Formation of β-Metallanaphthalenes by the Coupling of a Benzo-Iridacyclopentadiene with Olefins

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Supporting Information Placeholder

ABSTRACT: We have synthesized a new type of metallaaromatic complexes, namely the hydride-β-iridanaphthalenes $[Tp^{Me2}Ir(H)[C(CH_2R')\text{-}C_6H_4\text{-}o\text{-}C(R)=C(R)]$ (*benzo*-**3**-H,CH_2R'), by reaction of the benzo-iridacyclopentadiene $[Tp^{Me2}Ir[C_6H_4\text{-}o\text{-}C(R)=C(R)](OH_2)]$ (*benzo*-**1**-OH_2) (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate, R = CO_2Me) with olefins of the type CH_2=CHR' (R' = H, Me, C_6H_4-*p*-Me, OPh). These reactions are proposed to take place with the initial coordination of the olefin and isomerization to a carbene form, and subsequent insertion into the Ir–C(phenylic) bond and a final α-H elimination. The reaction with ethoxyethylene does not afford the corresponding derivative but rather it is obtained a mixture of three, isolable, compounds, which are proposed to derive from three different types of insertion of the olefin, one of them a typical 1,2-insertion, and the other two as (different) carbenes. The related reactions of the iridacyclopentadiene $[Tp^{Me2}Ir[C(R)=C(R)\text{-}C(R)=C(R)](OH_2)]$ (**1**-OH_2) are also discussed. For different combinations of precursor and olefin, we have observed differences in the regio- and stereochemistry of the insertions.

INTRODUCTION

Metalloaromatic species continue to attract the attention of both experimental[1] and theoretical chemists.[2] Since the first report in 1982 by Roper *et al.* of an osmabenzene,[3] several types of metallabenzenes have been reported. Many of them were obtained by serendipitous procedures, but several routes have been designed for the rational synthesis of derivatives of different metals, as for instance the reaction described by Haley *et al.*,[4] which uses the C_5 precursor *Z*-3-(2-iodovinyl)-1,2-diphenylcyclopropene and has been applied to the synthesis of Ir and Pt metallabenzenes. Almost all the metallabenzenes reported contain in the ring one or more substituents, in many cases as a consequence of the method of preparation, or as a tool to provide stability to the metallaaromatic ring.[2c] The simplest one, a parent metallabenzene without substituents on the C atoms of the aromatic ring, has been published recently and was generated by the coupling in an iridium compound of two molecules of acetylene and a CH_2 fragment of a molecule of CH_2Cl_2, the solvent of the reaction.[5] Higher metallaaromatics as metallanaphthalenes or metallaanthracenes are much less common.[6] For the case of metallanaphthalenes, to the best of our knowledge, only the three transition metal complexes shown in Figure 1 have been described to date[7] and, as can be observed, in all these cases the metal occupies the α-position of the aromatic ring.[8] The first derivative reported, the Tp^{Me2}-α-iridanaphthalene,[7a] was generated by the mild oxidation of a bicyclic derivative (Scheme 1), for which also exists an analogous without the fused benzo ring, and it also transforms upon oxidation into a metallaaromatic structure, the iridabenzene of Scheme 1. This indicates that the fused benzo ring does not alter essentially the reactivity of the metallacycle, and in this paper we make use of this observation.

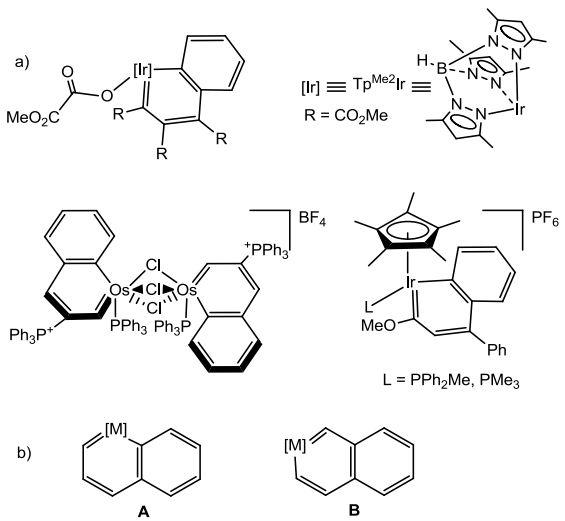
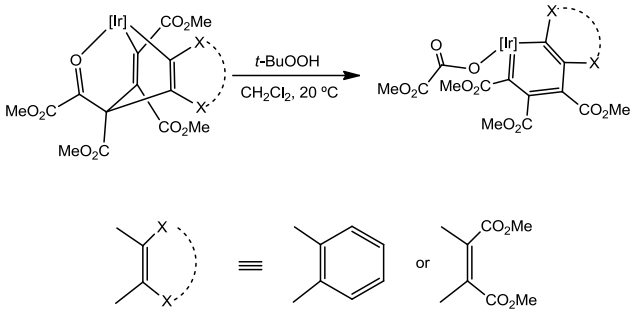


Figure 1. a) The three known metallanaphthalenes.[7] b) The structures of α-metallanaphthalenes (**A**) and β-metallanaphthalenes (**B**).

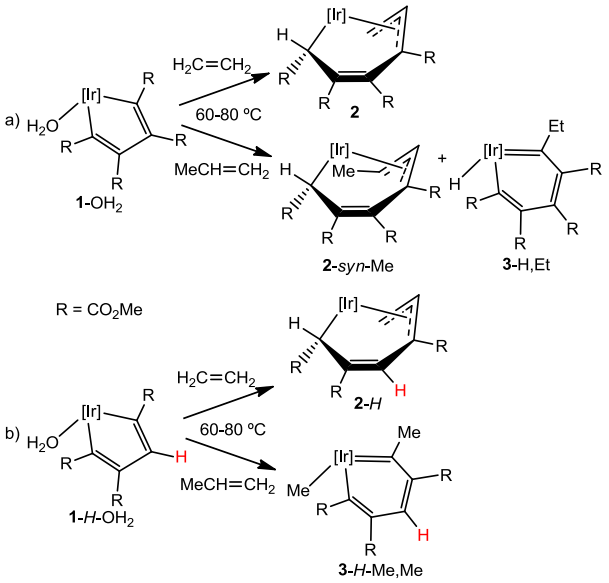
Scheme 1. Synthesis of iridanaphthalene and iridabenzene derivatives by oxidation of related bicyclic precursors.



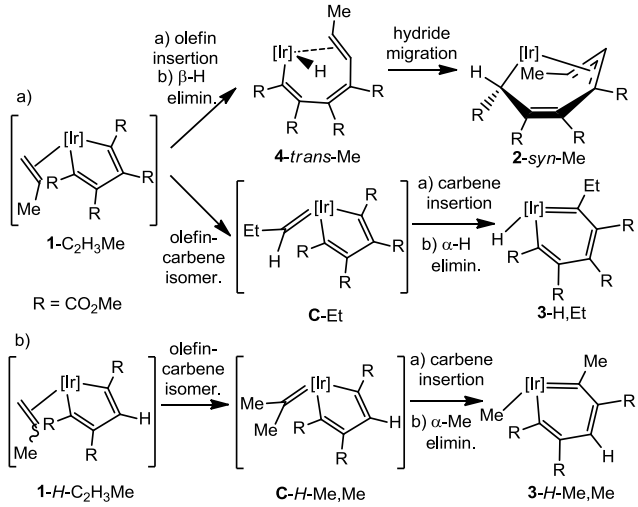
The osmanaphthalene of Figure 1 was prepared upon orthometallation of a Ph group on the γ position of the alkenylcarbyne ligand in the compound $[OsH\{\equiv C\text{-}C(PPh_3)=CHPh\}(PPh_3)_2Cl_2]BF_4$ upon heating under N_2.[7b] A somehow similar reaction leads to the formation of the Cp*Ir derivative, the precursor of the metallaaromatic ring being in this case an alkenylcarbene iridium complex of formula $[IrCp^*Cl\{=C(OMe)CH=CPh_2\}(PR_3)]PF_6$, which experiences orthometallation of one of the Ph substituents of the carbene ligand when treated with $AgPF_6$.[7c]

On the other hand, a few years ago we reported the reactions of the iridacyclopentadienes **1**-OH_2 and **1**-*H*-OH_2 with the small olefins ethylene and propene, to give the products shown in Scheme 2.[9] While the first species, the symmetrical **1**-OH_2, reacts with C_2H_4 forming the η^1-allyl-η^3-allyl complex **2** as the final reaction product, its reaction with C_2H_3Me gives a mixture of the related species **2**-*syn*-Me[10] and the hydride-iridabenzene **3**-H,Et. The corresponding reactions of the less substituted iridacyclopentadiene **1**-*H*-OH_2 give exclusively and respectively the η^1-allyl-η^3-allyl complex **2**-*H* and the unexpected methyliridabenzene **3**-*H*-Me,Me. The mechanisms proposed for the formation of the reaction products, starting with the unobserved propene adducts **1**-C_2H_3Me and **1**-*H*-C_2H_3Me (notice that in this case two stereoisomers may be formed), are summarized in Scheme 3,[9] where upon the initial insertion of the olefin leads to the η^1-allyl-η^3-allyl derivative while the metallaaromatic structures are proposed to be formed in processes in which the olefin converts into an alkylidene ligand before insertion.

Scheme 2. The final products observed in the reactions of the iridacyclopentadienes 1-OH_2 (a) and 1-*H*-OH_2 (b) with ethylene and propene.[9] In this and all other Schemes, complexes and intermediates labelled with *H* represent species whit an unsubstituted position in the metallacycle (H instead of CO_2Me). The numbering of iridabenzenes and iridanaphthalenes are followed by descriptors of the co-ligand (hydride or alkyl) directly bonded to the metal center and of the alkyl substituent in the position adjacent to Ir in the aromatic ring.



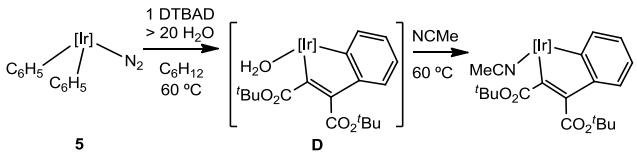
Scheme 3. Mechanisms proposed for the formation of 2-*syn*-Me, 3-H,Et and 3-*H*-Me,Me from the, initially formed but unobserved, propene adducts 1-C_2H_3Me (a) and 1-*H*-C_2H_3Me (b).[9] The substituents of the carbene ligands in the intermediates shown in this and other Schemes are specifically indicated, with the exception of H, after the corresponding label.



