Functionalization of 3-iridacyclopentenes

Margarita Gómez,[a] Nuria Rendón,[a] Eleuterio Álvarez,[a] Kurt Mereiter,[b] Manuel L. Poveda,*[a] and Margarita Paneque*[a]

Abstract: A series of iridacyclopentenes of composition [Tp^{Me2}Ir(k^2-C,C-$CH_2CR'=CRCH_2$)(CO)] (Tp^{Me2} = hydrotris(3,5-dimethyl-pyrazolyl)borate; R = R' = H, **1**; R = Me, R' = H, **2**; R = R' = Me, **3**) have been subjected to common organic chemistry procedures for hydrogenation, cyclopropanation, epoxidation, water addition through hydroboration, *cis*-dihydroxylation and ozonolysis. The stability of metallacycles **1**-**3**, provided by the presence of the coligands Tp^{Me2} and CO, directs the reactivity towards the C=C double bonds, and further the stereochemistry of the products formed is strongly dictated by the steric demands of the Tp^{Me2} ligand. While the products obtained in some of the above mentioned reactions are the expected ones from an organic chemistry point of view, in other cases the results differ from the outcomes of similar reactions carried out with the all-carbon counterparts.

Introduction

Some years ago we briefly reported the transformation of the Ir^{III} 18 e^-, 3-iridacyclopentene complex [Tp^{Me2}Ir(k^2-C,C-$CH_2CH=CHCH_2$)(CO)] (**1**) (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate) into the methylene-3-iridacyclobutanone shown in Scheme 1a.[1] The overall process involved several synthetic steps that can be described as typical using standard organic chemistry reagents, work-up and purification techniques. It started with the hydration of the double bond of **1** *via* a hydroboration-oxidation sequence and finished with a Wolff rearrangement of a carbene intermediate. The success of this synthesis heavely relies on the well-known non-labile nature of the coligands Tp^{Me2} and CO on the Ir^{III} coordination sphere,[2] which prevents thermal substitution reactions, as well as their kinetic chemical stability towards many reagents even under forcing conditions (notice that the C—H of the aromatic pyrazolyls, the B—H, and the B—N bonds of the Tp^{Me2} ligand are sterically protected from chemical attack by the 3,5-Me substituents). Last but not least the Ir—C bonds of the iridacycle of all the complexes reported herein are very highly stable *vs.* common acids and bases, and this, among other consequences, greatly facilitates the work-up of many reactions.

The use of Organic Chemistry procedures on synthetic organometallic chemistry is not new, and has been for long applied to, for instance, the well-studied functionalization of aromatic ligands such as cyclopentadienyls (*e.g.* ferrocene) and benzenes (*e.g.* [(η^6-C_6H_6)Cr($CO)_3$]), and Schemes 1b[3] and 1c[4] show, respectively, an old and a quite recent further examples of these types of reactions. In this contribution we fully report the results obtained in the functionalization, and subsequent chemistry derived thereof, of the 3-metallacyclopentene Ir^{III} complexes **1**-**3** which are easily obtained by the reaction of the corresponding η^4-Ir^I butadienes with carbon monoxide (Scheme 1d).[5] Among other findings, we have obtained interesting organometallic species which would be very difficult to obtain by alternative methods. As already mentioned part of this work has been communicated.[1]

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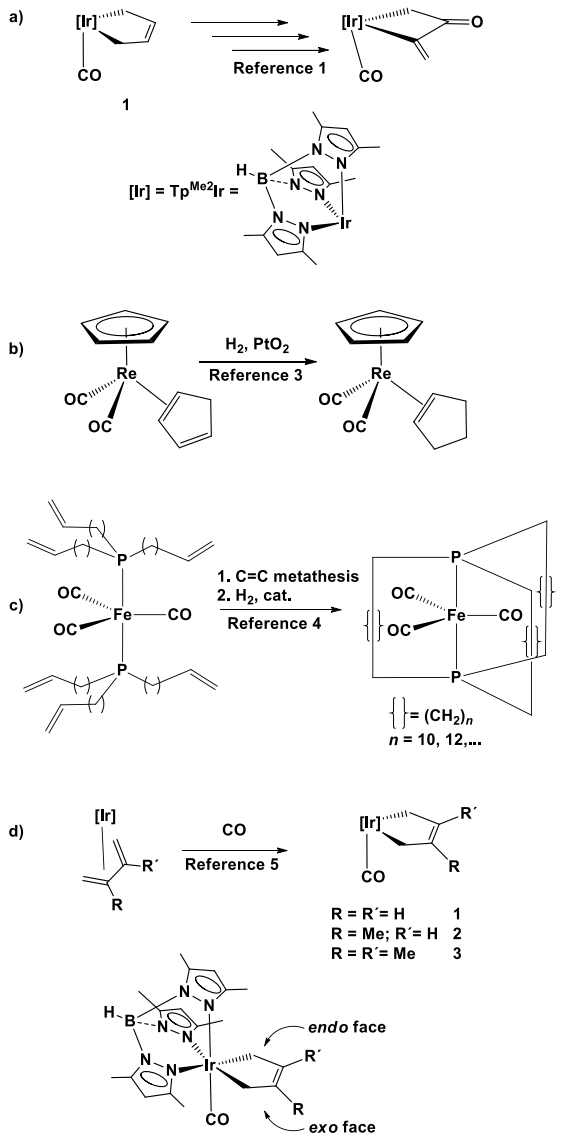


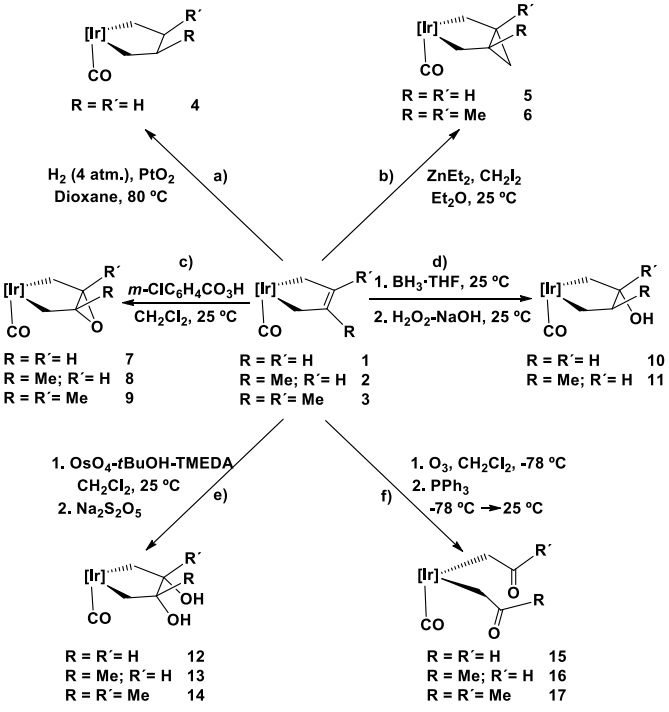
Scheme 1. a) Multi-step conversion of the 3-iridacyclopentene **1** into a methylene-3-iridacyclobutanone. b) Catalytic hydrogenation of the free C=C double bond of the cyclopentadiene adduct of a Re^{I} complex. c) An interesting application of C=C metathesis, using a Grubbs catalyst, to a $Fe(CO)_3(PR_3)_2$ complex. d) Synthesis of the 3-iridacyclopentenes **1**-**3** studied in this work. In addition, the designation of the *exo* and *endo* faces of these metallacycles is depicted. This nomenclature also applied to the faces of all others iridacycles described herein and also to the stereochemistry of the substituents.

Results and Discussion

Some common reactions of unactivated C=C double bonds carried out with complexes 1-3

Hydrogenation: Compound **1** very slowly added H_2, under forcing conditions (4 atm, dioxane, 80 ºC) and in the presence of PtO_2 as a catalyst, to give the iridacyclopentane **4**. As expected from the known trend that increasing substitution in the C=C double bond of olefins increases the difficulty of this reaction, complexes **2** and **3**, which contain 1 and 2, respectively, Me groups on the olefinic moiety, did not afford detectable amounts of the hydrogenated products after a similar treatment. Although no demonstrated, it is proposed that the addition of H_2 takes place in *cis*,[6] and through the less sterically hindered *exo* face of the olefin, as is the case for all other additions studied in this section (Scheme 2a).

Cyclopropanation: The room temperature reaction of complex **1** with an excess of the Simmons-Smith carbenoid,[7] *i.e.* the result of the interaction between $ZnEt_2$ and CH_2I_2 in diethyl ether, led to the clean formation (*ca*. 80% conversion) of the expected metallabicyclic complex **5** (Scheme 2b). This species could not be isolated in pure form from the mixture with compound **1**, neither by fractional crystallization nor by column chromatography on silica gel. Its purification was carried out by conversion of the remaining starting material **1** into its epoxide derivative (by reaction with *m*-chloroperbenzoic acid, see below) and subsequent separation by column chromatography. Complex **5** was completely characterized by NMR spectroscopy, its stereochemistry deduced from the NOESY spectrum and unambiguously corroborated crystallographically (Figure 1).



Scheme 2. Some common reactions of unactivated C=C double bonds as applied to complexes **1**-**3**: a) Catalytic hydrogenation. b) Cyclopropanation. c) Epoxidation. d) Hydration by a hydroboration-oxidation sequence. e) *Cis*-dihydroxylation. f) Ozonolysis.

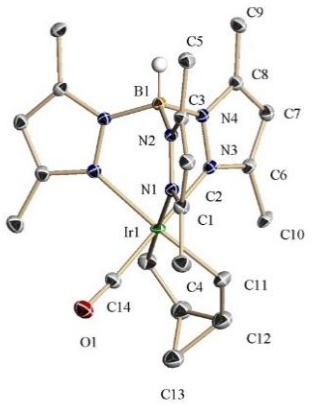


Figure 1. X-ray structure of complex **5** (30% displacement ellipsoids; H atoms are omitted for clarity). Selected bond lengths [Å]: Ir—N(1) 2.155(4), Ir—N(3) 2.169(7), Ir—C(11) 2.072(5), C(11)—C(12) 1.506(10), C(12)—C(13) 1.567(13).

The two methyl substituents of the C=C double bond of complex **3** should, in principle, sterically inhibit a similar carbenoid attack but, in the other hand, the electron-donating character of these groups makes this functionality more susceptible to the reaction with the electrophilic ":CH_2" reagent. In practise, **3** reacted with a $ZnEt_2$:CH_2I_2 mixture, under the same conditions used for complex **1**, giving the cyclopropanated compound **6** (which was characterized by NMR spectroscopy only) although with less than 80% conversion.

Epoxidation: The epoxidation of complexes **1**-**3** was carried out with *m*-chloroperbenzoic acid[8] (CH_2Cl_2, 25 ºC) to cleanly afford species **7**-**9** (Scheme 2c; of them, compound **8** was characterised by NMR spectroscopy only). As expected, the epoxidation takes place in the *exo*-face of the olefin, as deduced from their NOESY spectra. For complex **7** the structure was also proven crystallographically (Figure S2).

Water addition through hydroboration: We have applied the hydroboration-oxidation method (an *anti*-Markovnikov addition of water) to obtain alcohols.[6,9] Thus, when complexes **1** and **2** were reacted with the adduct BH_3·THF in THF, and the corresponding borane derivatives oxidized with H_2O_2-NaOH, the alcohols **10** and **11** were obtained in high yields (94 and 91% respectively; **11** characterized only by NMR) (Scheme 2d). The *exo* disposition of the OH group in both derivatives and the *transoid* stereochemistry of the methyl group, with respect to the OH, in compound **11** were deduced from NOESY studies. In addition, compound **10** has been characterized crystallographically (Figure S3).

Surprisingly, complex **3** did not yield the expected tertiary alcohol under the same reaction conditions shown in Scheme 2d. In fact, it was recovered unaltered and this strongly contrasts with the facility with which 1,2-dimethylcyclopentene gives the corresponding alcohol. It may be possible that in this case the hydroboration-oxidation process has taken place, but with the resultant alcohol being much more prone to back-dehydration than its all-carbon organic counterpart.

Cis-dihydroxylation: Derivatives **1**-**3** reacted with stoichiometric amounts of OsO_4 with formation of stable osmiate derivatives which, when decomposed with $Na_2S_2O_5$ yielded the expected *cis*-diol derivatives **12**-**14** (Scheme 2e).[6,10,11] These compounds were characterized only by NMR spectroscopy and for complex **12** also by X-ray crystallography (Figure 2). Clearly OsO_4 attacks the *exo*-face of the C=C double bonds.

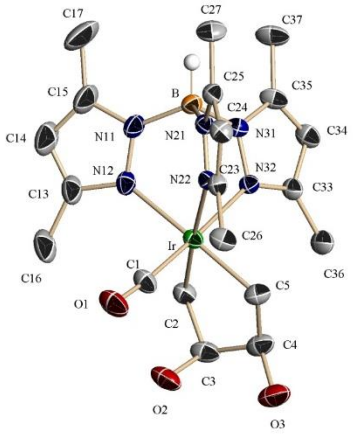
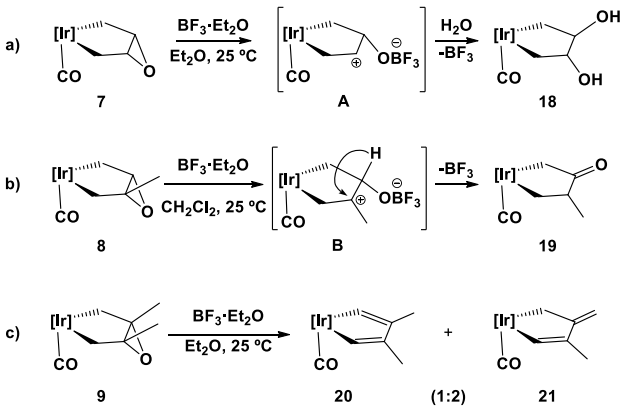


Figure 2. X-ray structure of complex **12** (30% displacement ellipsoids; H atoms are omitted for clarity). Selected bond lengths [Å]: Ir—N(12) 2.168(5), Ir—N(22) 2.183(4), Ir—N(32) 2.165(4), Ir—C(1) 1.827(6), Ir—C(2) 2.086(6), Ir—C(5) 2.081(6).

Ozonolysis: Finally in this section, the reactions of complexes **1**-**3** with O_3 were carried out as usual[6] and the resulting products **15**-**17** (Scheme 2f; **16** and **17** characterized only by NMR) purified by column chromatography on silica gel. The structure of compound **15** was, in addition, authenticated by X-ray crystallography (Figure S5).

Lewis acid promoted ring-opening of the epoxides 7-9

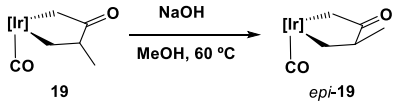
Ring-opening of epoxides is commonly carried out[6] with BF_3·Et_2O and thus, when epoxide **7** was reacted with an excess of this reagent (diethyl ether, room temperature), quantitative formation of the *trans*-diol **18** took place (Scheme 3a). It is proposed that intermediate **A**, resulting from the addition of BF_3 to the epoxide, easily hydrates to give the observed product.



Scheme 3. Ring-opening of epoxides **7**-**9** by the action of BF_3·Et_2O.

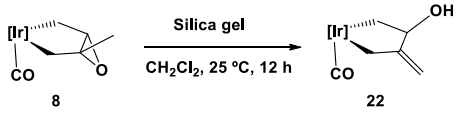
In contrast, ketone **19** was obtained when compound **8**, with only one methyl substituent, was subjected to the action of $BF_3{\cdot}Et_2O$ in dichloromethane. Complex **19** has been completely characterized by NMR spectroscopy and crystallographically (Figure S6). To explain the stereoselectivity shown in Scheme 3b, *i.e*. with the Me of **19** being in the *exo* position, we propose that in the reaction of **8** with BF_3 the intermediate **B** experiences a suprafacial migration of the methine hydrogen atom. Therefore, we have to conclude that the presence of the methyl substituent in intermediate **B**, as compared to **A**, enhances the mobility of the C—H hydrogen and/or makes the former species less susceptible to water addition.

The CHMe group adjacent to the keto functionality in **19** must be easily epimerizable and, in fact, when this compound was treated with NaOH in methanol at 60 ºC the thermodynamically more stable isomeric species *epi*-**19** was obtained in 80% spectroscopic yield (Scheme 4). We propose that subtle steric factors, rather than electronic ones, are responsible for the energetic difference between these two ketones. Interestingly, and in comparison to similar organic compounds,[12] this isomerization requires quite drastic conditions and this fact is probably due to the steric protection of the enolizable hydrogen.



Scheme 4. Epimerization of ketone **19** in basic medium.

Epoxide **8** was also opened by the action of silica gel in dichloromethane but, surprisingly, the allylic alcohol **22** was obtained instead of ketone **19** (Scheme 5). Compound **22** has been completely characterized by NMR spectroscopy and the *endo* disposition of the OH group was deduced from the NOESY spectrum.



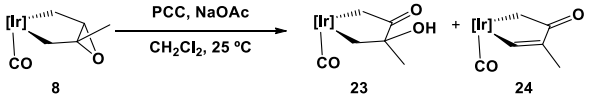
Scheme 5. Ring-opening of epoxide **8** by silica gel in CH_2Cl_2.

This kind of isomerization is of great interest in organic synthesis and is usually carried out by indirect methods.[13] It has been reported that the epoxide of 1-methylcyclopentene gives, in the presence of activated alumina, an allylic alcohol related to **22** but in admixture with other products.[14] However, in a control experiment, we have found that this substrate is not altered by silica gel using the conditions of Scheme 5.

Another different result was observed in the reaction of complex **9** with $BF_3{\cdot}Et_2O$ in Et_2O (Scheme 3c). In this case a dehydration process took place giving a mixture, in a *ca.* 1:2 ratio, of the dienes **20** and **21**. In the case of derivative **20** the two lost hydrogen atoms derive from the two Ir—CH_2 groups while in the formation of derivative **21** one of the hydrogen atoms comes from a methyl group. The same mixture of products are more satisfactorily obtained by an alternative procedure (see below).

