4}J_{HP}$ = 1.6 Hz, C$_5$(CH_3)$_5$); 2.41 (s, 3H, CH_3); 4.35 (s, 3H, OCH_3); 6.58 (s, 1H, C^2*H*); 6.94–7.00 (m, 1H, C^5*H*); 7.39–7.42 (m, 2H, *Ph*); 7.51–7.56 (m, 4H, *H^4* + *Ph*); 7.66–7.68 (m, 1H, C^7*H*) ppm. ^{31}P{^{1}H} NMR: δ –144.17 (sept, $^{1}J_{PF}$ = 710.4 Hz, *P*F$_6$); –34.87 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR: δ 9.7 (s, C$_5$(*C*H$_3$)$_5$); 14.2 (d, $^{1}J_{CP}$ = 40.7 Hz, P(*C*H$_3$)$_3$); 21.3 (s, *C*H$_3$); 63.4 (s, O*C*H$_3$); 99.9 (d, $^{2}J_{CP}$ = 1.8 Hz, *C*$_5$(CH$_3$)$_5$); 117.7 (d, $^{3}J_{CP}$ = 2.0 Hz, *C^2*); 124.8 (s, *C^5*); 128.6–129.9 (all s, *Ph*); 131.4 (s, *C^9*); 137.8 (s, *C^4*); 142.1 (s, *C$_{ipso}$*); 142.9 (s, *C^6*); 143.9 (d, $^{3}J_{CP}$ = 4.9 Hz, *C^7*); 157.0 (d, $^{2}J_{CP}$ = 10.2 Hz, *C^8*); 179.3 (s, *C^3*); 245.7 (d, $^{2}J_{CP}$ = 10.3 Hz, *C^1*) ppm. **6B:** ^{1}H NMR: δ 1.25 (d, 9H, $^{2}J_{HP}$ = 10.9 Hz, P(CH_3)$_3$); 1.78 (d, 15H, $^{4}J_{HP}$ = 1.6 Hz, C$_5$(CH_3)$_5$); 2.47 (s, 3H, CH_3); 4.37 (s, 3H, OCH_3); 6.63 (s, 1H, C^2*H*); 7.10–7.14 (m, 2H, C^5*H* + C^6*H*); 7.32–7.35 (m, 4H, C$_6$*H$_4$*CH$_3$); 7.66–7.70 (m, 1H, C^4*H*); 7.81–7.84 (m, 1H, C^7*H*) ppm. ^{31}P{^{1}H} NMR: δ –144.17 (sept, $^{1}J_{PF}$ = 710.4 Hz, *P*F$_6$); –35.05 (s, *P*(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR: δ 9.7 (s, C$_5$(*C*H$_3$)$_5$); 14.1 (d, $^{1}J_{CP}$ = 40.8 Hz, P(*C*H$_3$)$_3$); 21.5 (s, *C*H$_3$); 63.6 (s, O*C*H$_3$); 100.0 (d, $^{2}J_{CP}$ = 1.9 Hz, *C*$_5$(CH$_3$)$_5$); 118.7 (d, $^{3}J_{CP}$ = 2.1 Hz, *C^2*); 123.6 (s, *C^5*); 128.6–129.9 (all s, *C*$_6$H$_4$CH$_3$); 131.7 (s, *C^6*); 134.4 (s, *C^9*); 137.9 (s, *C^4*); 139.1 (s, *C$^{1'}$*); 140.7 (s, *C$^{4'}$*); 143.0 (d, $^{3}J_{CP}$ = 5.0 Hz, *C^7*); 156.1 (d, $^{2}J_{CP}$ = 10.1 Hz, *C^8*); 179.0 (s, *C^3*); 247.6 (d, $^{2}J_{CP}$ = 10.4 Hz, *C^1*) ppm.

Note: During NMR characterization the formation of **9b** (~5%) was observed.

Preparation of 6-Nitro-3-phenylindan-1-one (7a) and 3-(4-Nitrophenyl)indan-1-one (7b)