In view of the transformations shown in Schemes 1 and 2, we decided to explore the reactivity towards olefins of a related iridacyclopentadiene, in which one of the moieties –C(R)=C(R)–, present in **1**-OH_2, was replaced by a benzo, *o*-C_6H_4-, group. This precursor could serve as the starting material for the formation of metallanaphthalenes if reactions like those leading to compounds **3** were taking place. The appropriate starting metallacycle has been proposed to exist as an intermediate species in the synthesis of iridacycloheptatrienes formed by the reaction of $[Tp^{Me2}Ir(C_6H_5)_2(N_2)]$ (**5**) with 2 equiv. of dimethylacetylene dicarboxylate (DMAD).[11] In addition, some of us have reported the synthesis of the analogous benzoiridacyclopentadiene shown in Scheme 4, by the reaction of compound **5** with 1 equiv. of DTBAD (di(*tert*-butyl)acetylen dicarboxylate) in the presence of an excess of water (intended as stabilizing ligand). Nevertheless, the purported aquo complex is

very sensitive to oxygen and consequently the stabilization of the iridacycle requires the addition of another Lewis base such as NCMe.[12]

Scheme 4. Formation of the $CO_2{}^tBu$- substituted benzo-iridacyclopentadiene from the reaction of $[Tp^{Me2}Ir(C_6H_5)_2(N_2)]$ (5) with 1 equiv. of DTBAD in the presence of H_2O and its stabilization by NCMe.[12]

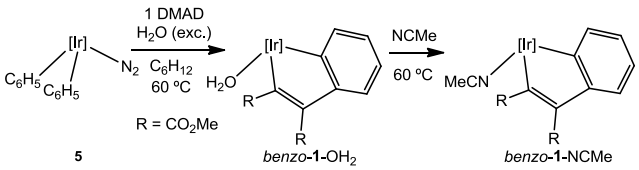


We have now observed that the $-CO_2Me$ derivative analogous to **D** is less prone to oxidation, and in this paper we report its isolation and the study of its reactions with the monosubstituted olefins CH_2=CHR' (R' = H, Me, C_6H_4-*p*-Me, OPh, OEt, SEt). For the sake of completeness, we have also studied the reactions of the metallacycle **1**-OH_2 with the additional olefins included in this contribution (R' = OPh, OEt, SEt), and compared the results. Some of these reactions have allowed the isolation of the first examples of transition metals β-metallanaphthalenes (Figure 1b).[8]

RESULTS AND DISCUSSION

Synthesis and characterization of $[Tp^{Me2}Ir[C_6H_4$-*o*-$C(R)=C(R)](OH_2)]$ (*benzo*-1-OH_2). As advanced above this aquo complex can be obtained in very good yield by the reaction of $[Tp^{Me2}Ir(C_6H_5)_2(N_2)]$ (**5**) with 1 equivalent of $MeO_2CC{\equiv}CCO_2Me$ (DMAD) in water-saturated C_6H_{12} at 60 °C (Scheme 5).[13] This species was completely characterized by NMR and thus the phenylic and vinylic Ir-bonded carbon nuclei resonate at 142.3 and 146.3 ppm respectively.

Scheme 5. Synthesis of the complex *benzo*-1-OH_2 and its substitution with NCMe.



As expected, the water ligand of *benzo*-**1**-OH_2 is highly labile and easily displaced by acetonitrile at 25 °C (CH_2Cl_2-NCMe, $t_{1/2}$ ≈ 2 h) to give the species *benzo*-**1**-NCMe (Scheme 5). This adduct has been characterized by single crystal X-ray crystallographic studies whose results are shown in Figure 2 as an ORTEP representation. The benzo-iridacyclopentadiene ring is almost planar and exhibits normal[9c,11,14] Ir–C bond distances of 2.035(5) (phenylic) and 2.039(5) Å respectively.

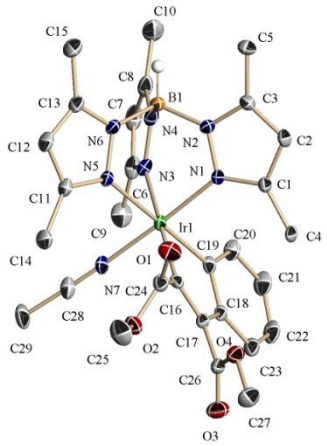
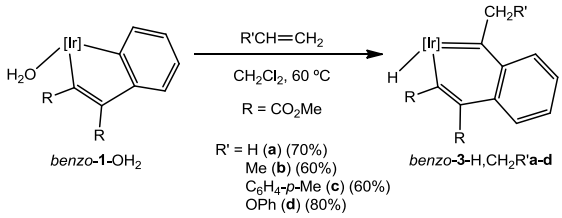


Figure 2. ORTEP representation of the species *benzo*-**1**-NCMe. Thermal ellipsoids are set at 30% probability and most H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ir1–C16 2.039(5), Ir1–C19 2.035(5), C16–C17 1.344(8), C17–C18 1.461(8), C18–C19 1.396(8), Ir1–N7 1.992(5), N7–C28 1.133(8), C28–C29 1.449(9), C19–Ir1–C16 78.4(2), Ir1–C16–C17 116.5(4), Ir1–C19–C18 115.5(4).

Reactivity of complex *benzo*-1-OH_2 towards the olefins CH_2=CHR' (R' = H, Me, C_6H_4-*p*-Me, OPh). Complex *benzo*-**1**-OH_2 reacted with an excess of the titled olefins giving in all cases, in high (spectroscopic) yields (60-80%), the hydride β-iridanaphthalenes *benzo*-**3**-H,CH_2R'**a-d** as the only isolable, in pure form, products by chromatography on silica gel (Scheme 6).

Scheme 6. Reactions of complex *benzo*-1-OH_2 with the olefins CH_2=CHR' (R' = H, Me, C_6H_4-*p*-Me, OPh). Spectroscopic yields are indicated in parentheses.



All these complexes have been completely characterized by the usual techniques and, in the case of the complexes *benzo*-**3**-H,CH_2R'**a,b** (R' = H, Me) also by X-ray crystallography (Figures 3 and S1). The Ir–C(CH_2R') carbon nuclei resonate in the 285-305 ppm interval while the signals for Ir–C(R) appear at *ca.* 155 ppm in the ^{13}C NMR spectra. These resonances are much further apart than those observed for the corresponding nuclei in the Tp^{Me2}-α-iridanaphthalene depicted in Figure 1 (255.0 and 177.9 ppm for the Ir–C(R) and the Ir–C(phenylic) respectively[7a]).This is probably due to the higher weight of the resonance forms in which the benzo ring is fully aromatic. In agreement with this is also the slightly longer distance of the Ir–C(R) bond with respect to the Ir–C(CH_2R'). Both of them are intermediate between single and double Ir–C bonds and, for the case of *benzo*-**3**-H,CH_3 have values of 1.987(6) and 1.900(6) Å, respectively. The iridium atoms show a deviation of *ca.* 0.7 Å with respect to the mean planes defined by the five carbon atoms that form the metallacyclic rings. This deviation is similar to

these observed in the previously reported metallanaphthalenes.[7] The C–C bonds of the IrC_5 fragment as well all the C–C distances of the fused benzene ring compare well with those found in naphthalene.[15]

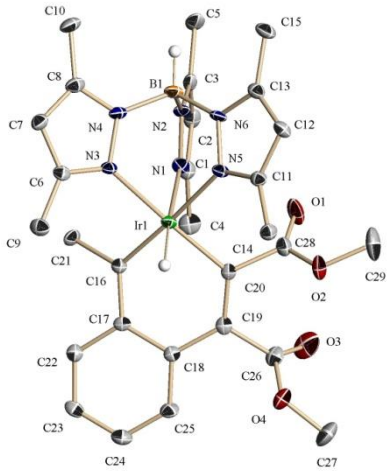
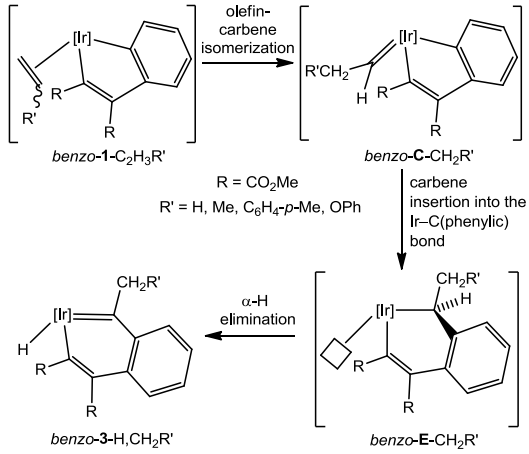


Figure 3. ORTEP representation of complex *benzo*-**3**-H,CH_3. Thermal ellipsoids are set at 30% probability and most H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ir1–C16 1.900(6), Ir1–C20 1.987(6), C16–C17 1.441(8), C17–C18 1.437(9), C18–C19 1.465(9), C19–C20 1.357(9); C16–Ir1–C20 89.1(3).

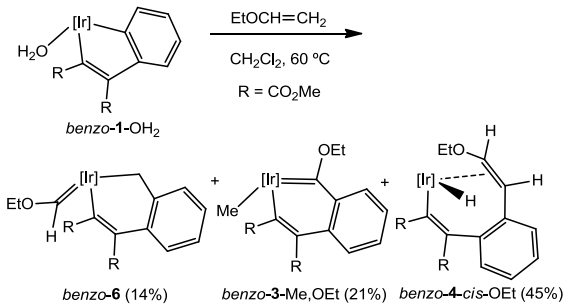
The mechanism proposed for the formation of these β-iridanaphthalenes, based on the analogy with refer. 9, is shown in Scheme 7. The olefin is proposed to coordinate (notice that, as was the case of the complex **1**-*H*-C_2H_3Me of the Introduction, the corresponding adduct may form as two stereoisomers) and transform into an alkylidene ligand, to insert selectively into one of the two different Ir–C bonds (as also happens in the case of Scheme 3b), in this case the Ir–C(phenylic) one. This regiochemical selectivity allows for the unprecedented formation of β-metallanaphthalenes, while the insertion into the Ir-alkenyl bond would have provided the α-iridanaphthalenes. Remarkably even ethylene, the olefin less prone to the isomerization, affords the corresponding β-iridanaphthalene unlike in the reactions of Scheme 2. We conclude, therefore, that the presence of the benzo moiety in the iridacyclopentadiene ring drives the insertion towards the Ir-C(phenylic) bond and also favours the olefin-to-alkylidene isomerization in the iridium coordination sphere.

Scheme 7. Mechanism propose for the formation of the β-iridanaphthalenes *benzo*-3-H,CH_2R' (R' = H, Me, C_6H_4-*p*-Me, OPh).



Reaction of complex *benzo*-1-OH_2 with CH_2=CHOEt. A much more complex reaction took place when complex *benzo*-1-OH_2 reacted with ethoxyethylene. Instead of the expected β-iridanaphthalene *benzo*-**3**-H,CH_2R' (R' = OEt) a mixture of the three main species shown in Scheme 8 was actually formed.

Scheme 8. Reaction of the species *benzo*-1-OH_2 with CH_2=CHOEt. Spectroscopic yields are shown in parentheses.



One of them, complex *benzo*-**6**, represents a new structural type in this study and contains the Fischer's carbene ligand =C(H)OEt and a six-membered, non-aromatic, iridacycle with an Ir–CH_2 bond. These two functionalities give rise to ^{13}C NMR resonances at 256.8 ($^1J_{CH}$ = 153 Hz)[16] and 3.8 ($^1J_{CH}$ = 130 Hz)[17] ppm respectively. The solid-state structure has been confirmed by X-ray crystallography (Figure 4).