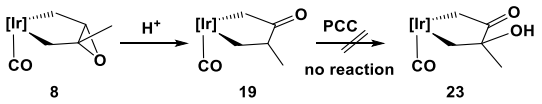
Ring-opening of epoxide 8 under oxidative conditions

Epoxide **8** also experienced a ring-opening process when reacted with pyridinium chlorochromate (PCC)[15] which, under the conditions specified in Scheme 6 afforded a mixture of ketones **23** and **24**. The former compound is an α-hydroxyl ketone with the OH group in an *endo* disposition (NOESY evidence) while the latter, characterized only by NMR, is an α,β-enone, which formally derives from **23** by a simple dehydration, although this point has not been tested experimentally. In comparison, when the epoxide of 1-methylcyclopentene was treated similarly a complex mixture of products was obtained.



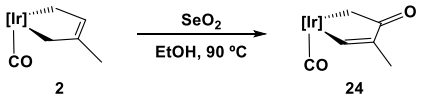
Scheme 6. Reaction of epoxide **8** with PCC.

A reasonable mechanism that may explain the formation of compound **23**, with ketone **19** acting as an intermediate, is shown in Scheme 7. However, this is clearly no the case as this ketone did not react when treated similarly with PCC and so far we can not offer a mechanistic explanation for its formation.



Scheme 7. A plausible, but incorrect, mechanism for the formation of compound **23** in the reaction of **8** with PCC.

Interestingly, we have found a simple method for the synthesis, in almost quantitative yield, of ketone **24**. This consists on the reaction of complex **2** with SeO_2 in ethanol at 90 ºC (Scheme 8). This result is quite surprising since, if present as is the case, this reagent usually reacts with allylic C—H moieties.[16]

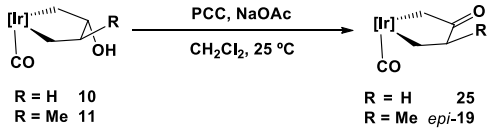


Scheme 8. Unexpected outcome of the oxidation of complex **2** with SeO_2.

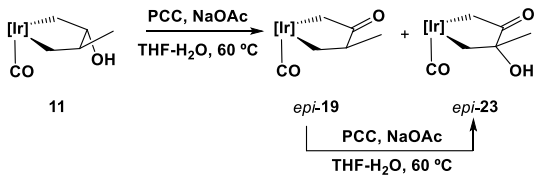
Oxidation of alcohols 10-11

The reaction of alcohols **10** and **11** with PCC, in CH_2Cl_2 at 25 ºC, afforded the corresponding ketones **25**[17] (characterized by X-ray crystallography, Figure S7) and *epi*-**19** (Scheme 9). However, we have found that if the reaction of complex **11** with PCC was carried out under more forcing conditions (THF-H_2O, 60 ºC) an overoxidation took place and the α-hydroxylketone *epi*-**23** slowly

appeared, in admixture with *epi*-**19**, in the reaction mixture. As expected, and with the aid of a control experiment, it was demonstrated that the latter species is an intermediate in the formation of the former (Scheme 10). Clearly PCC attacks the *exo* face of *epi*-**19**.

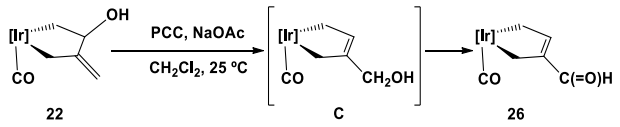


Scheme 9. Oxidation of alcohols **10** and **11** with PCC.



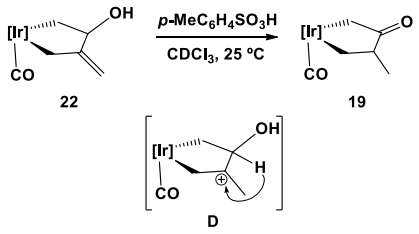
Scheme 10. Reaction of complex **11** with PCC under more forcing conditions than those depicted in Scheme 9.

Surprisingly, the oxidation of the allylic alcohol **22** with PCC gave the α,β-unsaturated aldehyde **26** (Scheme 11; **26** characterized only by NMR) instead of the expected α-methylenketone. This reaction may be explained by invoking that an isomerization of **22** to the thermodynamically more stable primary alcohol **C**, takes place followed by its oxidation to **26**.



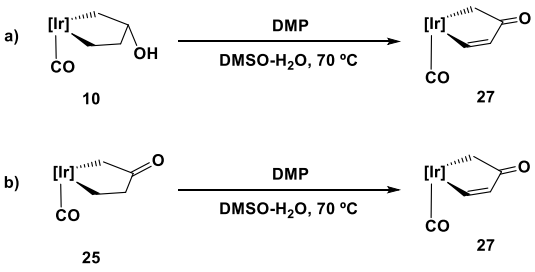
Scheme 11. Oxidation of the allylic alcohol **22** with PCC.

The proposed isomerization can not be based on acid catalysis because, first, the reaction took place in the presence of NaOAc and second, and more importantly, complex **22** experienced a fast isomerization to **19** in the presence of *p*-toluenesulfonic acid at room temperature (Scheme 12). If this last reaction occurs through formation of the carbocation **D** shown in Scheme 12, *i.e.* by protonation of the methylene group, this has to be followed by a suprafacial migration of the hydrogen and final deprotonation of the hydroxyl group, and the resulting product would be *epi*-**19**, *i.e.* the thermodynamically more stable of the two epimers. Consequently, for the time being we do not have a satisfactory mechanistic explanation for the formation of complex **19** in this reaction.



Scheme 12. Isomerization of complex **22** in the presence of a strong acid. Carbocation **D** can not be an active intermediate in this transformation.

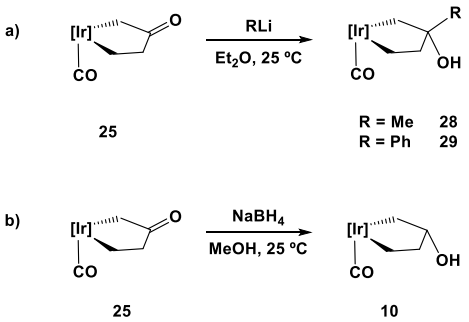
We have also studied the oxidation of alcohol **10** with Dess-Martin periodinane (DMP), in a mixture of DMSO and H_2O at 70 ºC, to find out that this reaction gave the conjugated enone **27** (Scheme 13). Clearly, a double oxidation has taken place which consists on the transformation of the alcohol onto a keto functionality and on the dehydrogenation of the Ir-CH_2CH_2- moiety with formation of a Ir-CH=CH- group. It is well-known that DMP oxidizes alcohol functionalities to keto groups,[18] while use of this reagent, and related species, in the dehydrogenation of suitable ketones with formation of conjugated enones,[19] has been studied in detail.[20] In fact, ketone **25** yielded **27** under the same reaction conditions (Scheme 13b).



Scheme 13. Reaction of alcohol **10** (a) and of ketone **25** (b) with DMP.

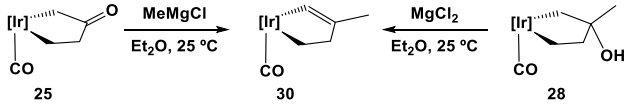
Reactions of ketone 25 and enone 24 with RLi and RMgX

Ketone **25** reacted with MeLi and PhLi with formation of the alcohols **28** and **29**, respectively (Scheme 14a; **28** characterized only by NMR). Quite surprisingly both the R^- nucleophiles added to the C=O carbon through the *endo* face (NOESY evidence), *i.e*. the one that "apparently" is the sterically less favoured. Interestingly, this is also the case for its reaction with $NaBH_4$ that gave alcohol **10** (Scheme 14b).



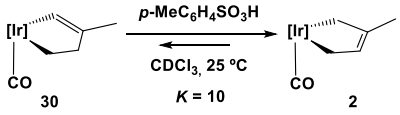
Scheme 14. Reaction of ketone **25** with a) MeLi and PhLi and with b) $NaBH_4$.

By contrast, and upon reaction with MeMgCl,[21] ketone **25** afforded the 2-iridacyclopentene derivative **30** (Scheme 15).[22] This compound seems to be the result of the addition of Me^- to the ketone group to give alcohol **28** followed by a regiospecific dehydration (no isomers of **30** were observed). If this alcohol is an intermediate in this transformation it is quite plausible that the magnesium cation, acting as a Lewis acid, is responsible for the dehydration process, and in fact **28** gave **30** upon interaction with $MgCl_2$ in Et_2O (Scheme 15). It is worthy of remark that the formation of the C=C double bond is somehow specially favored in this system since the reaction of cyclopentanone with MeMgCl (Et_2O, 25 ºC) yields only the corresponding tertiary alcohol.



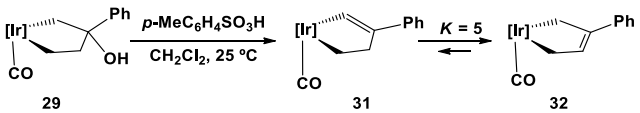
Scheme 15. Reaction of ketone **25** with MeMgCl to give complex **30** and formation of the latter species by treatment of alcohol **28** with $MgCl_2$.

We have also found that compound **30** isomerized to compound **2**, in $CDCl_3$ in the presence of *p*-toluenesulfonic acid, with a thermodynamic equilibrium being stablished with the latter species predominating (*K* = 10, Scheme 16).



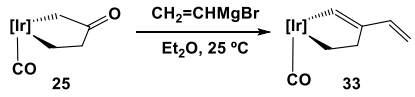
Scheme 16. Complex **30** equilibrates with its isomer **2** in the presence of *p*-toluenesulfonic acid.

Dehydration of the phenyl derivative **29** can also be induced easily, but slowly, by stirring its CH_2Cl_2 solutions, at 25 ºC, in the presence of silica gel. Under these conditions, a mixture of the isomeric olefins **31** (characterized only by NMR) and **32** was formed with the former being the kinetic product which then transformed into the more stable species **32**. This isomerization was faster in the presence of *p*-toluensulfonic acid ($CDCl_3$) and this has allowed for the thermodynamic ratio 5:1 to be easily reached (Scheme 17).



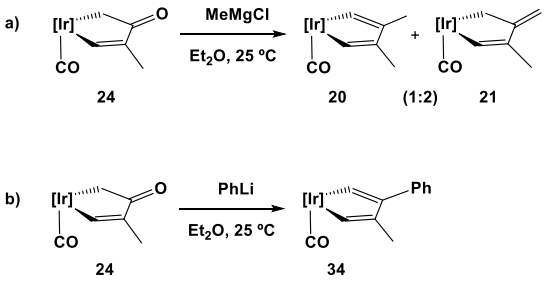
Scheme 17. Ketone **31** is the kinetic product of the acid-catalyzed dehydration of alcohol **29** but its isomer **32** is thermodynamically favoured.

We have also studied the reaction of ketone **25** with CH_2=CHMgBr to find out that it gave exclusively the conjugated diene **33** (Scheme 18). In addition to being characterized by NMR spectroscopy, this compound has also been subjected to X-ray crystallography (Figure S8). It is quite possible that, in accord with the results already presented, this may be the kinetic product while the isomer having the internal C=C double bond in the 3-position being the thermodynamically favored.



Scheme 18. Reaction of ketone **25** with CH_2=CHMgBr.

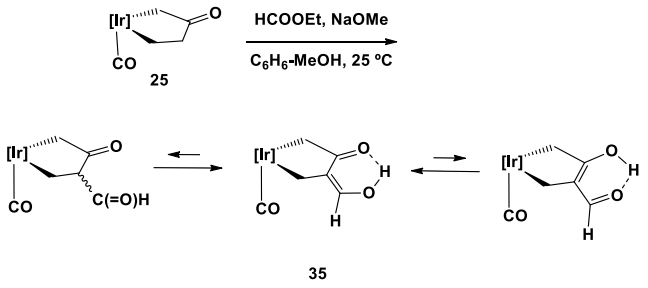
Finally in this section, it was observed that enone **24** reacted with MeMgCl with formation of a 1:2 mixture of the previously described dienes **20** and **21** (Scheme 19a). It is quite probable that this ratio is under thermodynamic control as it is also the one obtained by the very different synthetic method depicted in Scheme 3c. By contrast, its reaction with PhLi gave diene **34** exclusively (characterized only by NMR) (Scheme 19b).[23]



Scheme 19. Reactions of enone **24** with a) MeMgCl and with b) PhLi.

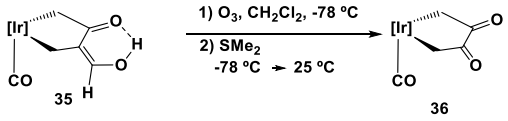
α-Formylation of the 3-iridacyclopentanone 25 and further functionalization of the resulting product 35

The room temperature reaction of **25** with ethyl formate in a mixture of benzene-methanol, in the presence of NaOMe, gave the α-formylketone **35** (Scheme 20). This Claisen condensation is a commonly used procedure in Organic Chemistry to introduce a formyl group in α to an enolizable ketone.[24] Compound **35** (characterized only by NMR) could, in principle, exists as the four isomeric structures represented in Scheme 20.[25] In this case, and in general in related organic derivatives, the hydroxymethylene species predominates in $CDCl_3$ solutions, as suggested by resonances at 8.58 and 121.2 ppm, in the ^1H NMR and the $^{13}C\{^1H\}$ NMR spectra, respectively, in accord with a =CH(OH) functionality.



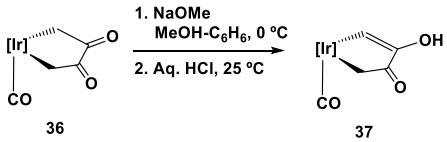
Scheme 20. α-Formylation of ketone **25** and the four possible equilibrating structures of the resulting product **35**.

Ozonolysis of compound **35** yielded diketone **36** (Scheme 21).[26] It is worth to mention that, contrary to some cases described in the literature, a Baeyer-Villiger overoxidation process, yielding an acid anhydride by the oxidative rupture of the -C(=O)—C(=O)- bond, did not take place.[6] However, this acid anhydride has been obtained by an alternative procedure (see below).



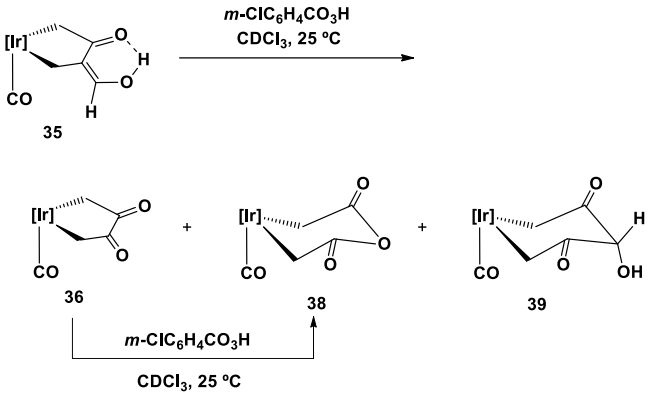
Scheme 21. Ozonolysis of compound **35**.

Diketone **36** is characterized by an absorption at 1712 cm^{-1} in the IR spectrum and its symmetric structure is manifested by quite simple ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra. Interestingly, its solutions in $CDCl_3$ are stable for long periods of time while α,β-cyclopentadione appears to exist, in solution, mainly as the enolic form with the diketo-keto/enol equilibrium being quite fast at room temperature in the laboratory time scale. The enhanced stability of the diketo tautomer of **36** seems to be kinetic in nature since it was transformed quantitatively to the keto-enol isomer **37** by reaction with an excess of NaOMe, in a benzene:methanol mixture, followed by acid treatment (Scheme 22).



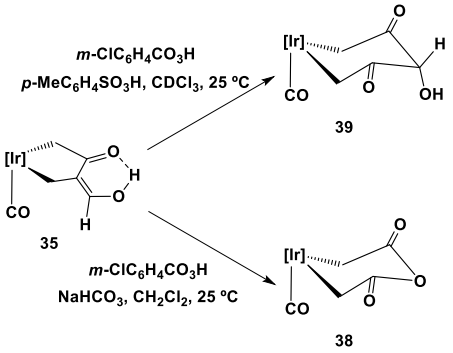
Scheme 22. Isomerization of diketone **36** into the enol **37** by sequential treatment with an excess of NaOMe and of HCl.

^{1}H NMR monitoring of the reaction of derivative **35** with an excess of *m*-chloroperbenzoic acid, in $CDCl_3$ at 25 ºC, showed the formation of three products, the diketone **36**, the acid anhydride **38** (having one carbon atom less than the starting material; only characterized by NMR) and the diacylcarbinol **39** (with an expanded ring) (Scheme 23).[27]



Scheme 23. Reaction of complex **35** with an excess of *m*-$ClC_6H_4CO_3H$ in $CDCl_3$ at 25 ºC.

From this monitoring, and supported by other control experiments, it is concluded that acid anhydride **38** appears at the expenses of diketone **36** *via* a Baeyer-Williger oxidation.[26] Curiously, the competitive paths leading to the diketone and to the diacylcarbinol are kinetically controlled by the acidity of the solution and thus, when the oxidation of **35** was carried out in the presence of the stronger acid *p*-toluenesulfonic acid, derivative **39** was exclusively obtained (Scheme 24; characterized only by NMR), while in the presence of sodium bicarbonate derivative **38** was mainly formed (Scheme 24).

