Reactivity of Tp^{Me2}-Containing Hydride-Iridafurans with Alkenes, Alkynes and H$_2$

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ABSTRACT: The Tp^{Me2}-containing hydride-iridafurans **2a,b** (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate) cleanly reacted with ethylene to give the bicyclic derivatives **6a,b**. Formation of the latter complexes is a reversible process and it is proposed to occur by an electrocyclic ring closure that takes place between C$_2$H$_4$ and the 16e$^-$ unsaturated intermediates **A** resulting from hydride migration to the α-carbon of the metallacycle. Similar reactions were observed with a variety of alkynes RC≡CR (R = H, Ph, CO$_2$Me) and R´C≡CH (R´= CO$_2$Me, Ph, CMe$_3$) with the regioselectivity observed for the latter substrates depending on the nature of R´. In the case of Me$_3$SiC≡CH the structure of an

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unexpected byproduct indicates that an alkyne-vinylidene rearrangement has taken place on the metal coordination sphere during the reaction and this observation suggests that in the mechanism of all these coupling processes the corresponding π-adducts are active intermediates. Finally, complexes **2a,b** reacted with H₂ to give products derived from the hydrogenation of their alkenyl arms.


R = CO₂Me
Ar = C₆H₄-*p*-OMe, a; C₆H₄-*p*-NO₂, b
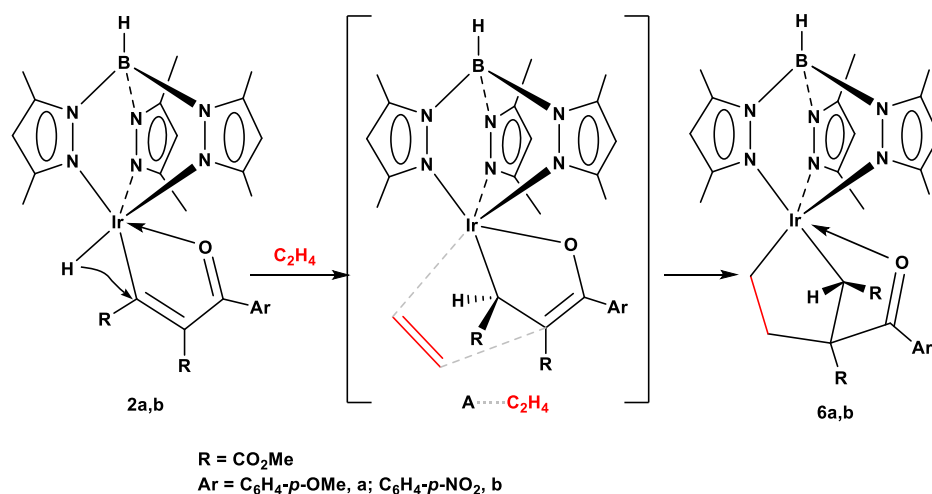
INTRODUCTION

Metallafurans[1] are the most common members of the family of 6π-aromatic metallacycles, which also include the growing type of metallabenzenes.[2] They are known for quite a few transition metals and have been synthetized by a variety of methods. In a recent paper[3] we have described the synthesis of hydride-iridafurans of structure **2** by the reaction of the bis(ethylene) Ir(I) species $Tp^{Me2}Ir(C_2H_4)_2$ (**1**) (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate) with dimethyl acetylenedicarboxylate (DMAD) in the presence of aromatic aldehydes ArCHO (CH₂Cl₂, 60 ºC, 14 h, Scheme 1). Both electron-donating and electron-withdrawing substituents in the *para* position of the phenyl ring of the aldehyde were successfully used for iridafuran formation and DMAD and 1 equiv. of aldehyde formally coupled in the iridium coordination sphere to form the metallacycle. However, a second molecule of the aldehyde is required for the formation of complexes **2**. Thus, the reaction of **1** and ArCHO (1:2, 25 ºC), gives rise to the very fast and almost quantitative formation of intermediates **3**, and these species eventually convert

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into the final compounds **2**. However, species **3** evolve differently depending of the nature of the aldehyde. At variance with what we have reported for **3a** (Scheme 2), where a mixture of the iridafuran **2a** and the aldehyde adduct **4a** is initially formed, we have noticed that for the case of p-O$_2$N-C$_6$H$_4$-CHO, a new compound, resulting from the formal addition of the released C$_2$H$_4$ to the corresponding hydride-iridafuran **2b**, was slowly formed. This unexpected result launched the study reported herein where we describe the reactivity of complexes **2a,b** against alkenes, alkynes and finally H$_2$.

Scheme 1. Formation of the hydride-iridafurans 2 by the reaction of complex 1 with DMAD and aromatic aldehydes
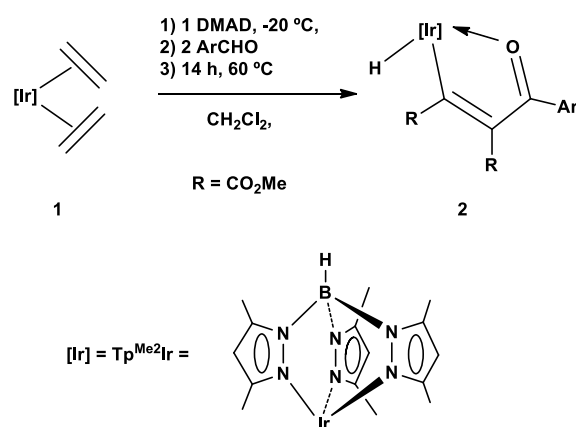

Scheme 2. Formation of the alkoxyde intermediate 3a in route to complex 2a and evolution of the former species in CH$_2$Cl$_2$

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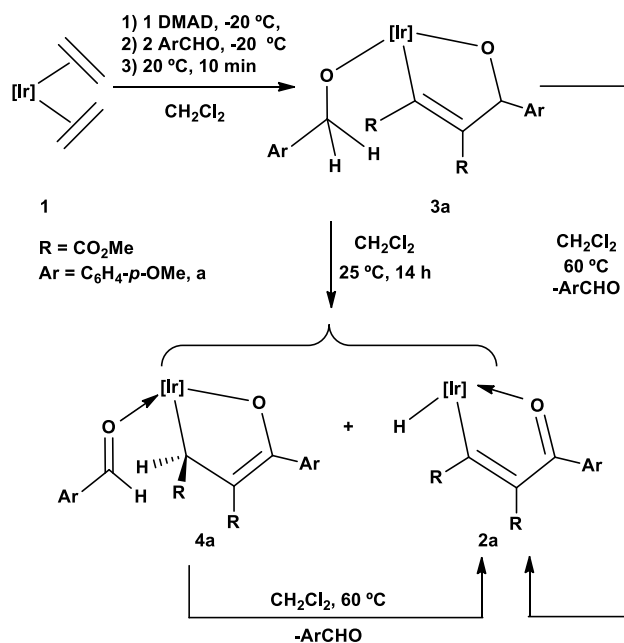
RESULTS AND DISCUSSION

Reactivity of the hydride-iridafurans 2a,b with olefins. Monitorization (^{1}H NMR, CD$_2$Cl$_2$, 25 °C) of the reaction of **1** with 1 eq. of DMAD and 2 eq. of p-O$_2$N-C$_6$H$_4$-CHO indicated very fast quantitative formation of intermediate **3b**, which slowly evolved ([Ir] ≈ 0.07 mM, CH$_2$Cl$_2$, 25 °C, 14 h) at room temperature to a mixture of the products depicted in Scheme 3. In addition of **2b**, two other species, **5b** and **6b**, were also formed.

Scheme 3. Formation and room temperature evolution of complex 3b in CH$_2$Cl$_2$ (spectroscopic yields in parenthesis)


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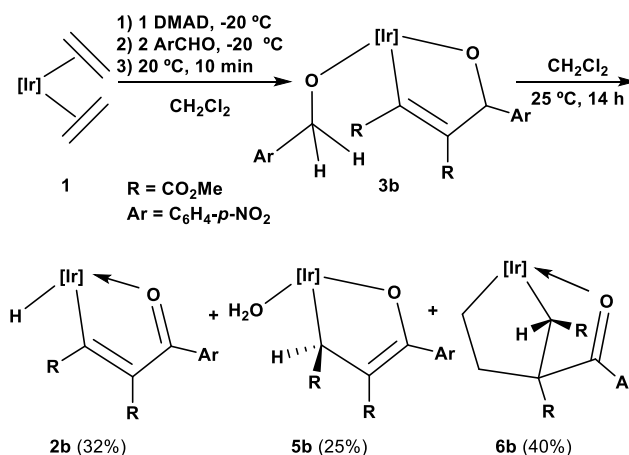
Complex **5b**, a water adduct,[4] was easily isolated in pure form due to its insolubility in CH_2Cl_2 and probably derived from the reaction of **2b** with adventitious water and, in fact, it is formed in *ca.* 80% yield if the reaction was carried out in the presence of added water. Interestingly, only the iridafuran **2b** affords an aquo adduct as neither **2a** nor the parent species derived from benzaldehyde[3] reacted with water in this way. Species **6b**, with a metallabicyclic structure, was easily purified by chromatography, and completely characterized by the usual analytical and spectroscopic methods. Thus, the two adjacent CH_2 groups resonate at 3.00 and 2.46 (IrCH_2CH$_2$) and at 2.08 (IrCH$_2$CH_2) ppm in the ^{1}H NMR spectrum while the corresponding ^{13}C signals appear at 37.8 (IrCH$_2$CH$_2$) and at -15.2 (IrCH$_2$CH$_2$) ppm. The β carbon $=C(CO_2Me)$ in **2b** was transformed in a β aliphatic quarternary carbon atom in **6b** and consequently the corresponding ^{13}C resonance shifts upfield from 137.0 ppm to 75.8 ppm. From the structure of complex **6b** it can be concluded that its formation is the formal result of the coupling of a molecule of free ethylene, released from complex **1**, with the iridafuran **2b** and in fact this species cleanly reacted with C_2H_4 at 25 ºC to give **6b** (Scheme 4). The stereochemistry of the Ir-CHR-carbon, easily deduced from the NOESY spectrum, is in accord with the mechanism proposed for its formation (see below).

Scheme 4. Reversible reaction of 2a,b with ethylene

R = CO$_2$Me
Ar = C$_6$H$_4$-*p*-OMe, a; C$_6$H$_4$-*p*-NO$_2$, b
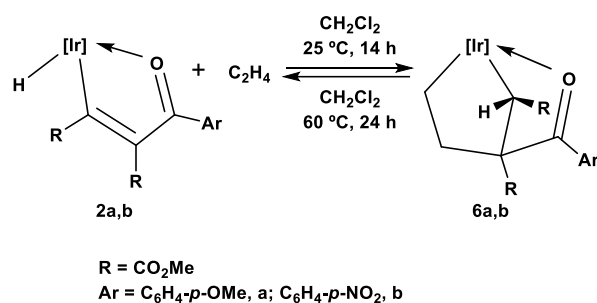
Formation of complex **6b** is a reversible process and, upon heating (CH_2Cl_2, 60 ºC), it returned to the starting hydride-iridafuran **2b** (Scheme 4). It was also found that the reactivity just commented

was independent on the nature of the Ar-substituent of the iridafuran as complex **2a** also experienced the processes shown in Scheme 4 but, in contrast, neither propene (CH_2=CHMe) nor methyl acrylate (CH_2=$CHCO_2Me$) were effective reaction partners and this may reflect, at least partially, the influence of the steric effects on the addition process. The structure of complex **6a** has been confirmed by single crystal X-ray diffraction studies (Figure 1).
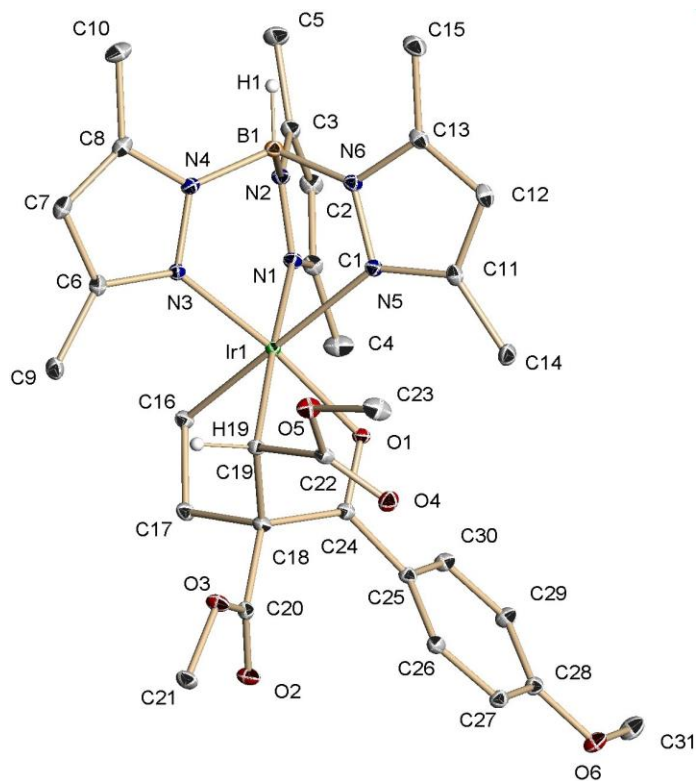

Figure 1. X-ray structure of compound **6a** (30% displacement ellipsoids, H atoms except the H atoms on C(19) and B(1) omitted for clarity). Selected bond lengths (Å) and angles (deg): Ir(1)—C(16) = 2.077(2), Ir(1)—C(19) = 2.1004(19), Ir(1)—O(1) = 2.0587(15), Ir(1)—N(1) = 2.1294(17), Ir(1)—N(3) = 2.0530(17), Ir(1)—N(5) = 2.2075(17), C(16)—C(17) = 1.536(3), C(16)—Ir(1)—C(19) = 82.07(8), C(16)—Ir(1)—O(1) = 83.29(7), C(19)—Ir(1)—O(1) = 78.56(7).