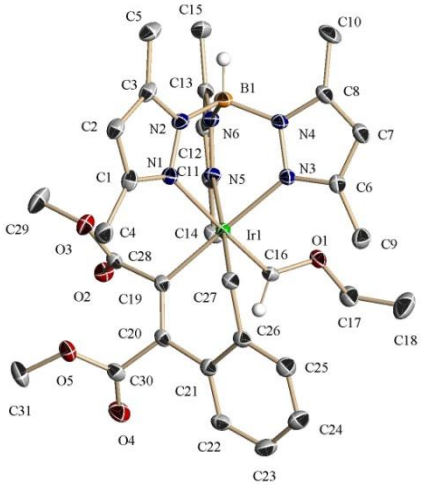
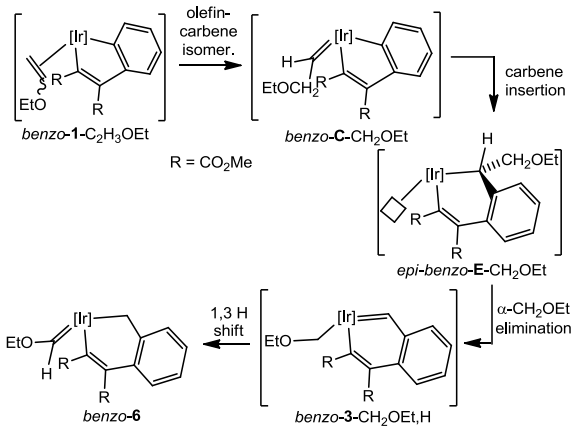


Figure 4. X-ray structure of complex *benzo*-**6**. Thermal ellipsoids are set at 30% probability and most H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ir1–C16 1.880(3), Ir1–C19 2.041(3), Ir1–C27 2.080(3), C19–C20 1.352(4), C20–C21 1.486(4), C21–C26 1.419(4), C26–C27 1.493(4), C19–Ir1–C27 83.04(11), C16–Ir1–C19 87.60(11), C16–Ir1–C27 92.91(11).

Formation of *benzo*-**6** is best explained as shown in Scheme 9 where we proposed an olefin-to-carbene isomerization identical to the invoked for CH_2=CHOPh (Scheme 7) but with the subsequent insertion into the Ir–C(phenylic) bond having the opposite stereoselectivity. This leads to the intermediate *epi*-*benzo*-**E**-CH_2OEt, from which a α-CH_2OEt elimination process[9a,b,18] gives rise to the unobserved intermediate *benzo*-**3**-CH_2OEt,H which eventually experiences a simple 1,3 H shift. Clearly, Fischer's type carbenes in these Tp^{Me2}Ir(III) systems are sufficiently more stable thermodynamically than Schrock's ones[19] to overcome the partial loss of aromaticity associated with the metallanaphthalene *benzo*-**3**-CH_2OEt,H to *benzo*-**6** transformation.

Scheme 9. Mechanism proposed for the formation of complex *benzo*-6.



The structure of the methyl-β-iridanaphthalene *benzo*-**3**-Me,OEt was deduced from the NMR spectral data obtained. Thus, the carbon nucleus of the methyl ligand resonates at -18.4 ppm while the iridium-bonded carbon of the C(OEt) moiety does so at 256.4 ppm *i.e.* at higher field than those collected for species *benzo*-**3**-H,CH_2R'. This displacement is clearly the result of the different electron donating properties of the OEt and the CH_2R' substituents on the corresponding carbons. Complex *benzo*-**3**-Me,OEt was also characterized by X-ray diffraction and its structure is shown in Figure 5.

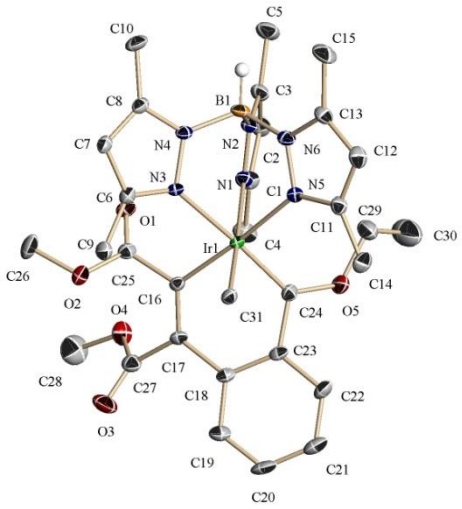
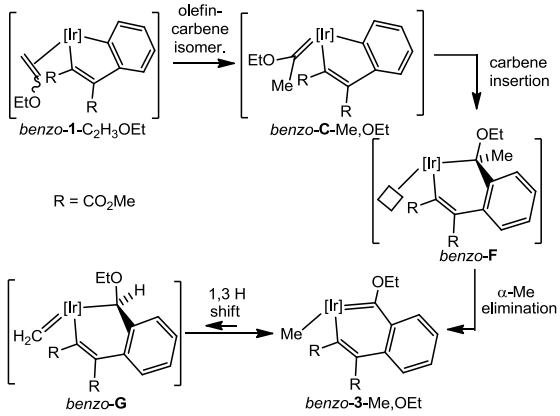


Figure 5. ORTEP representation of complex *benzo*-**3**-Me,OEt. Thermal ellipsoids are set at 30% probability and most H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ir1–C24 1.907(5), Ir1–C16 2.026(5), Ir1–C31 2.095(4), C16–C17 1.343(7), C17–C18 1.479(7), C18–C23 1.396(7), C23–C24 1.475(7), C16–Ir1–C24 87.2(2), C24–Ir1–C31 88.2(2), C16–Ir1–C31 91.15(2).

The structure of *benzo*-**3**-Me,OEt is reminiscent of that of complex **3**-*H*-Me,Me (Schemes 2 and 3), with a Me ligand generated from the olefin, and consequently its formation can be explained as shown in Scheme 10: the olefin-to-alkylidene isomerization in the Ir(III) coordination sphere is of the type CH_2=CHOEt → =C(Me)OEt with formation of intermediate *benzo*-**F**, following the stereoselective insertion of the carbene ligand into the Ir–C(phenylic) bond, and a final α-Me elimination event. Notice that, in this case, the purported methylidene species *benzo*-**G** resulting from a 1,3 H shift from the alkyl to the carbene ligands is not favoured thermodynamically, for the reasons commented above for complex *benzo*-**6** (see Scheme 9), and therefore *benzo*-**G** is not observed among the reaction products.

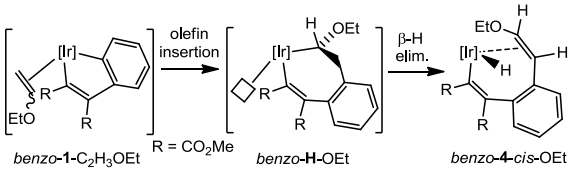
Scheme 10. Proposed mechanism for the formation of the methyl-β-iridanaphthalene complex *benzo*-3-Me,OEt.



Lastly, the third product isolated in the reaction shown in Scheme 8 is the hydride-olefin complex *benzo*-**4**-*cis*-OEt in which the Ir(III) center completes the 18 e⁻ count by coordination to

the cisoid olefin terminus of the -C_6H_4-*o*-CH=CHOEt chain. This species is closely related to **4**-*trans*-Me depicted in Scheme 3 of the Introduction and is clearly the result of the olefin insertion into the Ir–C(phenylic) bond of complex *benzo*-**1**-OH_2 followed by a β-H elimination event (Scheme 11). Interestingly in both cases the regioselectivity of the insertion of both propene and CH_2=CHOEt is the same but the stereoselectivity is just opposite, with the latter giving rise to a cisoid disposition of the two C–H sp^2 bonds ($^3J_{HH}$ = 9.0 Hz and NOESY evidence). Obviously the hydride migration experienced by species **4**-*trans*-Me in Scheme 3 is prevented in complex *benzo*-**4**-*cis*-OEt as this process will result in the loss of the aromatic stability of the benzo ring.

Scheme 11. Mechanistic proposal for the formation of complex *benzo*-4-*cis*-OEt.

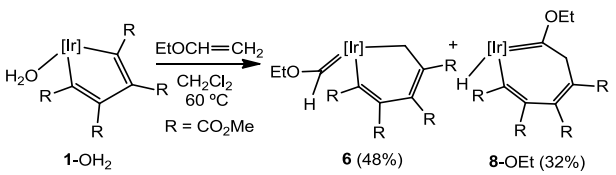


The experimental results of Schemes 6 and 8, and the mechanistic proposals of Schemes 7, 9-11, suggest that the OEt substituent disfavours to some extent the olefin-to-carbene rearrangement compared to OPh.

Reaction of complex 1-OH_2 with the olefins CH_2=CHR' (R' = OEt, OPh). To complete the comparative study of the reactivity of *benzo*-**1**-OH_2 and **1**-OH_2 towards olefins, we carried out the reactions of the latter complex with the olefins CH_2=CHR' (OEt, OPh) which had not been studied before.

Complex **1**-OH_2 reacted with ethoxyethylene with formation of mainly two products, namely **6** and **8**-OEt (Scheme 12). The first one is the corresponding carbene-iridacyclohexadiene analogue to *benzo*-**6** and has been completely characterized by NMR spectroscopy and single crystal X-ray studies (Figure S2) but the second one, the hydride-Fischer's carbene **8**-OEt represents a new type of structure in this system.

Scheme 12. Reaction of complex 1-OH_2 with CH_2=CHOEt. Spectroscopic yields are shown in parentheses.



Complex **8**-OEt has been completely characterized by NMR spectroscopy and thus the $^{13}C\{^1H\}$ NMR spectrum shows resonances at 277.7 and 61.1 ppm for the Ir–C(OEt) and C–CH_2–C nuclei of the iridacycle, respectively. Its structure has been confirmed by X-ray diffraction and an ORTEP view of **8**-OEt is shown in Figure 6.

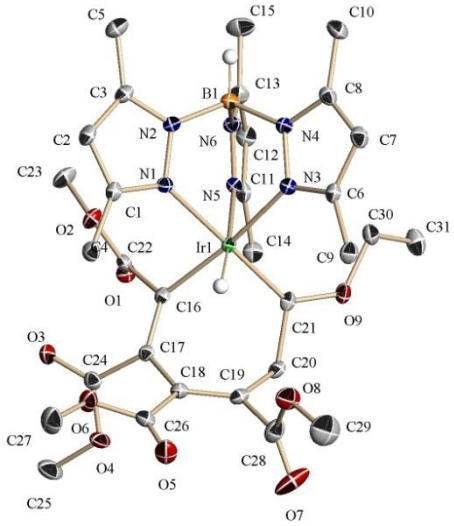
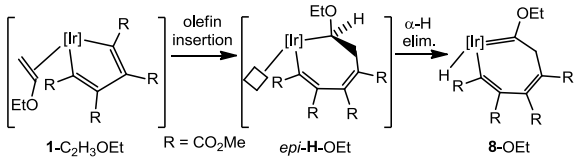


Figure 6. X-ray structure of complex **8**-OEt. Thermal ellipsoids are set at 30% probability and most H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ir1–C16 2.035(3), Ir1–C21 1.917(3), C16–C17 1.354(4), C17–C18 1.480(4), C18–C19 1.338(4), C19–C20 1.497(4), C20–C21 1.534(4), Ir1–H 1.577(18), C16–Ir1–C21 90.49(12).

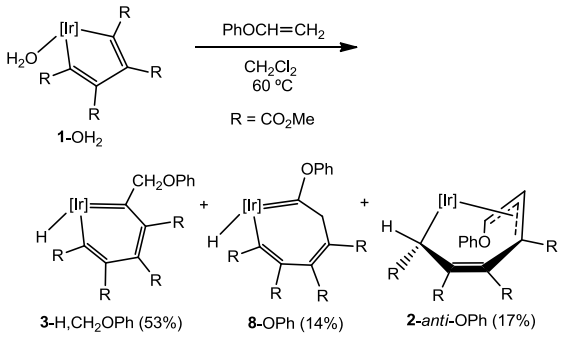
While the formation of **6** does not need further comments (see Scheme 9), the simplest mechanism that can explain that of complex **8**-OEt is shown in Scheme 13. It is proposed that the olefin inserts into an Ir–C bond giving the stereoisomer intermediate *epi*-**H**-OEt, so named to shown its relationship with the intermediate *benzo*-**H**-OEt of Scheme 11, which transforms into the Fischer's carbene **8**-OEt through a α-H elimination process. This mechanistic proposal implies that the α-H elimination is preferred in this case over the β-H corresponding process[20] and this strongly contrasts with the opposite selectivity (β-H elimination preferred over α-H elimination) needed for the formation of the complex **4**-*trans*-Me, the result of the corresponding reaction with propene commented in the Introduction (Scheme 3).