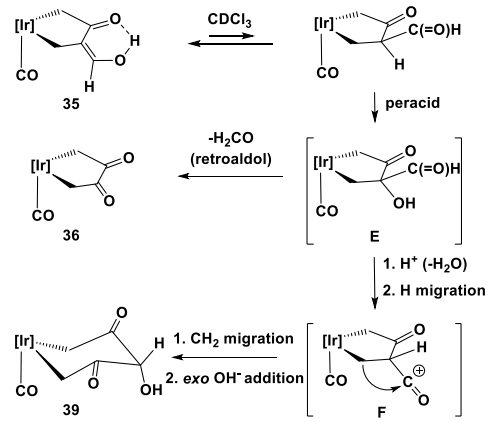


Scheme 24. Influence of the medium acidity in the outcome of the oxidation of complex **35** with *m*-$ClC_6H_4CO_3H$.

Compounds **38** and **39** were characterized by NMR spectroscopy, and the configuration of the CH(OH) moiety of the latter species based on its NOESY spectrum. Interestingly, the structure of compound **39** contrasts with those found for pure organic derivatives in which the enol form predominates, at least in solution. More specifically, and for unknown reasons, **39** does not adopt the expected enodiolic form, -C(OH)=C(OH)-C(=O)-, which is stabilized by two hydrogen bonding interactions. Compounds with such a structure, called acireductones,[27] are very susceptible to oxidation, even by air, to give α,β,γ-triketones. Perhaps compound **39** can not be overoxidized because its enolic form is not kinetically available.

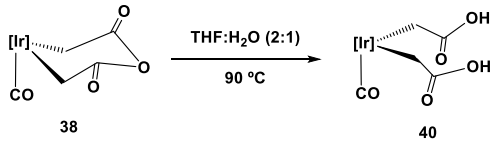
Scheme 25 shows a plausible mechanism for these oxidations in which intermediate **E**, responsible for the formation of both **38** and **39**, is obtained by hydroxylation[28] of the less

stable *endo*-formyl tautomer of compound **35** previously depicted in Scheme 20.



Scheme 25. Proposed mechanism for the formation of compounds **38** and **39**.

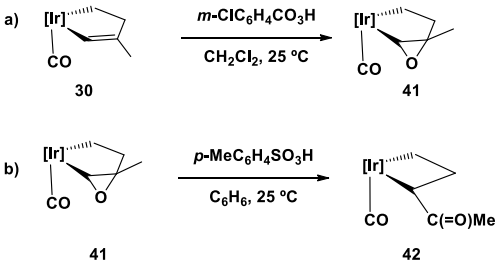
Finally, in this section, we have to mention that the acid anhydride **38** can be hydrolyzed, but with great difficulty, to the diacid **40** (Scheme 26; **40** characterized only by NMR).



Scheme 26. Hydrolisis of acid anhydride **38**.

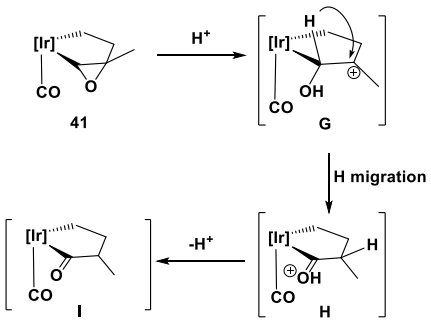
Five to four iridacycle-ring contraction reactions

Complex **30** reacted with *m*-chloroperbenzoic acid, in CH_2Cl_2 at 25 ºC, with formation of the corresponding epoxide **41** (Scheme 27a) and, as expected, the peracid has attacked the *exo* face of the olefin (NOESY evidence). This epoxide further reacted with the stronger acid *p*-toluenesulfonic acid, in benzene at 25 ºC, to give complex **42**, an iridacyclobutane[29] with an *exo*-acetyl substituent in the α-position with respect to the metal center (Scheme 27b). Both compounds **41** and **42** have been fully characterized only by NMR spectroscopy and their stereochemistry deduced from their NOESY spectra.



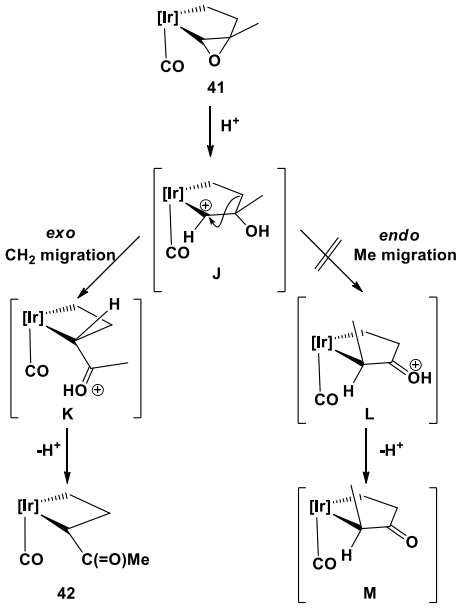
Scheme 27. a) Epoxidation of complex **30** to give **41** and b) ring contraction of the latter compound in the presence of a strong acid.

Formation of complex **42** may be explained by an acid-catalyzed isomerization in which the epoxide first opened and the resulting intermediate then contracted. However, this process description is not satisfactory since the protonation of the epoxide oxygen is expected to form carbocation **G**, in which a suprafacial migration of the hydrogen atom converts it to **H**, an intermediate that should afford the acyl **I** by deprotonation (Scheme 28).



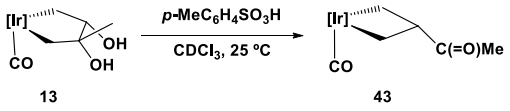
Scheme 28. Expected, but unobserved, acid-mediated isomerization of epoxide **41**.

Therefore complex **42** must result from a preferred alternative kinetic route and a reasonable mechanism for its formation is shown in Scheme 29. Here, the protonation of **41** is followed by the formation of the alternative carbocation **J** in which the positive charge is in α position with respect to the metal. This species then contracts to **K** by a Wagner-Meerwein *exo* migration of the β-CH_2 group (notice that this process must be preferred to an alternative methyl migration that would give ketone **M**) which finally deprotonates to give the observed product. In consequence, it has to be proposed that the iridium atom should somehow stabilize a carbocation in α, *i.e*. **J** versus **G** in Scheme 28, and also that the *exo* migration of a carbon to this cationic center must be specially favoured (the CH_2 group may migrate *exo* or *endo* while the methyl substituent has to migrate *endo*).



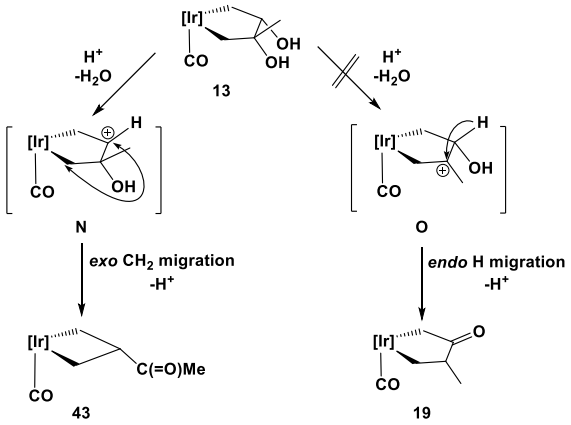
Scheme 29. Proposed mechanism for the formation of the iridacyclobutane **42** by the acid-catalyzed isomerization of epoxide **41**.

A positional isomer of compound **42**, ketone **43**, was obtained when the *cis*-diol **13** was treated with *p*-toluenesulfonic acid (Scheme 30). This reaction may be described as an acid-catalyzed dehydration coupled to a ring contraction of the metallacycle with formation of an *exo*-acetyl substituent in the β position with respect to the metal center. Again, the *exo* disposition of the C(=O)Me group was deduced from the analysis of its NOESY spectrum.



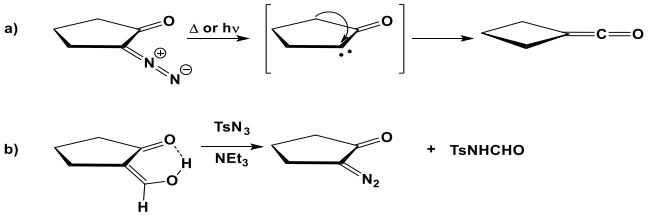
Scheme 30. Reaction of diol **13** with *p*-toluenesulfonic acid.

Formation of complex **43** (characterized only by NMR) is best explained through the formation of intermediate **N** (Scheme 31) which then contracts similarly to **J** in Scheme 29. However, it is difficult to understand why the alternative intermediate **O**, which should give derivative **19**, is not formed at all.[30]



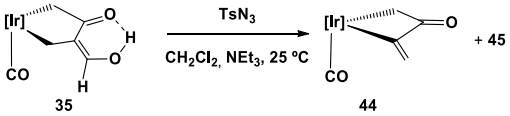
Scheme 31. Proposed mechanism for the formation of complex **43** by the reaction of diol **13** with acid.

The Wolff rearrangement consists on the transformation/s of a diazoalkane having an adjacent keto group, *i.e.* the functionality R-C(=N_2)-C(=O)-R´, which takes place *via* thermal (with or without a metal-based catalyst) or photochemical activation. Carbene R-C(:)-C(=O)-R´ seems to be the main, unstable, reaction product which evolves depending on the nature of R, R´ and the reaction media.[31] One of the most interesting cases of this reaction occurs when the α-diazoketone functionality belongs to a carbocycle because, in general, it yields derivatives having a contracted ring. This is particularly important for the synthesis of cyclobutanes[32] from five-membered rings and the simplest example is shown in Scheme 32a. As can be observed, the carbene intermediate gives a ketene functionality by migration of a CH_2 moiety, in the β position with respect to the carbene, with concomitant formation of the cyclobutane ring. Generally, the ketene is not isolated but it is trapped by any adequate reagent present in the reaction mixture.



Scheme 32. a) Thermal (with or without a metal-based catalyst) or photochemical evolution of α-diazocyclopentanone. b) Transformation of α-formylcyclopentanone (for convenience the enol tautomer is the one depicted herein) to the corresponding α-diazoketone by its reaction with TsN_3 in the presence of NEt_3.

Of the different methods reported to obtain α-diazoketones, one of particular interest to us, is the reaction of α-formylketones with tosyl azide in the presence of a base[30] (Scheme 32b). Interestingly, when this reaction was carried out with compound **35**, in CH_2Cl_2 at 25 ºC in the presence of NEt_3, the expected diazoalkane was not observed but instead compound **44** formed in *ca.* 45% isolated yield (Scheme 33)[33] along with an insoluble product, namely compound **45** (see below).



Scheme 33. Reaction of the α-formylketone **35** with TsN_3 in the presence of NEt_3.

As can be observed compound **44** is a 3-iridacyclobutanone with an exocyclic methylene group. This derivative has been completely characterized, among others methods, by IR and NMR spectroscopy. It is interesting to note that the corresponding organic derivative of **44**, a four-membered carbocycle (-$CH_2CH_2CH_2(=CH_2)C(=O)$-), is a liquid with high tendency to polymerization.[34] In the other hand, 3-metallacyclobutanones have been described in the literature, including the Ir^{III} derivative **P** (Figure 3) which has been characterized, among other techniques, by crystallography.[35] As this metallacycle presents a dihedral angle of 139º between the planes CH_2-Ir-CH_2 and CH_2-C(=O)-CH_2, it was deduced that resonance form **Q** contributes notably to the fundamental state of the molecule. As an X-ray diffraction study carried out with **44**[1] clearly shows that the four membered ring is almost planar, we can deduce that formulation **R** is not contributing, to any extent, to its structure.[36]

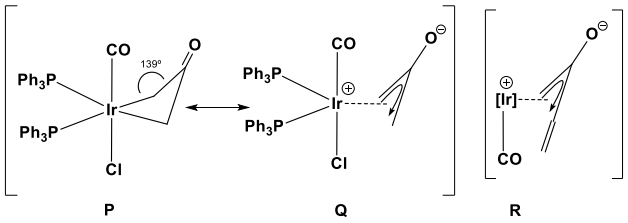
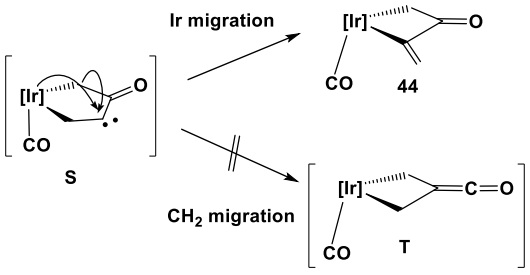


Figure 3. The two resonance forms **P** and **Q** that contributed to the ground state of the Ir^{III} 3-metalobutanone of reference 35. By comparison, resonance form **R** does not contribute to any extent to the structure of **44**.

We propose that formation of ketone **44** results (Scheme 34) from migration of the iridium to the carbene carbon of intermediate **S** that would be the result of N_2 extrusion of a purported unobserved intermediate irida-diazoalkane. Clearly this pathway should be preferred to the alternative CH_2 migration that would give the otherwise expected ketene **T** (*endo* migrations have been represented in this scheme but it is obvious that *exo* processes afford the same structures).[37]



Scheme 34. The two possible migration pathways of intermediate **S**.

The structure of the byproduct of the reaction of Scheme 33, compound **45**, has been shown by X-ray crystallography (Figure S9) to be a metallacycle-degradation species that contains an alkyl chain (1 C) and a *trans*-alkenyl chain (2 C) both with tosylamide ending groups bonded to the iridium center (Figure 4).

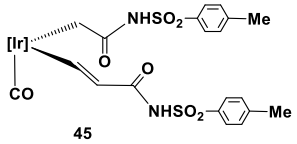
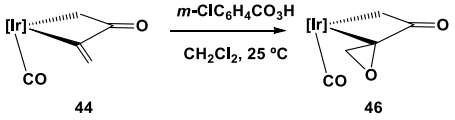


Figure 4. Structure of compound **45** as deduced from single crystal X-ray diffraction studies.

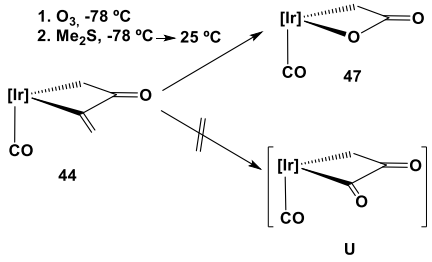
Compound **44** showed an interesting reactivity towards some oxidizing reagents. Thus, with *m*-chloroperbenzoic acid in CH_2Cl_2 at room temperature, it was epoxidized to complex **46** (Scheme 35). The stereochemistry of this species was deduced from its NOESY spectrum and confirmed crystallographically.[1] It is concluded, therefore, that the peracid, once again, attacks the *exo* olefin face. In contrast with the 3-iridabutanone **44**, this metallacycle considerably deviates from planarity and the dihedral angle is *ca*. 145º. This and the fact that the C=O bond length of the keto function (1.311(18) Å) is longer than expected for a C=O double bond (1.22 Å), suggest a large contribution to the fundamental state of the molecule of a resonance form related to **R** of Figure 3, at least in the solid state.

The reaction just described is somewhat unexpected as α,β-unsaturated ketones do not usually react with this electrophilic reactant (when they do, the Baeyer-Villiger oxidation is the most common transformation) and their epoxidation normally requires nucleophilic agents, such as H_2O_2 in basic media.[8] It is quite probable that the α iridium center increases the electronic density of the olefinic function thus allowing this reaction to proceed.



Scheme 35. Reaction of complex **44** with *m*-chloroperbenzoic acid.

Ozonolysis of **44** also gave a surprising result as metallalactone[38] **47** was obtained instead of the expected α,β-diketone **U** (Scheme 36). Compound **47** had been completely characterized by spectroscopy including X-ray crystallography.[1] As can be observed a carbon atom of the starting metallacycle has been lost and substituted by an oxygen atom. Although this behavior is unusual in ozonolysis processes it has been reported before in the case of an α,β-unsaturated ketone.[39]



Scheme 36. Ozonolysis of compound **44**.

Conclusions

In this paper we have demonstrated, in sufficient extent, that organometallic species with reactive functionalities like -CH=CH-, >C=O, etc., more or less distanced from a M—C bond, if certain premises of the coligands and the metal center apply are able to be the subjects of common organic procedures to give novel organometallic structures that would be very dificcult to obtain by other methods. More importantly, we have also shown that, in a number of cases, the metal strongly influences the outcome of some of these reactions leading to unexpected products as compared with all-carbon systems.

Experimental Section

General methods. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were obtained by the use of a Bruker Vector 22 spectrometer. The NMR Instruments were Bruker DRX-500, DRX-400, and DPX-300 spectrometers. Spectra were referenced to external $SiMe_4$ (δ 0 ppm) using the residual protio solvent peaks as internal standards (^{1}H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). Spectral assignments were made by means of routine one- and two-dimensional NMR experiments where appropriate. Unless obviously unnecessary all manipulations were performed under dinitrogen, following conventional Schlenk techniques. Solvents were freshly dried and distilled prior to use where appropriate. Compounds **1**, **2** and **3** were obtained by using published procedures.[5] Elemental analysis have been obtained only for selected compounds.

Supporting Information for this paper contains the synthesis and characterization of all the new products, along with the X-ray data for products **5** (CCDC 1565331), **7** (CCDC 1565332), **10** (CCDC 1565333), **12** (CCDC 1565334), **15** (CCDC 1565335), **19** (CCDC 1565336), **25** (CCDC 1565337), **33** (CCDC 1565338), and **45** (CCDC 1565339).

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Keywords: Iridium • Metallacycles • C=C Reactivity • Ring-contraction • Wolff rearrangement

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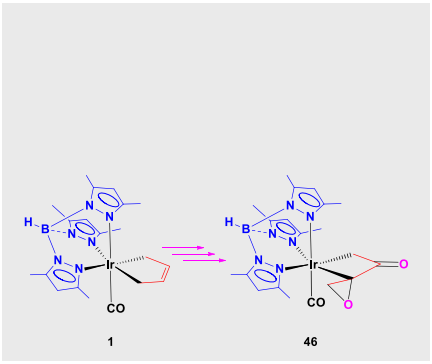
Entry for the Table of Contents

Layout 1:

FULL PAPER

Using methods commonly applied in Organic Chemistry, the 3-iridacyclopentenes of complexes [Tp^{Me2}Ir(k^2-C,C-CH_2CR'=$CRCH_2$)(CO)] (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate; R = R' = H, **1**; R = Me, R' = H, **2**; R = R' = Me, **3**), have been functionalized, in some cases with unexpected outcomes, to give organometallic species with new structural motivs, as the example shown in the Scheme.