With respect to the mechanism of formation of the bicyclic derivatives **6** it is proposed that after hydride migration to the α-carbon of species **2**[3] the resulting unsaturated species **A** of Scheme 5 experiences a 1,3-electrocyclic coupling with C_2H_4 to give the final products.[5] The same mechanism is probably responsible for the reaction of complexes **2** with the alkynes described below, and acetylene

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has been used as the representative reacting species in Scheme 5. In these couplings it is not known if π-adduct formation is a necessary step previous to the electrocyclic closure, *i.e.* if we are dealing with a neat, more or less isochronous, concerted step or with a mechanism consisting of two well defined steps. As will be discussed later, the formation of compound **19a** (see below) may suggest a two-steps mechanism.

Scheme 5. Proposed mechanism for the reaction of complexes 2 with C_2H_4 and C_2H_2.
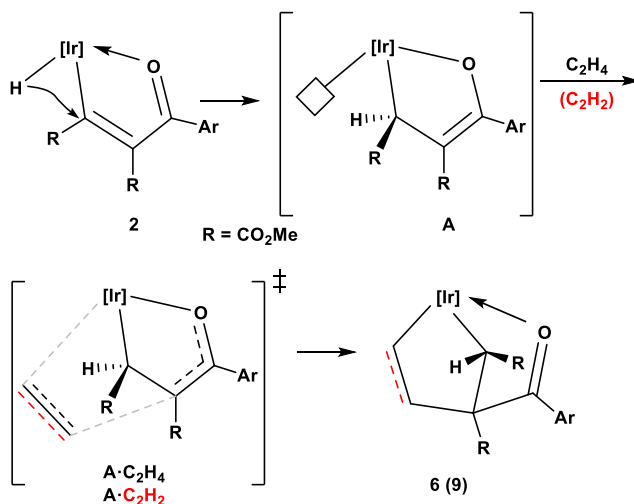

Reactivity of complexes 2 with $MeO_2CC\equiv CCO_2Me$ (DMAD), $HC\equiv CH$ and $PhC\equiv CPh$. On the basis of the ethylene reactivity already commented we studied the reaction of complexes **2a,b** with DMAD. Thus, complex **2b** reacted with an excess (3 equiv.) of this alkyne (CH_2Cl_2, 80 ºC, 48 h) to form a related bicyclic species **7b** isolated in almost quantitative yield (Scheme 6a). Complex **7b** was completely characterized by, among other analytical techniques, NMR spectroscopy (see Experimental Section). Interestingly, when the same reaction was carried out with **2a** the corresponding species **7a** was not selectively formed but the carboxylate-bound[6] compound **8a** (*ca.* 3:1 ratio, Scheme 6b) was also generated. These two species were easily separated and purified by chromatography and both have been characterized unambiguously, among other techniques, by single crystal X-ray studies (Figures 2 and 3). Complex **8a** seems to proceed from **7a** by hydrolysis of the $\beta-CO_2Me$ substituent of **7a**, coordination of

the resulting carboxylate group to the iridium center and transfer of the released proton to the carbon atom of the cyclic structure which was previously bound to the Ir center. However, attemps to induce this hydrolysis reaction in dichloromethane solutions by a variety of methods were fruitless.

Scheme 6. Reactions of complexes 2a,b with DMAD (isolated yields in parenthesis)
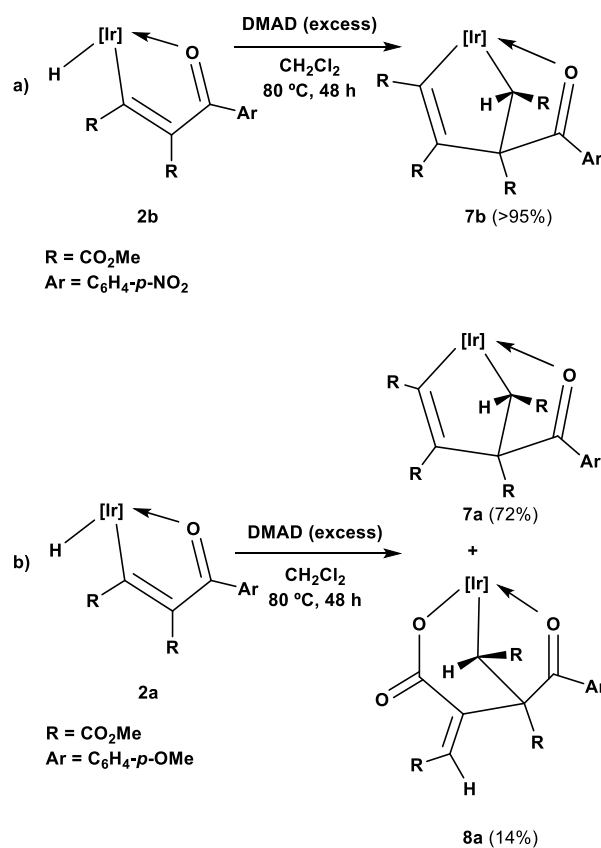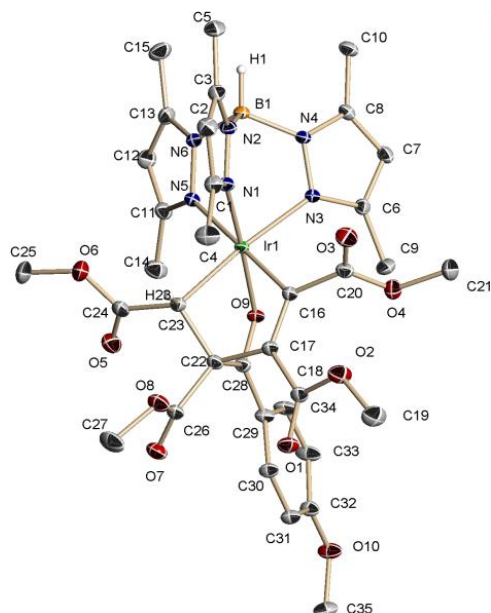
Figure 2. X-ray structure of compound **7a** (30% displacement ellipsoids, H atoms except the H atom on C(23) and B(1) omitted for clarity). Selected bond lengths (Å) and angles (deg): Ir(1)—C(16) = 2.001(2), Ir(1)—C(23) = 2.072(2), Ir(1)—O(9) = 2.0599(16), Ir(1)—N(1) = 2.0459(19), Ir(1)—N(3) = 2.1451(19), Ir(1)—N(5) = 2.180(2), C(16)—Ir(1)—C(23) = 78.77(9), C(16)—Ir(1)—O(9) = 84.28(8), C(23)—Ir(1)—O(9) = 84.28(8).
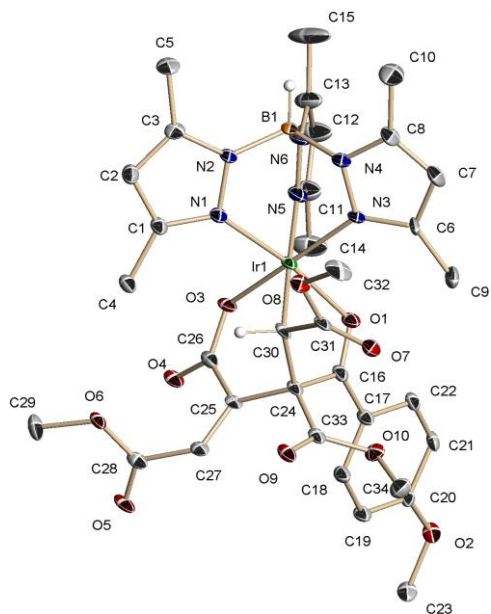

Figure 3. X-ray structure of compound **8a** (30% displacement ellipsoids, H atoms except the H atoms on C(30) and B(1) omitted for clarity). Selected bond lengths (Å) and angles (deg): Ir(1)—C(30) =

2.060(6), Ir(1)—O(1) = 2.063(4), Ir(1)—O(3) = 2.037(4), Ir(1)—N(1) = 2.036(5), Ir(1)—N(3) = 2.057(5), Ir(1)—N(5) = 2.105(5), C(30)—Ir(1)—O(1) = 81.45(18), C(30)—Ir(1)—O(3) = 89.76(18), O(1)—Ir(1)—O(3) = 83.84(15).

It is worth of comment that the order of addition of the reagents in these reactions is a determining factor on the results. Thus, and although compound **7a** is made up formally from two molecules of DMAD and one of anisaldehyde, it has to be obtained following strictly the procedure described herein. In fact, if two equiv. of DMAD are added first to compound **1**, the substitution of the two ethylenes is kinetically very favorable, and the iridacyclopentadiene fragment [Tp^{Me2}Ir(-C(R)=C(R)-C(R)=C(R))] is formed.[4,7] Addition of aldehyde to this species gives rise to a different product,[8] a bicyclic isomer of **7** with a different functionality derived from the aldehyde moiety: a carbene instead of a keto group, with an unexpected configuration of the carbon atom of the Ir-CHR moiety (Scheme 7).[8]

Scheme 7. Influence of the order of addition of the reagents to the reaction of complex 1 with 2 equiv. of DMAD and 1 equiv. of ArCHO.

R = CO$_2$Me
Ar = C$_6$H$_4$-*p*-OMe, a; C$_6$H$_4$-*p*-NO$_2$, b
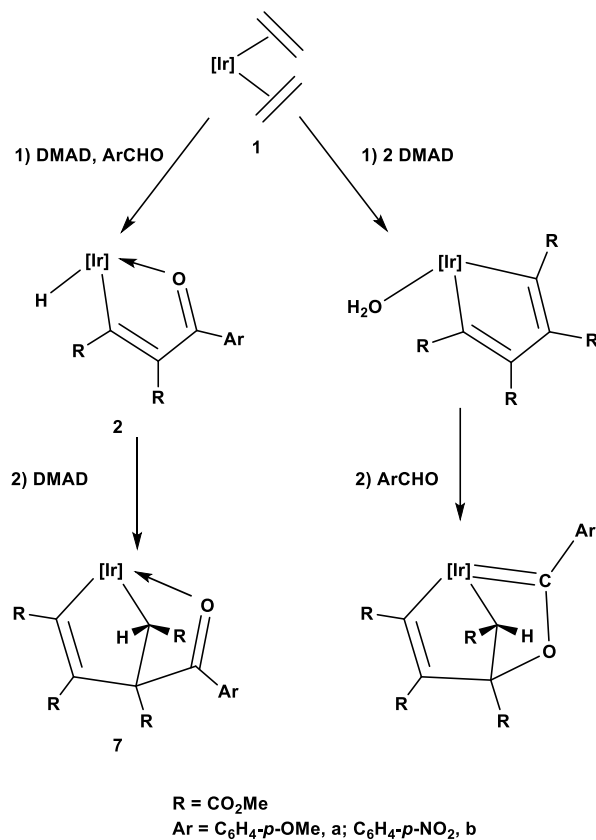
As commented before the formation of compounds **2a,b** requires the use of 2 equiv. of aldehyde, with one of them recovered at the end of the reaction. Therefore, purification of these complexes normally requires silica gel column chromatography although we have now found that, for the case of **2a**, a simple washing of the crude product with several portions of cold hexane removes the excess of aldehyde and gives the iridafuran in pure form (90% yield *vs.* 75% following chromatography). However, since an excess of aldehyde does not retard nor interfere the reaction of **2a,b** with DMAD, the synthesis of the bicyclic keto compounds **7a,b** can be carried out in an "one-pot, two-steps" procedure, which, for obvious reasons, are higher yield processes.

We have studied the reaction with the alkynes acetylene and diphenylacetylene only for the case of **2a** and the results obtained are shown in Scheme 8. Complexes **9a** and **10a** have been completely characterized by the usual analytical and spectroscopic techniques and no additional comments are necessary.

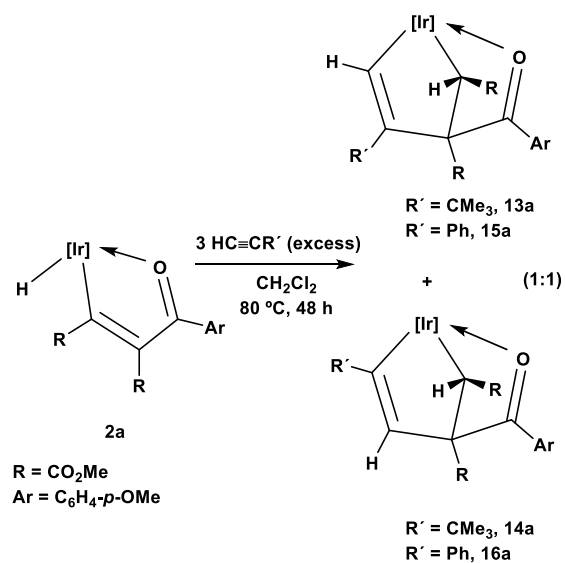**Scheme 8. Reactivity of complex 2a with HC≡CH and PhC≡CPh**

2a

R = CO$_2$Me
Ar = C$_6$H$_4$-p-OMe

R´= H, 9a
R´= Ph, 10a
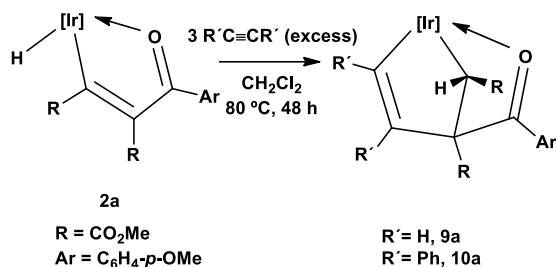
Reactivity of complexes 2a,b with the terminal alkynes MeO$_2$CC≡CH (MP), Me$_3$CC≡CH, PhC≡CH and Me$_3$SiC≡CH. The reactions of iridafurans **2a,b** with an excess of MP furnished related bicyclic structures with a regioselectivity that depends on the starting iridafuran. Thus, complex **2a** reacted with MP (CH$_2$Cl$_2$, 80 ºC, 48 h) to give exclusively the regioisomer **11a** (Scheme 9a) with the CO$_2$Me group in β position but, in contrast, the addition of this alkyne to **2b** was not completely regioselective and the isomers **11b** and **12b** were formed in *ca*. 4:1 ratio (Scheme 9b). It is interesting to note the considerable chemical shift difference, in the ^{1}H NMR spectra, between the CH alkenyl hydrogens of **11b** and **12b**. Thus, while the signal for the former appears at a very low field, 11.43 ppm, in the latter case it is located at 7.20 ppm. It is well known that metal alkenyls exhibit nucleophilic reactivity at the β-carbon because of the contribution of a carbene canonical form to the resonance hybrid (see for instance reference 9 and references cited therein). For compound **11b**, a CO$_2$Me substituent in this β-carbon stabilizes this carbene form and shiftes the C$_\alpha$H resonance to a lower field. In comparison, the corresponding signals for **13a** and **15a** (with CMe$_3$ and Ph substituent, respectively) are located at *ca*. 9 ppm (see below) indicating less contribution of the carbene form.