A dark brown solution of a **4(A,B)** mixture (~57:43 mole ratio, 106 mg, 0.13 mmol) in 10 mL of 1,2-dichloroethane was stirred and heated at 338 K for 24 hours. The brown solution obtained was vacuum-concentrated yielding a brown oil from which the indanone **7b** was extracted with diethylether. The solid that remains after the extraction was washed with pentane (3 × 4 mL) and it was identified as the complex **4A** without alteration (60.4 mg, 0.074 mmol). On the other hand, the indanone **7b** was purified through a silica column using hexane/AcOEt (7:4) as eluent. **7b:** Yield (calculated on the complex **4B**): 12.8 mg (90%). Anal. Calcd for $C_{15}H_{11}O_3N$ (253.26 g/mol): C 71.14, H 4.38, N 5.53; found: C 71.21, H 4.40, N 5.57. MS (m/z): 254.0769 $[M+1]^+$; 253.0736 [M]; 207.08 $[M–NO_2]^+$. IR (cm^{-1}): *v* (CO) 1712 (s); (NO_2) 1518 (s) and 1348 (s). ^{1}H NMR: δ 2.64 (dd, 1H, $^{2}J_{HH}$ = 19.2 Hz, $^{3}J_{HH}$ = 3.9 Hz, C^2*H*$_2$); 3.26 (dd, 1H, $^{2}J_{HH}$ = 19.2 Hz, $^{3}J_{HH}$ = 8.2 Hz, C^2*H*$_2$); 4.74 (dd, 1H, $^{3}J_{HH}$ = 8.2 Hz, $^{3}J_{HH}$ = 3.7 Hz, C^3*H*); 7.24–7.28 (m, 1H, C^4*H*); 7.30–7.34 (m, 2H, C$^{2'}$*H* + C$^{6'}$*H*); 7.45–7.51 (m, 1H, C^6*H*); 7.60–7.65 (m, 1H, C^5*H*); 7.79–7.83 (m, 1H, C^7*H*); 8.14–8.19 (m, 2H, C$^{3'}$*H* + C$^{5'}$*H*) ppm. ^{13}C{^{1}H} NMR: δ 44.5 (s, *C^3*); 46.7 (s, *C^2*); 123.9 (s, *C^7*); 124.5 (s, *C$^{3'}$* + *C$^{5'}$*); 127.2 (s, *C^4*); 128.8 (s, *C^6*); 129.0 (s, *C$^{2'}$* + *C$^{6'}$*); 135.7 (s, *C^5*); 137.3 (s, *C^8*); 147.4 (s, *C$^{4'}$*); 151.8 (s, *C$^{1'}$*); 156.7 (s, *C^9*); 204.6 (s, *C*O) ppm.

A dark brown solution of the complex **4A** previously isolated (60.4 mg, 0.074 mmol) in 10 mL of 1,2-dichloroethane was stirred and heated at 368 K for 24 hours. The brown solution obtained was vacuum-concentrated yielding a brown oil. The mixture of **7(a,b)** (~30:70 mole ratio estimated by NMR, respectively) was extracted with diethylether and purified through a silica column using hexane/AcOEt (7:4) as eluent. Yield (isolated mixture): 17 mg (91%) (~27% for **7a**, ~64% for **7b**). **7a:** ^{1}H NMR: δ 2.81 (dd, 1H, $^{2}J_{HH}$ = 19.5 Hz, $^{3}J_{HH}$ = 4.1 Hz, C^2*H*$_2$); 3.35 (dd, 1H, $^{2}J_{HH}$ = 19.4 Hz, $^{3}J_{HH}$ = 8.2 Hz, C^2*H*$_2$); 4.69 (dd, 1H, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 4.0 Hz, C^3*H*); 7.12–7.38 (*Ph*, overlapped with isomer **7b**); 7.45 (d, 1H, $^{3}J_{HH}$ = 8.4 Hz, C^4*H*); 8.40 (dd, 1H, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HH}$ = 2.2 Hz, C^5*H*); 8.56 (d, 1H, $^{4}J_{HH}$ = 2.1 Hz, C^7*H*) ppm. ^{13}C{^{1}H} NMR: δ 45.0 (s, *C^3*); 47.5 (s, *C^2*); 119.0 (s, *C^7*); 126.7–130.4 (*Ph* + *C^4*, overlapped with isomer **7b**); 129.5 (s, *C^5*); 138.1 (s, *C^8*); 142.6 (s, *C^6*); 136.4 (s, *C$^{1'}$*); 163.8 (s, *C^9*); 203.8 (s, *C*O) ppm.

Preparation of 6-Methoxy-3-phenylindan-1-one (8a) and 3-(4-Methoxyphenyl)indan-1-one (8b)