Margarita Gómez, Nuria Rendón, Eleuterio Álvarez, Kurt Mereiter, Manuel L. Poveda, and Margarita Paneque**

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Functionalization of 3-iridacyclopentenes

Supporting Information

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Compounds **4**-**47**.

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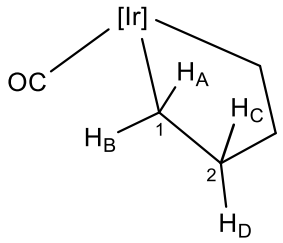
III REFERENCES

I SYNTHESIS AND CHARACTERIZATION

General methods. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were obtained by the use of a Bruker Vector 22 spectrometer. The NMR Instruments were Bruker DRX-500, DRX-400, and DPX-300 spectrometers. Spectra were referenced to external $SiMe_4$ (δ 0 ppm) using the residual protio solvent peaks as internal standards (^{1}H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). Spectral assignments were made by means of routine one- and two-dimensional NMR experiments where appropriate. Unless obviously unnecessary all manipulations were performed under dinitrogen, following conventional Schlenk techniques. Solvents were freshly dried and distilled prior to use where appropriate. Compounds **1**, **2** and **3** were obtained by using published procedures.[1] Elemental analysis have been obtained only for selected compounds. Some of the samples obtained for X-ray crystallography and for elemental analysis where crystallized from solvent mixtures different to those used for the bulk isolation of the products during the work-up procedures. In some cases solvates were obtained, as observed in the unit cell (compounds **12** and **45**) of the X-ray structures. For the case of the elemental analysis of compounds **9**, **27**, **29** and **45**, integration of these signals in the NMR is not reported due to the normally small amount of sample obtained by these recrystallization procedures and also to the very different relaxation time corresponding to the protons of the solvents in comparison to the organometallic products, which make difficult to obtain an accurate measure.

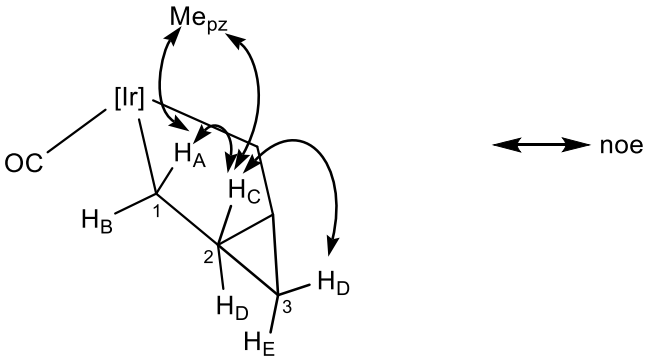
Compound 4. To a solution of complex **1** (0.10 g, 0.17 mmol) in dioxane (10 mL), a small quantity of PtO_2 was added and the resulting mixture was treated with 4 bar of H_2 in a Fisher porter vessel. The solution was stirred at 80 ºC for 3 days and then centrifugated, filtered and taken to dryness. ^{1}H NMR analysis of the crude reaction product showed quantitative formation of compound **4** which

was purified by column chromatography on silica gel using a mixture of *n*hexane:Et_2O (10:1) as eluent. Yield: 44 mg, 0.077 mmol (45%). R_f = 0.27 [silica gel; *n*hexane:Et_2O (1:5)]. An analytically pure sample, as white needles, was obtained by crystallization from a mixture of *n*hexane:CH_2Cl_2 (1:2) at -20 ºC.



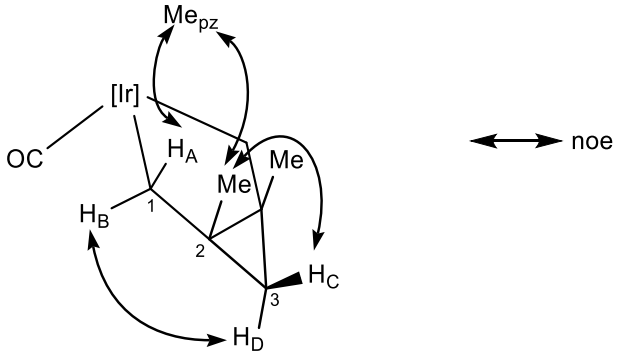
^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.81 (s, 3 H, 3 CH_{pz}), 2.64, 2.16 (m, 2 H each, 2 CH_AH_B), 2.52, 2.40, 2.36 (s, 1:2:3, 6 Me_{pz}), 1.88, 1.66 (m, 2 H each, 2 CH_CH_D); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ = 169.7 (CO), 151.0, 150.8, 144.0, 143.5 (2:1:1:2, C_{qpz}), 109.3, 107.2 (1:2, CH_{pz}), 35.3 (C^2, $^1J_{CH}$ = 122 Hz), 15.2, 14.6, 13.5, 12.8 (1:2:1:2, Me_{pz}), 2.8 (C^1, $^1J_{CH}$ = 125 Hz); IR (Nujol): ν 1987 cm^{-1} (Ir—CO); elemental analysis calcd (%) for $C_{20}H_{30}BN_6OIr$: C 41.9, H 5.2, N 14.7; found: C 41.4, H 5.2, N 15.0.

Compound 5. To a solution of compound **1** (0.10 g, 0.17 mmol) in diethyl ether (5 mL), an excess of $ZnEt_2$ (2.8 mL, 1 M in hexane, 2.8 mmol) and CH_2I_2 (0.34 mL, 4.2 mmol) were added sequentially. The resulting mixture was stirred at room temperature for 12 h and, after this period of time a NH_4Cl-saturated water solution was added. The organic phase was separated, dried with $MgSO_4$ and taken to dryness. ^{1}H NMR analysis of the resulting product showed that only a partial transformation of **1** into compound **5** has occurred (80% conversion). **5** could not be separated from **1** by column chromatography on silica gel, hence the crude mixture was treated with *m*-chloroperbenzoic acid to transform **1** into **7** (see below). In this way **5** was separated by column chromatography on silica gel eluting with a mixture of *n*hexane:Et_2O (10:1). Yield: 65 mg, 0.11 mmol (65%). R_f = 0.55 (silica gel; *n*hexane: Et_2O, 5:1). An analytically pure sample, as white crystals, was obtained by crystallization from a mixture of *n*hexane:CH_2Cl_2 (1:2) at -20 ºC.



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.79, 5.75 (s, 1:2, 3 H, 3 CH_{pz}), 2.54 (d, 2 H, $^2J_{AB}$ = 11.1 Hz, 2 H_B), 2.52, 2.33, 2.32, 2.29 (s, 1:1:2:2, 18H, 6 Me_{pz}), 2.36 (dd, 2H, $^3J_{CA}$ = 2.8 Hz, 2 H_A), 0.77 (m, 2 H, 2 H_C), 0.33 (td, 1 H, $^3J_{BD}$ = 8.3 Hz, $^2J_{ED}$ = 4.5 Hz, H_D), 0.20 (q, 1 H, $^3J_{CE}$ = 4.5 Hz, H_E); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 170.9 (CO), 150.7, 150.6, 143.6, 143.3 (1:2:1:2, C_{qpz}), 108.7, 106.8 (1:2, CH_{pz}), 27.3 (C^2, $^1J_{CH}$ = 157 Hz), 14.4, 13.1, 13.0, 12.5 (2:1:1:2, Me_{pz}), 9.7 (C^3, $^1J_{CH}$ = 157 Hz), 4.6 (C^1, $^1J_{CH}$ = 129 Hz); IR (Nujol): ν 1986 cm^{-1} (Ir—CO); elemental analysis calcd (%) for $C_{21}H_{30}BN_6OIr$: C 43.1, H 5.1, N 14.4; found: C 43.4, H 5.1, N 15.2.

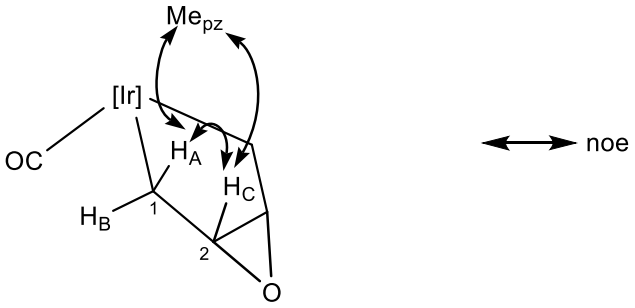
Compound 6. Following the same procedure described above for the synthesis of **5**, but starting with complex **3**, a 1:4 mixture of compounds **3**:**6** was obtained. Complex **6** was characterized by NMR spectroscopy in admixture with **3**.



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.77 (s, 3 H, 3 CH_{pz}), 2.77 (d, 2 H, $^2J_{AB}$ = 11.2 Hz, 2 H_B), 2.36, 2.33, 2.32 (s, 1:1:1, 18 H, 6 Me_{pz}), 2.05 (d, 2 H, 2 H_A), 1.16 (s, 6 H, 2 Me), 0.54 (d, 1 H, $^2J_{CD}$ = 4.2 Hz, H_D), -0.34 (d, 1 H, H_C); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 170.8 (CO), 150.6-143.1 (C_{qpz}), 108.1, 106.8 (1:2, CH_{pz}), 34.2 (C^2),

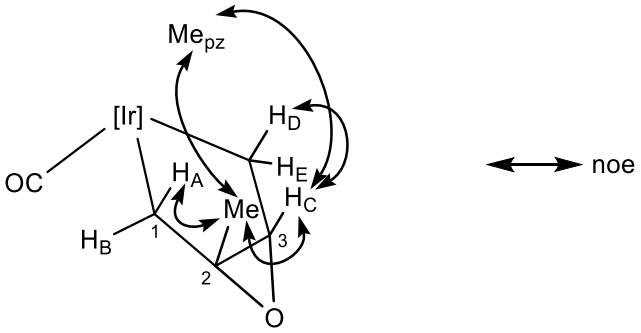
22.5 (C^3, $^1J_{CH}$ = 164 Hz), 21.6 (Me), 14.5, 12.8, 12.5, 11.9 (2:1:2:1, Me_{pz}), 13.1 (C^1, $^1J_{CH}$ = 130 Hz).

Compound 7. A solution of *m*-$ClC_6H_4CO_3H$ (0.13 g, 0.75 mmol) in dichloromethane (5 mL) was added to a solution of compound **1** (0.30 g, 0.52 mmol) in the same solvent (5 mL) at 0 ºC. The resulting solution was stirred at room temperature for 1 h and, after this period of time, a $NaHCO_3$-saturated water solution added. The organic phase was separated, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the resulting product revealed quantitative formation of compound **7**. An analytically pure sample, as white needles, was obtained by crystallization from a mixture of Et_2O:CH_2Cl_2 (1:2) at -20 ºC. Yield: 180 mg, 0.31 mmol (60%).



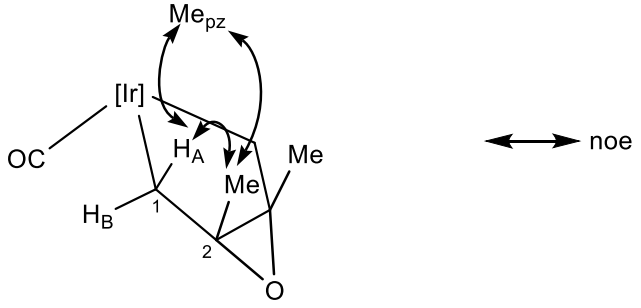
^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.82, 5.79 (s, 1:2, 3 H, 3 CH_{pz}), 2.89 (s, 2 H, 2 CH_C), 2.66 (d, 2 H, $^2J_{AB}$ = 13.0 Hz, 2 H_B), 2.36, 2.34, 2.33, 2.28 (s, 1:2:2:1, 18H, 6 Me_{pz}), 2.17 (d, 2 H, 2 H_A); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 168.9 (CO), 151.0, 150.4, 144.0, 143.7 (2:1:1:2, C_{qpz}), 109.3, 107.2 (1:2, CH_{pz}), 65.8 (C^2, $^1J_{CH}$ = 170 Hz), 14.7, 13.6, 13.2, 12.8 (2:1:1:2, Me_{pz}), 2.1 (C^1, $^1J_{CH}$ = 127 Hz); IR (Nujol): ν 1999 cm^{-1} (Ir—CO); elemental analysis calcd (%) for $C_{20}H_{28}BN_6O_2Ir$: C 40.9, H 4.8, N 14.3; found: C 40.8, H 4.6, N 13.9.

Compound 8. Following the same procedure described above for complex **7**, but starting with **2** (0.30 g, 0.51 mmol) complex **8** was quantitatively obtained. A spectroscopically pure sample, a microcrystalline pale yellow solid, was obtained by crystallization from a mixture of Et_2O:CH_2Cl_2 (1:2) at -20 ºC. Yield: 235 mg, 0.39 mmol (76%).



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.82, 5.77 (s, 1:2, 3 H, 3 CH_{pz}), 2.82 (s, 1 H, H_C), 2.65 (d, 1 H, $^2J_{DE}$ = 12.8 Hz, H_E), 2.61 (d, 1 H, $^2J_{AB}$ = 12.8 Hz, H_B), 2.35, 2.34, 2.33, 2.32 (s, 1:1:2:2, 18 H, 6 Me_{pz}), 2.14 (dd, 1 H, $^3J_{CD}$ = 1.7 Hz, H_D), 2.05 (d, 1 H; H_A), 1.55 (s, 3 H, Me); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ = 169.1 (CO), 151.0, 150.5, 144.0, 143.7 (2:1:1:2, C_{qpz}), 109.1, 107.2 (1:2, CH_{pz}), 72.4 (C^3, $^1J_{CH}$ = 168 Hz), 71.4 (C^2), 19.5 (Me), 14.8, 14.7, 13.4, 13.3, 12.8 (1:1:1:1:2, Me_{pz}), 6.0 (C^1, $^1J_{CH}$ = 127 Hz), 0.9 (C^4, $^1J_{CH}$ = 134, 127 Hz); IR (Nujol): ν 2007 cm^{-1} (Ir—CO).

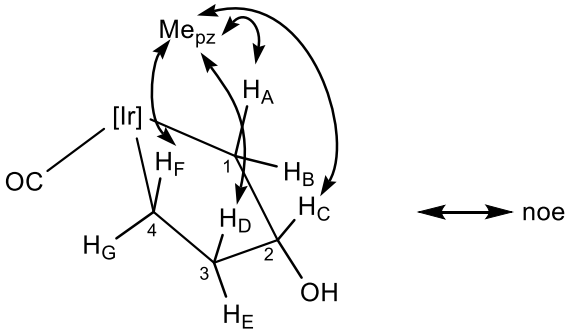
Compound 9. Following the same procedure described above for complex **7**, but starting with **3** (0.30 g, 0.50 mmol), complex **9** was quantitatively obtained. An analytically pure sample, a microcrystalline pale yellow solid, was obtained by crystallization from a mixture of Et_2O:CH_2Cl_2 (1:2) at -20 ºC. Yield: 240 mg, 0.38 mmol (76%).



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.81, 5.77 (s, 1:2, 3 H, 3 CH_{pz}), 2.79 (d, 2 H, $^2J_{AB}$ = 13.0 Hz, 2 H_B), 2.34, 2.23 (s, 5:1, 18 H, 6 Me_{pz}), 2.08 (d, 2 H, 2 H_A), 1.40 (s, 6 H, 2 Me); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ = 168.9 (CO), 150.9, 150.5, 144.0, 143.6 (2:1:1:2, C_{qpz}), 108.9, 107.1 (1:2, CH_{pz}), 73.8 (C^2), 19.3 (Me), 14.7, 13.2, 12.8, 12.6 (2:1:2:1, Me_{pz}), 8.5 (C^1, $^1J_{CH}$ = 127 Hz); IR (Nujol): ν 2007 cm^{-1} (Ir—

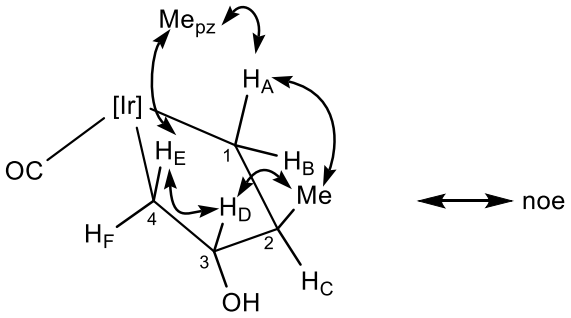
CO); elemental analysis calcd (%) for $C_{22}H_{32}BN_6O_2Ir{\cdot}H_2O$: C 42.9, H 5.2, N 13.6; found: C 41.7, H 5.7, N 13.1.

Compound 10. To a cold (0 ºC) solution of **1** (0.20 g, 0.35 mmol) in THF (10 mL) an excess of $BH_3{\cdot}THF$ (2.5 mL, 1 M in THF, 2.5 mmol) was added. The reaction mixture was stirred at 0 ºC for 30 min and then at room temperature for 4 h. After cooling the system at 0 ºC, NaOH (2.5 mL, 3 M in H_2O) and H_2O_2 (2.5 mL, 30% in H_2O) were added and the resulting mixture stirred for 2 h at room temperature. Upon addition of 10 mL of Et_2O the organic phase was separated, washed with NaCl-saturated water, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude product revealed quantitative formation of **10**, which was purified by crystallization from a mixture of Et_2O:CH_2Cl_2 (1:2) at -20 ºC as white needles. Yield: 195 mg, 0.33 mmol (94%).