Scheme 9. Reactions of complexes 2a,b with methyl propiolate (MP)

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a)

2a

R = CO$_2$Me
Ar = C$_6$H$_4$-p-OMe

11a

b)

2b

R = CO$_2$Me
Ar = C$_6$H$_4$-p-NO$_2$

11b

+   (4:1)

12b
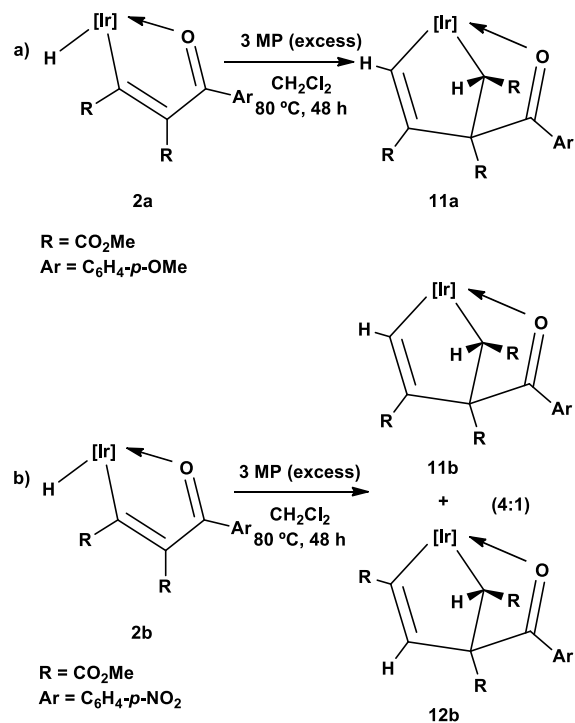
For the rest of the alkynes in this section only the reactivity of the iridafuran **2a** was tested and the reactions of this complex with Me$_3$CC≡CH and PhC≡CH afforded almost equimolar mixtures of the regioisomers **13a**, **14a** and **15a**, **16a**, respectively (Scheme 10).

Scheme 10. Reactions of complex 2a with Me₃CC≡CH and PhC≡CH

R′ = CMe$_3$, 13a
R′ = Ph, 15a

2a

R = CO$_2$Me
Ar = C$_6$H$_4$-p-OMe

3 HC≡CR′ (excess)
CH$_2$Cl$_2$
80 °C, 48 h

+   (1:1)

R′ = CMe$_3$, 14a
R′ = Ph, 16a

However, the reaction of **2a** with Me₃SiC≡CH is somewhat more interesting in the sense that, in addition to the expected mixture of the regioisomers **17a** and **18a** the formation of a new bicyclic structure, *i.e.* complex **19a**, completely characterized by NMR spectroscopy (see Experimental Section), was observed (Scheme 11). In this latter species the alkyne gives rise to a C=CH$_2$ group[10] acting as a bridge between the metal and the β-C(R) carbon atom of the starting iridafuran.

Scheme 11. Reaction of complex 2a with Me₃SiC≡CH
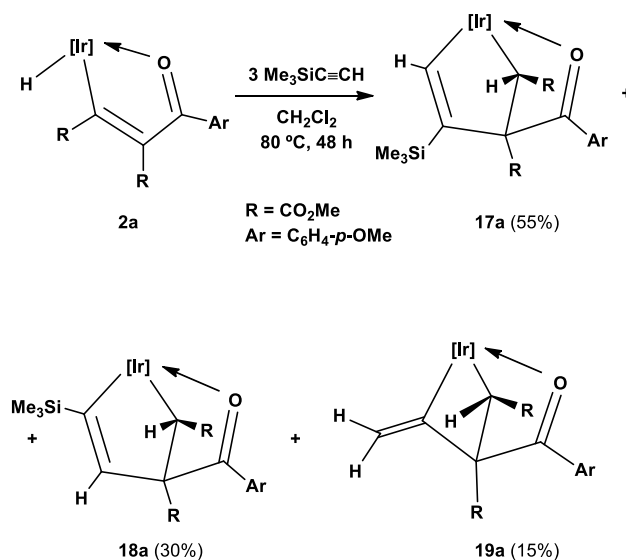
Formation of **19a** is best explained (Scheme 12) if an initial π-alkyne species **B** experiences a, well-precedented,[11] rearrangement to the vinylidene species **C** followed by electrocyclization and hydrolysis of the C—SiMe$_3$ bond. As SiMe$_3$ substituents in vinylidenes are not prone to adventitious hydrolysis in Tp^{Me2}Ir(III) systems[11h] we inferred that the C—SiMe$_3$ hydrolytic cleavage takes place after the cyclization step.[11c] As anticipated, this result may be an indication of the two steps nature of the mechanism shown in Scheme 5 for the all addition outcomes of intermediates **A** with unsaturated substrates.

Scheme 12. Proposed mechanism for the formation of complex 19a

R = CO₂Me
Ar = C₆H₄-*p*-OMe

19a
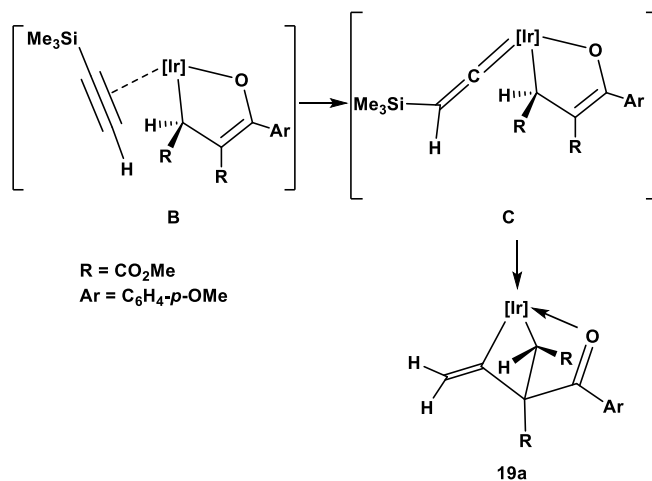
Reactivity of iridafurans 2a,b towards H₂. In an attempt to cleave the Ir—C bond of intermediate **A** of Scheme 5 by hydrogenolysis, the reaction of complex **2a** with H_2 was carried out in cyclohexane (90 °C, 2 atm, 24 h) but instead of the desired process, the formation of two isomeric metallacycles, compounds **20a** and **21a**, in a *ca.* 4:1 ratio was observed (Scheme 13).

Scheme 13. Reaction of complex 2a with H₂

R = CO₂Me
Ar = C₆H₄-*p*-OMe; R´= OMe
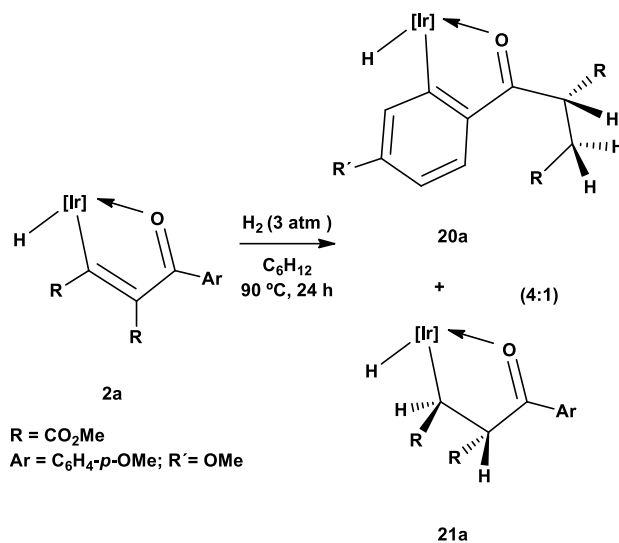
The benzoiridafuran **20a** is the formal result of the hydrogenation of the alkenyl moiety in **2a** followed by an *ortho*-metallation of the aromatic ring. This compound was obtained as an unique stereoisomer, shown by NMR spectroscopy to have the structure depicted in Scheme 13 but existing in

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solution as an equilibrated mixture of conformational rotamers (*i.e.* atropoisomers) (NOESY evidence) in a *ca.* 1:0.2 ratio. We proposed that the presence of the two CO_2Me substituents in the -$CHRCH_2R$ chain generates two rotameric, energetic local minima. Compound **21a** is, in turn, the result of a *trans* (NOESY evidence) stereospecific hydrogenation of the alkenyl moiety of **2a** and it is best characterized by the two doublets (5.29 and 5.13 ppm, $^3J_{HH}$ = 1.6 Hz) in the ^{1}H NMR spectrum which correspond to the Ir-CH(R)-CH(R)- hydrogens respectively.

When **2a** was reacted with D_2 under identical conditions (C_6H_{12}, 3 atm, 90 ºC, 24 h) **20a**-$d_{1.8}$ was obtained thus confirming the stoichiometry of the reaction and showing, as deduced from the ^{1}H NMR spectrum, that no further scrambling, with excess of D_2, occurred. The label was found to be distributed among the hydride ligand and the three CH positions and a similar distribution of deuteriums was observed for **21a**-$d_{1.8}$.

Having in mind the experimental fact that **21a** did not afford complex **20a** after prolonged heating in C_6H_{12} at 90 ºC and the distribution of deuterium just mentioned, the formation of both species may be explained with the mechanism shown in Scheme 14. First, an iridium(V) trishydride[12] intermediate **D**, having a κ^2-Tp^{Me2} ligand, is formed with all the three hydrides (D_2H in the reaction with D_2) behaving as equivalent. From this intermediate different routes can be advanced for the formation of **20a** and **21a** and two of them, not described textually in any detail, are shown in Scheme 14. In both cases, the keto-enol tautomerization proposed as the final step should be a reversible process and therefore the isomer with a *cisoid* H,H chain stereochemistry (*i.e. epi-***21a**) should also be accessible kinetically but we believe that its unfavourable thermodynamics is preventing its detection.

Scheme 14. Proposed mechanisms for the reaction of complex 2a with hydrogen
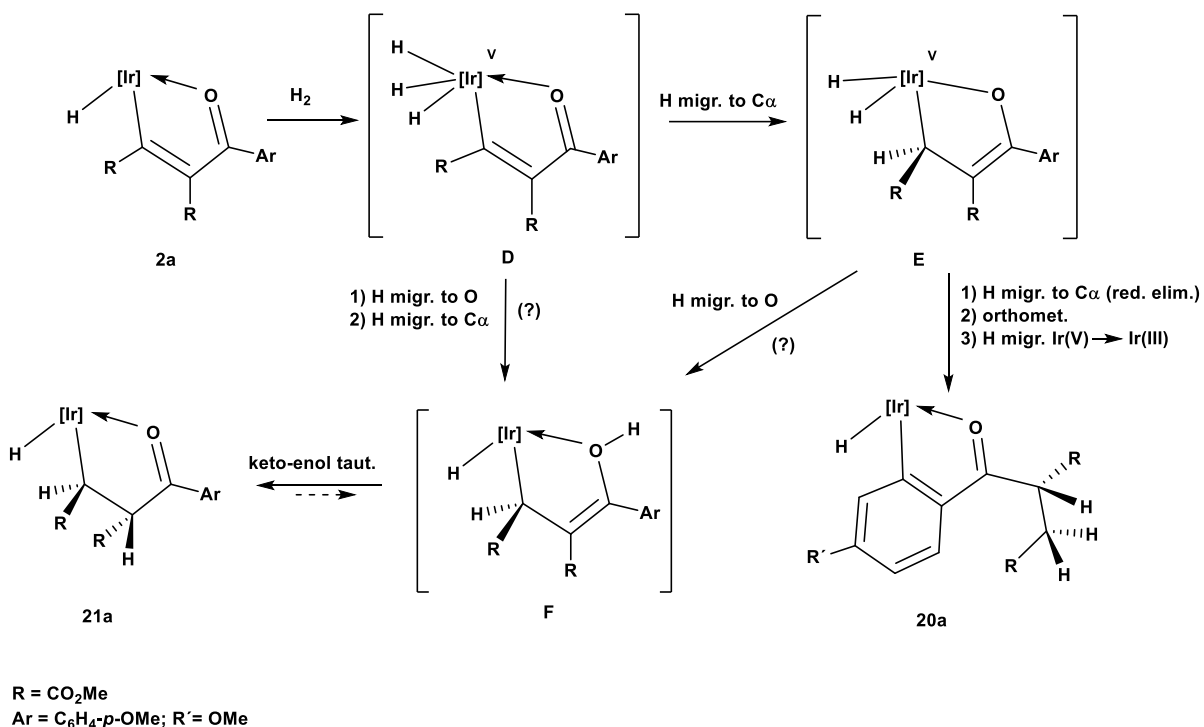
Hydrogenation of compound **2b** under the same reaction conditions (C$_6$H$_{12}$, 3 atm, 90 ℃, 24 h) gave rise to complex **20b** as the main reaction product. In this case the expected hydride **21b** was not detected but the carbonyl derivative **22b** was formed instead (Scheme 15). Both compounds were easily separated and purified by chromatography and fully characterized by the usual methods. The carbonyl ligand of **22b** is responsible for a strong absorption, at 2040 cm^{-1}, in the IR spectrum and a ^{13}C{^{1}H} NMR resonance at 163.0 ppm. In turn, the Ir-CH$_2$ group gives rise to two doublets in the ^{1}H NMR spectrum (4.00 and 3.62 ppm, $^2J_{HH}$ = 13.9 Hz) and to a signal at 3.4 ppm in the ^{13}C{^{1}H} NMR spectrum. With respect to the mechanism of its formation, it can be proposed that the α-CO$_2$Me group in **2b** has been hydrogenated according to the formal equation: H-Ir-C(CO$_2$Me)= + H$_2$ → OC-Ir-CH$_2$- + MeOH. This is not the first time that a CO$_2$Me substituent in this type of iridacycles is involved in a reaction.[6]

Scheme 15. Reactivity of complex 2b with hydrogen

17

20b

2b

3 atm H$_2$
C$_6$H$_{12}$
90 °C, 24 h

+   (2.7:1)

R = CO$_2$Me
Ar = C$_6$H$_4$-*p*-NO$_2$; R´= NO$_2$

22b

CONCLUDING REMARKS

The Tp^{Me2}-containing hydride-iridafurans studied in this report normally react through 16e$^-$ unsaturated intermediates that result from the hydride migration to the α-carbon of the metallacycle. In contrast to the adduct formation observed previously for hard or soft (NCMe, CO) Lewis bases, with ethylene and alkynes as substrates they experience electrocyclic ring closure to give bicyclic structures. Based in some experimental evidence it is suggested that π-adducts species act as active intermediates before the electrocyclic coupling takes place.