A dark brown solution of a **5(A,B)** mixture (~33:66 mole ratio, 100 mg, 0.125 mmol) in 10 mL of 1,2-dichloroethane was stirred and heated at 338 K for 24 hours. The brown solution obtained was vacuum-concentrated yielding a brown oil from which **8(a,b)** were extracted with diethylether. The solid that remains after the extraction was washed with pentane (3 × 4 mL) and it was identified as the complex **5A** (80% recovered regarding initial quantity, 26.4 mg, 0.033 mmol). On the other hand, the mixture **8(a,b)** (~13:87 mole ratio estimated by NMR, respectively) was purified through a silica column using hexane/AcOEt (7:4) as eluent. Yield (isolated mixture): 15 mg (50%) (~19% for **8a** calculated on complex **5A**, ~65% for **8b** calculated on complex **5B**). Anal. Calcd for $C_{16}H_{14}O_2$ (238.29 g/mol): C 80.65, H 5.92; found: C 80.92, H 6.01. MS (m/z): 239.1024 $[M+1]^+$; 238.0992 [M]; 223.08 $[M–CH_3]^+$. IR (cm^{-1}): *v* (CO) 1710 (s). **8b:** ^{1}H NMR: δ 2.60 (dd, 1H, $^{2}J_{HH}$ = 19.1 Hz, $^{3}J_{HH}$ = 3.9 Hz, C^2*H*$_2$); 3.18 (dd, 1H, $^{2}J_{HH}$ = 19.2 Hz, $^{3}J_{HH}$ = 8.0 Hz, C^2*H*$_2$); 3.77 (s, 3H, OCH_3); 4.55 (dd, 1H, $^{3}J_{HH}$ = 7.9 Hz, $^{3}J_{HH}$ = 3.9 Hz, C^3*H*); 6.84 (d, 2H, $^{3}J_{HH}$ = 8.7 Hz, C$^{3'}$*H* + C$^{5'}$*H*); 7.05 (d, 2H, $^{3}J_{HH}$ = 8.7 Hz, C$^{2'}$*H* + C$^{6'}$*H*); 7.26 (d, 1H, $^{3}J_{HH}$ = 7.7 Hz, C^4*H*); 7.41 (t, 1H, $^{3}J_{HH}$ = 7.4 Hz, C^6*H*); 7.55–7.61 (m, 1H, C^5*H*); 7.75 (d, 1H, $^{3}J_{HH}$ = 7.6 Hz, C^7*H*) ppm. ^{13}C{^{1}H} NMR: δ 44.0 (s, *C^3*); 47.3 (s, *C^2*); 55.6 (s, OCH$_3$); 114.5 (s, *C$^{3'}$* + *C$^{5'}$*); 123.4 (s, *C^7*); 127.2 (s, *C^4*); 128.1 (s, *C^6*); 129.0 (s, *C$^{2'}$* + *C$^{6'}$*); 135.3 (s, *C^5*); 136.3 (s, *C$^{1'}$*); 137.1 (s, *C^8*); 158.7 (s, *C^9*); 159.0 (s, *C$^{4'}$*); 206.0 (s, *C*O) ppm.

A dark brown solution of the complex **5A** previously isolated (26.4 mg, 0.033 mmol) in 10 mL of 1,2-dichloroethane was stirred and heated at 368 K for 24 hours. The brown solution obtained was vacuum-concentrated yielding a brown oil. A mixture of **8a** and 6-methoxy-3-phenylinden-1-one (~70:30 mole ratio, respectively) was extracted with diethylether and purified through a silica column using hexane/AcOEt (7:4) as eluent. Yield (isolated mixture): 1.6 mg (~14% for **8a**). The solid that remains after the extraction was washed with pentane (3 × 4 mL) and it was identified as the complex **5A** (78% recovered regarding initial quantity, 16.4 mg, 0.033 mmol). **8a:** ^{1}H NMR: δ 2.64 (dd, 1H, $^{2}J_{HH}$ = 19.2 Hz, $^{3}J_{HH}$ = 3.6 Hz, C^2*H*$_2$); 3.22 (dd, 1H, $^{2}J_{HH}$ = 19.1 Hz, $^{3}J_{HH}$ = 7.9 Hz, C^2*H*$_2$); 3.86 (s, 3H, OCH_3); 4.53 (dd, 1H, $^{3}J_{HH}$ = 7.8 Hz, $^{3}J_{HH}$ = 3.7 Hz, C^3*H*); 7.10–7.14 (m, 2H, *Ph*); 7.15–7.17 (m, 2H, C^4*H* + C^5*H*); 7.20–7.25 (m, 2H, C^7*H* + *Ph*); 7.28–7.33 (m, 2H, *Ph*) ppm. ^{13}C{^{1}H} NMR: δ 44.1 (s, *C^3*); 47.9 (s, *C^2*); 56.1 (s, OCH$_3$); 104.8 (s, *C^7*); 124.4 (s, *C^5*); 127.2 (s, 2C *Ph*); 127.8 (s, 1C *Ph*); 127.9 (s, 2C *Ph*); 128.0 (s, *C^4*); 160.2 (*C^6*, observed by {^{1}H, ^{13}C} HMBC correlations) ppm. Due to the final product mixture, the rest of the signals could not be assigned.