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.78, 5.77 (s, 1:2, 3 H, 3 CH_{pz}), 4.40 (m, 1 H, H_C), 2.59 (dd, 1 H, J_{HH} = 12.4 and 6.6 Hz, H_D), 2.50, 2.45 (m, 1 H each, 2 H, H_E and H_G), 2.41, 2.38, 2.36, 2.32 (s, 1:1:1:3, 18 H, 6 Me_{pz}), 2.26 (m, 1 H, H_A), 1.82 (td, 1 H, J_{HH} = 10.2 and 7.2 Hz, H_F), 1.50 (m, 1 H, H_B); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 168.7 (CO), 150.8, 150.7, 150.1, 143.9, 143.3 (1:1:1:1:2, C_{qpz}), 109.0, 107.0, 106.9 (CH_{pz}), 80.7 (C^2, $^1J_{CH}$ = 141 Hz), 45.2 (C^3, $^1J_{CH}$ = 123 Hz), 15.0, 14.4, 14.2, 13.2, 12.52, 12.5 (Me_{pz}), 10.5 (C^1, $^1J_{CH}$ = 127 Hz), -6.1 (C^4, $^1J_{CH}$ = 129 Hz); IR (Nujol): ν 2001 cm^{-1} (Ir—CO); elemental analysis calcd (%) for $C_{20}H_{30}BN_6O_2Ir$: C 40.7, H 5.1, N 14.3; found: C 40.6, H 4.8, N 14.0.

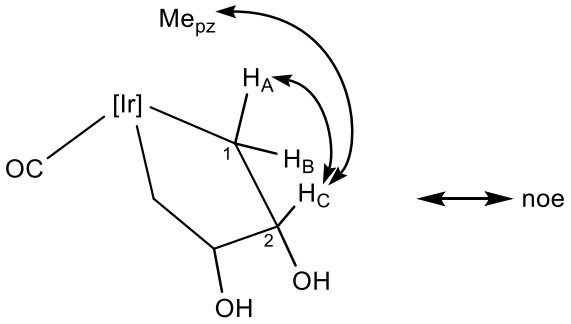
Compound 11. Following the same procedure described above for complex **10**, but starting with **2** (0.20 g, 0.34 mmol), complex **11** was quantitatively obtained. A spectroscopically pure sample, a pale brown solid, was obtained by crystallization from a mixture of Et_2O:CH_2Cl_2 (1:2) at -20 ºC. Yield: 185 mg, 0.31 mmol (91%).



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.80, 5.78, 5.75 (s, 1 H each, 3 H, 3 CH_{pz}), 4.04 (q, 1 H, $^3J_{ED}$ = $^3J_{FD}$ = $^3J_{CD}$ = 8.2 Hz, H_D), 2.63, 2.57 (dd, 1 H each, $^2J_{EF}$ = 12.1 Hz, H_E and H_F), 2.42, 2.41, 2.33, 2.32, 2.31 (s, 1:1:1:1:2, 18 H, 6 Me_{pz}), 2.35 (dd, 1 H, $^2J_{AB}$ = 11.0, $^3J_{CB}$ = 5.5 Hz, H_B), 1.66 (m, 1 H, H_C), 1.51 (dd, 1 H, $^3J_{CA}$ = 13.2 Hz, H_A), 1.14 (d, 3 H, $^3J_{CMe}$ = 6.0 Hz, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 168.7 (CO), 151.0, 150.2, 144.3, 143.6 (2:1:1:2, C_{qpz}), 109.4, 107.4, 107.1 (CH_{pz}), 84.5 (C^3, $^1J_{CH}$ = 138 Hz), 53.8 (C^2, $^1J_{CH}$ = 131 Hz), 21.7 (Me), 16.0, 14.6, 13.5, 12.7 (1:1:1:1:2, Me_{pz}), 6.2 (C^4, $^1J_{CH}$ = 129 Hz), 2.3 (C^1, $^1J_{CH}$ = 127 Hz); IR (Nujol): ν 1994 cm^{-1} (Ir—CO).

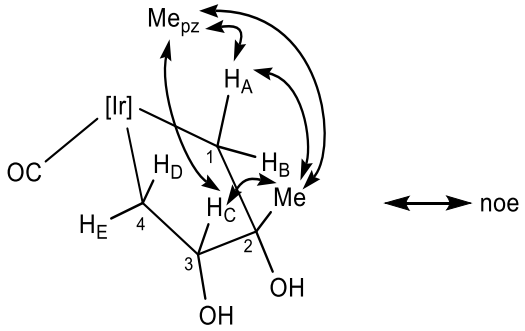
Compound 12. TMEDA (0.1 mL) was added to a cold (0 ºC) solution of compound **1** (0.10 g, 0.17 mmol) in CH_2Cl_2 (15 mL). After cooling the system at -78 ºC an excess of OsO_4 (3 mL, 0.1 M in *t*BuOH, 0.3 mmol) was added. The resulting mixture was stirred for 10 min at -78 ºC and then for 4 h at room temperature. The volatiles were removed under reduced pressure and upon addition of 10 mL of THF and $Na_2S_2O_5$-saturated water (10 mL), the resulting mixture was refluxed for 3 h. The organic phase was separated and the aqueous phase washed twice with CH_2Cl_2 (2 x 5 mL). The organic phases were combined, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude product revealed the formation of compound **12**, which was purified by crystallization from a mixture of Et_2O:CH_2Cl_2 (1:2) at -20 ºC as a pale yellow

solid. Yield: 85 mg, 0.14 mmol (82%). Slow evaporation of a solution of compound **12** in C_6H_{12}:CH_2Cl_2 (1:1) provided quality crystals for X-ray crystallography.



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.77 (s, 3 H, 3 CH_{pz}), 4.22 (m, 2 H, 2 H_C), 2.40 (dd, 2 H, $^2J_{AB}$ = 12.7, $^3J_{CB}$ = 4.0 Hz, 2 H_B), 2.38, 2.36, 2.32 (s, 1:2:3, 18 H, 6 Me_{pz}), 2.28 (dd, 2 H, $^3J_{CA}$ = 6.1 Hz, 2H_A); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 167.9 (CO), 150.8, 149.8, 144.1, 143.3 (2:1:1:2, C_{qpz}), 109.1, 107.0 (1:2, CH_{pz}), 80.8 (C^2, $^1J_{CH}$ = 142 Hz), 15.4, 14.3, 13.2, 12.5 (1:2:1:2, Me_{pz}), 2.1 (C^1, $^1J_{CH}$ = 130 Hz); IR (Nujol): ν 2009 (Ir—CO).

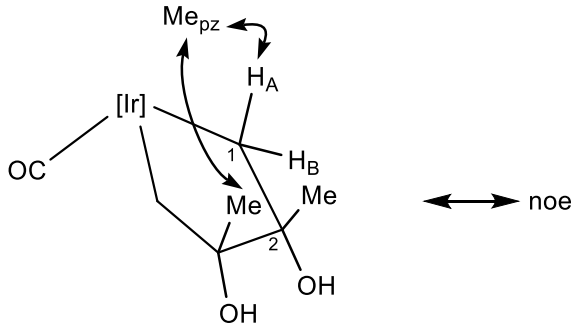
Compound 13. Following the same procedure described above for complex **12**, but starting with **2** (0.10 g, 0.17 mmol), complex **13** was quantitatively obtained. A spectroscopically pure sample, a pale yellow solid, was obtained by crystallization from a mixture of hexane:CH_2Cl_2 (1:2) at -20 ºC. Yield: 83 mg, 0.13 mmol (77%).



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.81, 5.78, 5.76 (s, 1 H each, 3 H, 3 CH_{pz}), 4.26 (t, 1 H, $^3J_{DC}$ = $^3J_{EC}$ = 8.1 Hz, H_C), 2.48, 2.42 (m, 1 H each, H_D and H_E), 2.46, 2.41, 2.35, 2.34, 2.33, 2.31 (s, 3 H each, 18 H, 6 Me_{pz}), 2.41 (d, 1 H, $^2J_{AB}$ = 12.0 Hz,

H_B), 2.11 (d, 1 H, H_A), 1.38 (s, 3 H, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 167.7 (CO), 150.9, 150.8, 149.8, 144.1, 143.4, 143.3 (C_{qpz}), 109.1, 107.1, 106.9 (CH_{pz}), 83.4 (C^2), 82.9 (C^3, $^1J_{CH}$ = 139 Hz); 27.4 (Me), 15.3, 14.7, 13.9, 13.3, 12.5, 12.4 (Me_{pz}), 9.9 (C^1, $^1J_{CH}$ = 129 Hz), 1.6 (C^4, $^1J_{CH}$ = 129 Hz); IR (Nujol): ν 2004 cm^{-1} (Ir—CO).

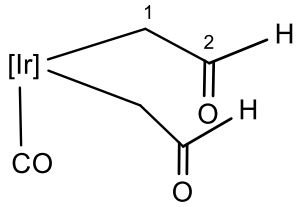
Compound 14. Following the same procedure described above for complex **12**, but starting with **3** (0.10 g, 0.17 mmol), complex **14** was quantitatively obtained, which was crystallized as a pale yellow solid from a mixture of hexane:CH_2Cl_2 (1:2) at -20 ºC. Yield: 82 mg, 0.13 mmol (76%).



^1H NMR ($CDCl_3$, 25 ºC): δ = 5.79, 5.76 (s, 2:1, 3 H, 3 CH_{pz}), 2.62 (s, 4 H, 2 H_A and 2 H_B), 2.48, 2.45, 2.32, 2.31 (s, 1:2:2:1, 18 H, 6 Me_{pz}), 1.38 (s, 6 H, 2Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 166.1 (CO), 150.9, 150.2, 144.1, 143.6 (2:1:1:2, C_{qpz}), 109.7, 107.1 (1:2, CH_{pz}), 85.2 (C^2), 28.8 (Me, $^1J_{CH}$ = 125 Hz), 17.9 (C^1, $^1J_{CH}$ = 129 Hz), 15.7, 14.8, 13.5, 12.7 (1:2:1:2, Me_{pz}); IR (Nujol): ν 1996 cm^{-1} (Ir—CO).

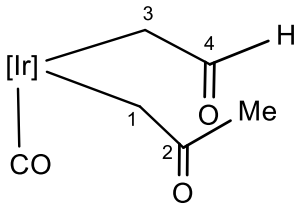
Compound 15. In a two-necks round-bottom flask, a flow of O_3 was passed through a cold (-70 ºC) solution of compound **1** (0.10 g, 0.17 mmol) in dichloromethane (20 mL) for 15 min. PPh_3 (0.05 g, 0.17 mmol) was then added and the resulting suspension stirred at -70 ºC until the phosphine was dissolved. This solution was stirred at room temperature for 30 min. and the volatiles were removed under reduced pressure. ^1H NMR analysis of the crude product revealed the formation of compound **15**, which was purified by column

chromatography on silica gel using a mixture of *n*hexane:Et_2O (1:5) as eluent. Yield: 40 mg, 0.066 mmol (39%) (white crystals). R_f = 0.16 [silica gel; *n*hexane:Et_2O (1:5)].



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 9.40 (dd, 2 H, $^3J_{HH}$ = 5.3 and 4.2 Hz, 2 CHO), 5.87, 5.83 (s, 1:2, 3 H, 3 CH_{pz}), 3.43, 3.07 (dd, 2 H each, $^2J_{HH}$ = 9.9 Hz, 2C^1H_2), 2.61, 2.37, 2.36, 2.34 (s, 1:2:1:2, 18 H, 6 Me_{pz}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 207.9 (C^2, $^1J_{CH}$ = 166 Hz), 165.0 (CO), 152.5, 151.2, 144.7, 144.6 (1:2:1:2, C_{qpz}), 109.9, 108.0 (1:2, CH_{pz}), 15.6, 14.7, 13.2, 12.8 (1:2:1:2, Me_{pz}), 8.5 (C^1, $^1J_{CH}$ = 132 Hz); IR (Nujol): ν 2036 (Ir—CO), 1668 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{20}H_{28}BN_6O_3Ir$: C 39.8, H 4.6, N 13.9; found: C 40.0, H 4.3, N 14.5.

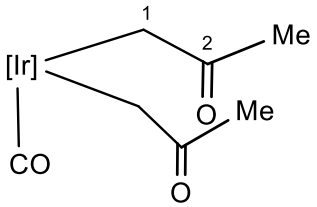
Compound 16. Following the same procedure described above for complex **15**, but starting with **2** (0.10 g, 0.17 mmol), complex **16** was obtained. It was purified by column chromatography on silica gel using a mixture ofhexane:Et_2O (1:5) as eluent to give a white solid. Yield: 46 mg, 0.075 mmol (44%). R_f = 0.29 [silica gel; *n*hexane:Et_2O (1:5)].



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 9.24 (dd, 1 H, $^3J_{HH}$ = 5.7 and 3.5 Hz, CHO), 5.87, 5.84, 5.80 (s, 1 H each, 3 H, 3 CH_{pz}), 3.52, 3.13 (d, 1 H each, $^2J_{HH}$ = 10.8 Hz, C^1H_2), 3.41, 2.95 (dd, 1 H each, $^2J_{HH}$ = 10.1 Hz, C^3H_2), 2.66, 2.38, 2.36, 2.35, 2.34, 2.33 (s, 3 H each, 18 H, 6 Me_{pz}), 2.16 (s, 3 H, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 215.6 (C^2), 208.4 (C^4, $^1J_{CH}$ = 167 Hz), 165.5 (CO), 152.1, 151.2, 150.4, 144.3, 144.3, 144.2 (C_{qpz}), 109.7, 107.8, 107.7 (CH_{pz}), 30.9 (Me), 14.5,

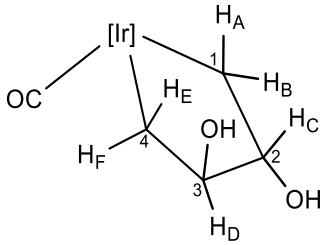
14.3, 14.1, 12.9, 12.6, 12.5 (Me_{pz}), 10.8 (C^1, $^1J_{CH}$ = 130 Hz), 6.8 (C^3, $^1J_{CH}$ = 130 Hz); IR (Nujol): ν 2021 (Ir—CO), 1685 cm^{-1} (C=O).

Compound 17. Following the same procedure described above for complex **15**, but starting with **3** (0.10 g, 0.17 mmol), complex **17** was obtained in *ca.* 90% spectroscopic yield. This compound was purified by column chromatography on silica gel using a mixture of *n*hexane:Et_2O (1:5) as eluent. Yield: 70 mg, 0.11 mmol (65%) (white solid). R_f = 0.13 [silica gel; *n*hexane:Et_2O (1:5)].



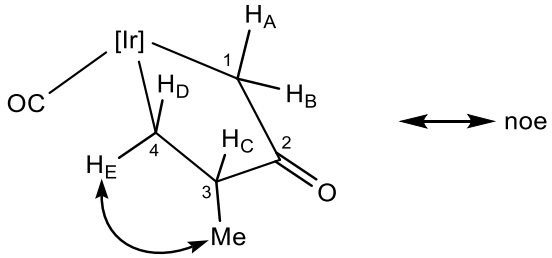
^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.86, 5.82 (s, 1:2, 3 H, 3 CH_{pz}), 3.36, 3.15 (AB spin system, 2 H each, $^2J_{HH}$ = 12.1 Hz, 2 $IrCH_2$), 2.75, 2.35, 2.33, 2.32 (s, 1:1:2:2, 18 H, 6 Me_{pz}), 2.13 (s, 6 H, 2 Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 216.1 (C^2), 166.8 (CO), 151.9, 150.5, 144.4, 144.3 (1:2:2:1, C_{qpz}), 109.8, 107.9 (1:2, CH_{pz}), 30.7 (Me), 15.5, 14.6, 13.2, 12.9 (1:2:1:2, Me_{pz}), 11.8 (C^1, $^1J_{CH}$ = 127 Hz); IR (Nujol): ν 2026 (Ir—CO), 1672 cm^{-1} (C=O).

Compound 18. An excess of BF_3 in Et_2O was added dropwise to a solution of compound **7** (0.12 g, 0.20 mmol) in dichloromethane (5 mL) at -78 ºC. The cooling bath was then removed and the resulting reaction mixture stirred while allowing to reach room temperature. CH_2Cl_2 (5 mL) was then added and the resulting solution washed sequentially with $NaHCO_3$-saturated water (10 mL), NaOH (10 mL, 1 M) and NaCl-saturated water (10 mL). The organic phase was separated, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude product revealed formation of compound **18**. This compound was purified by column chromatography on silica gel using a mixture of *n*hexane:Et_2O (7:1) as eluent. Yield: 78 mg, 0.13 mmol (65%) (white solid). R_f = 0.61 [silica gel; *n*hexane:Et_2O (1:1)].



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.90, 5.83 (s, 2:1, 3 H, 3 CH_{pz}), 4.20 (q, 1 H, J_{HH} = 8.8 Hz, H_C or H_D), 3.51 (m, 1 H, H_D or H_C), 2.63, 2.45, 2.39, 2.38, 2.36, 2.33 (s, 3 H each, 18 H, 6 Me_{pz}), 2.30, 2.10, 1.82 (m, dd, dd, 2:1:1, J_{HH} = 11.5, 9.3, 12.6, 9.5 Hz, 4 H, 2 $IrCH_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ = 167.6 (CO), 151.5, 151.4, 145.3, 144.3, 144.2 (1:1:1:1:2, C_{qpz}), 109.6, 107.6, 107.3 (CH_{pz}), 92.1 (C^2 or C^3, $^1J_{CH}$ = 141 Hz), 84.5 (C^3 or C^2, $^1J_{CH}$ = 138 Hz), 16.6, 14.6, 14.2, 13.4, 12.6, 12.5 (Me_{pz}), -4.2 (C^1 or C^4, $^1J_{CH}$ = 128 Hz), -10.7 (C^4 or C^1, $^1J_{CH}$ = 132 Hz); IR (Nujol): ν 2007 cm^{-1} (Ir—CO); elemental analysis calcd (%) for $C_{20}H_{30}BN_6O_3Ir$: C 39.7, H 5.0, N 13.9; found: C 40.0, H 4.5, N 13.6.