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EXPERIMENTAL SECTION

General Considerations. All the manipulations were carried out under an inert atmosphere, following Schlenk techniques. The solvents employed were dried before use. The elemental analyses of the new compounds were carried out using a Perkin-Elmer Series II CHNS/O 2400 analyzer at the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla). IR spectra were recorded on a Perkin-Elmer system 2000 FT-IR. NMR instruments were Bruker models DPX-300, DRX-400, and DRX-500. ^{1}H and ^{13}C resonances were referenced with respect to SiMe$_4$ using the residual protio solvent peaks as internal standard (^{1}H NMR) and the characteristic resonances of the solvent ^{13}C nuclei (^{13}C NMR). Most of the ^{1}H and ^{13}C assignments were based in one- and two-dimensional experiments (^{13}C{^{1}H} gated, COSY, NOESY, ^{1}H-^{13}C HSQC, and HMBC). Compounds **2a,b** were prepared by the procedures described in the literature.[3]

One-pot synthesis of compound 2a. To a solution of compound **1** (0.30 g, 0.55 mmol) in dichloromethane (10 mL) at -20 ºC, MeO$_2$CC≡CCO$_2$Me (0.066 mL, 0.55 mmol) and *p*-anisaldehyde (0.135 g, 1.10 mmol) were added sequentially. The cold bath was then removed and the resulting mixture stirred at 60 ºC 20 h. The volatiles were then removed under reduced pressure and the residue washed with hexane at -30 ºC (8x6 mL). Yield: 0.393 g (93%) of compound **2a** with enough purity to be use as starting material.

Synthesis of compound 5b. To a solution of compound **1** (0.10 g, 0.18 mmol) in dichloromethane (4 mL) at -20 ºC, MeO$_2$CC≡CCO$_2$Me (0.022 mL, 0.18 mmol) and water (0.2 ml, 11.0 mmol) were added sequentially. After stirring for 10 min at this temperature, *p*-nitrobenzaldehyde (0.056 g, 0.36 mmol) was added. The cold bath was then removed and the resulting mixture stirred at

room temperature for 14 h. After this period of time, a bright yellow precipitate of **5b** was formed, which was separated by filtration from a dark brown solution and dried under vacuum. Yield: 0.12 g (80%).
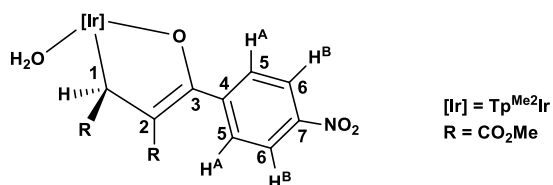

^{1}H NMR (Acetone-d_6, 25 °C; δ (ppm)): 8.13, 7.75 (d, 2 H each, $^3J_{HH}$ = 8.6 Hz, 2 H^B, 2 H^A, resp.), 6.55 (br s, 2 H, H_2O), 6.12 (s, 1 H, C^{1}H), 5.84, 5.81, 5.59 (s, 1 H each, 3 CH$_{pz}$), 3.41, 2.93 (s, 3 H each, 2 CO$_2$Me), 2.65, 2.45, 2.44, 2.37, 2.37, 2.34 (s, 3 H each, 6 Me$_{pz}$). ^{13}C{^{1}H} NMR (Acetone-d_6, 25 °C; δ (ppm)): 185.0 (C^3), 184.3, 168.0 (*C*O$_2$Me), 154.6, 154.0, 152.0, 145.2, 144.0, 143.8 (C$_{qpz}$), 148.6 (C^4), 147.7 (C^7), 130.9, 122.6 (C^5, C^6, resp.), 112.0 (C^2), 108.8, 108.5, 107.3 (CH$_{pz}$), 50.0, 49.6 (CO$_2$*Me*), 17.7 (C^1, $^1J_{CH}$ = 132 Hz), 14.8, 13.9, 13.1, 12.6, 12.6, 12.0 (Me$_{pz}$). Elemental analysis for C$_{28}$H$_{35}$BN$_7$O$_8$Ir·0.5CH$_2$Cl$_2$ (sample crystallized from CH$_2$Cl$_2$:Et$_2$O): C, 40.6; H, 4.1; N, 11.6. Found: C, 40.8; H, 4.4; N, 11.2. IR (Nujol): υ(OH) 3361, (CO, CO$_2$Me) 1704, 1681, (NO$_2$) 1550 cm^{-1}.

Synthesis of compound 6a. Complex **2a** (0.15 g, 0.19 mmol) was dissolved in dichloromethane (7 mL) and the solution placed in a Fisher-Porter vessel which was pressurized with C$_2$H$_4$ (3 atm). The resulting mixture was stirred at 60 °C for 14 h. The volatiles were removed under vacuum and quantitative conversion into compound **6a** was ascertained by ^{1}H NMR. This compound was purified by column chromatography on silica gel using diethylether:hexane (1:3) → diethylether:hexane (1:1) mixtures as eluent. Yield: 0.14 g (90%). An analytically pure sample, as dark red crystals, was obtained by slow diffusion of pentane into a dichloromethane solution at room temperature.
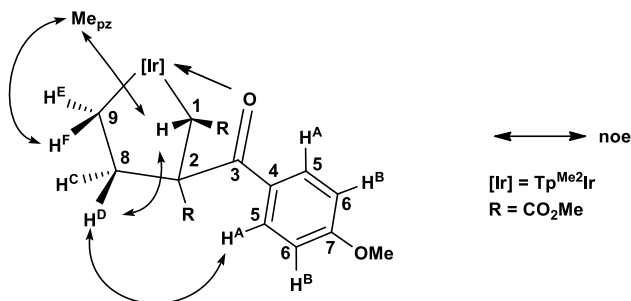
^{1}H NMR (CDCl$_3$, 25 ºC; δ (ppm)): 7.79, 6.89 (d, 2 H each, $^3J_{HH}$ = 8.0 Hz, 2 CH^A, 2 CH^B, resp.),

5.81, 5.68, 5.65 (s, 1 H each, 3 CH$_{pz}$), 5.43 (s, 1 H, C^{1}H), 3.84 (s, 3 H, C^{7}OMe), 3.68, 3.25 (s, 3 H each,

2 CO$_2$Me), 2.95, 2.39 (td, m, 1 H each, $^2J_{HH}$ = 11.3, $^3J_{HH}$ = 3.3 Hz, H^E, H^F, resp.), 2.62, 2.46, 2.35, 2.31,

2.14, 1.91 (s, 3 H each, 6 Me$_{pz}$), 2.20, 2.03 (m, 1 H each, H^C, H^D, resp.). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 ºC;

δ (ppm)): 222.4 (C^3), 184.7, 172.3 (*CO$_2$Me), 163.2 (C^7), 152.5, 152.1, 149.6, 143.7, 143.2, 142.5 (C$_{qpz}$),

131.1, 113.3 (C^5, C^6, resp.), 129.4 (C^4), 109.1, 107.0, 106.9 (CH$_{pz}$), 75.8 (C^2), 55.5 (C^{7}O*Me*), 51.8, 50.4

(CO$_2$*Me*), 38.8 (C^8, $^1J_{CH}$ = 131 Hz), 24.7 (C^1, $^1J_{CH}$ = 138 Hz), 16.0, 13.4, 13.3, 13.2, 12.8, 12.5 (Me$_{pz}$), -

15.9 (C^9, $^1J_{CH}$ = 130 Hz). Elemental analysis for C$_{31}$H$_{40}$BN$_6$O$_6$Ir**:** C, 46.8; H, 5.0; N, 10.5. Found:

C, 47.2; H, 5.4; N, 10.0. Rf = 0.29 (silica gel, 1:1 diethylether:hexane). IR (Nujol): υ(CO, CO$_2$Me)

1721, 1678 cm^{-1}.

Synthesis of compound 6b. To a solution of Tp^{Me2}Ir(C$_2$H$_4$)$_2$ (**1**) (0.50 g, 0.92 mmol) in

dichloromethane (7 mL) at -20 ºC, MeO$_2$CC≡CCO$_2$Me (0.11 mL, 0.92 mmol) was added. After stirring

for 10 min at this temperature, *p*-nitrobenzaldehyde (0.28 g, 1.83 mmol) was added. The cold bath was

then removed and the resulting mixture stirred at room temperature for 14 h. The volatiles were

removed under reduced pressure and ^{1}H NMR monitoring revealed the presence of **2b**, **6b** and **5b** in 35,

40 and 25% spectroscopic yield, respectively. Only the title compound was isolated by column

chromatography on silica gel using diethylether:hexane (1:5) → diethylether mixtures as eluent. Yield:

0.23 g (30%) of a violet microcrystalline solid.
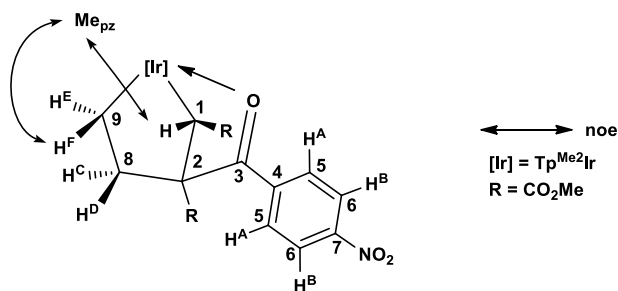
^{1}H NMR (CDCl$_3$, 25 °C; δ (ppm)): 8.25, 7.90 (d, 2 H each, $^3J_{HH}$ = 8.4 Hz, 2 H^B, 2 H^A, resp.), 5.83, 5.69, 5.65 (s, 1 H each, 3 CH$_{pz}$), 5.64 (s, 1 H, C^{1}H), 3.62, 3.31 (s, 3 H each, 2 CO$_2$Me), 3.00, 2.46 (ddd, m, 1 H each, $^2J_{HH}$ = 11.2, $^3J_{HH}$ = 6.0, 2.3 Hz, H^E and H^F, resp.), 2.61, 2.47, 2.35, 2.31, 2.13, 1.86 (s, 3 H each, 6 Me$_{pz}$), 2.08 (m, 2 H, H^C and H^D). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C; δ (ppm)): 226.3 (C^3), 185.9, 171.2 (*C*O$_2$Me), 152.5, 152.0, 149.5, 143.8, 143.8, 142.8 (C$_{qpz}$), 149.0 (C^7), 143.9 (C^4), 128.0, 123.1 (C^5, C^6, resp.), 109.3, 107.1, 107.0 (CH$_{pz}$), 78.4 (C^2), 52.0, 50.8 (CO$_2$*Me*), 37.9 (C^8, $^1J_{CH}$ = 131 Hz), 25.5 (C^1, $^1J_{CH}$ = 141 Hz), 16.1, 13.3, 13.3, 13.2, 12.8, 12.4 (Me$_{pz}$), -15.2 (C^9, $^1J_{CH}$ = 133 Hz). Elemental analysis for C$_{30}$H$_{37}$BN$_7$O$_7$Ir·CH$_2$Cl$_2$ (sample crystallized from CH$_2$Cl$_2$-Et$_2$O): C, 41.6; H, 4.4; N, 11.0. Found: C, 41.2; H, 4.8; N, 11.2. Rf = 0.20 (silica gel, 1:1 diethylether:hexane). IR (Nujol): υ(CO, CO$_2$Me) 1737 (br), (NO$_2$) 1550 cm^{-1}.

Synthesis of compounds 7a and 8a. To a solution of compound **2a** (0.15 g, 0.19 mmol) in dichloromethane (7 mL), MeO$_2$CC≡CCO$_2$Me (0.07 mL, 0.58 mmol) was added. The resulting mixture was stirred at 80 °C for 48 h, and then the volatiles were removed under reduced pressure. ^{1}H NMR analysis revealed the formation of **7a** and **8a** in 80 and 10% spectroscopic yield, respectively. They were isolated by column chromatography on silica gel using diethylether:hexane (1:1) → ethylacetate:diethylether (1:1) mixtures as eluent. Yield: 0.13 g (72%, yellow solid) and 0.025 g (14%, orange solid) of **7a** and **8a**, respectively. Analytically pure samples of both were obtained by slow diffusion of pentane into dichloromethane solutions at room temperature (bright yellow crystals, **7a**; bright orange crystals, **8a**).