Scheme 13. Mechanism proposed for the formation of complex 8-OEt.



The three products of the reaction of complex **1**-OH_2 with phenoxyethylene are shown in Scheme 14. The outcome of this reaction, as compared with these already commented, is in accord with the high sensitivity of these systems to changes in both the starting aquo-complex and/or the reacting olefin.

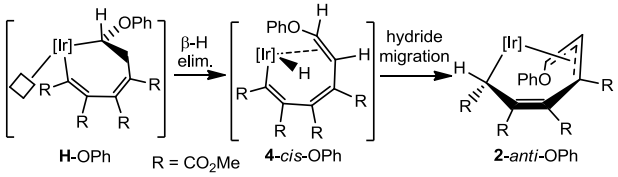
Scheme 14. Reaction of complex 1-OH_2 with CH_2=CHOPh. Spectroscopic yields are presented in parentheses.



In addition to the hydride-iridabenzene **3**-H,CH_2OPh (analogous to *benzo*-**3**-H,CH_2OPh and hence the result of an olefin-to-carbene isomerization and insertion, see Schemes 6 and 7), there were formed two other products that derived from olefin insertion events, the non-aromatic species hydride-carbene, **8**-OPh, and the η^1-allyl-η^3-allyl complex **2**-*anti*-OPh. Remarkably, the latter species differs in stereochemistry (Scheme 15) with the related species **2**-*syn*-Me obtained in the reaction of **1**-OH_2 with propene (Scheme 2) and this outcome implies that the, unobserved, intermediate hydride **4**-*cis*-OPh has the same stereochemistry than the thermally stable *benzo*-**4**-*cis*-OEt (Scheme 8).

Comparing the results of the reactions of **1**-OH_2 and *benzo*-**1**-OH_2 with the two olefins CH_2=CHR' (R' = OEt, OPh) and in particular the nature of derivatives **6** and *benzo*-**6** (for R' = OEt) and **3**-H,CH_2OPh and *benzo*-**3**-H,CH_2OPh (for R' = OPh), all of them deriving from carbene insertion processes, we have to infer that subtle differences between the OEt and OPh substituents are the responsible for the opposite stereochemistry in the insertion of the carbene =C(H)(OR') into the Ir–C bonds of the starting iridacyclopentadienes.

Scheme 15. Mechanism proposed for the formation of complex 2-*anti*-OPh.



The three compounds have all been unequivocally characterized by NMR spectroscopy and other techniques including single crystal X-ray studies for the case of **3**-H,CH_2OPh (Figure 7).

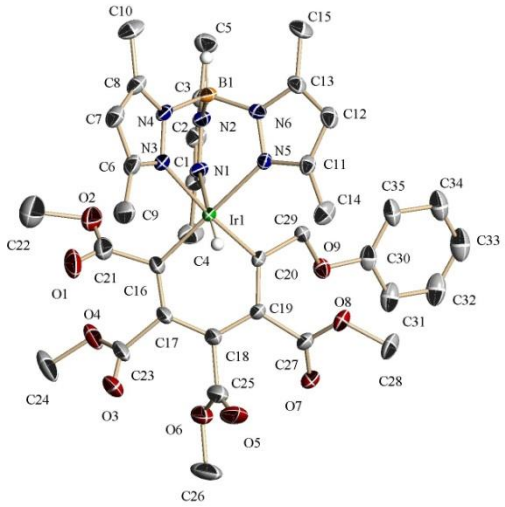
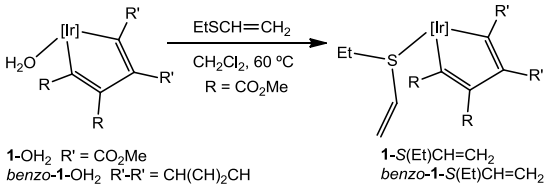


Figure 7. ORTEP representation of complex **3**-H,CH_2OPh. Thermal ellipsoids are set at 30% probability and most H atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Ir1–C16 1.981(6), Ir1–C20 1.929(5), C16–C17 1.355(9), C17–C18 1.414(9), C18–C19 1.364(8), C19–C20 1.411(8), Ir1–H 1.44(2), C16–Ir1–C20 88.3(3).

Reactions of complexes 1-OH_2 and *benzo*-1-OH_2 with CH_2=CHSEt. Finally, the reactions of complexes**1**-OH_2 and *benzo*-**1**-OH_2 with a sulphur-containing olefin, namely ethyl vinyl sulphide, were investigated. In both cases, at 60 °C, simple adducts bounded to the Ir center *via* the sulphur atom were obtained (Scheme 16), from which no further transformations related to their oxygen counterpart were observed. These species were found to be stable up to 120 °C.

Scheme 16. Reactivity of complexes 1-OH_2 and *benzo*-1-OH_2 towards CH_2=CHSEt.



The structure of complex **1**-S(Et)CH=CH_2 was confirmed by X-ray diffraction studies and its ORTEP view is shown in Figure 8.

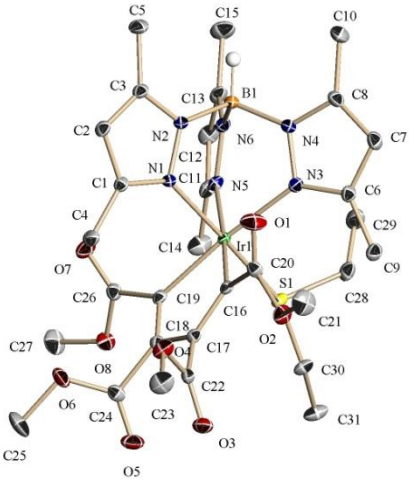


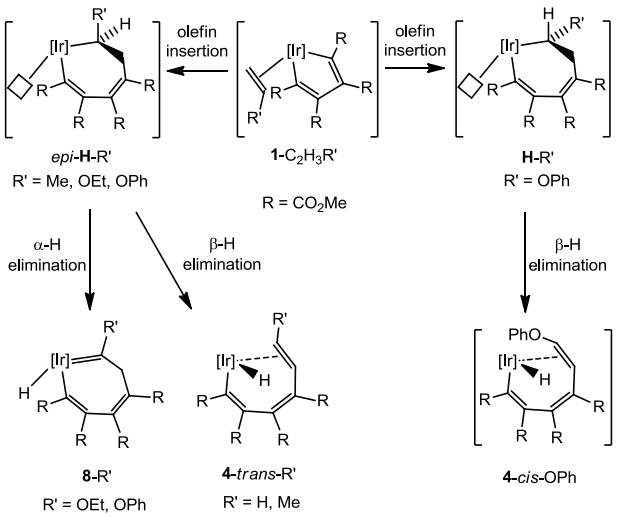
Figure 8. ORTEP representation of complex **1**-S(Et)CH=CH_2. Thermal ellipsoids are set at 30% probability and most H atoms are omitted for clarity. Selected bond distances (Å) and angles (º): Ir1–C16 2.012(2), Ir1–C19 2.043(2), Ir1–S1 2.3292(6), C16–C17 1.357(3), C17–C18 1.459(3), C18–C19 1.362(3), C16–Ir1–C19 79.02(9), C16–Ir1–S1 96.15(6), C19–Ir1–S1 83.47(7).

CONCLUSIONS

The reactions of compound *benzo*-**1**-OH_2 with olefins have allowed the isolation of the first examples in the literature, to our knowledge, of β-metallanaphthalenes of a transition element. The results are explained by the isomerisation of the corresponding olefins into a carbene ligand before insertion into the Ir–C(phenylic) bond. This reaction is general for a series of olefins CH_2=CHR' (R' = H, Me, C_6H_4-*p*-Me, OPh), but for the case of ethoxyethylene, the isomerization olefin-to-carbene seems to be less favoured and furthermore the insertion process takes place with the opposite stereochemistry and subsequently the reaction rather produces an iridacyclohexadiene with an ethoxycarbene co-ligand.

A comparative study carried out with the iridacyclopentadiene **1**-OH_2 shows that while, in general, it can be said that the presence of the benzo moiety in the iridacyclopentadiene ring favours the olefin-to-carbene isomerization in the iridium coordination sphere, the results of these reactions are highly dependent to changes in the nature of both the starting aquo complex and the olefin, as was also observed previously for **1**-OH_2 and the less substituted **1**-*H* (see refer. 9). Thus, in some instances, the reactions observed are the result of the simple insertion of the corresponding olefin (*i.e.* without previous transformation into carbene ligands), but in a process which can take place with variable stereochemistry. Scheme 17 summarizes the differences between the stereochemical preference of the CH_2=CHR' (R' = H, Me, OEt, OPh) insertion into the Ir–C bond of **1**-OH_2 depending on R', and also a comparison of the elimination processes, α-H *vs.* β-H, in intermediates *epi*-**H**-R' (the stereochemistry in **H**-R' doesn't allow for the α-H elimination process). While for the case of R' = OPh both these intermediates are proposed to form in view of the products obtained in this reaction (Scheme 14), for R' = Me and OEt, only *epi*-**H**-R' seems to form. From these latter species, the α-H elimination is much more favoured when R' = OEt or OPh but for the case of propene the β-H elimination is preferred, yielding a derivative related to the compound formed with ethylene (the precursor of compound **2** of Scheme 2).

Scheme 17. Stereoselectivity of the insertion of the CH_2=CHR' (R' = Me, OEt, OPh) olefins into the Ir–C(phenylic) bond of the iridacyclopentadiene 1-C_2H_3R' as a function of the nature of the R' substituent and the consequent transformation of the corresponding intermediates depending of the α-H *vs.* β-H elimination processes. The *trans* label in 4 is only for R' = Me.



EXPERIMENTAL SECTION

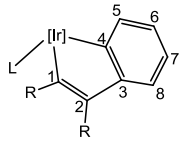
General Considerations. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). IR spectroscopy was performed on a Bruker Vector 22 spectrometer. NMR spectroscopy was performed on Bruker Avance DRX-500, DRX-400, DPX-300 and Avance^{III}-400/R spectrometers; the spectra were referenced to external $SiMe_4$ (δ = 0 ppm) by using residual protonated solvent peaks (^{1}H) or to characteristic resonances of the solvent nuclei as internal standards (^{13}C). Spectroscopic assignments were performed by routine 1D and 2D NMR experiments where appropriate. All of the $^3J_{HH}$ aromatic coupling constants were about 7.5 Hz. The assignments for the NMR Tp^{Me2} signals were labelled as CH_{pz}, Me_{pz} and C_{qpz} for the CH of the pyrazolyl ring, methyl substituent and quaternary carbons respectively. Almost all of the manipulations were performed under a dry, oxygen-free nitrogen atmosphere, by following conventional Schlenk techniques. Complexes **1**-OH_2 and [Tp^{Me2}Ir(C_6H_5)$_2$(N_2)] (**5**) were synthesized according to literature procedures.[21,22]

X-ray structure analysis of complexes *benzo*-1-NCMe, *benzo*-3-CH_2R'a,b (R' = H, Me), *benzo*-6, *benzo*-3-Me,OEt, 6, 8-OEt, 3-H,CH_2OPh and *benzo*-1-S(Et)CH=CH_2. 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 K_α) = 0.71073 Å, by means of ω and φ scans with a width of 0.50 degree. The datawere reduced (SAINT)[23] and corrected for absorption effects by the multi-scan method (SADABS).[24] The structures were solved by direct methods (SIR-2002)[25] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12)[26] 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 (*U*iso values) fixed at 1.2

times (1.5 times for methyl groups) those *U*eq values of the corresponding attached atoms.