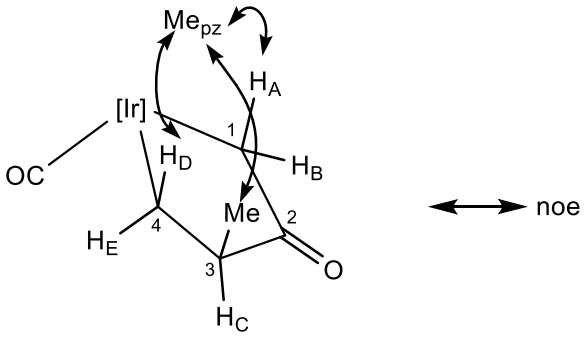
Compound 19. Following the same procedure described above for the synthesis of **18** but starting with complex **8** (0.20 g, 0.33 mmol), complex **19** was quantitatively formed. A spectroscopically pure sample, a microcrystalline pale yellow solid, was obtained by crystallization from a mixture of hexane:CH_2Cl_2 (1:2) at -20 ºC. Yield: 119 mg, 0.19 mmol (58%).



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.83, 5.81, 5.80 (s, 1 H each, 3 H, 3 CH_{pz}), 3.33 (d, 1 H, $^2J_{BA}$ = 14.0 Hz, H_A), 2.96 (m, 1H, H_C), 2.91 (d, 1 H, H_B), 2.40, 2.35, 2.31 (s, 2:3:1, 18 H, 6 Me_{pz}), 2.28 (m, 2 H, H_D and H_E), 1.24 (d, 3 H, $^3J_{CMe}$ = 7.0 Hz, Me); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ = 230.2 (C^2), 167.2 (CO), 151.1, 150.6, 144.4, 143.9 (2:1:1:2, C_{qpz}), 109.6, 107.5, 107.3 (CH_{pz}), 43.8 (C^3, $^1J_{CH}$ = 124

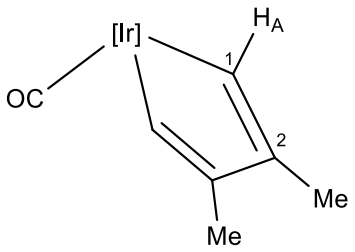
Hz), 18.7 (Me), 14.6, 14.5, 14.4, 13.4, 12.8, 12.8 (Me_{pz}), 13.5 (C^1, $^1J_{CH}$ = 128 Hz), -7.9 (C^4, $^1J_{CH}$ = 124 Hz); IR (Nujol): ν 2005 (Ir—CO), 1682 cm^{-1} (C=O).

Compound *epi*-19. NaOH (0.02 g) was added to a solution of compound **19** (0.10 g, 0.17 mmol) in methanol (2 mL). The resulting mixture was stirred at 60 ºC for 12 h and, after this period of time, the volatiles were removed under reduced pressure. The residue was then dissolved in CH_2Cl_2 (5 mL) and washed sequentially with water (10 mL) and NaCl-saturated water (10 mL). The organic phase was separated, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude product revealed the formation of compound **21** in *ca*. 80% spectroscopic yield. An analytically pure sample was obtained by crystallization from a mixture of Et_2O:CH_2Cl_2 (1:2) at -20 ºC (66 mg, 0.11 mmol, 65%).

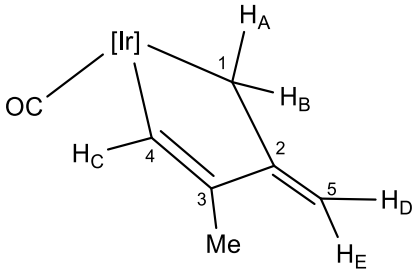


^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.85, 5.80, 5.77 (s, 1 H each, 3 H, 3 CH_{pz}), 3.47 (br d, 1 H, $^2J_{AB}$ = 17.6 Hz, H_B), 2.78 (dd, 1 H, $^2J_{ED}$ = 10.4 Hz, $^3J_{CD}$ = 8.8 Hz, H_D), 2.57 (d, 1 H, H_A), 2.47, 2.38, 2.36, 2.35, 2.28, 2.06 (s, 3 H each, 18 H, 6 Me_{pz}), 2.33 (m, 1 H, H_C), 1.67 (dd, 1H, $^3J_{CE}$ = 12.1 Hz, H_E), 1.16 (d, 3 H, $^3J_{CMe}$ = 6.6 Hz, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 230.8 (C^2), 168.6 (CO), 151.0, 150.8, 144.0, 143.8 (2:1:1:2, C_{qpz}), 109.4, 107.5, 107.1 (CH_{pz}), 51.6 (C^3, $^1J_{CH}$ = 118 Hz), 18.3 (Me, $^1J_{CH}$ = 126 Hz), 14.9, 14.6, 14.2, 13.2, 12.7, 12.7 (Me_{pz}), 10.6 (C^1, $^1J_{CH}$ = 130 and 124 Hz), -2.8 (C^4, $^1J_{CH}$ = 135 Hz); IR (Nujol): ν 2012 (Ir—CO), 1705 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{21}H_{30}BN_6O_2Ir$: C 41.9, H 4.9, N 13.9; found: C 41.6, H 4.9, N 13.3.

Compounds 20 and 21. An excess of MeMgCl (1.2 mL, 0.33 M in THF, 0.4 mmol) was added to a solution of compound **24** (0.10 g, 0.17 mmol) in diethyl ether (10 mL) at 0 ºC. The resulting solution was stirred at room temperature for 24 h and, after this period of time, the volatiles were removed under reduced pressure. The residue was then dissolved in CH_2Cl_2 (10 mL) and the solution washed with NH_4Cl-saturated water. The organic phase was separated, dried with Na_2SO_4 and taken to dryness to yield 70 mg of a white solid. A ^{1}H NMR analysis of the crude product revealed the formation, in a *ca.* 1:2 ratio, of the isomeric diene complexes **20** and **21**, which could not be separated by column chromatography.



20



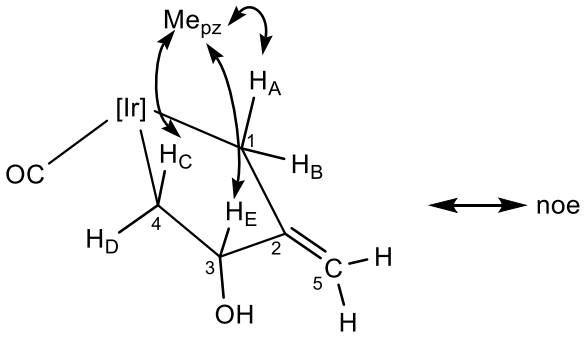
21

Selected NMR data for **20**: ^{1}H NMR ($CDCl_3$, 25 ºC): δ = 6.76 (q, 2 H, $^4J_{MeA}$ = 0.9 Hz, 2 H_A), 5.82, 5.58 (s, 2:1, 3 H, 3 CH_{pz}), 2.37-2.16 (6 Me_{pz}), 1.93 (d, 6 H, 2 Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 153.9 (C^2), 117.7 (C^1, $^1J_{CH}$ = 151 Hz), 108.7, 107.2, 106.6 (CH_{pz}), 20.5 (Me).

Selected NMR data for **21**: ^{1}H NMR ($CDCl_3$, 25 ºC): δ = 6.85 (q, 2 H, $^4J_{MeC}$ = 1.1 Hz, 2 H_C), 5.83, 5.79, 5.65 (s, 1 H each, 3 H, 3 CH_{pz}), 4.79 (m, 2 H, CH_DCH_E), 3.25, 3.14 (d, dd, 1 H each, $^2J_{AB}$ = 14.0, $^4J_{HH}$ = 2.6 Hz, CH_AH_B), 2.37-2.16 (6 Me_{pz}), 1.89 (d, 3 H, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 162.8, 152.3 (C^2 and C^3), 123.3 (C^4, $^1J_{CH}$ = 151 Hz), 109.1, 106.8, 106.5 (CH_{pz}), 102.9 (C^5, $^1J_{CH}$ = 156 Hz), 19.7 (Me), 14.4-11.4 (Me_{pz}), 5.8 (C^1, $^1J_{CH}$ = 129 Hz).

Compound 22. Silica gel (0.1 g) was added to a solution of compound **8** (0.30 g, 0.50 mmol) in dichloromethane (10 mL). The resulting suspension was stirred at room temperature for 12 h and, after this period of time, the mixture was filtered and the volatiles from the filtrate were removed under reduced pressure.

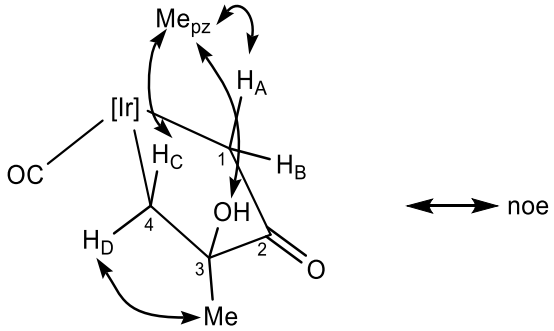
Water (10 mL) was added, the resulting mixture shaken vigorously and the organic phase separated, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude product revealed the formation of compound **22** which was purified by crystallization from a mixture of Et_2O:CH_2Cl_2 (1:2) at -20 ºC as a yellow solid. Yield: 180 mg, 0.30 mmol (60%).



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.79, 5.77 (s, 1:2, 3 H, 3 CH_{pz}), 5.01, 4.90 (q, 1 H each, $^2J_{HH}$ = $^4J_{HH}$ = 1.6 Hz, C^5H_2), 4.65 (t, 1 H, $^3J_{CE}$ = $^3J_{DE}$ = 4.4 Hz, H_E), 3.36, 2.70 (dt, 1 H each, $^2J_{AB}$ = 13.7 Hz, CH_AH_B), 2.44 (m, 2 H, CH_CH_D), 2.37, 2.36, 2.33 (s, 1:2:3, 18 H, 6 Me_{pz}). The NOESY spectrum in $CDCl_3$ was not of much help due to the coincidence of some Me_{pz}. Drawn interactions correspond to those observed in C_6D_6. In this solvent the important resonances appear at δ = 4.66 (dd, 1 H, $^3J_{CE}$ = 4.9, $^3J_{DE}$ = 2.3 Hz, H_E), 3.67, 2.92 (dt, 1 H each, $^2J_{AB}$ = 14.3, $^4J_{HH}$ = 1.6 Hz, H_B and H_A), 2.79, 2.66 (dd, 1 H each, $^2J_{CD}$ = 12.0 Hz, H_D and H_C); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 168.3 (CO), 167.5 (C^2), 151.1, 151.0, 144.2, 143.6 (2:1:1:2, C_{qpz}), 109.3, 107.3, 107.2 (CH_{pz}), 101.9 (C^5, $^1J_{CH}$ = 152 Hz), 81.4 (C^3, $^1J_{CH}$ = 143 Hz), 15.1, 14.7, 14.4, 13.4, 12.8 (1:1:1:1:2, Me_{pz}), 5.2 (C^4, $^1J_{CH}$ = 129 Hz), 0.8 (C^1, $^1J_{CH}$ = 128 Hz).

Compound 23. A solution of compound **8** (0.10 g, 0.17 mmol) in dichloromethane (5 mL) was added to a cold (0 ºC) suspension of a mixture of anhydrous sodium acetate (0.03 g, 0.36 mmol), celite (0.1 g), pyridinium chlorochromate (0.11 g, 0.5 mmol) and molecular sieves (0.05 g) in dichloromethane (5 mL). The resulting mixture was stirred for 30 min at 0 ºC and *ca*. 1 h at room temperature, filtered through celite, eluted with dichloromethane and taken to dryness. ^{1}H NMR analysis of the crude product

revealed formation of compounds **23** and **24** in 6:1 ratio. Compound **23** was purified by column chromatography on silica gel using a mixture of *n*hexane:Et_2O (10:1) as eluent to give a white solid. Yield: 35 mg, 0.057 mmol (33%). R_f = 0.26 [silica gel; *n*hexane: Et_2O (1:1)].

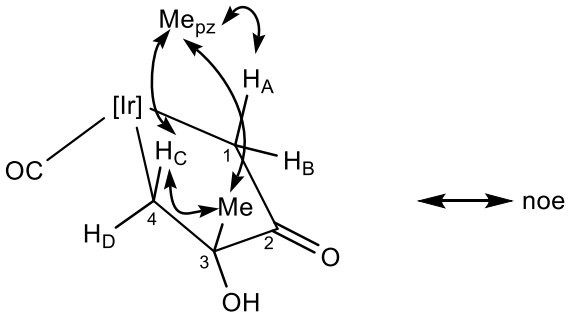


^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.83, 5.81, 5.72 (s, 1 H each, 3 H, 3 CH_{pz}), 3.49 (d, 1 H, $^2J_{AB}$ = 17.5 Hz, H_B), 3.30 (br s, 1 H, OH), 2.72 (d, 1 H, $^2J_{CD}$ = 11.9 Hz, H_D), 2.40 (d, 1 H, H_A), 2.43, 2.36, 2.34, 2.32, 2.26, 2.04 (s, 3 H each, 18 H, 6 Me_{pz}), 2.27 (d, 1 H, H_C), 1.4 (s, 3 H, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 231.4 (C^2), 168.3 (CO), 151.4, 150.8, 150.6, 143.9, 143.8, 143.7 (C_{qpz}), 109.3, 107.4, 107.1 (CH_{pz}), 80.8 (C^3), 27.3 (Me), 14.5, 14.0, 13.1, 12.5, 12.4 (2:1:1:1:1, Me_{pz}), 4.2 (C^1, $^1J_{CH}$ = 131 and 125 Hz), 3.3 (C^4, $^1J_{CH}$ = 136 Hz).

Compound *epi*-23. *Method A*: A solution of PCC (0.22 g, 1.02 mmol) and sodium acetate (0.09 g, 1.09 mmol) in H_2O (3 mL) was added to a solution of **11** (0.15 g, 0.25 mmol) in THF (10 mL) and the resulting mixture stirred for 18 h at 60 ºC. Upon addition of 10 mL of Et_2O the organic phase was separated, washed with NaCl-saturated water, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude product revealed formation of compounds ***epi*-23** and ***epi*-19** in a *ca*. 7:3 ratio. Compound ***epi-23*** was separated and purified by column chromatography on silica gel using a mixture of *n*hexane:Et_2O (10:1) as eluent. Yield: 92 mg, 0.15 mmol (60%) (yellow solid). R_f = 0.31 [silica gel; *n*hexane: Et_2O (1:1)].

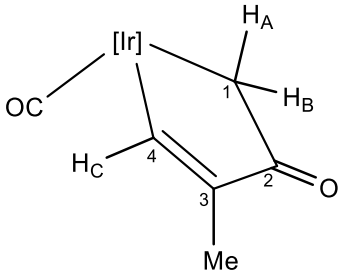
Method B: A solution of PCC (0.075 g, 0.35 mmol) and sodium acetate (0.09 g, 1.09 mmol) in H_2O (3 mL) was added to a solution of ***epi*-19** (0.05 g, 0.075 mmol) in THF (5 mL) and the resulting mixture stirred for 18 h at 60 ºC. Upon

addition of 10 mL of Et_2O, the organic phase was separated, washed with NaCl-saturated water, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude product revealed formation of compound ***epi*-23** which was purified by crystallization from a mixture of Et_2O:CH_2Cl_2 (1:2) at -20 ºC as a yellow solid. Yield: 30 mg, 0.05 mmol (67%).



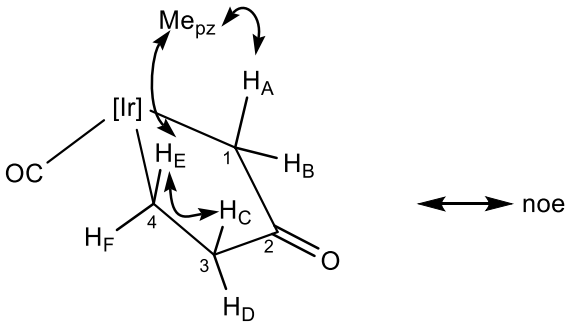
^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.58, 5.80, 5.78 (s, 1 H each, 3 H, 3 CH_{pz}), 3.30 (d, 1 H, $^2J_{AB}$ = 15.9 Hz, H_B), 2.96 (d, 1 H, H_A), 2.69 (d, 1 H, $^2J_{CD}$ = 12.7 Hz, H_D), 2.47, 2.35, 2.34, 2.28, 2.21 (s, 1:1:2:1:1, 18 H, 6 Me_{pz}), 2.06 (d, 1 H, H_C), 1.36 (s, 3 H, Me). OH resonance has not been located; ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ = 226.3 (C^2), 166.4 (CO), 151.0, 150.7, 150.5, 144.0, 143.7, 143.6 (C_{qpz}), 109.4, 107.2, 106.9 (CH_{pz}), 78.4 (C^3), 26.3 (Me, $^1J_{CH}$ = 127 Hz), 14.8, 14.6, 14.1, 13.1, 12.5, 12.4 (Me_{pz}), 8.8 (C^1, $^1J_{CH}$ = 130 Hz), 2.5 (C^4, $^1J_{CH}$ = 129 Hz); IR (Nujol): ν 2016 (Ir—CO), 1693 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{21}H_{30}BN_6O_3Ir$: C 40.8, H 4.8, N 13.6; found: C 41.4, H 4.9, N 13.0.

Compound 24: An excess of SeO_2 (0.41 g, 3.7 mmol) in ethanol (10 mL) was added to a solution of compound **2** (0.20 g, 0.36 mmol) in the same solvent (5 mL). The resulting mixture was stirred at 90 ºC for 3 h and the volatiles were then removed under reduced pressure. To the residue dichloromethane (10 mL) was added, the resulting suspension filtered through celite and the filtrate dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude product revealed quantitative formation of **24**, which was purified by crystallization from a mixture of Et_2O:CH_2Cl_2 (1:2) at -20 ºC as a red solid. Yield: 202 mg, 0.34 mmol (94%).