$[Ir] = Tp^{Me2}Ir$
$R = CO_2Me$

7a   **8a**
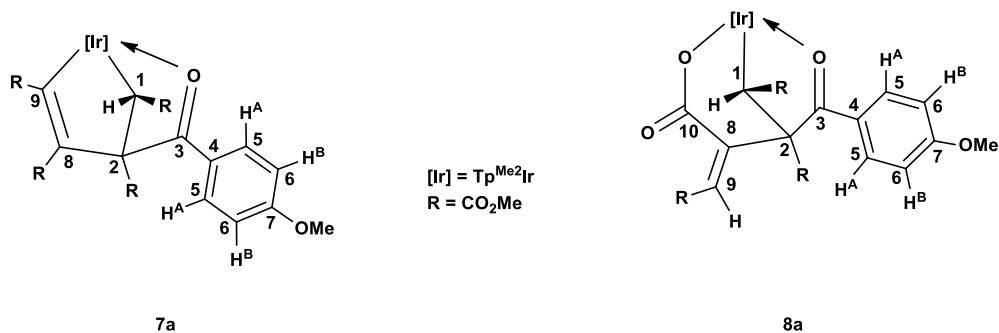
7a: ^1H NMR (CDCl$_3$, 25 °C; δ (ppm)): 8.34, 6.89 (d, 2 H each, $^3J_{HH}$ = 9.0 Hz, 2 H^A, 2 H^B, resp.),

5.90 (s, 1 H, C^{1}H), 5.80, 5.71, 5.61 (s, 1 H each, 3 CH$_{pz}$), 3.84 (s, 3 H, C^{7}OMe), 3.73, 3.70, 3.31, 3.22

(s, 3 H each, 4 CO$_2$Me), 2.48, 2.48, 2.36, 2.31, 2.10, 1.58 (s, 3 H each, 6 Me$_{pz}$). $^{13}C\{^1H\}$ NMR (CDCl$_3$,

25 °C; δ (ppm)): 214.8 (C^3), 182.5, 175.1, 169.4, 162.3 (*CO*$_2$Me), 169.3 (C^9), 164.4 (C^7), 155.1, 152.7,

150.6, 144.3, 143.7, 142.8 (C$_{qpz}$), 134.7 (C^8), 133.6, 113.2 (C^5, C^6, resp.), 128.7 (C^4), 108.6, 107.5,

106.1 (CH$_{pz}$), 79.7 (C^2), 55.5 (C^{7}O*Me*), 52.1, 51.8, 50.7, 50.5 (CO$_2$*Me*), 37.1 (C^1, $^1J_{CH}$ = 141 Hz), 17.1,

13.5, 13.3, 12.6, 12.5, 12.3 (Me$_{pz}$). Elemental analysis for C$_{35}$H$_{42}$BN$_6$O$_{10}$Ir: C, 46.2; H, 4.6; N, 9.2.

Found: C, 46.0; H, 4.8; N, 8.7. Rf = 0.50 (silica gel, 6:1 diethylether:hexane). IR (Nujol): υ(CO,

CO$_2$Me) 1758, 1721, 1691 cm^{-1}.

8a: ^1H NMR (CDCl$_3$, 25 °C; δ (ppm)): 7.97, 6.87 (d, 2 H each, $^3J_{HH}$ = 9.0 Hz, 2 H^A, 2 H^B, resp.),

6.82 (s, 1 H, C^{9}H), 6.05 (s, 1 H, C^{1}H), 5.76, 5.74, 5.66 (s, 1 H each, 3 CH$_{pz}$), 3.87 (s, 3 H, C^{7}OMe),

3.76, 3.74, 2.89 (s, 3 H each, 3 CO$_2$Me), 2.49, 2.44, 2.41, 2.33, 2.07, 2.00 (s, 3 H each, 6 Me$_{pz}$). $^{13}C\{^1H\}$

NMR (CDCl$_3$, 25 °C; δ (ppm)): 218.0 (C^3), 183.2, 169.5, 168.3 (*CO*$_2$Me), 166.6 (C^{10}), 165.7 (C^7),

152.7, 152.6, 150.7, 145.0, 143.2, 142.9 (C$_{qpz}$), 140.0 (C^8), 133.8, 114.2 (C^5, C^6, resp.), 128.5 (C^4),

128.0 (C^9, $^1J_{CH}$ = 162 Hz), 108.7, 108.6, 106.6 (CH$_{pz}$), 73.8 (C^2), 55.8 (C^{7}O*Me*), 52.4, 52.4, 50.6

(CO$_2$*Me*), 26.0 (C^1, $^1J_{CH}$ = 138 Hz), 14.6, 14.6, 12.9, 12.7, 12.0, 12.0 (Me$_{pz}$). Elemental analysis for

C$_{34}$H$_{40}$BN$_6$O$_{10}$Ir: C, 45.6; H, 4.5; N, 9.4. Found: C, 45.2; H, 5.0; N, 9.9. Rf = 0.14 (silica gel,

diethylether). IR (Nujol): υ(CO, CO$_2$Me, CO$_2$Ir) 1728, 1702 cm^{-1}.

**Synthesis of compound 7b.** To a solution of compound **2b** (0.075 g, 0.137 mmol) in dichloromethane (5 mL), $MeO_2CC\equiv CCO_2Me$ (0.05 mL, 0.411 mmol) was added. The resulting mixture was stirred at 80 ºC for 48 h, and then the volatiles were removed under reduced pressure. ^1H NMR analysis revealed the formation of **7b** in 90% spectroscopic yield. Compound **7b** was purified by column chromatography on silica gel using diethylether:hexane (1:1) → ethylacetate mixtures as eluent. Yield: 0.05 g (56%) of a dark red microcrystalline solid.


$[Ir] = Tp^{Me2}Ir$
$R = CO_2Me$
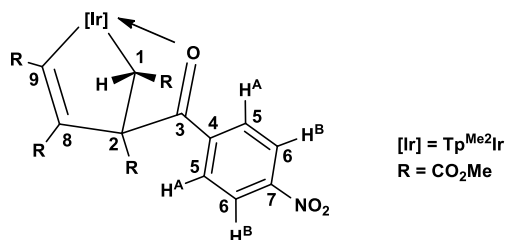
^1H NMR (CDCl$_3$, 25 ºC; δ (ppm)): 8.39, 8.25 (d, 2 H each, $^3J_{HH}$ = 8.5 Hz, 2 H^A, 2 H^B, resp.), 6.03 (s, 1 H, C^{1}H), 5.83, 5.76, 5.62 (s, 1 H each, 3 CH$_{pz}$), 3.74, 3.70, 3.33, 3.27 (s, 3 H each, 4 CO$_2$Me), 2.51, 2.48, 2.38, 2.32, 2.14, 1.50 (s, 3 H each, 6 Me$_{pz}$). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 25 ºC; δ (ppm)): δ 219.5 (C^3), 183.1, 174.6, 168.7, 162.4 (*C*O$_2$Me), 170.9 (C^9), 155.2, 152.7, 150.5, 144.7, 144.1, 143.1 (C$_{qpz}$), 149.9 (C^7), 142.2 (C^4), 133.7 (C^8), 130.3, 122.8 (C^5, C^6, resp.), 108.9, 107.7, 106.3 (CH$_{pz}$), 81.3 (C^2), 52.3, 52.2, 50.9, 50.9 (CO$_2$*Me*), 37.6 (C^1, $^1J_{CH}$ = 143 Hz), 17.2, 13.6, 13.3, 12.9, 12.4, 12.3 (Me$_{pz}$). Elemental analysis for C$_{34}$H$_{39}$BN$_7$O$_{11}$Ir: C, 44.2; H, 4.2; N, 10.6. Found: C, 44.0; H, 4.6; N, 10.3. Rf = 0.42 (silica gel, 3:1 diethylether:hexane). IR (Nujol): υ(CO, CO$_2$Me) 1757, 1723, 1699, (NO$_2$) 1551 cm^{-1}.

Synthesis of compound 9a. Method a: Compound **2a** (0.09 g, 0.12 mmol) was dissolved in dichloromethane (5 mL), placed in a Fisher-Porter vessel, pressurized with C$_2$H$_2$ (2 atm) and then stirred at 60 ºC for 14 h. The volatiles were removed under vacuum and quantitative conversion into compound **9a** was ascertained by ^1H NMR. This compound, a bright orange microcrystalline solid, was purified by

column chromatography on silica gel using a diethylether:hexane (1:1) mixture as eluent. Yield: 0.075 g (81%).
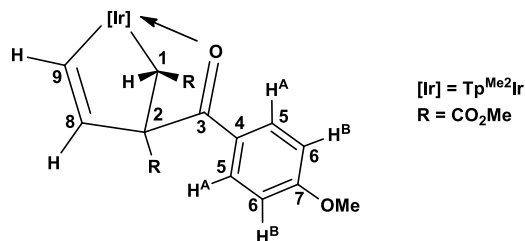
Method b: To a solution of compound **1** (0.10 g, 0.18 mmol) in dichloromethane (3 mL) at -20 ºC, $MeO_2C{\equiv}CCO_2Me$ (0.022 mL, 0.18 mmol) and *p*-anisaldehyde (0.045 mL, 0.36 mmol) were added sequentially. The cold bath was then removed and the resulting mixture stirred at 60 ºC for 20 h. After cooling at 25 ºC, the reaction mixture was placed in a Fisher Porter vessel, pressurized with C_2H_2 (2 atm) and then stirred at 60 ºC for 14 h. Compound **9a** was purified by column chromatography on silica gel using diethylether:pentane (1:1) mixture as eluent. Yield: 0.111 g (76%).

^{1}H NMR (CDCl$_3$, 25 ºC; δ (ppm)): 9.18 (d, $^3J_{HH}$ = 5.8 Hz, 1 H, C^{9}H), 7.76, 6.87 (d, 2 H each, $^3J_{HH}$ = 8.9 Hz, 2 H^A and 2 H^B, resp.), 6.19 (d, 1 H, C^{8}H), 5.73, 5.71, 5.31 (s, 1 H each, 3 CH$_{pz}$), 5.31 (s, 1 H, C^{1}H), 3.83 (s, 3 H, C^{7}OMe), 3.77, 3.30 (s, 3 H each, 2 CO$_2$Me), 2.47, 2.40, 2.38, 2.34, 1.95, 1.80 (s, 3 H each, 6 Me$_{pz}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 ºC; δ (ppm)): 215.8 (C^3), 184.3, 171.9 (*C*O$_2$Me), 162.7 (C^7), 153.7, 153.0, 149.5, 143.8, 143.6, 142.4 (C$_{qpz}$), 149.1 (C^9), 130.9 (C^5), 129.5 (C^4), 127.6 (C^8), 113.6 (C^6), 108.3, 107.4, 105.7 (CH$_{pz}$), 82.0 (C^2), 55.3 (C^{7}O*Me*), 51.8, 50.4 (CO$_2$*Me*), 34.5 (C^1), 15.7, 13.2, 13.1, 12.7, 12.2, 10.9 (Me$_{pz}$). Elemental analysis for C$_{31}$H$_{38}$BIrN$_6$O$_6$: C, 46.9; H, 4.8; N, 10.6. Found: C, 46.8; H, 4.9; N, 10.3. Rf = 0.24 (silica gel, 1:1 diethylether:hexane). IR (Nujol): υ(CO, CO$_2$Me) 1720, 1680, 1600 cm^{-1}.

Synthesis of compound 10a. To a solution of compound **2a** (0.07 g, 0.09 mmol) in dichloromethane (3.5 mL), PhC≡CPh (0.048 g, 0.29 mmol) was added. The resulting mixture was stirred at 80 ºC for 48 h and then the volatiles were removed under reduced pressure. Quantitative conversion into **10a** was ascertained by ^{1}H NMR. An analytically pure sample of **10a** was obtained by column chromatography on silica gel using a diethylether:hexane (1:1) mixture as eluent. Yield: 0.071g (82%) of bright orange crystals.
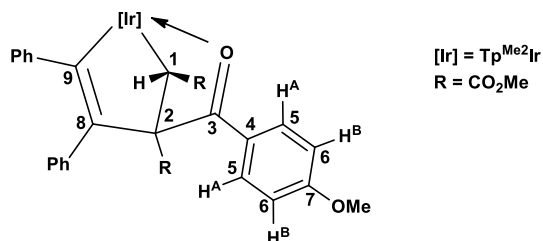
^{1}H NMR (CDCl$_3$, 25 ºC; δ (ppm)): δ 7.98, 6.93 (d, 2 H each, $^3J_{HH}$ = 8.6 Hz, 2 H^A and 2 H^B, resp.), 7.05 (m, 3 H, 3 CH(Ph)), 6.88 (d, 2 H, 2 CH(Ph)), 6.74 (t, 1 H, CH(Ph)), 6.56 (t, 2 H, 2 CH(Ph)), 6.36 (d, 2 H, 2 CH(Ph)), 6.02 (s, 1 H, C^{1}H), 5.88, 5.65, 5.36 (s, 1 H each, 3 CH$_{pz}$), 3.87 (s, 3 H, C^{7}OMe), 3.29, 3.21 (s, 3 H each, 2 CO$_2$Me), 2.60, 2.59, 2.38, 2.31, 1.87, 1.31 (s, 3 H each, 6 Me$_{pz}$).

^{13}C{^{1}H} NMR (CDCl$_3$, 25 ºC; δ (ppm)): 219.5 (C^3), 185.4, 169.7 (CO$_2$Me), 162.1 (C^7), 154.1, 151.9, 149.2, 143.8, 143.3, 132.3 (C$_{qpz}$), 153.6 (C^9), 145.7, 140.7 (C$_{qar}$), 138.0 (C^8), 132.2 (C^4), 131.3 (C^5), 130.3, 129.0, 127.5, 126.2, 125.6, 124.2 (2:2:2:2:1:1, CH(Ph)), 112.6 (C^6), 108.5, 107.2, 105.2 (CH$_{pz}$), 87.0 (C^2), 55.2 (C^{7}O*Me*), 51.1, 50.5 (CO$_2$*Me*), 33.2 (C^1), 15.8, 13.3, 12.9, 12.6, 12.3, 12.2 (Me$_{pz}$). Elemental analysis for C$_{43}$H$_{46}$BIrN$_6$O$_6$: C, 54.6; H, 4.9; N, 8.9. Found: C, 54.4; H, 5.1; N, 8.7. Rf = 0.42 (silica gel, 1:1 diethylether:hexane). IR (KBr): υ(CO, CO$_2$Me) 1750, 1720, 1690 cm^{-1}.