A summary of the crystallographic data and structure refinement of these new crystalline compounds is given at the end of the experimental and spectroscopic data for each compound.

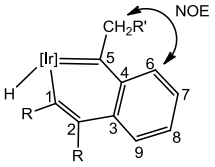
Synthesis and characterization of complex *benzo*-1-L (L = OH_2). To a stirred suspension of $[Tp^{Me2}Ir(C_6H_5)_2(N_2)]$ (**5**) in C_6H_{12} (0.50 g, 0.74 mmol; 10 mL) was added DMAD (92 μL, 0.74 mmol) and H_2O (~280 μL, 15.6 mmol) and the mixture stirred at 60 °C for 12 h. The solvent was removed under vacuum and the resultant solid washed with pentane (3x5 mL). The ^{1}H NMR spectrum of the resulting dark yellow solid was in accord with the formation of compound *benzo*-**1**-OH_2 in almost quantitative spectroscopic yield. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 7.09 (d, 1 H, C^5H), 7.06 (d, 1 H, C^8H), 6.82 (t, 1 H, C^7H), 6.68 (t, 1 H, C^6H), 5.87, 5.80, 5.44 (s, 1 H each, 3 CH_{pz}), 4.01 (s, 2 H, H_2O), 3.72, 3.33 (s, 3 H each, 2 CO_2Me), 2.46, 2.44, 2.40, 2.07, 2.01, 1.36 (s, 3 H each, 6 Me_{pz}). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 175.0, 170.8 (CO_2Me), 156.7 (C^3), 155.1, 150.6, 143.8, 143.4 (C_{qpz}), 152.5 (C^2), 146.3 (C^1), 142.3 (C^4), 137.9 (C^5), 123.1 (C^6),122.3 (C^7, C^8), 107.5, 107.1, 106.3 (CH_{pz}), 52.0, 50.7 (CO_2*Me*), 14.3, 13.2, 12.8, 12.5, 11.9 (Me_{pz}). HRMS (FAB): *m*/*z* calcd. for $C_{27}H_{34}BN_6O_5IrNa$: 749.2211; found: 749.2197.



Synthesis and characterization of complex *benzo*-1-L (L = NCMe). A suspension of *benzo*-**1**-OH_2 in MeCN (0.10 g, 0.14 mmol; 10 mL) was stirred at 60 °C for 3 h. Thereafter the solvent was removed under vacuum and the ^{1}H NMR spectrum of the crude of the reaction was in accord with the formation of compound *benzo*-**1**-NCMe in almost quantitative spectroscopic yield. This complex was purified, as a dark yellow solid, by column chromatography on silica gel using a mixture of hexane/Et_2O (1:1) → Et_2O as eluent. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 7.34 (d, 1 H, C^8H), 7.13 (d, 1 H, C^5H), 6.94 (t, 1 H, C^7H), 6.73 (t, 1 H, C^6H), 5.89, 5.82, 5.49 (s, 1 H each, 3 CH_{pz}), 3.84, 3.47 (s, 3 H each, 2 CO_2Me), 2.43, 2.42, 2.37, 2.23, 1.37 (s, 1:1:1:2:1, 6 Me_{pz}), 2.34 (s, 3 H, NCMe). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 174.3, 167.9 (CO_2Me), 156.3 (C^3), 154.3, 150.3, 150.2, 143.5, 143.3, 142.6 (C_{qpz}), 150.0 (C^2), 145.2 (C^1), 142.1 (C^4), 136.2 (C^5), 123.4 (C^6), 122.6 (C^7), 122.3 (C^8), 114.7 (NCMe), 107.8, 107.1, 106.3 (CH_{pz}), 51.4, 50.7 (CO_2*Me*), 15.1, 13.8, 13.2, 12.6, 11.9 (Me_{pz}), 3.9 ($^1J_{CH}$ = 138 Hz, NC*Me*). HRMS (FAB): *m*/*z* calcd. for $C_{29}H_{35}BN_7O_4IrNa$: 772.2371; found: 772.2386. Crystal data for *benzo*-**1**-NCMe: $2(C_{29}H_{35}BIrN_7O_4)\bullet CH_2Cl_2$, *M* = 1582.23, monoclinic, *a* = 11.1035(5) Å, *b* = 19.2926(10) Å, *c* = 15.4230(7) Å, *α* = 90.00°, *β* = 100.9400(10)°, *γ* = 90.00°, *V* = 3243.8(3) Å^3, *T* = 173(2) K, space group $P2_1/n$, *Z* = 2, *μ* = 4.244 mm^{-1}, 34098 reflections measured, 5870 independent reflections (R_{int} = 0.0332). The final R_1 values were 0.0332 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0949 ($I > 2\sigma(I)$). The final R_1 values were 0.0412 (all data). The final $wR(F^2)$ values were 0.0992 (all data). The goodness of fit on F^2 was 1.077. CCDC 1017019.

Synthesis and characterization of complex *benzo*-3-H,CH_2R'a (R' = H). A stirred solution of *benzo*-**1**-OH_2 (0.10 g, 0.14 mmol) in CH_2Cl_2 (5 mL) was placed in a Fischer-Porter vessel and heated, under 2 atm of C_2H_4, at 60 °C for 12 h. The solvent was removed under vacuum and a ^{1}H NMR spectrum of the crude of the reaction showed the presence of compound *benzo*-**3**-H,Me in *ca.* 70% spectroscopic yield. This complex was purified, as a green solid, by column chromatography on silica gel using a mixture of hexane/Et_2O (2:1) as eluent. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 7.95 (d, 1 H, C^9H), 7.79 (d, 1 H, C^6H), 7.75 (t, 1 H, C^8H), 7.24 (t, 1 H, C^7H), 5.80, 5.79, 5.75 (s, 1 H each, 3 CH_{pz}), 3.77, 3.12 (s, 3 H each, 2 CO_2Me), 2.52, 2.45, 2.44, 2.22, 1.83, 1.35 (s, 3 H each, 6 Me_{pz}), 1.94 (s, 3 H, CH_3), -20.47 (s, 1 H, Ir–H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 294.2 (C^5), 177.1, 170.3 (CO_2Me), 156.0 (C^1), 153.9 (C^4), 153.7, 150.1, 149.5, 145.2, 144.5, 142.7 (C_{qpz}), 139.9 (C^3), 133.7 (C^2), 132.6 (C^8), 129.6 (C^9), 126.2 (C^7), 118.5 (C^6), 106.3, 105.8, 105.4 (CH_{pz}), 52.0, 50.8 (CO_2*Me*), 49.0 ($^1J_{CH}$ = 127 Hz, CH_3), 15.9, 15.4, 13.1, 12.9, 12.8, 12.7 (Me_{pz}). Elemental analysis calcd. (%) for $C_{29}H_{36}BIrN_6O_4$: C 47.3; H 4.9; N 11.4; found: C 47.1; H 5.1; N 11.1.

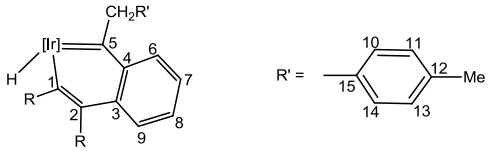
Crystal data for *benzo*-**3**-H,Me: $C_{29}H_{36}BIrN_6O_4$, *M* = 735.65, monoclinic, *a* = 25.5107(14) Å, *b* = 22.5877(11) Å, *c* = 15.2104(8) Å, *α* = 90.00°, *β* = 90.6890(10)°, *γ* = 90.00°, *V* = 8764.0(8) Å^3, *T* = 173(2) K, space group $P2_1/c$, *Z* = 12, *μ* = 4.616 mm^{-1}, 99523 reflections measured, 15827 independent reflections (R_{int} = 0.0550). The final R_1 values were 0.0380 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0895 ($I > 2\sigma(I)$). The final R_1 values were 0.0648 (all data). The final $wR(F^2)$ values were 0.0989 (all data). The goodness of fit on F^2 was 1.097. CCDC 1017021.



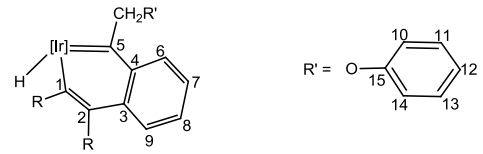
Synthesis and characterization of complex *benzo*-3-H,CH_2R'b (R' = Me). A stirred solution of *benzo*-1-OH_2 (0.10 g, 0.14 mmol) in CH_2Cl_2 (5 mL) was placed in a Fischer-Porter vessel and heated, under 2 atm of C_3H_8, at 60 °C for 12 h. The solvent was removed under vacuum and the ^{1}H NMR spectrum of the crude of the reaction showed formation of compound *benzo*-3-H,Et in *ca.* 60% spectroscopic yield. This complex was purified, as a green solid, by column chromatography on silica gel using a mixture of hexane/Et_2O (3:1) as eluent. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 8.00 (d, 1 H, C^9H), 7.69 (t, 1 H, C^8H), 7.64 (d, 1 H, C^6H), 7.21 (t, 1 H, C^7H), 5.78, 5.76, 5.75 (s, 1 H each, 3 CH_{pz}), 3.78, 3.15 (s, 3 H each, 2 CO_2Me), 3.74, 1.48 (m, 1 H each, CH_2 (Et)), 2.52, 2.45, 2.41, 2.17, 1.85, 1.47 (s, 3 H each, 6 Me_{pz}), 0.95 (t, 3 H, $^3J_{HH}$ = 7.5 Hz, CH_3(Et)), -20.64 (s, 1 H, Ir–H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 302.1 (C^5), 176.8, 170.4 (CO_2Me), 155.4 (C^1), 152.2 (C^4), 153.5, 150.2, 150.1, 145.1, 144.5, 143.0 (C_{qpz}), 140.5 (C^3), 134.2 (C^2), 131.9 (C^8), 130.0 (C^9), 125.7 (C^7), 118.7 (C^6), 106.2, 105.8, 105.3 (CH_{pz}), 53.8 (CH_2), 52.0, 50.8 (CO_2*Me*), 15.8, 15.7, 14.3, 12.9, 12.8, 12.7 (Me_{pz}), 11.9 (CH_3). HRMS (FAB): *m*/*z* calcd. for $C_{30}H_{38}BN_6O_4IrNa$: 772.2575; found: 772.2574. Elemental analysis calcd. (%) for $C_{30}H_{38}BIrN_6O_4$: C 48.1; H 5.1; N 11.2; found: C 48.0; H 5.1; N 11.1. Crystal data for *benzo*-**3**-H,Et: $C_{30}H_{38}BIrN_6O_4$, *M* = 749.67, triclinic, *a* = 10.8738(4) Å, *b* = 11.0633(5) Å, *c* = 13.0304(5) Å, *α* = 84.9390(10)°, *β* = 73.7790(9)°, *γ* = 89.6870(10)°, *V* = 1498.99(11) Å^3, *T* = 173(2) K, space group $P\bar{1}$, *Z* = 2, *μ* = 4.499 mm^{-1}, 26597 reflections measured, 5385 independent reflections (R_{int} = 0.0265). The final R_1 values were 0.0161 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0396 ($I > 2\sigma(I)$). The final R_1 values were 0.0183 (all data). The final $wR(F^2)$ values were 0.0400 (all data). The goodness of fit on F^2 was 1.064. CCDC 1017020.