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 8.58 (s, 1 H, H_C), 5.89, 5.81, 5.67 (s, 1 H each, 3 H, 3 CH_{pz}), 2.99, 2.78 (d, 1 H each, $^{2}J_{AB}$ = 16.4 Hz, CH_AH_B), 2.37, 2.35, 2.34, 2.31, 2.30, 2.09 (s, 3 H each, 18 H, 6 Me_{pz}), 1.83 (s, 3 H, Me); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25 ºC): δ 218.3 (C^2), 164.9 (CO), 152.4, 151.5, 150.1, 148.6, 144.2, 143.9, 143.8 (C_{qpz} and C^3), 145.5 (C^4, $^{1}J_{CH}$ = 149 Hz), 109.5, 107.1, 106.9 (CH_{pz}), 17.6 (Me, $^{1}J_{CH}$ = 126 Hz), 14.4, 14.1, 13.7, 13.0, 12.5, 12.4 (Me_{pz}), 11.3 (C^1, $^{1}J_{CH}$ = 128 Hz).

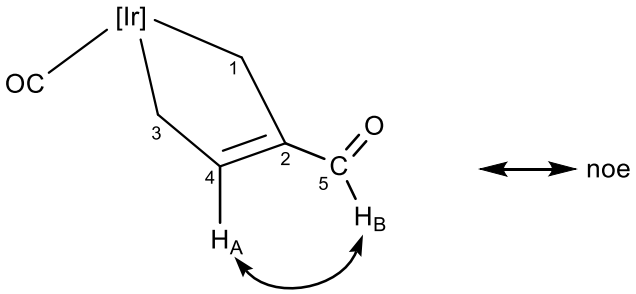
Compound 25. A solution of complex **10** (0.20 g, 0.34 mmol) in CH_2Cl_2 (5 mL) was added to a cold (0 ºC) mixture of PCC (0.22 g, 1.02 mmol), sodium acetate (0.05 g, 0.61 mmol), celite (0.6 g) and molecular sieves (0.1 g) in CH_2Cl_2 (10 mL). After stirring for 30 min at 0 ºC and for 1 h at room temperature, the resulting suspension was filtered through celite, the cake was washed with CH_2Cl_2 and the volatiles were removed under reduced pressure. ^{1}H NMR analysis of the crude product revealed the formation of **25**, which was purified by crystallization from a mixture of Et_2O:CH_2Cl_2 (1:2) at -20 ºC as white needles. Yield: 110 mg, 0.19 mmol (56%).



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.81, 5.80, 5.79 (s, 1 H each, 3 H, 3 CH_{pz}), 3.19 (d, 1 H, $^{2}J_{AB}$ = 17.0 Hz, H_B), 2.80 (dd, 1 H, $^{4}J_{HH}$ = 1.5 Hz, H_A), 2.73 (dd, 1 H, $^{2}J_{DC}$ = 17.9, $^{3}J_{EC}$ = 7.3 Hz, H_C), 2.58 (t, 1 H, $^{2}J_{EF}$ = $^{3}J_{DF}$ = 10.6 Hz, H_F), 2.44 (dt, 1 H,

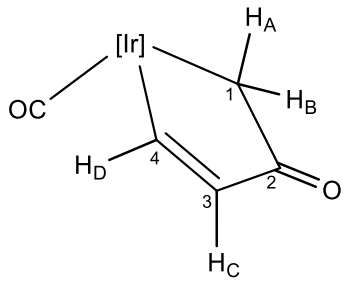
$^{3}J_{ED}$ = 10.0 Hz, H_D), 2.40, 2.34, 2.33, 2.27, 2.22 (s, 1:1:2:1:1, 18 H, 6 Me_{pz}), 1.80 (dt, 1 H, H_E); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25 ºC): δ = 231.8 (C_2), 167.9 (CO), 150.8, 150.7, 150.7, 143.9, 143.7 (1:2:1:1:1, C_{qpz}), 109.3, 107.2, 106.9 (CH_{pz}), 46.1 (C^3), 14.4, 14.3, 14.1, 13.0, 12.5, 12.4 (Me_{pz}), 11.8 (C^1), –15.3 (C^4); IR (Nujol): ν 2000 (Ir—CO), 1696 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{20}H_{28}BN_6O_2Ir$: C 40.9, H 4.8, N 14.3; found: C 40.6, H 4.6, N 14.0.

Compound 26. A solution of compound **22** (0.10 g, 0.16 mmol) in dichloromethane (5 mL) was added to a cold (0 ºC) mixture of anhydrous sodium acetate (0.03 g, 0.36 mmol), celite (0.2 g), pyridinium chlorochromate (0.11 g, 0.5 mmol) and molecular sieves (0.04 g) in dichloromethane (10 mL). The resulting mixture was stirred for 30 min at 0 ºC and for 4 h at room temperature before the suspension was filtered through celite, the cake washed with dichloromethane and the filtrate taken to dryness. ^{1}H NMR analysis of the crude product revealed formation of compound **26**, which was purified by crystallization from a mixture of Et_2O:CH_2Cl_2 (1:2) at -20 ºC as a white solid. Yield: 51 mg, 0.085 mmol (53%).



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 9.83 (s, 1 H, H_B), 6.98 (m, 1 H, H_A), 5.80, 5.79, 5.73 (s, 1 H each, 3 H, 3 CH_{pz}), 3.27, 2.91 (dm, dq, 1 H each, $^{2}J_{HH}$ = 18.6, J_{HH} = 2.3 Hz, C^1H_2 or C^3H_2), 3.24, 2.66 (d, dq, 1 H each, $^{2}J_{HH}$ = 15.5, J_{HH} = 2.6 Hz, C^3H_2 or C^1H_2), 2.36, 2.35, 2.34, 2.34, 2.32, 2.01 (s, 3 H each, 18 H, 6 Me_{pz}); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25 ºC): δ = 190.7 (C^5, $^{1}J_{CH}$ = 169 Hz), 169.8 (C^4, $^{1}J_{CH}$ = 150 Hz), 167.8 (CO), 158.4 (C^2), 151.5, 151.1, 150.7, 143.8, 143.5 (1:1:1:1:2, C_{qpz}), 108.8, 107.0 (1:2, CH_{pz}), 14.4, 14.2, 13.0, 12.5, 12.4, 12.4 (Me_{pz}), 2.1 (C^1 or C^3, $^{1}J_{CH}$ = 131 Hz), -3.3 (C^3 or C^1, $^{1}J_{CH}$ = 136 Hz); IR (Nujol): ν 2014 (Ir—CO), 1682 cm^{-1} (C=O).

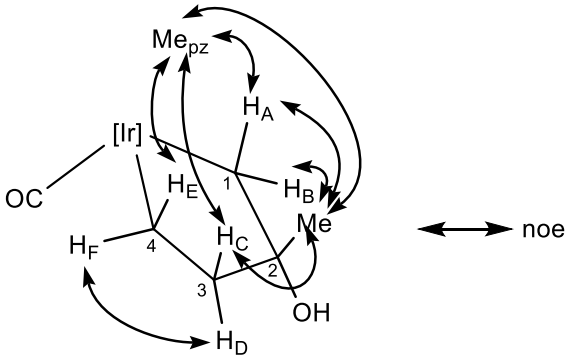
Compound 27. An excess of DMP (0.36 g, 0.85 mmol) was added to a solution of **10** (0.10 g, 0.17 mmol) in DMSO (5 mL), the resulting mixture stirred for 5 min at room temperature, H_2O (0.08 mL, 2.5 equiv.) then added and the mixture stirred at 70 ºC for 12 h. Et_2O (5 mL) was then added and, after vigorously shaken, the organic phase was separated, washed sequentially with $NaHCO_3$-saturated and NaCl-saturated water, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude product revealed formation of compound **27**, which was purified by crystallization from a mixture of Et_2O:CH_2Cl_2 (1:2) at -20 ºC. Yield: 75 mg, 0.13 mmol (77%) (white solid). A sample of analytical purity was obtained by crystallization from a mixture of *n*hexane:CH_3OH (1:1).



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 9.12 (d, 1 H, $^3J_{CD}$ = 7.6 Hz, H_D), 6.73 (d, 1 H, H_C), 5.89, 5.82, 5.68 (s, 1 H each, 3 H, 3 CH_{pz}), 2.93, 2.85 (d, 1 H each, $^2J_{AB}$ = 16.4 Hz, CH_AH_B), 2.37, 2.35, 2.32, 2.32, 2.31, 2.24 (s, 3 H each, 18 H, 6 Me_{pz}); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ = 220.4 (C^2), 164.7 (CO), 153.4 (C^4, $^1J_{CH}$ = 153 Hz), 152.9, 151.6, 150.1, 144.2, 144.0, 143.9 (C_{qpz}), 144.3 (C^3, $^1J_{CH}$ = 161 Hz), 109.5, 107.2, 106.9 (CH_{pz}), 14.4, 14.1, 14.0, 13.0, 12.5, 12.4 (Me_{pz}), 11.5 (C^1, $^1J_{CH}$ = 130 Hz); IR (Nujol): ν 2021 (Ir—CO), 1665 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{20}H_{26}BN_6O_2Ir \cdot 5/2CH_3OH$: C 40.6, H 5.4, N 12.6; found: C 40.4, H 4.9, N 12.1.

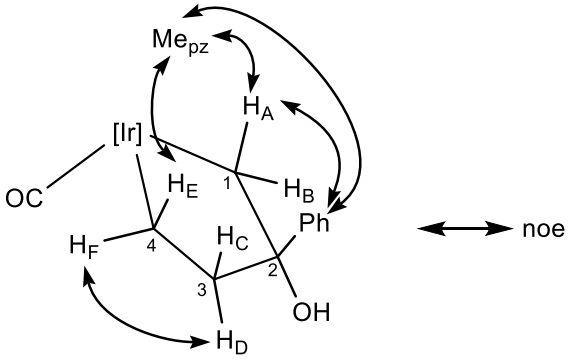
Compound 28. An excess of MeLi (0.14 mL, 1.6 M in Et_2O, 0.22 mmol) was added to a cooled (0 ºC) solution of compound **25** (0.05 g, 0.085 mmol) in diethyl ether (5 mL), the resulting mixture stirred for 24 h at room temperature, NH_4Cl-saturated water (10 mL) was then added and, after vigorously shaken, the organic phase was separated, dried with Na_2SO_4 and taken to dryness. ^{1}H

NMR analysis of the crude product (white solid, 20 mg) revealed the formation of compound **28** but also the presence of starting material, which could not be separated.



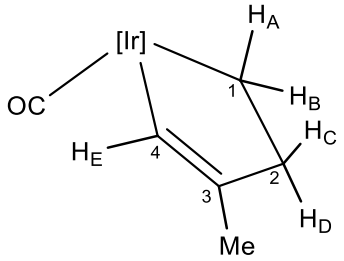
^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.80, 5.78, 5.75 (s, 1 H each, 3 CH_{pz}), 2.69 (ddd, 1 H, $^2J_{EF}$ = 10.6, $^3J_{CF}$ = 18.4, $^3J_{DF}$ = 7.7 Hz, H_F), 2.43, 2.41, 2.34, 2.33, 2.32 (s, 1:1:1:2:1, 6 Me_{pz}), 2.40 (d, 1 H, $^2J_{BA}$ = 12.4 Hz, H_A), 2.25 (dd, 1 H, $^4J_{EB}$ = 2.6 Hz, H_B), 2.11 (ddd, 1 H, $^2J_{DC}$ = 7.7, $^3J_{EC}$ = 10.9 Hz, H_C), 1.95 (td, 1 H, H_E), 1.53 (m, 1 H, H_D), 1.49 (s, 3 H, Me). Represented NOEs in the figure have been deduced from NOESY spectra in C_6D_6, $CDCl_3$ and different mixtures of them; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 169.1 (CO), 150.9, 150.7, 150.2, 143.9, 143.3 (1:1:1:1:2, C_{qpz}), 109.0, 106.9 (1:2, CH_{pz}), 87.0 (C^2), 45.4 (C^3, $^1J_{CH}$ = 123 Hz), 28.8 (Me), 19.0 (C^1, $^1J_{CH}$ = 123 Hz), 14.8, 14.4, 14.0, 13.2, 12.6, 12.5 (Me_{pz}), -7.5 (C^4, $^1J_{CH}$ = 128 Hz). IR (Nujol): ν 1999 cm^{-1} (Ir—CO).

Compound 29. An excess of PhLi (0.5 mL, 3 M in hexane, 1.5 mmol) was added to a cooled (0 ºC) solution of compound **25** (0.20 g, 0.34 mmol) in diethyl ether (10 mL), the resulting mixture stirred for 24 h at room temperature, NH_4Cl-saturated water was then added and, after vigorously shaken, the organic phase was separated, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude product revealed formation of compound **34** which was purified by column chromatography on silica gel using a mixture of *n*hexane:AcOEt (10:1) as eluent to give a white solid. Yield: 160 mg, 0.24 mmol (71%). R_f = 0.66 [silica gel; *n*hexane: Et_2O (10:1)]. The sample used for elemental analysis was obtained by crystallization from a mixture of *n*hexane: CH_2Cl_2 (1:1).



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 7.74, 7.45, 7.33 (d, t, t, 2:1:2, Ph), 5.85, 5.81, 5.80 (s, 1 H each, 3 CH_{pz}), 3.00 (d, 1 H, $^2J_{BA}$ = 11.9 Hz, H_A), 2.87 (ddd, 1 H, $^2J_{EF}$ = 11.5, $^3J_{HH}$ = 10.1, 8.2 Hz, H_F), 2.49 (dd, 1 H, J_{EB} = 2.1 Hz, H_B), 2.46, 2.40, 2.39, 2.37, 2.36 (s, 2:1:1:1:1, 6 Me_{pz}), 2.41 (m, 1 H, H_C), 2.07 (td, 1 H, $^3J_{HH}$ = 11.0, 2.1 Hz, H_E), 1.87 (m, 1 H, H_D). OH resonance has not been located. NOESY experiment was registered in a mixture of $CDCl_3$:C_6D_6 (4:1); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 168.8 (CO), 150.9, 150.7, 150.3, 148.9, 144.1, 143.4 (1:1:1:1:1:2, C_{qpz} + C_{qPh}), 128.1, 126.1, 125.4 (2:1:2, CH_{Ph}), 109.0, 107.1, 107.0 (CH_{pz}), 89.9 (C^2), 45.6 (C^3, $^1J_{CH}$ = 123 Hz), 17.5 (C^1, $^1J_{CH}$ = 126 Hz), 14.8, 14.7, 13.9, 13.3, 12.6, 12.5 (Me_{pz}), -8.3 (C^4, $^1J_{CH}$ = 131 Hz); IR (Nujol): ν 2004 cm^{-1} (Ir—CO); elemental analysis calcd (%) for $C_{26}H_{34}BN_6O_2Ir\cdot 1/2CH_2Cl_2$: C 44.9, H 4.9, N 11.9; found: C 45.3, H 5.2, N 11.6.

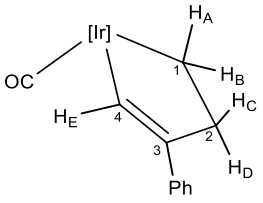
Compound 30. An excess of MeMgCl (0.53 mL, 0.68 M in THF, 0.36 mmol) was added to a cooled (0 ºC) solution of compound **25** (0.10 g, 0.17 mmol) in diethyl ether (10 mL), the resulting mixture stirred for 24 h at room temperature and the volatiles were then removed under reduced pressure. CH_2Cl_2 (10 mL) and NH_4Cl-saturated water (10 mL) were then added and, after vigorously shaken, the organic phase was separated, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude product revealed formation of compound **30** with *ca.* 10% of starting material remaining. Complex **30** was purified by column chromatography on silica gel using a mixture of *n*hexane:Et_2O (100:1) as eluent to give a white solid. Yield: 90 mg, 0.15 mmol (88%).



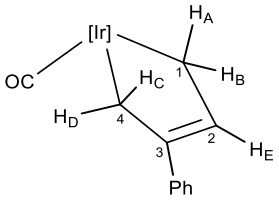
^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.96 (s, 1 H, H_E), 5.81, 5.78, 5.68 (s, 1 H each, 3 CH_{pz}), 2.56, 2.50 (m, 1 H each, CH_AH_B), 2.49, 2.37 (m, 1 H each, CH_CH_D), 2.38, 2.34, 2.33, 2.31, 2.30 (s, 1:2:1:1:1, 6 Me_{pz}), 1.87 (s, 3 H, Me); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ = 168.4 (CO), 153.3 (C^3), 151.7, 150.9, 150.3, 143.5, 143.2 (1:1:1:1:2, C_{qpz}), 110.6 (C^4, $^1J_{CH}$ = 148 Hz), 109.0, 106.7, 106.3 (CH_{pz}), 43.9 (C^2, $^1J_{CH}$ = 125 Hz), 21.1 (Me, $^1J_{CH}$ = 130 Hz), 13.8, 13.5, 12.9, 12.5, 12.4, 11.8 (Me_{pz}), -1.3 (C^1, $^1J_{CH}$ = 133 Hz); IR (Nujol): ν 2001 cm^{-1} (Ir—CO); elemental analysis calcd (%) for $C_{21}H_{30}BN_6OIr$: C 43.1, H 5.1, N 14.5; found: C 43.2, H 5.1, N 14.0.

Compounds 31 and 32. *Method A*: To a solution of compound **29** (0.05 g, 0.075 mmol) in acetic anhydride (2 mL), Na_2SO_4 (0.1 g) was added and the resulting mixture stirred at 60 ºC for 3 days. The solvent was then removed under reduced pressure and ^{1}H NMR analysis of the crude product showed the formation of a *ca.* 1:2 mixture of compounds **31** and **32** which could not be separated by column chromatography.