Synthesis of compound 11a. To a solution of compound **2a** (0.09 g, 0.12 mmol) in dichloromethane (3.5 mL), MeO$_2$CC≡CH (0.032 mL, 0.35 mmol) was added. The resulting mixture was stirred at 80 ºC for 48 h, and then the volatiles were removed under reduced pressure. ^{1}H NMR analysis

revealed the formation of **11a** in ≥90% spectroscopic yield. Compound **11a** was purified by column chromatography on silica gel using a diethylether:hexane (2:1) mixture as eluent. Yield: 0.065 g (76%) of red crystals.

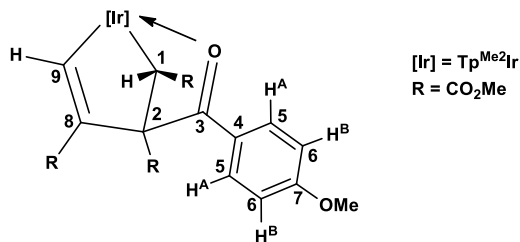^{1}H NMR (CDCl$_3$, 25 ºC; δ (ppm)): 11.14 (s, 1 H, C^{9}H), 8.21, 6.79 (d, 2 H each, $^3J_{HH}$ = 9.0 Hz, 2 H^A, 2 H^B resp.), 5.72, 5.67, 5.58 (s, 1 H each, 3 CH$_{pz}$), 5.60 (s, 1 H, C^{1}H), 3.74 (s, 3 H, C^{7}OMe), 3.67, 3.63, 3.17 (s, 3H each, 3 CO$_2$Me), 2.40, 2.35, 2.27, 2.24, 2.08, 1.38 (s, 3 H each, 6 Me$_{pz}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 ºC; δ (ppm)): 215.3 (C^3), 183.0, 170.0, 161.9 (*C*O$_2$Me), 176.1 (C^9), 163.9 (C^7), 153.6, 152.9, 149.6, 144.2, 144.0, 142.6 (C$_{qpz}$), 134.7 (C^8), 133.1 (C^5), 129.0 (C^4), 113.1 (C^6), 108.5, 107.6, 105.9 (CH$_{pz}$), 79.1 (C^2), 55.4 (C^{7}O*Me*), 51.9, 51.4, 50.5 (CO$_2$*Me*), 38.1 (C^1), 15.5, 13.5, 13.2, 12.8, 12.2, 10.8 (Me$_{pz}$). Elemental analysis for C$_{33}$H$_{40}$BIrN$_6$O$_8$: C, 46.5; H, 4.7; N, 9.9. Found: C, 46.7; H, 5.0; N, 9.5. IR (Nujol): υ(CO, CO$_2$Me) 1740, 1690, 1600 cm^{-1}.

Synthesis of compounds 11b and 12b. To a solution of compound **2b** (0.140 g, 0.18 mmol) in dichloromethane (5 mL), MeO$_2$CC≡CH (0.048 mL, 0.54 mmol) was added. The resulting mixture was stirred at 80 ºC for 48 h, and then the volatiles were removed under reduced pressure. ^{1}H NMR analysis of the resulting residue revealed the formation of **11b** and **12b** in 75 and 20% spectroscopic yield, respectively. They were isolated, as dark red microcrystalline solids, by column chromatography on silica gel using a diethylether:hexane (1:1) mixture as eluent. Yield: 0.065 g (40%) and 0.015 g (10%) of **11b** and **12b**, respectively.
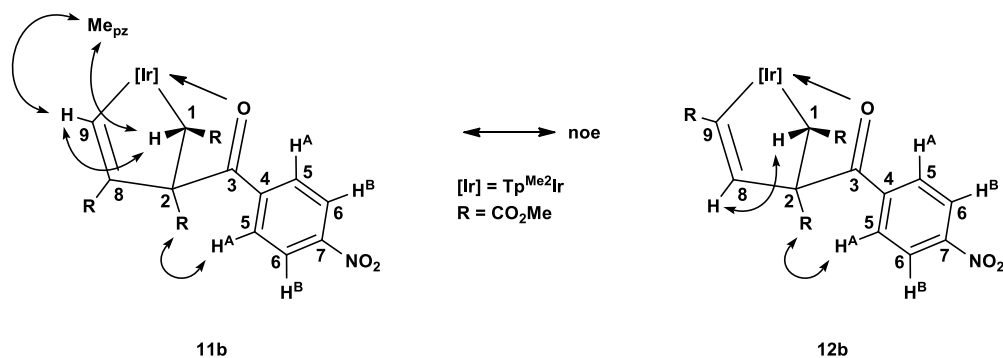
11b: ^{1}H NMR (CDCl$_3$, 25 °C; δ (ppm)): 11.43 (s, 1 H, C^{9}H), 8.32, 8.22 (d, 2 H each, $^3J_{HH}$ = 8.9 Hz, 2 H^A, 2 H^B, resp.), 5.83, 5.71, 5.67 (s, 1 H each, 3 CH$_{pz}$), 5.78 (s, 1 H, C^{1}H), 3.75, 3.72, 3.28 (s, 3 H each, 3 CO$_2$Me), 2.49, 2.44, 2.35, 2.31, 2.18, 1.39 (s, 3 H each, 6 Me$_{pz}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C; δ (ppm)): 219.2 (C^3), 183.5, 169.3, 162.0 (*C*O$_2$Me), 178.1 (C^9, $^1J_{CH}$ = 158 Hz), 153.7, 152.9, 149.5, 144.5, 144.4, 142.9 (C$_{qpz}$), 149.7 (C^7), 142.5 (C^4), 133.3 (C^8), 130.0, 122.8 (C^5, C^6, resp.), 108.8, 107.8, 106.1 (CH$_{pz}$), 80.7 (C^2), 52.2, 51.7, 50.8 (CO$_2$*Me*), 38.5 (C^1, $^1J_{CH}$ = 143 Hz), 15.6, 13.6, 13.2, 12.8, 12.2, 10.7 (Me$_{pz}$). Elemental analysis for C$_{32}$H$_{37}$BN$_7$O$_9$Ir·0.5Et$_2$O (sample crystallized from CH$_2$Cl$_2$:Et$_2$O): C, 45.1; H, 4.6; N, 10.8. Found: C, 44.7; H, 4.7; N, 10.5. Rf = 0.19 (silica gel, 1:1 diethylether:hexane). IR (Nujol): υ(CO, CO$_2$Me) 1749, 1685, (NO$_2$) 1548 cm^{-1}.

12b: ^{1}H NMR (CDCl$_3$, 25 °C; δ (ppm)): 8.24, 7.90 (d, 2 H each, $^3J_{HH}$ = 8.8 Hz, 2 H^B, 2 H^A, resp.), 7.20 (s, 1 H, C^{8}H), 5.74, 5.70, 5.64 (s, 1 H each, 3 CH$_{pz}$), 5.60 (s, 1 H, C^{1}H), 3.71, 3.34, 3.33 (s, 3 H each, 3 CO$_2$Me), 2.50, 2.39, 2.34, 2.24, 1.92, 1.59 (s, 3 H each, 6 Me$_{pz}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C; δ (ppm)): 219.2 (C^3), 185.1, 170.1, 170.0 (*C*O$_2$Me), 153.8, 153.0, 150.5, 144.4, 143.6, 142.3 (C$_{qpz}$), 149.2 (C^9), 148.8 (C^7), 143.2 (C^4), 136.9 (C^8, $^1J_{CH}$ = 174 Hz), 128.5, 123.2 (C^5, C^6, resp.), 108.3, 107.9, 105.6 (CH$_{pz}$), 84.0 (C^2), 52.4, 51.1, 51.0 (CO$_2$*Me*), 35.3 (C^1, $^1J_{CH}$ = 143 Hz), 16.0, 13.3, 13.3, 12.8, 12.4, 11.4 (Me$_{pz}$). Elemental analysis for C$_{32}$H$_{37}$BN$_7$O$_9$Ir·0.5CH$_2$Cl$_2$ (sample crystallized from CH$_2$Cl$_2$:Et$_2$O): C, 42.9; H, 4.2; N, 10.8. Found: C, 42.5; H, 4.0; N, 10.4. Rf = 0.31 (silica gel, 3:1 diethylether:hexane). IR (Nujol): υ(CO, CO$_2$Me) 1790, 1715, 1684, (NO$_2$) 1549 cm^{-1}.

Synthesis of compounds 13a and 14a. To a solution of compound **1** (0.10 g, 0.18 mmol) in dichloromethane (3 mL) at -20 ºC, $Me_3CC \equiv CH$ (0.022 mL, 0.18 mmol) and *p*-anisaldehyde (0.045 mL, 0.36 mmol) were added sequentially. The cold bath was then removed and the resulting mixture stirred at 60 ºC for 20 h. After cooling at 25 ºC, *terc*-butylacetylene (0.134 mL, 1.10 mmol) was added and the resulting mixture stirred at 80 ºC for 48 h to afford a *ca.* 1:1 mixture of **13a** and **14a**. They were separated, as orange and red microcrystalline solids, by column chromatography on silica gel using a diethylether:hexane (1:1) mixture as eluent. Yield: 0.052 g (33%) and 0.056 g (36%) of **13a** and **14a**, respectively.

13a   14a
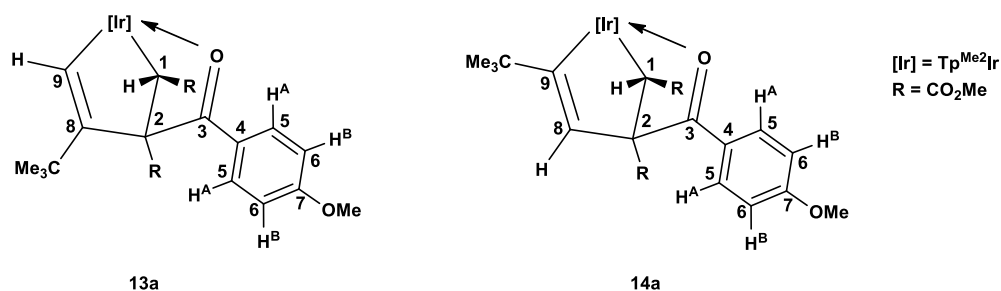
13a: ^1H NMR (CDCl$_3$, 25 ºC; δ (ppm)): 9.06 (s, 1 H, C^{9}H), 7.79, 6.84 (d, 2 H each, $^3J_{HH}$ = 8.7 Hz, 2 H^A and H^B, resp.), 5.73, 5.71, 5.67 (s, 1 H each, 3 CH$_{pz}$), 5.61 (s, 1 H, C^{1}H), 3.82 (s, 3 H, C^{7}OMe), 3.71, 3.31 (s, 3 H each, 2 CO$_2$Me), 2.46, 2.39, 2.33, 1.85, 1.81 (s, 1:2:1:1:1, 6 Me$_{pz}$), 1.02 (s, 9 H, CMe$_3$). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 25 ºC; δ (ppm)): 220.7 (C^3), 185.9, 171.8 (*C*O$_2$Me), 161.4 (C^7), 153.4, 152.2, 149.1, 143.6, 143.3, 142.3 (C$_{qpz}$), 145.5 (C^8), 140.9 (C^9), 132.6 (C^4), 130.9 (C^5), 112.1 (C^6), 108.3, 107.0, 105.7 (CH$_{pz}$), 83.5 (C^2), 55.1 (C^{7}O*Me*), 51.4, 50.5 (CO$_2$*Me*), 37.0 (*C*Me$_3$), 35.6 (C^1), 30.6 (C*Me$_3$*), 15.2, 13.1, 12.7, 12.6, 12.1, 11.1 (Me$_{pz}$). Elemental analysis for C$_{35}$H$_{46}$BIrN$_6$O$_6$: C, 49.5; H, 5.5; N, 9.9. Found: C, 49.6; H, 5.7; N, 9.5. Rf = 0.39 (silica gel, 1:1 diethylether:hexane). IR (Nujol): υ(CO, CO$_2$Me) 1735, 1680, 1600 cm^{-1}.

14a: ^1H NMR (CDCl$_3$, 25 ºC; δ (ppm)): 7.89, 6.89 (d, 2 H each, $^3J_{HH}$ = 8.9 Hz, 2 H^A and H^B, resp), 5.80 (s, 1 H, C^{1}H), 5.76, 5.72, 5.70 (s, 1 H each, 3 CH$_{pz}$), 5.24 (s, 1 H, C^{8}H), 3.84 (s, 3 H,

C^7OMe), 3.81, 3.45 (s, 3 H each, 2 CO_2Me), 2.54, 2.44, 2.37, 2.36, 2.12, 1.83 (s, 3 H each, 6 Me_{pz}), 0.54

(s, 9 H, CMe_3). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 25 °C; δ (ppm)): 217.3 (C^3), 182.7, 170.8 (CO_2Me), 163.5 (C^7),

153.7, 152.2, 145.0, 143.9, 143.2, 142.3 (C_{qpz}), 137.0 (C^8), 132.8 (2C^5), 128.3 (C^4), 115.1 (C^9), 113.4

(C^6), 108.7, 106.5, 106.3 (CH_{pz}), 88.9 (C^2), 55.3 (C^7OMe), 51.4, 51.0 (CO_2Me), 32.6 (CMe_3), 29.2

(CMe_3), 17.5, 13.7, 13.2, 12.6, 12.4, 12.2 (Me_{pz}), 9.5 (C^1). Elemental analysis for $C_{35}H_{46}BIrN_6O_6$: C,

49.5; H, 5.6; N, 9.9. Found: C, 49.3; H, 5.3; N, 9.8. Rf = 0.21 (silica gel, 1:1 diethylether:hexane). IR

(Nujol): υ(CO, CO_2Me) 1725, 1690, 1605 cm^{-1}.