Preparation of 6-Methyl-3-phenylindan-1-one (9a) and 3-(4-Methylphenyl)indan-1-one (9b)

A dark green suspension of **6(A,B)** (~50:50 mole ratio, 80 mg, 0.10 mmol) in 10 mL of 1,2-dichloroethane was stirred and heated at 338

K for 24 hours. The brown solution obtained was filtered and vacuum-concentrated giving a brown oil. The mixture of **9(a,b)**

(~45:55 mole ratio, respectively) was purified through a silica column using hexane/AcOEt (95:5) as eluent. Yield (isolated mixture): 20.2 mg (91%) (~41% for **9a** calculated on complex **6A**, ~50% for **9b** calculated on complex **6B**).
Anal. Calcd for $C_{16}H_{14}O$ (222.29 g/mol): C 86.45, H 6.35; found: C 86.62, H 6.39. MS (m/z): 223.1079 $[M+1]^+$; 222.1040 [M]; 207.08 $[M–CH_3]^+$; 145.06 $[M–Ph]^+$; 130.04 $[M–C_6H_4–CH_3]^+$. IR (cm^{-1}): ν (CO) 1713 (s).**9a:** ^{1}H NMR: δ 2.42 (s, 3H, CH_3); 2.64 (dd, 1H, $^2J_{HH}$ = 19.1 Hz, $^3J_{HH}$ = 3.6 Hz, C$^2H_2$); 3.20 (dd, 1H, $^2J_{HH}$ = 19.1 Hz, $^3J_{HH}$ = 8.0 Hz, C$^2H_2$); 4.55 (dd, 1H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 3.9 Hz, C^3H); 7.13–7.18 (m, 4H, C^4H + *Ph*); 7.28–7.33 (m, 2H, *Ph*); 7.39–7.44 (m, 1H, C^5H); 7.55–7.60 (m, 1H, C^7H) ppm. ^{13}C{^{1}H} NMR: δ 21.2 (s, CH_3); 44.4 (s, C^3); 47.5 (s, C^2); 123.3 (s, C^7); 126.8 (s, C^4); 127.2 (s, 1C *Ph*); 128.0 (s, 2C *Ph*); 129.2 (s, 2C *Ph*); 135.6 (s, C^5); 137.1 (s, C^8); 138.4 (s, C^6); 144.6 (s, $C^{1'}$); 155.8 (s, C^9); 205.9 (s, CO) ppm. **9b:** ^{1}H NMR: δ 2.32 (s, 3H, CH_3); 2.63 (dd, 1H, $^2J_{HH}$ = 19.1 Hz, $^3J_{HH}$ = 3.8 Hz, C$^2H_2$); 3.18 (dd, 1H, $^2J_{HH}$ = 19.1 Hz, $^3J_{HH}$ = 8.0 Hz, C$^2H_2$); 4.56 (dd, 1H, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 3.9 Hz, C^3H); 7.02 (d, 2H, $^3J_{HH}$ = 8.1 Hz, C$^{2'}H$ + C$^{6'}H$); 7.13 (d, 2H, $^3J_{HH}$ = 7.7 Hz, C$^{3'}H$ + C$^{5'}H$); 7.22–7.29 (m, 1H, C^4H); 7.39–7.44 (m, 1H, C^6H); 7.55–7.60 (m, 1H, C^5H); 7.76 (d, 1H, $^3J_{HH}$ = 7.7 Hz, C^7H) ppm. ^{13}C{^{1}H} NMR: δ 21.1 (s, CH_3); 44.4 (s, C^3); 47.1 (s, C^2); 123.4 (s, C^7); 127.1 (s, C^4); 127.8 (s, $C^{2'}$ + $C^{6'}$); 128.0 (s, C^6); 129.8 (s, $C^{3'}$ + $C^{5'}$); 135.3 (s, C^5); 137.0 (s, $C^{4'}$); 137.1 (s, C^8); 141.3 (s, $C^{1'}$); 158.6 (s, C^9); 206.0 (s, CO) ppm.

Acknowledgements

We thank the University of Vigo CACTI services for recording the NMR spectra. M. T. thank University of Vigo for funding through a Predoctoral Fellowship.

Notes and references

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7 In order to obtain more information about this reaction, a solution of the mixture **4(A,B)** (~57:43 mole ratio) was prepared in CD_2Cl_2. After six days at 308 K, **4A** remained unaltered and **4B** had almost completely evolved to the intermediate [IrCp*{η^3–(C_9H_5)(OMe)(*p*–NO_2–C_6H_4)}(PMe_3)]PF_6 (**D**) (~10:90 mole ratio estimated by NMR, respectively) in accordance with our results in a previous work.[3c]

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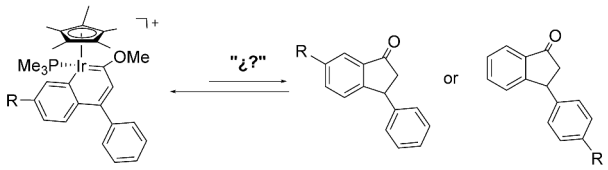

How do the substituents on the naphthalene skeleton affect the stability of the iridanaphthalene complex [IrCp*{=C(OMe)CH=C(o–C_6H_4)(Ph)}(PMe_3)]PF_6?