Synthesis and characterization of complex *benzo*-3-H,CH_2R'c (R' = C_6H_4-*p*-Me). To a stirred solution of *benzo*-**1**-OH_2 in CH_2Cl_2 (0.15 gr, 0.21 mmol; 6 mL) was added *p*-methyl styrene (80.6μL, 0.62 mmol) and heated at 60 °C for 3 h. The solvent was removed under vacuum and the ^{1}H NMR spectrum of the crude of the reaction showed formation of complex *benzo*-**3**-H,CH_2R'**c** in *ca.* 60% spectroscopic yield. This complex was purified, as a green solid, by column chromatography on silica gel using a mixture of pentane/Et_2O (3:1) → (2:1) as eluent. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 7.97 (d, 1 H, C^9H), 7.63 (t, 1 H, C^8H), 7.48 (d, 1 H, C^6H), 7.00 (t, 1 H, C^7H), 6.79 (d, 2 H, C^{11}H, C^{13}H), 6.49 (d, 2 H, C^{10}H, C^{14}H), 5.83, 5.74, 5.59 (s, 1 H each, 3 CH_{pz}), 4.68, 2.73 (d, 1 H each, $^2J_{HH}$ = 18.7 Hz, CH_2), 3.76, 3.10 (s, 3 H each, 2 CO_2Me), 2.50, 2.48, 2.40, 2.15, 1.91, 1.07 (s, 3 H each, 6 Me_{pz}), 2.17 (s, 3 H, Me),
-20.72 ppm (s, 1 H, Ir–H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 295.3

(C^5), 176.7, 170.6 (CO_2Me), 155.4 (C^1), 154.4 (C^4), 153.7, 151.0, 150.3, 145.2, 144.8, 143.2 (C_{qpz}), 140.6 (C^3), 135.4 (C^{12}), 134.9 (C^2), 133.6 (C^{15}), 131.9 (C^8), 130.0 (C^9), 129.8 (C^{10}, C^{14}), 128.9 (C^{11}, C^{13}), 125.4 (C^7), 119.5 (C^6), 106.4, 106.3, 105.4 (CH_{pz}), 66.3 ($^1J_{CH}$ = 121, 133 Hz, CH_2), 52.2, 51.0 (CO_2Me), 21.2 ($^1J_{CH}$ = 126 Hz, Me), 16.0, 15.7, 14.1, 13.1, 13.0, 12.0 (Me_{pz}). Elemental analysis calcd. (%) for $C_{36}H_{42}BIrN_6O_4$: C 52.4; H 5.1; N 10.2; found: C 52.5; H 5.2; N 9.9.

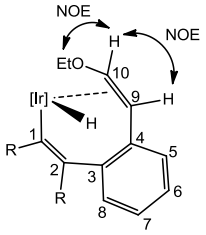


Synthesis and characterization of complex *benzo*-3-H,CH_2R'd (R' = OPh). To a stirred solution of *benzo*-**1**-OH_2 in CH_2Cl_2 (0.15 gr, 0.21 mmol; 7 mL) was added PhOCH=CH_2 (78.8μL, 0.6 mmol) and heated at 60 °C for 1 h. The solvent was removed under vacuum and the ^{1}H NMR spectrum of the crude of the reaction showed formation of complex*benzo*-**3**-H,CH_2R'd in *ca.* 80% spectroscopic yield. This complex was purified, as a green solid, by column chromatography on silica gel using a mixture of pentane/Et_2O (4:1) → (1:1) as eluent. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 8.00 (d, 1 H, C^9H), 7.75 (t, 1 H, C^8H), 7.67 (d, 1 H, C^6H), 7.18 (t, 2 H, C^{11}H, C^{13}H), 7.13 (t, 1 H, C^7H), 6.89 (t, 1 H, C^{12}H), 6.63 (d, 2 H, C^{10}H, C^{14}H), 5.81, 5.78, 5.63 (s, 1 H each, 3 CH_{pz}), 4.87, 3.23 (d, 1 H each, $^2J_{HH}$ = 17.2 Hz, CH_2O), 3.76, 3.10 (s, 3 H each, 2 CO_2Me), 2.49, 2.47, 2.42, 2.20, 1.88, 1.38 (s, 3 H each, 6 Me_{pz}), -20.58 (s, 1 H, Ir–H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 285.9 (C^5), 176.8, 170.0 (CO_2Me), 158.0 (C^{15}), 155.5 (C^1), 153.7, 150.3, 149.8, 145.2, 144.9, 142.7 (C_{qpz}), 151.1 (C^4), 140.9 (C^3), 134.2 (C^2), 132.7 (C^8), 129.6 (C^9), 129.4 (C^{11},C^{13}), 125.4 (C^7), 121.4 (C^6), 121.1 (C^{12}), 114.8 (C^{10}, C^{14}), 106.3, 105.9, 105.5 (CH_{pz}), 88.5 ($^1J_{CH}$ = 136 Hz, CH_2O), 52.0, 50.8 (CO_2Me), 15.8, 15.6, 12.9, 12.7, 12.6, 12.0 (Me_{pz}). HRMS (FAB): *m*/*z* calcd. for $C_{35}H_{38}BN_6O_5IrNa$: 849.2524; found: 849.2537.

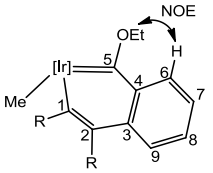


Synthesis and characterization of complexes *benzo*-6, *benzo*-3-Me,OEt and *benzo*-4-cis,OEt. To a solution of *benzo*-**1**-OH_2 in CH_2Cl_2 (0.20 gr, 0.27 mmol; 6 mL) was added EtOCH=CH_2 (80 μL, 0.8 mmol) and the mixture was heated at 60 °C for 2 h. The solvent was removed under vacuum and the ^{1}H NMR spectrum of the crude of the reaction showed formation of complexes *benzo*-**4**-cis,OEt (*ca.* 45%), *benzo*-**3**-Me,OEt (*ca.* 21%) and *benzo*-**6** (*ca.* 14%). These complexes were separated by column chromatography on silica gel using a mixture of hexane/Et_2O (3:1) as eluent.

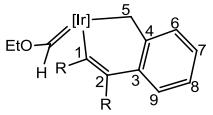
Complex *benzo*-**4**-cis,OEt was isolated from the second fraction (pale yellow solid). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 7.36 (d, 1 H, C^8H), 7.15 (d, $^3J_{HH}$ = 9.0 Hz, 1 H, C^{10}H), 7.14 (t, 1 H, C^6H), 7.11-7.05 (m, 2 H, C^5H, C^7H), 6.31 (d, 1 H, C^9H), 5.76, 5.69, 5.63 (s, 1 H each, 3 CH_{pz}), 3.71, 3.11 (s, 3 H each, 2 CO_2Me), 2.84, 1.96 (m, 1 H each, OCH_2CH$_3$), 2.40, 2.33, 2.29, 2.27, 2.13, 1.86 (s, 3 H each, 6 Me_{pz}), 0.61 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, OCH$_2$CH_3), -25.24 (s, 1 H, Ir–H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 173.8, 167.4 (CO_2Me), 152.0, 151.7, 151.2, 145.0, 143.3, 142.4 (C_{qpz}), 146.6 (C^3), 145.5 (C^1), 138.6 (C^4), 136.8 (C^2), 126.9, 126.8, 126.7, 120.5 (C^5-C^8), 109.0 ($^1J_{CH}$ = 184 Hz, C^{10}), 107.1, 106.4, 105.4 (CH_{pz}), 65.2 ($^1J_{CH}$ =145 Hz; OCH_2CH$_3$), 59.4 ($^1J_{CH}$ = 166 Hz, C^9), 51.6, 50.6 (CO_2Me), 15.4, 15.3, 15.2, 12.8 (Me_{pz}), 14.6 ($^1J_{CH}$ = 128 Hz, OCH$_2$CH_3). HRMS (FAB): *m*/*z* calcd. for $C_{31}H_{40}BN_6O_5IrNa$: 803.2680; found: 803.2665. Elemental analysis calcd. (%) for $C_{31}H_{40}BIrN_6O_5$: C 47.7; H 5.2; N 10.8; found: C 47.7; H 5.4; N 10.5.



Complex *benzo*-**3**-Me,OEt was isolated from the first fraction as an orange solid. Crystals suitable for single crystal X-ray studies were obtained by slow solvent evaporation, at 25 °C, from its solutions in hexane-Et_2O mixtures. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 7.92 (d, 1 H, C^9H), 7.51 (d, 1 H, C^6H), 7.50 (t, 1 H, C^8H), 7.27 (t, 1 H, C^7H), 5.74, 5.71, 5.69 (s, 1 H each, 3 CH_{pz}), 3.71, 3.08 (s, 3 H each, 2 CO_2Me), 3.62 (m, 2 H, OCH_2), 2.44, 2.40, 2.35, 2.21, 2.03, 1.62 (s, 3 H each, 6 Me_{pz}), 1.12 (t, 3 H, OCH$_2$CH_3), 0.40 (s, 3 H, Ir–Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 256.4 (C^5), 175.7, 170.4 (CO_2Me), 152.7, 150.7, 150.3, 144.0, 143.4, 142.4 (C_{qpz}), 152.3 (C^1), 142.7 (C^4), 139.7 (C^3), 133.9 (C^2), 131.5 (C^8), 127.7 (C^9), 125.8 (C^7), 122.3 (C^6), 107.6, 107.1, 105.4 (CH_{pz}), 71.8 ($^1J_{CH}$ =150 Hz, OCH_2CH$_3$), 51.8, 50.7 (CO_2Me), 14.9 (OCH$_2$CH$_3$), 14.8, 14.1, 13.7, 12.9, 12.8 (Me_{pz}), -18.4 ($^1J_{CH}$ = 128 Hz, Ir–CH_3). HRMS (FAB): *m*/*z* calcd. for $C_{31}H_{40}BN_6O_5IrNa$: 803.2680; found: 803.2700. Elemental analysis calcd. (%) for C 47.7; H 5.2; N 10.8; found: C 47.6; H 5.6; N 9.9. Crystal data for *benzo*-**3**-Me,OEt: $2(C_{31}H_{40}BIrN_6O_5)\bullet C_4H_{10}O$, M = 1633.52, monoclinic, *a* = 32.6015(14) Å, *b* = 10.4977(5) Å, *c* = 23.3279(12) Å, α = 90.00°, β = 119.4920(10)°, γ = 90.00°, *V* = 6949.3(6) Å^3, *T* = 213(2) K, space group *C*2/*c*, Z = 4, μ = 3.892 mm^{-1}, 39151 reflections measured, 6223 independent reflections (R_{int} = 0.0490). The final R_1 values were 0.0319 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0827 ($I > 2\sigma(I)$). The final R_1 values were 0.0416 (all data). The final $wR(F^2)$ values were 0.0856 (all data). The goodness of fit on F^2 was 1.073. CCDC 1017022.