Synthesis of compounds 15a and 16a. To a solution of compound **2a** (0.10 g, 0.13 mmol) in

dichloromethane (6 mL), PhC≡CH (0.043 g, 0.39 mmol) was added and the resulting mixture stirred at

80 °C for 14 h to afford a *ca*. 1:1 mixture of **15a** and **16a**. They were separated by column

chromatography on silica gel using a diethylether:hexane (1:1) mixture as eluent. Yield: 0.058g (50%,

bright red crystals) and 0.048g (40%, of bright red crystals) of **15a** and **16a**, respectively.

15a   16a

15a: ^1H NMR (CDCl$_3$, 25 °C; δ (ppm)): 9.34 (s, 1 H, C^9H), 7.69, 6.74 (d, 2 H each, $^3J_{HH}$ = 8.7

Hz, 2 H^A and 2H^B, resp.), 7.10, 7.04 (m, 2 H, 3 H, 5 CH(Ph)), 5.80 (s, 1 H, C^1H), 5.68, 5.67, 5.62 (s, 1

H each, 3 CH_{pz}), 3.74 (s, 3 H, C^7OMe), 3.44, 3.25 (s, 3 H each, 2 CO_2Me), 2.41, 2.40, 2.34, 2.27, 1.91,

1.68 (s, 3 H each, 6 Me_{pz}). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 25 °C; δ (ppm)): 218.1 (C^3), 185.2, 170.6 (CO_2Me),

162.3 (C^7), 153.6, 152.6, 149.5, 143.8, 143.7, 142.5 (C_{qpz}), 150.5 (C^9), 140.7 (C_{qar}), 139.6 (C^8), 131.4

(C^4), 131.1 (C^5), 127.8, 127.6, 125.8 (CH(Ph)), 112.7 (C^6), 108.5, 107.3, 105.9 (CH_{pz}), 84.9 (C^2), 55.3

(C^7OMe), 51.6, 50.6 (CO_2Me), 36.4 (C^1), 15.5, 13.3, 13.1, 12.8, 12.3, 11.1 (Me_{pz}). Elemental analysis

for $C_{37}H_{42}BIrN_6O_6$: C, 51.1; H, 4.9; N, 9.7. Found: C, 51.1; H, 5.0; N, 9.4. IR (Nujol): υ(CO, CO₂Me) 1740, 1690, 1600 cm⁻¹.

16a: ¹H NMR (CDCl₃, 25 ºC; δ (ppm)): 7.83, 6.83 (d, 2 H each, $^3J_{HH}$ = 8.9 Hz, 2 H^A and 2 H^B, resp.), 6.72 (t, 1 H, p-CH(Ph)), 6.58 (m, 4 H, 4 CH(Ph)) 6.44 (s, 1 H, C^{8}H) 5.70 (s, 2 H, C^{1}H and CH$_{pz}$), 5.59, 5.39 (s, 1 H each, 2 CH$_{pz}$), 3.82, 3.43 (s, 3 H each, 2 CO₂Me), 3.77 (s, 3 H, C^{7}OMe), 2.43, 2.34, 2.31, 2.27, 1.83, 1.64 (s, 3 H each, 6 Me$_{pz}$). ¹³C{¹H} NMR (CDCl₃, 25 ºC; δ (ppm)): 216.9 (C^3), 182.8, 171.1 (CO₂Me), 164.0 (C^7), 154.7, 152.5, 151.3, 144.3, 143.6, 142.5 (C$_{qpz}$), 137.7 (C$_{qar}$), 133.0 (C^5), 128.6 (C^9), 128.2 (C^8), 128.0 (C^4), 127.0, 126.5, 125.5 (CH(Ph)), 113.7 (C^6), 108.6, 107.0, 106.0 (CH$_{pz}$), 88.5 (C^2), 55.6 (C^{7}OMe), 52.0, 51.4 (CO₂Me), 15.6, 13.3, 12.7, 12.6, 12.3, 12.1 (Me$_{pz}$), 9.0 (C^1). Elemental analysis for $C_{37}H_{42}BIrN_6O_6$: C, 51.1; H, 4.9; N, 9.7. Found: C, 50.9; H, 5.1; N, 9.4. IR (Nujol): υ(CO, CO₂Me) 1725, 1690, 1600 cm⁻¹.

Synthesis of compounds 17a, 18a and 19a: To a solution of compound **2a** (0.07 g, 0.09 mmol) in dichloromethane (4 mL), Me₃SiC≡CH (0.324 mL, 2.29 mmol) was added and the resulting mixture stirred at 80 ºC for 48 h. After evaporation of the volatiles ¹H NMR analysis of the resulting residue revealed the presence of **17a**, **18a** and **19a** in *ca*. 4:2:1 ratio. Column chromatography on silica gel using diethylether:hexane (1:2) → diethylether:hexane (1:1) mixtures as eluent furnished **17a** (0.031 g, 39% orange solid) and **18a** in admixture with **19a**.

17a   18a   19a

[Ir] = Tp^{Me2}Ir
R = CO₂Me
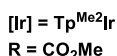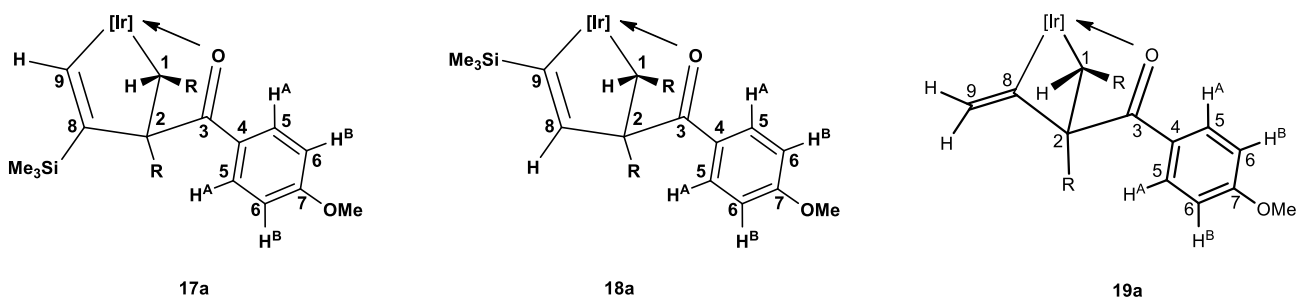
17a: ^{1}H NMR (CDCl$_3$, 25 ºC; δ (ppm)): 10.13 (s, 1 H, C^{9}H), 7.73, 6.85 (d, 2 H each, $^3J_{HH}$ = 8.9 Hz, 2 H^A and 2 H^B, resp.), 5.73, 5.70, 5.69 (s, 1 H each, 3 CH$_{pz}$), 5.41 (s, 1 H, C^{1}H), 3.83 (s, 3 H, C^{7}OMe), 3.74, 3.31 (s, 3 H each, 2 CO$_2$Me), 2.46, 2.39, 2.34, 2.32, 1.89, 1.77 (s, 3 H each, 6 Me$_{pz}$), -0.06 (s, 9 H, SiMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 ºC; δ (ppm)): 217.9 (C^3), 185.0, 171.5 (*C*O$_2$Me), 169.4 (C^9), 162.0 (C^7), 153.5, 152.8, 149.3, 143.7, 143.6, 142.4 (C$_{qpz}$), 139.9 (C^2), 130.8 (C^5), 130.7 (C^4), 112.5 (C^6), 108.3, 107.2, 105.8 (CH$_{pz}$), 85.2 (C^8), 55.2 (C^{7}O*Me*), 51.5, 50.4 (CO$_2$*Me*), 35.6 (C^1), 15.3, 13.1, 13.0, 12.7, 12.2, 10.8 (Me$_{pz}$), 0.0 (SiMe$_3$). Elemental analysis for C$_{34}$H$_{46}$BIrN$_6$O$_6$Si: C, 47.2; H, 5.3; N, 9.7. Found: C, 47.0; H, 5.2; N, 9.7. Rf = 0.30 (silica gel, 1:1 diethylether:hexane). IR (Nujol): υ(CO, CO$_2$Me) 1720, 1685, 1600 cm^{-1}.

18a: ^{1}H NMR (CDCl$_3$, 25 ºC; δ (ppm)): 7.78, 6.89 (d, 2 H each, $^3J_{HH}$ = 8.9 Hz, 2 H^A and 2 H^B, resp.), 6.57 (s, 1 H, C^{8}H), 5.77, 5.69, 5.66 (s, 1 H each, 3 CH$_{pz}$), 5.40 (s, 1 H, C^{1}H), 3.87 (s, 3 H, C^{7}OMe), 3.80, 3.33 (s, 3 H each, 2 CO$_2$Me), 2.52, 2.39, 2.34, 2.18, 1.92, 1.75 (s, 3 H each, 6 Me$_{pz}$), -0.41 (s, 9 H, SiMe$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 ºC; δ (ppm)): 214.9 (C^3), 184.7, 171.8 (*C*O$_2$Me), 164.3 (C^9), 162.6 (C^7), 153.8, 152.9, 149.3, 143.7, 143.7, 142.5 (C$_{qpz}$), 138.8 (C^2), 130.8 (C^5), 129.7 (C^4), 113.3 (C^6), 108.4, 107.1, 105.8 (CH$_{pz}$), 84.5 (C^8), 55.3 (C^{7}O*Me*), 51.9, 50.4 (CO$_2$*Me*), 33.2 (C^1), 17.5, 13.2, 13.1, 12.8, 12.6, 12.2 (Me$_{pz}$), 0.3 (SiMe$_3$).

19a: ^{1}H NMR (CDCl$_3$, 25 ºC; δ (ppm)): 7.90, 6.92 (d, 2 H each, $^3J_{HH}$ = 8.9 Hz, 2 H^A and 2 H^B, resp.), 5.79, 5.75, 5.74 (s, 1 H each, 3 CH$_{pz}$), 5.70 (s, 1 H, C^{1}H), 5.27, 4.61 (s, 1 H each, CH$_2$), 3.87 (s, 3 H, C^{7}OMe), 3.85, 3.51 (s, 3 H each, 2 CO$_2$Me), 2.52, 2.45, 2.42, 2.38, 2.16, 1.91 (s, 3 H each, 6 Me$_{pz}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 ºC; δ (ppm)): 216.5 (C^3), 182.8, 171.3 (*C*O$_2$Me), 164.0 (C^7), 154.0, 152.4, 150.9, 144.1, 143.4, 142.6 (C$_{qpz}$), 132.8 (C^5), 132.5 (C^8), 128.0 (C^4), 113.8 (2C^6), 112.2 (C^9), 108.8, 106.7, 106.4 (CH$_{pz}$), 88.0 (C^2), 55.6 (C^{7}O*Me*), 51.8, 51.3 (CO$_2$*Me*), 16.5, 13.3, 13.0, 12.7, 12.5, 12.4 (Me$_{pz}$), 9.8 (C^1). Elemental analysis for C$_{31}$H$_{39}$BIrN$_6$O$_6$: C, 46.9; H, 4.8; N, 10.6. Found: C, 47.0; H, 4.9; N, 10.8. Rf = 0.37 (silica gel, 2:1 diethylether:hexane). IR (Nujol): υ(CO, CO$_2$Me) 1725, 1690, 1600 cm^{-1}.

Synthesis of compounds 20a and 21a: Compound **2a** (0.10 g, 0.13 mmol) was suspended in cyclohexane (7 mL), placed in a Fisher-Porter vessel and pressurized with H_2 (3 atm). The resulting mixture was stirred at 90 ºC for 24 h and the volatiles removed under vacuum. ^1H NMR analysis of the resulting residue revealed the formation of **20a** (as a mixture of rotamers in 1:0.2 ratio) and **21a** in 80% and 20% spectroscopic yield, respectively. They were separated by column chromatography on silica gel, using diethylether:hexane (1:10) → (1:1) mixtures as eluent. Yield: 0.075 g (75%, orange microcrystalline solid) and 0.012 g (12%, orange microcrystalline solid) of **20a** and **21a**, respectively.

20a   21a

20a, major rotamer: ^1H NMR (CDCl$_3$, 25 ºC; δ (ppm)): 7.83, 7.04, 6.55 (d, d, dd, 1 H each, $^3J_{HH}$ = 9.1, $^4J_{HH}$ = 2.2 Hz, H^A, H^C, H^B, resp.), 5.88, 5.80, 5.54 (s, 1 H each, 3 CH$_{pz}$), 4.88 (dd, 1 H, $^3J_{HH}$ = 9.3, 4.9 Hz, C^{2}H), 3.78 (s, 3 H, C^{7}OMe), 3.71, 3.61 (s, 3 H each, 2 CO$_2$Me), 3.33, 2.94 (dd, 1 H each, $^2J_{HH}$ = 17.6 Hz, C^{1}H$_2$), 2.41, 2.39, 2.37, 2.16, 1.08 (s, 1:2:1:1:1, 6 Me$_{pz}$), -22.54 (s, 1 H, Ir–H). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 25 ºC; δ (ppm)): 209.7 (C^3), 179.8 (C^9), 171.7, 169.5 (CO$_2$Me), 164.1 (C^7), 151.9, 151.6, 151.5, 143.8, 143.3, 142.8 (C$_{qpz}$), 138.7 (C^4), 134.1, 119.4, 109.4 (C^5, C^8, C^6, resp.), 106.4, 106.4, 105.8 (CH$_{pz}$), 55.3 (C^{7}OMe), 52.8, 52.6 (CO$_2$Me), 46.0 (C^2, $^1J_{CH}$ = 135 Hz), 33.4 (C^1, $^1J_{CH}$ = 134, 131 Hz), 16.6, 14.3, 13.1, 12.4, 12.3, 10.8 (Me$_{pz}$).