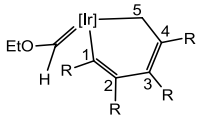


Complex *benzo*-**6** was isolated in the third fraction as a yellow solid. Crystals of analytical purity and suitable for single crystal X-ray studies were obtained by slow solvent evaporation from its solutions in hexane-Et_2O mixtures. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 13.95 (s, 1 H, Ir=CH), 7.68, 7.03, 6.98 (m, 1:1:2, C^6H-C^9H), 5.81, 5.76, 5.67 (s, 1 H each, 3 CH_{pz}), 5.06. 2.60 (d, 1 H each, $^2J_{HH}$=11.5 Hz, C^5H_2), 4.16, 3.83 (m, 1 H each, OCH_2CH$_3$), 3.73, 3.13 (s, 3 H each, 2 CO_2Me), 2.62, 2.35, 2.32, 2.16, 1.74 (s, 1:2:1:1:1:1, 6 Me_{pz}), 0.94 (t, 3 H, $^3J_{HH}$=7.2 Hz, OCH$_2$CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ = 256.8 ($^1J_{CH}$ = 153 Hz, Ir=C), 175.9, 169.5 (CO_2Me), 153.3, 149.4, 148.3, 143.7, 144.0, 143.0 (C_{qpz}), 149.9, 142.5, 137.1, 137.0 (C^1-C^4), 128.2, 126.6, 123.7 (C^6-C^8), 108.3, 106.8, 105.9 (CH_{pz}), 80.1 ($^1J_{CH}$=147 Hz, OCH_2CH$_3$), 51.8, 50.5 (CO_2Me), 16.1, 14.8, 14.2, 13.0, 12.9, 12.8 (Me_{pz}), 15.0 (OCH$_2$CH$_3$), 3.8 ($^1J_{CH}$=130 Hz, C^5). Elemental analysis calcd. (%) for $C_{31}H_{40}BIrN_6O_5$: C 47.7; H 5.2; N 10.8; found: C 47.5; H 5.2; N 10.6. Crystal data for *benzo*-**6**: $C_{31}H_{40}BIrN_6O_5$, M = 779.70, triclinic, *a* = 10.8057(4) Å, *b* = 12.4169(5) Å, *c* = 14.0635(9) Å, α = 101.592(2)°, β = 99.841(2)°, γ = 115.4170(10)°, *V* = 1597.47(13) Å^3, *T* = 213(2) K, space group $P\bar{1}$, Z = 2, μ = 4.228 mm^{-1}, 19887 reflections measured, 5724 independent reflections (R_{int} = 0.0278). The final R_1 values were 0.0149 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0336 ($I > 2\sigma(I)$). The final R_1 values were 0.0171 (all data). The final $wR(F^2)$ values were 0.0338 (all data). The goodness of fit on F^2 was 1.020. CCDC 1017023.

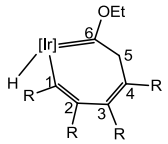


Synthesis and characterization of complexes 6 and 8-OEt. To a solution of **1**-OH_2in CH_2Cl_2 (0.20 gr, 0.25 mmol; 10 mL) was added $EtOCH{=}CH_2$ (73μL, 0.8 mmol) and the stirred mixture heated at 60 °C for 12 h. The solvent was removed under vacuum and the ^1H NMR spectrum of the crude of the reaction showed formation of complexes **6** (*ca.* 48%) and **8**-OEt (*ca.* 32%). These complexes were separated by column chromatography on silica gel using a mixture of hexane/Et_2O (1:1) → Et_2O as eluent.

Complex **6** was isolated in the second fraction as a yellow solid. Crystals of analytical purity and suitable for single crystal X-ray studies were obtained by slow solvent evaporation, at 25 °C, from its solutions in hexane-CH_2Cl_2 mixtures. ^1H NMR ($CDCl_3$, 25 °C): δ = 14.70 (s, 1 H, Ir=CH), 5.82, 5.79 (s, 1:2, 3 CH_{pz}), 5.08, 2.28 (d, 1 H each, $^2J_{HH}$ = 13 Hz, C^5H_2), 4.54 (m, 2 H, OCH_2CH_3), 3.77, 3.69, 3.23 (s, 2:1:1, 4 CO_2Me), 2.63, 2.39, 2.04, 1.95 (s, 1:3:1:1, 6 Me_{pz}), 1.48 (m, 3 H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 260.2 ($^1J_{CH}$ = 150 Hz, Ir=C), 176.2, 170.9, 169.0, 164.4 (CO_2Me), 156.3, 151.0, 131.8, 131.5 (C^1-C^4), 153.4, 149.4, 149.0, 143.9, 143.6, 143.3 (C_{qpz}), 108.7, 107.0, 106.3 (CH_{pz}), 82.4 ($^1J_{CH}$ = 150 Hz, OCH_2CH_3), 51.9, 51.8, 51.6, 50.3 (CO_2Me), 16.9, 15.2, 15.0, 13.0, 12.8 (Me_{pz}), 14.3 ($^1J_{CH}$ = 128 Hz, OCH_2CH_3), -2.1 ($^1J_{CH}$ = 128 Hz, C^5H_2). HRMS (FAB): *m/z* calcd. for $C_{31}H_{42}BN_6O_9IrNa$: 869.2633; found: 869.2634. Elemental analysis calcd. (%) for $C_{31}H_{42}BIrN_6O_9$: C 44.0; H 5.0; N 9.9; found: C 43.8; H 4.7; N 9.7. Crystal data for **6**: $C_{31}H_{42}BIrN_6O_9 \bullet CH_2Cl_2$, M = 930.64, monoclinic, *a* = 21.7786(8) Å, *b* = 10.7975(4) Å, *c* = 16.5848(7) Å, *α* = 90.00°, *β* = 97.368(2)°, *γ* = 90.00°, *V* = 3867.8(3) Å^3, *T* = 213(2) K, space group $P2_1/c$, *Z* = 4, *μ* = 3.647 mm^{-1}, 45671 reflections measured, 6887 independent reflections (R_{int} = 0.0410). The final R_1 values were 0.0339 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0839 ($I > 2\sigma(I)$). The final R_1 values were 0.0432 (all data). The final $wR(F^2)$ values were 0.0874 (all data). The goodness of fit on F^2 was 1.070. CCDC 1017017.



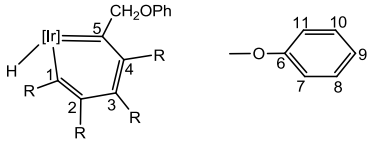
Complex **8**-OEt was isolated in the first fraction as a yellow solid. Crystals of analytical purity and suitable for single crystal X-ray studies were obtained by slow solvent evaporation, at 25 °C, from its solutions in hexane-Et_2O mixtures. ^1H NMR ($CDCl_3$, 25 °C): δ = 5.84, 5.76, 5.69 (s, 1 H each, 3 CH_{pz}), 4.33, 1.94 (br d, 1 H each, $^2J_{HH}$=14.5 Hz, C^5H_2), 3.81, 3.80, 3.66, 3.06 (s, 3 H each, 4 CO_2Me), 3.60, 3.52 (m (from COSY), 1 H each, OCH_2CH_3), 2.47, 2.36, 1.83, 1.74 (s, 1:3:1:1, 6 Me_{pz}), 1.12 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), -17.63 (s, 1 H, Ir–H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 277.7 (C^6), 177.2, 169.2, 168.2, 165.3 (CO_2Me), 154.2, 150.6, 150.1, 144.6, 144.1, 143.1 (C_{qpz}), 134.5 (C^4), 106.0, 105.6 (CH_{pz}), 72.9 (OCH_2CH_3), 61.1 (C^5H_2, (br signal)), 52.3, 52.1, 51.5, 50.4 (CO_2Me), 15.9, 14.9, 14.8, 14.6, 12.7 (Me_{pz} + OCH_2CH_3). Resonances corresponding to C^1-C^3were not found. HRMS (FAB): *m/z* calcd. for $C_{31}H_{42}BN_6O_9IrNa$: 869.2633; found: 869.2634. Crystal data for **8**-OEt: $C_{31}H_{42}BIrN_6O_9$, M = 845.72, triclinic, *a* = 9.7953(4) Å, *b* = 12.8887(4) Å, *c* = 15.6815(6) Å, *α* = 99.9000(10)°, *β* = 105.7370(10)°, *γ* = 109.0050(10)°, *V* = 1726.44(11) Å^3, *T* = 213(2) K, space group $P\bar{1}$, *Z* = 2, *μ* = 3.927 mm^{-1}, 32079 reflections measured, 6160 independent reflections (R_{int} = 0.0361). The final R_1 values were 0.0204 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0513 ($I > 2\sigma(I)$). The final R_1 values were 0.0233 (all data). The final $wR(F^2)$ values were 0.0519 (all data). The goodness of fit on F^2 was 1.079. CCDC 1017018.



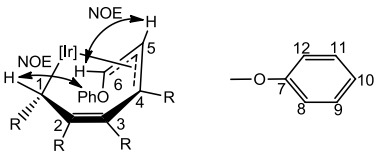
Synthesis and characterization of complexes 3-H,CH_2OPh, 8-OPh and 2-*anti*-OPh. To a solution of *benzo*-**1**-OH_2in CH_2Cl_2 (0.15 gr, 0.19 mmol; 6 mL) was added $PhOCH{=}CH_2$ (70 μL, 0.6 mmol) and the stirred mixture heated at 60°C for 12 h. Thereafter the solvent was removed under vacuum. The ^1H NMR spectrum of the crude of the reaction showed formation of complexes **3**-H,CH_2OPh (*ca.* 53%), **8**-OPh (*ca.* 14%) and **2**-*anti*-OPh(*ca.* 17%). These complexes were separated by column chromatography on silica gel using a mixture of hexane/Et_2O (4:1) → (1:4) as eluent.

Complexes **3**-H,CH_2OPh and **2**-*anti*-OPh were obtained as a mixture in the first fraction. These complexes were separated by cristallization. Complex **3**-H,CH_2OPh crystallized as a dark yellow crystals, suitable for X-ray studies, by slow solvent evaporation, at 25 °C, from its solutions in hexane-Et_2O mixtures and complex **2**-*anti*-OPh was obtained as a yellow solid after taken to dryness the mother liquor.

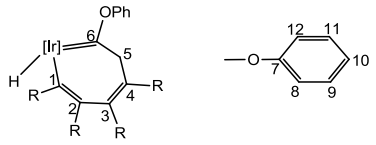
Complex **3**-H,CH_2OPh. ^1H NMR ($CDCl_3$, 25 °C): δ =7.14 (t, 2 H, C^8H, $C^{10}H$), 6.85 (t, 1 H, C^9H), 6.62 (d, 2 H, C^7H, $C^{11}H$), 5.87, 5.77, 5.62 (s, 1 H each, 3 CH_{pz}), 4.36, 3.83 (d, 1 H each, $^2J_{HH}$ = 17 Hz, CH_2O), 3.88, 3.72, 3.51, 3.18 (s, 3 H each, 4 CO_2Me), 2.47, 2.46, 2.41, 2.16, 2.10, 1.10 (s, 3 H each, 6 Me_{pz}), -21.29 (s, 1 H, Ir–H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 256.2 (C^5), 206.4 (C^1), 179.2, 170.4, 167.7, 166.1 (CO_2Me), 157.8 (C^6), 154.3, 152.3, 149.6, 146.1, 146.0, 143.0 (C_{qpz}), 153.2 (C^3), 137.8 (C^4), 132.2 (C^2), 129.4 (C^8, C^{10}), 121.2 (C^9), 114.5 (C^7,C^{11}), 106.7, 106.6, 105.6 (CH_{pz}), 85.8 ($^1J_{CH}$ = 147 Hz, CH_2O), 52.8, 52.5, 51.1 (CO_2Me), 16.3, 16.1, 13.0, 12.8, 12.6, 11.5 (Me_{pz}). HRMS (FAB): *m/z* calcd. for $C_{35}H_{42}BN_6O_9IrNa$: 917.2633; found: 917.2626. Crystal data for **3**-H,CH_2OPh: $C_{35}H_{42}BIrN_6O_9$, M = 893.76, orthorhombic, *a* = 11.0403(6) Å, *b* = 11.2173(6) Å, *c* = 30.0051(16) Å, *α* = 90.00°, *β* = 90.00°, *γ* = 90.00°, *V* = 3715.9(3) Å^3, *T* = 213(2) K, space group $P2_12_12_1$, *Z* = 4, *μ* = 3.654 mm^{-1}, 72029 reflections measured, 6714 independent reflections (R_{int} = 0.0379). The final R_1 values were 0.0262 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0639 ($I > 2\sigma(I)$). The final R_1 values were 0.0269 (all data). The final $wR(F^2)$ values were 0.0642 (all data). The goodness of fit on F^2 was 1.058. CCDC 1017016.