20a, minor rotamer: ^1H NMR (CDCl$_3$, 25 ºC; δ (ppm)): 7.77, 7.06, 6.55 (d, d, dd, 1 H each, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 2.2 Hz, H^A, H^C, H^B, resp.), 5.88, 5.80, 5.54 (s, 1 H each, 3 CH$_{pz}$), 4.88 (dd, 1 H, $^3J_{HH}$ = 9.3, 4.9 Hz, C^{2}H), 3.78 (s, 3 H, C^{7}OMe), 3.74, 3.66 (s, 3 H each, 2 CO$_2$Me), 3.28, 2.72 (dd, 1 H each, $^2J_{HH}$ = 17.6 Hz, C^{1}H$_2$), -22.56 (s, 1 H, Ir–H). Resonances corresponding to the methyl groups of the

pyrazolyl rings have not been assigned. $^{13}C\{^1H\}$ NMR (CDCl$_3$, 25 °C; δ (ppm)): 210.2 (C^3), 180.3 (C^9), 171.7, 170.0 (CO$_2$Me), 162.5 (C^7), 151.9, 151.6, 151.5, 143.8, 143.3, 142.8 (C$_{qpz}$), 138.5 (C^4), 134.7, 119.6, 109.5 (C^5, C^8, C^6, resp.), 106.4, 106.4, 105.9 (CH$_{pz}$), 55.3 (C^{7}O*Me*), 52.7, 52.6 (CO$_2$Me), 45.9 (C^2, $^1J_{CH}$ = 135 Hz), 34.1 (C^1, $^1J_{CH}$ = 131 Hz). Resonances corresponding to the methyl groups of the pyrazolyl rings have not been assigned.

Elemental analysis for C$_{29}$H$_{38}$BN$_6$O$_6$Ir·0.5CH$_2$Cl$_2$ (sample crystallized from CH$_2$Cl$_2$:Et$_2$O): C, 43.6; H, 4.8; N, 10.4. Found: C, 43.9; H, 5.1; N, 10.2. Rf = 0.41 (silica gel, 1:1 diethylether:hexane). IR (Nujol): υ(Ir–H) 2152 (CO, CO$_2$Me) 1739 (br) cm^{-1}.

21a: ^1H NMR (CDCl$_3$, 25 °C; δ (ppm)): 8.01, 6.89 (d, 2 H each, $^3J_{HH}$ = 8.9 Hz, 2 H^A and 2 H^B, resp.), 5.75, 5.71, 5.62 (s, 1 H each, 3 CH$_{pz}$), 5.29, 5.13 (d, 1 H each, $^3J_{HH}$ = 1.6 Hz, C^{1}H and C^{2}H, resp.), 3.86 (s, 3 H, C^{7}OMe), 3.75, 2.92 (s, 3 H each, 2 CO$_2$Me), 2.40, 2.37, 2.32, 2.18, 1.75 (s, 2:1:1:1:1, 6 Me$_{pz}$), -22.52 (s, 1 H, Ir–H). $^{13}C\{^1H\}$ NMR (CDCl$_3$, 25 °C; δ (ppm)): 217.4 (C^3), 186.1, 170.8 (CO$_2$Me), 164.5 (C^7), 152.7, 152.7, 150.5, 143.1, 142.7, 142.7 (C$_{qpz}$), 132.0, 114.8 (C^5 and C^6, resp.), 128.1 (C^4), 106.9, 105.9, 105.2 (CH$_{pz}$), 63.1 (C^2, $^1J_{CH}$ = 128 Hz), 55.7 (C^{7}O*Me*), 52.6, 50.4 (CO$_2$Me), 15.9, 14.0, 13.7, 13.0, 12.6, 12.4 (Me$_{pz}$), 9.4 (C^1, $^1J_{CH}$ = 136 Hz). Elemental analysis for C$_{29}$H$_{38}$BN$_6$O$_6$Ir·0.5CH$_2$Cl$_2$ (sample crystallized from CH$_2$Cl$_2$:Et$_2$O): C, 43.6; H, 4.8; N, 10.4. Found: C, 44.1; H, 4.9; N, 10.2. Rf = 0.27 (silica gel, 1:1 diethylether:hexane). IR (Nujol): υ(Ir-H) 2147, (CO, CO$_2$Me) 1743 (br) cm^{-1}.

Synthesis of compounds 20b and 22b. Compound **2b** (0.135 g, 0.25 mmol) was suspended in cyclohexane (8 mL), placed in a Fisher-Porter vessel and pressurized with H$_2$ (3 atm). The resulting mixture was stirred at 90 °C for 24 h and the volatiles were removed under vacuum. ^1H NMR analysis of the resulting residue revealed the formation of **20b** (as a mixture of rotamers in 1:0.8 ratio) and **22b** in 53% and 20% spectroscopic yield, respectively. They were separated by column chromatography on

silica gel, using diethylether:hexane (1:5) → (1:1) mixtures as eluent. Yield: 0.065 g (48%, dark red microcrystalline solid) and 0.026 g (14%, brown microcrystalline solid) of **20b** and **22b**, respectively.

20b   22b
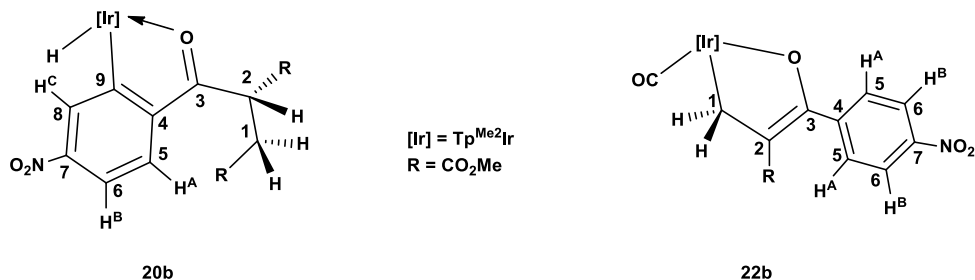
20b, major rotamer: ^{1}H NMR (CDCl$_3$, 25 °C; δ (ppm)): 8.30, 8.09, 7.75 (d, d, dd, 1 H each, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 1.8 Hz, H^C, H^A, H^B, resp.), 5.92, 5.88, 5.53 (s, 1 H each, 3 CH$_{pz}$), 5.05 (dd, 1 H, $^3J_{HH}$ = 14.7, 8.1 Hz, C^{2}H), 3.76, 3.65 (s, 3 H each, 2 CO$_2$Me), 3.30, 3.12 (dd, 1 H each, $^2J_{HH}$ = 17.6, C^{1}H$_2$), 2.42, 2.40, 2.40, 2.36, 2.10, 0.95 (s, 3 H each, 6 Me$_{pz}$), -22.33 (s, 1 H, Ir–H). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C; δ (ppm)): 215.9 (C^3), 177.7 (C^9), 171.7, 168.5 (*C*O$_2$Me), 152.1, 151.5, 151.3, 144.4, 143.8, 143.2 (C$_{qpz}$), 150.0 (C^7), 149.0 (C^4), 132.5, 131.8, 113.9 (C^5, C^8, C^6, resp.), 106.9, 106.7, 106.0 (CH$_{pz}$), 53.0, 52.3 (CO$_2$*Me*), 47.0 (C^2, $^1J_{CH}$ = 135 Hz), 33.3 (C^1, $^1J_{CH}$ = 133 Hz), 16.3, 14.3, 13.0, 12.3, 12.3, 11.1 (Me$_{pz}$).

20b, minor rotamer: ^{1}H NMR (CDCl$_3$, 25 °C; δ (ppm)): 8.32, 7.99, 7.75 (d, d, dd, 1 H each, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 1.8 Hz, H^C, H^A, H^B, resp.), 5.92, 5.88, 5.53 (s, 1 H each, CH$_{pz}$), 5.07 (dd, 1 H, $^3J_{HH}$ = 14.7, 8.1 Hz, C^{2}H), 3.71, 3.63 (s, 3 H each, 2 CO$_2$Me), 3.30, 2.91 (m, dd, 1 H each, $^2J_{HH}$ = 18.0 Hz, C^{1}H$_2$), -22.33 (s, 1 H, Ir–H). Resonances corresponding to the methyl groups of the pyrazolyl rings have not been assigned. ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C; δ (ppm)): 216.2 (C^3), 178.2 (C^9), 171.7, 169.1 (*C*O$_2$Me), 152.1, 151.6, 151.3, 144.4, 143.8, 143.2 (C$_{qpz}$), 150.0 (C^7), 148.9 (C^4), 132.3, 131.9, 114.0 (C^5, C^8, C^6, resp.), 106.9, 106.9, 106.1 (CH$_{pz}$), 53.2, 52.3 (CO$_2$*Me*), 47.0 (C^2, $^1J_{CH}$ = 135 Hz), 33.7 (C^1, $^1J_{CH}$ = 135 Hz). Resonances corresponding to the methyl groups of the pyrazolyl rings have not been assigned.

Rf = 0.34 (silica gel, 1:1 diethylether:hexane). IR (Nujol): υ(Ir–H) 2149, (CO, CO_2Me) 1743, 1738, (NO_2) 1548 cm^{-1}.

22b: ^{1}H NMR (CDCl$_3$, 25 ºC; δ (ppm)): 8.15, 7.57 (d, 2 H each, $^3J_{HH}$ = 7.3 Hz, 2 H^B and 2 H^A, resp.), 5.88, 5.83, 5.75 (s, 1 H each, 3 CH$_{pz}$), 4.00, 3.62 (d, 1 H each, $^2J_{HH}$ = 13.9 Hz, C^{1}H$_2$), 3.57 (s, 3 H, CO$_2$Me), 2.51, 2.43, 2.39, 2.35, 2.31, 2.27 (s, 3 H each, 6 Me$_{pz}$). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 ºC; δ (ppm)): 180.6 (C^3), 167.7 (*C*O$_2$Me), 163.0 (CO), 152.6, 151.6, 150.9, 145.0, 144.0, 143.7 (C$_{qpz}$), 147.2 (C^7), 145.4 (C^4), 129.4, 122.8 (C^5 and C^6, resp.), 113.5 (C^2), 108.9, 108.1, 107.0 (CH$_{pz}$), 50.6 (CO$_2$*Me*), 15.0, 13.0, 12.9, 12.7, 12.1, 12.0 (Me$_{pz}$), 3.4 (C^1, $^1J_{CH}$ = 136 Hz). Elemental analysis for C$_{27}$H$_{31}$BN$_7$O$_6$Ir: C, 43.1; H, 4.1; N, 13.0. Found: C, 43.9; H, 4.4; N, 13.2. Rf = 0.27 (silica gel, 1:1 diethylether:hexane). IR (Nujol): υ(CO) 2040, (CO, CO$_2$Me) 1745, 1656, (NO$_2$) 1548 cm^{-1}.

Structural Analysis of complexes 6a, 7a and 8a. Crystals of suitable size for X-ray diffraction analysis, were coated with dry perfluoropolyether and mounted on glass fibers and fixed in a cold nitrogen stream (T = 213 K) to the goniometer head. Data collections were performed on a Bruker-Nonius X8Apex-II CCD diffractometer, using monochromatic radiation λ(Mo Kα) = 0.71073 Å, by means of ω and φ scans with a width of 0.50 degree. The data were reduced (SAINT)[13] and corrected for absorption effects by the multi-scan method (SADABS).[14] The structures were solved by direct methods (SIR-2002)[15] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12)[16] minimizing w[F_o^2-F_c^2]^2. All the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and allowed to ride on the attached atoms with the isotropic temperature factors (Uiso values) fixed at 1.2 times (1.5 times for methyl groups) those Ueq values of the corresponding attached atoms.

Crystal data for 6a: C$_{31}$H$_{40}$BIrN$_6$O$_6$, M = 795.70, triclinic, a = 8.2638(4) Å, b = 12.0184(5) Å, c = 18.0299(8) Å, α = 98.159(2)°, β = 90.250(2)°, γ = 105.906(2)°, V = 1702.93(13) Å^3, T = 100(2) K,

space group $P\bar{1}$, $Z = 2$, $\mu = 3.970$ mm^{-1}, 25739 reflections measured, 10343 independent reflections (R_{int} = 0.0190). The final R_1 values were 0.0176 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0605 ($I > 2\sigma(I)$). The final R_1 values were 0.0184 (all data). The final $wR(F^2)$ values were 0.0612 (all data). The goodness of fit on F^2 was 1.125. CCDC 1015996.

*Crystal data for **7a**:* $2(C_{35}H_{42}BIrN_6O_{10})\cdot CH_2Cl_2$, M = 1904.44, triclinic, a = 8.6180(2) Å, b = 12.6109(3) Å, c = 19.4614(4) Å, α = 107.9940(10)°, β = 93.4270(10)°, γ = 105.5080(10)°, V = 1914.86(7) Å^3, T = 173(2) K, space group $P\bar{1}$, Z = 1, μ = 3.620 mm^{-1}, 58223 reflections measured, 11583 independent reflections (R_{int} = 0.0269). The final R_1 values were 0.0234 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0673 ($I > 2\sigma(I)$). The final R_1 values were 0.0262 (all data). The final $wR(F^2)$ values were 0.0686 (all data). The goodness of fit on F^2 was 0.996. CCDC 1015997.

*Crystal data for **8a**:* $C_{34}H_{40}BIrN_6O_{10}$, M = 895.73, monoclinic, a = 17.2496(13) Å, b = 17.2877(14) Å, c = 25.6049(17) Å, α = 90.00°, β = 98.640(3)°, γ = 90.00°, V = 7548.9(10) Å^3, T = 100(2) K, space group $P2_1/n$, Z = 8, μ = 3.599 mm^{-1}, 68501 reflections measured, 15477 independent reflections (R_{int} = 0.0885). The final R_1 values were 0.0447 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1083 ($I > 2\sigma(I)$). The final R_1 values were 0.0687 (all data). The final $wR(F^2)$ values were 0.1180 (all data). The goodness of fit on F^2 was 0.997. CCDC 1015998.

ASSOCIATED CONTENT

Supporting Information. CIF file giving crystallographic data for compounds **6a**, **7a** and **8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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For table of contents use only:

2a,b   A·····C$_2$H$_4$ 6a,b

R = CO$_2$Me
Ar = C$_6$H$_4$-*p*-OMe, a; C$_6$H$_4$-*p*-NO$_2$, b