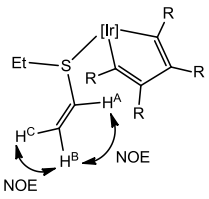
Complex **2**-*anti*-OPh. ^1H NMR ($CDCl_3$, 25 °C): δ = 7.41 (d, 1 H, $^3J_{HH}$ = 7.0 Hz, C^5H), 7.36 (t, 2 H, C^9H, $C^{11}H$), 7.14 (d, 2 H, C^8H, $C^{12}H$), 7.04 (t, 1 H, $C^{10}H$), 5.96, 5.82, 5.62 (s, 1 H each, 3 CH_{pz}), 5.73 (d, 1 H, C^6H), 4.98 (s, 1 H, C^1H), 3.84, 3.69, 3.49, 3.35 (s, 3 H each, 4 CO_2Me), 2.56, 2.50, 2.42, 2.31, 2.25, 2.21 (s, 3 H each, 6 Me_{pz}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 173.8, 166.4, 166.2 (CO_2Me), 158.2 (C^7), 152.6, 152.5, 144.6, 143.4 (C_{qpz}), 147.8, 138.4 (C^2,C^3), 129.7 (C^9, C^{11}), 121.5 (C^{10}), 115.1 (C^8, C^{12}), 110.2, 108.9, 107.7 (CH_{pz}), 87.1 ($^1J_{CH}$ = 171 Hz, C^5), 70.8 ($^1J_{CH}$ = 190 Hz, C^6), 52.4, 52.0, 51.9, 51.0 (CO_2Me), 46.8 (C^4), 17.2, 14.5, 13.8, 13.1, 12.7 (Me_{pz}), 13.4 (C^1). HRMS (FAB): *m/z* calcd. for $C_{35}H_{42}BN_6O_9IrNa$: 917.2633; found: 917.2629. Elemental analysis calcd. (%) for $C_{35}H_{42}BIrN_6O_9$: C 47.1; H 4.7; N 8.9; found: C 47.0; H 4.7; N 9.4.



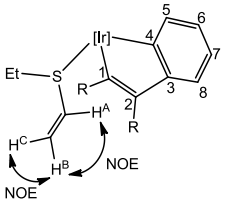
Complex **8**-OPh was obtained in the last fraction as a yellow solid. ^{1}H NMR ($CDCl_3$, 25 ºC): δ = 7.36 (t, 2 H, C^9H, C^{11}H), 7.25 (t, 1 H, C^{10}H), 6.92 (d, 2 H, C^8H, C^{12}H), 5.82, 5.76, 5.69 (s, 1 H each, 3 CH_{pz}), 4.49, 1.39 (d, 1 H each, $^2J_{HH}$ = 14.5 Hz, C^5H_2), 3.77, 3.72, 3.62, 3.05 (s, 3 H each, 4 CO_2Me), 2.42, 2.36, 2.35, 2.31, 1.98, 1.89 (s, 3 H each, 6 Me_{pz}), -17.27 (s, 1 H, Ir–H). ^{13}C NMR ($CDCl_3$, 25 ºC): δ = 277.9 (C^6), 177.3, 173.1, 168.5, 165.3 (CO_2Me), 155.8 (C^7), 154.5, 149.8, 149.1, 144.1, 143.9, 143.4 (C_{qpz}), 145.3, 133.8, 128.9 (C^1-C^4), 130.2 (C^9, C^{11}), 127.0 (C^{10}), 120.5 (C^8, C^{12}), 106.3, 106.1, 105.7 (CH_{pz}), 55.5 ($^1J_{CH}$ = 131 Hz, C^5H_2), 52.4, 52.3, 51.7, 50.6 (CO_2*Me*), 16.1, 15.7, 12.9 (Me_{pz}). HRMS (FAB): *m/z* calcd. for $C_{35}H_{42}BN_6O_9IrNa$: 917.2633; found: 917.2645.



Synthesis and characterization of complex 1-S(Et)CH=CH$_2$. To a solution of **1**-OH_2 in CH_2Cl_2 (0.10 gr, 0.13 mmol; 5 mL) was added ethyl vinyl sulfide (40 µL, 0.4 mmol) and the stirred mixture heated at 60 ºC for 12 h. Thereafter the solvent was removed under vacuum and the resultant solid washed with pentane (3x5 mL) and with Et_2O (2x5mL). The ^{1}H NMR spectrum of the resulting dark yellow solid was in accord with the formation of compound **1**-S(Et)CH=CH_2 in quantitative spectroscopic yield. Orange-brown crystals of analytical purity and suitable for single crystal X-ray studies were obtained by slow solvent evaporation, at 25 ºC, from its solutions in CH_2Cl_2-Et_2O mixtures. ^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.91 (dd, 1 H, $^3J_{AB}$ = 9.5, $^3J_{AC}$ = 16.4 Hz, H^A), 5.75, 5.51 (s, 2:1; 3 CH_{pz}), 5.64 (d, 1 H, $^3J_{AB}$ = 9.5 Hz, H^B), 5.51 (d, 1 H, $^3J_{AC}$ = 16.4 Hz, H^C), 3.70, 3.39 (s, 6 H each, 4 CO_2Me), 2.51 (q, 2 H, $^3J_{HH}$ = 7.1 Hz, S*CH*$_2$CH$_3$), 2.36, 2.31, 2.21, 1.98 (s, 2:1:2:1; 6 Me_{pz}), 1.21 (t, 3 H, $^3J_{HH}$ = 7.1 Hz, SCH$_2$*CH*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ = 172.5, 167.5 (CO_2Me), 154.7, 151.3, 143.9, 142.4 (C_{qpz}), 151.8, 145.8 (CCO_2Me), 125.6 ($^1J_{CH}$ = 161 Hz, CH=CH_2), 125.2 ($^1J_{CH}$ = 180 Hz, CH=CH_2), 108.3, 107.2 (CH_{pz}), 51.8, 51.0 (CO_2*Me*), 29.4 ($^1J_{CH}$ = 144 Hz, SCH_2CH_3), 15.1, 13.3, 13.0, 12.5 (Me_{pz}), 13.0 (SCH_2CH_3). Elemental analysis calcd. (%) for $C_{31}H_{42}BIrN_6O_8S$: C 43.2; H 4.9; N 9.7; S 3.7; found: C 43.4; H 5.2; N 9.5; S 3.5. Crystal data for **1**-S(Et)CH=CH_2: $C_{31}H_{42}BIrN_6O_8S$, *M* = 861.78, monoclinic, *a* = 10.2869(4) Å, *b* = 19.8342(7) Å, *c* = 17.0899(6) Å, *α* = 90.00°, *β* = 100.1010(10)°, *γ* = 90.00°, *V* = 3432.8(2) Å^3, *T* = 213(2) K, space group $P2_1/c$, *Z* = 4, *μ* = 4.008 mm^{-1}, 39783 reflections measured, 6207 independent reflections (R_{int} = 0.0189). The final R_1 values were 0.0170 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0394 ($I > 2\sigma(I)$). The final R_1 values were 0.0193 (all data). The final $wR(F^2)$ values were 0.0403 (all data). The goodness of fit on F^2 was 1.068. CCDC 1017015.



Synthesis and characterization of complex *benzo*-1-S(Et)CH=CH$_2$. To a solution of benzo-**1**-OH_2 in CH_2Cl_2 (0.10 gr, 0.14 mmol; 5 mL) was added ethyl vinyl sulfide (42µL, 0.4 mmol) and the mixture heated at 60 ºC for 2 h. Thereafter the solvent was removed under vacuum and the resultant solid washed with pentane (3x5 mL). The ^{1}H NMR spectrum of the resulting dark yellow solid was in accord with the formation of compound *benzo*-**1**-S(Et)CH=CH_2 in quantitative spectroscopic yield. ^{1}H NMR ($CDCl_3$, 25 ºC): δ = 7.11 (t, 2 H, C^5H, C^8H), 6.87 (t, 1 H, C^7H), 6.69 (t, 1 H, C^6H), 5.87, 5.79, 5.45 (s, 1 H each, 3 CH_{pz}), 5.83 (dd, 1 H, $^3J_{AB}$ = 9.6, $^3J_{AC}$ = 16.5 Hz, H^A), 5.45 (d, 1 H, $^3J_{AB}$ = 9.6 Hz, H^B), 5.28 (d, 1 H, $^3J_{AC}$ = 16.5 Hz, H^C), 3.81, 3.47 (s, 3 H each, 2 CO_2Me), 2.43, 2.41, 2.33, 2.30, 2.25, 1.29 (s, 3 H each, 6 Me_{pz}), 2.39 (m (from COSY), 2 H, S*CH*$_2$CH$_3$), 1.13 (t, 3 H, SCH$_2$*CH*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ = 173.6, 168.6 (CO_2Me), 156.7 (C^3), 153.9, 151.1, 150.8, 144.1, 143.7, 142.7 (C_{qpz}), 152.5 (C^2), 141.1 (C^4), 140.2 (C^1), 136.7 (C^5), 127.2 ($^1J_{CH}$ = 183 Hz, CH=CH_2), 123.9 ($^1J_{CH}$ = 161 Hz, CH=CH_2), 123.8 (C^6), 122.9 (C^8), 122.6 (C^7), 108.4, 107.9, 107.0 (CH_{pz}), 51.7, 51.0 (CO_2*Me*), 29.7 ($^1J_{CH}$ = 143 Hz, SCH_2CH_3), 16.4, 14.7, 14.1, 13.2, 12.3 (Me_{pz}), 13.4 (SCH_2CH_3). HRMS (FAB): *m/z* calcd. for $C_{31}H_{40}BN_6O_4IrSNa$: 819.2452; found: 819.2425. Elemental analysis calcd. (%) for $C_{31}H_{40}BIrN_6O_4S$: C 46.8; H 5.1; N 10.6; S 4.0; found: C 46.6; H 4.9; N 10.2; S 3.7.



ASSOCIATED CONTENT

Supporting Information

CIF file giving crystallographic data for compounds *benzo*-**1**-NCMe, *benzo*-**3**-CH_2R'a,b (R' = H, Me), *benzo*-**6**, *benzo*-**3**-Me,OEt, **6**, **8**-OEt, **3**-H,CH_2OPh and *benzo*-1-S(Et)CH=CH_2. Doc file containing Figures S1 and S2 with selected bond distances and angles (Tables 2 and 4 respectively), and structural data for all the nine compounds studied. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interests.

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