Method B: To a solution of compound **29** (0.05 g, 0.075 mmol) in dichloromethane (5 mL), silica gel was added (0.5 g) and the resulting suspension stirred at room temperature for 3 days. It was then filtered and the filtrate taken to dryness. ^{1}H NMR analysis of the crude product showed the formation of a *ca.* 1:2 mixture of compounds **31** and **32**.



31

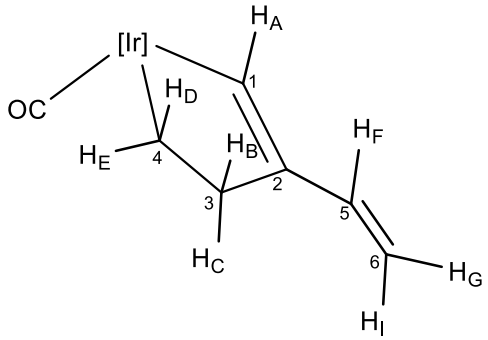


32

Selected NMR data for compound **31**: ^{1}H NMR ($CDCl_3$, 25 ºC): δ = 7.37 (d, 1 H, J_{HH} = 2.3 Hz, H_E), 3.06 (m, 2 H, CH_CH_D), 2.75 (m, 2 H, CH_AH_B); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ = 155.7 (C^3), 118.4 (C^4, $^{1}J_{CH}$ = 151 Hz), 41.3 (C^2, $^{1}J_{CH}$ = 123 Hz), -1.8 (C^1, $^{1}J_{CH}$ = 131 Hz).

Selected NMR data for compound **32**: ^{1}H NMR ($CDCl_3$, 25 ºC): δ = 6.22 (m, 1 H, H_E), 3.44, 3.07 (d, 1 H each, $^{2}J_{HH}$ = 15.0 Hz, CH_CH_D), 3.32, 2.73 (dm, 1 H each, $^{2}J_{HH}$ = 16.4 Hz, CH_AH_B); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ = 152.1 (C^3), 139.7 (C^2, $^{1}J_{CH}$ = 148 Hz), 5.1 (C^4, $^{1}J_{CH}$ = 141, 129 Hz), 2.6 (C^1, $^{1}J_{CH}$ = 130 Hz).

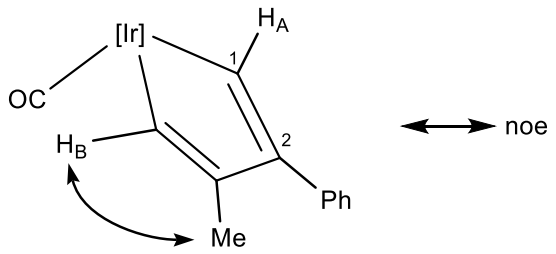
Compound 33. An excess of CH_2=CHMgBr (0.34 mL, 1 M in THF, 0.34 mmol) was added to a cooled (0 ºC) solution of compound **25** (0.10 g, 0.17 mmol) in diethyl ether (10 mL), the resulting mixture stirred for 24 h at room temperature, NH_4Cl-saturated water (10 mL) was then added and, after vigorously shaken, the organic phase was separated, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude product revealed formation of compound **33** which was purified by column chromatography on silica gel using a mixture of *n*hexane:AcOEt (10:1) as eluent to give a pale yellow solid. Yield: 45 mg, 0.075 mmol (44%). R_f = 0.63 [silica gel; *n*hexane: Et_2O (10:1)].



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 6.90 (s, 1 H, H_A), 6.48 (dd, $^{2}J_{IF}$ = 17.5, $^{2}J_{GF}$ = 10.6 Hz, H_F), 5.84, 5.81, 5.68 (s, 1 H each, 3 CH_{pz}), 4.93, 4.81 (dd, 1 H each, $^{2}J_{IG}$ = 1.4 Hz, CH_IH_G), 2.83, 2.57 (m, 2 H, CH_CH_B), 2.70, 2.59 (m, 2 H, CH_EH_D), 2.41, 2.35, 2.31, 2.24 (s, 1:2:2:1, 6 Me_{pz}); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ = 167.7 (CO), 158.2 (C^2), 151.9, 151.1, 150.4, 143.7, 143.4, 143.3 (C_{qpz}), 138.0 (C^5, $^{1}J_{CH}$ = 156 Hz), 126.5 (C^1, $^{1}J_{CH}$ = 148 Hz), 109.0, 106.9, 106.4 (CH_{pz}), 108.0

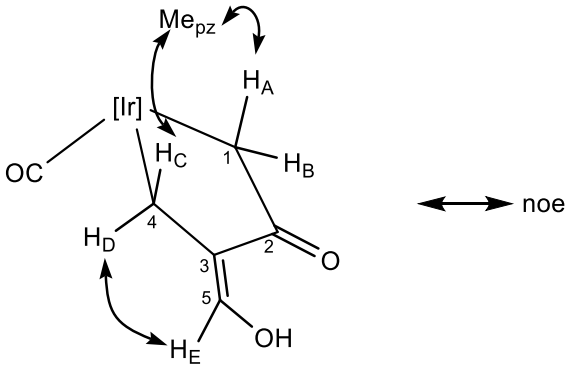
(C^6, $^1J_{CH}$ = 156 Hz), 37.4 (C^3, $^1J_{CH}$ = 125 Hz), 13.9, 13.8, 13.0, 12.6, 12.4, 14.4 (Me_{pz}), -1.8 (C^4, $^1J_{CH}$ = 131 Hz); IR (Nujol): ν 2011 cm^{-1} (Ir—CO).

Compound 34. An excess of PhLi (0.25 mL, 3 M in hexane, 0.75 mmol) was added to a cooled (0 ºC) solution of compound **24** (0.10 g, 0.17 mmol) in diethyl ether (10 mL), the resulting mixture stirred for 24 h at room temperature, NH_4Cl-saturated water was then added and, after vigorously shaken, the organic phase was separated, dried with Na_2SO_4 and taken to dryness. ^1H NMR analysis of the crude product revealed the formation of compound **34** (pale brown solid).



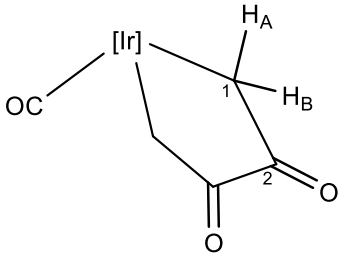
^1H NMR ($CDCl_3$, 25 ºC): δ = 7.44 (s, 1 H, H_A), 7.4-7.2 (m, 5 H, Ph), 7.00 (s, 1 H, H_B), 5.86, 5.84, 5.62 (s, 1 H each, 3 CH_{pz}), 2.41, 2.38, 2.36, 2.30 (1:1:3:1, 6 Me_{pz}), 2.02 (s, 3 H, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 163.0 (CO), 160.9 (C^2), 154.4, 151.2, 143.9, 143.7, 143.6 (C_{qpz} + C_{qPh}), 152.6 (C^3), 127.7, 127.4, 125.3 (2:2:1, CH_{Ph}), 127.8 (C^1, $^1J_{CH}$ = 154 Hz), 120.4 (C^4, $^1J_{CH}$ = 153 Hz), 108.7, 106.6 (1:2, CH_{pz}), 22.1 (Me), 14.4, 14.3, 13.0, 12.5, 11.6 (1:1:1:2:1, Me_{pz}).

Compound 35. To a cold (0 ºC) solution of complex **25** (0.10 g, 0.17 mmol) in C_6H_6 (5 mL), HCO_2Et (0.18 mL, 2.22 mmol) and methanol (0.1 mL) were added. The resulting mixture was then added dropwise over NaH (0.06 g, oil free), stirred a room temperature for 48 h and, in turn, added to cracked ice. The mixture was acidified with HCl (5 mL, 10% in H_2O), vigorously shaken, and the organic layer separated. After extraction of the aquous portions with Et_2O (3 x 5 mL), the combined organic phases were dried with Na_2SO_4 and taken to dryness. The resulting crude product was crystallized from Et_2O:CH_2Cl_2 (1:2) at -20 ºC. Isolated yield: 82 mg, 0.13 mmol (77%) (white solid).



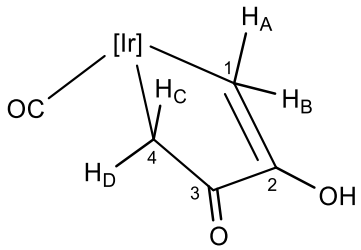
^{1}H NMR ($CDCl_3$, 25 ºC): δ = 8.58 (s, 1 H, H_E), 5.81, 5.80, 5.78 (s, 1 H each, 3 CH_{pz}), 3.25 (d, 1 H, $^2J_{CD}$ = 12.9 Hz, H_D), 3.09 (d, 1 H, $^2J_{AB}$ = 18.3 Hz, H_B), 2.98 (d, 1 H, H_A), 2.53 (d, 1 H, H_C), 2.39, 2.34, 2.32, 2.14 (s, 1:3:1:1, 6 Me_{pz}). The OH group has not been located; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 204.7 (C^2), 180.0 (C^5, $^1J_{CH}$ = 174 Hz), 167.1 (CO), 151.4, 150.9, 150.8, 143.9, 143.6 (1:1:1:1:2, C_{qpz}), 121.2 (C^3), 109.1, 107.2, 107.0 (CH_{pz}), 14.3, 14.2, 12.9, 12.7, 12.5, 12.4 (Me_{pz}), 4.2 (C^1, $^1J_{CH}$ = 129 Hz), -10.9 (C^4, $^1J_{CH}$ = 131 Hz); IR (Nujol): ν 2009 (Ir—CO), 1591 cm^{-1} (C=O).

Compound 36. In a two-necks round bottom flask O_3 was passed during 1 minute through a solution of compound **35** (0.10 g, 0.16 mmol) in dichloromethane (10 mL) at -78 ºC. Then, Me_2S (0.05 mL) was added, the cooling bath removed, and the resulting mixture stirred at room temperature for 3 h. Water (10 mL) was then added, the mixture shaken vigorously and the organic layer separated, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude reaction showed almost quantitative formation of the title compound along with a small quantity of starting material remaining. Complex **36** was purified by column chromatography on silica gel to give a yellow solid.



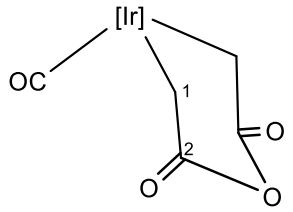
^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.85 (s, 3 H, 3 CH_{pz}), 3.07, 3.05 (AB spin system, 2 H each, $^2J_{AB}$ = 16.9 Hz, 2 CH_AH_B), 2.36, 2.31, 2.19 (s, 3:2:1, 6 Me_{pz}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 210.2 (C^2), 164.6 (CO), 150.9, 150.7, 144.3, 144.2 (2:1:1:2, C_{qpz}), 110.1, 107.5 (1:2, CH_{pz}), 14.8, 14.4, 12.9, 12.5 (1:2:1:2, Me_{pz}), 2.57 (C^1, $^1J_{CH}$ = 131 Hz); IR (Nujol): ν 2015 (Ir—CO), 1712 cm^{-1} (C=O).

Compound 37. A cold (0 ºC) solution of compound **36** (0.10 g, 0.16 mmol) in a C_6H_6 (5 mL) - methanol (0.10 mL) mixture was added dropwise to NaH (0.06 g) clean of oil. The resulting mixture was stirred at room temperature for 1 h and then added to a water-cracked ice mixture. The mixture was acidified with HCl (5 mL, 10% in H_2O) and then vigorously stirred for 10 minutes. After extraction of the aquous layer with Et_2O (3 x 5 mL), the combined organic phases were dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude reaction showed quantitative formation of **37** which was purified by column chromatography on silica gel using a mixture of *n*hexane:Et_2O (10:1) as eluent to give a pale yellow solid. Yield: 50 mg, 0.08 mmol (50%). R_f = 0.13 [silica gel; *n*hexane: Et_2O (1:1)].



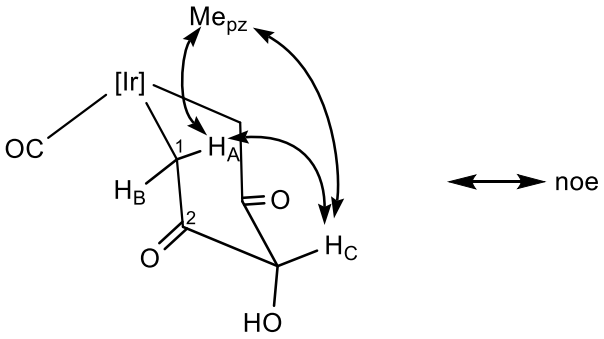
^{1}H NMR ($CDCl_3$, 25 ºC): δ = 7.39 (s, 1 H, H_A), 5.88, 5.82, 5.67 (s, 1 H each, 3 CH_{pz}), 5.78 (brs, 1 H, OH), 2.91, 2.50 (d, 1 H each, $^2J_{CD}$ = 17.1 Hz, CH_CH_D), 2.37, 2.36, 2.33, 2.32, 2.29, 2.08 (s, 3 H each, 6 Me_{pz}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 210.7 (C^3), 164.1 (CO), 154.2 (C^2), 152.4, 151.4, 150.5, 144.2, 143.9 (1:1:1:1:2, C_{qpz}), 109.6, 107.2, 106.9 (CH_{pz}), 109.5 (C^1, $^1J_{CH}$ = 150 Hz), 14.3, 14.2, 13.6, 12.9, 12.5, 12.4 (Me_{pz}), -4.2 (C^4, $^1J_{CH}$ = 130 Hz); IR (Nujol): ν 2023 (Ir—CO), 1642 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{20}H_{26}BN_6O_3Ir$: C 39.9, H 4.3, N 13.9; found: C 40.1, H 4.4, N 13.3.

Compound 38. To a cold (0 ºC) solution of compound **35** (0.10 g, 0.17 mmol) in dichloromethane (5 mL), an excess of *m*-chloroperbenzoic acid (0.11 g, 0.63 mmol) in dichloromethane (5 mL) and $NaHCO_3$-saturated water (5 mL) were added. The resulting mixture stirred at 0 ºC for 30 min and then at room temperature for another 30 min. The organic phase was separated and sequentially extracted with $Na_2S_2O_7$-saturated, $NaHCO_3$-saturated and NaCl-saturated water, then dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude reaction mixture showed formation of complex **38** which was purified by crystallization from a Et_2O:CH_2Cl_2 (1:2) mixture at -20 ºC to give a white solid. Yield: 74 mg, 0.12 mmol (71%).



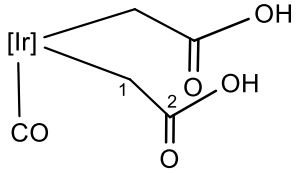
^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.88, 5.83 (s, 2:1, 3 CH_{pz}), 3.45, 2.86 (d, 2 H each, $^2J_{HH}$ = 12.3 Hz, 2 C^1H_2), 2.37 (s, 18 H, 6 Me_{pz}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 176.3 (C^2), 162.7 (CO) 151.7, 151.0, 144.6, 144.4 (1:2:1:2, C_{qpz}), 109.9, 107.8 (1:2, CH_{pz}), 14.8, 14.2, 13.0, 12.4 (1:2:1:2, Me_{pz}), -1.3 (C^1, $^1J_{CH}$ = 135 Hz); IR (Nujol): ν 2033 (Ir—CO), 1763 and 1723 cm^{-1} (C=O).

Compound 39. In a NMR tube a solution of compound **35** (0.10 g, 0.17 mmol) in $CDCl_3$ (0.5 mL) was treated with a few crystals of *p*-toluenesulfonic acid and the mixture kept at room temperature for 15 min. Then, an excess of *m*-chloroperbenzoic acid (0.04 g, 0.23 mmol) was added and after 10 min ^{1}H NMR monitoring revealed an almost quantitative formation of compound **39**. The reaction mixture was sequentially extracted with $Na_2S_2O_7$-saturated, $NaHCO_3$-saturated and NaCl-saturated water, the organic phase was dried with Na_2SO_4 and taken to dryness. Compound **39** was purified by crystallization from a Et_2O:CH_2Cl_2 (1:2) mixture at -20 ºC to give a white solid. Yield: 88 mg, 0.16 mmol (94%).



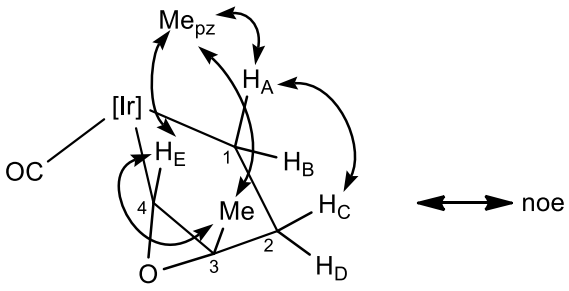
^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.90, 5.88 (s, 1:2, 3 CH_{pz}), 5.17 (brs, 1 H, H_C), 4.13 (brs, 1 H, OH), 3.46, 3.41 (AB spin system, 2 H each, $^2J_{AB}$ = 8.9 Hz, 2 H_A and 2 H_B resp.), 2.69, 2.42, 2.38, 2.36 (s, 1:2:1:2, 6 Me_{pz}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 206.1 (C^2), 161.5 (CO), 151.0, 150.3, 144.6, 144.5 (2:1:2:1, C_{qpz}), 110.4, 107.8 (1:2, CH_{pz}), 83.8 (C^3, $^1J_{CH}$ = 150 Hz), 16.1, 14.6, 13.1, 12.5 (1:2:1:2, Me_{pz}), 9.8 (C^1, $^1J_{CH}$ = 132 Hz); IR (Nujol): ν 2059 (Ir—CO), 1675 cm^{-1} (C=O).

Compound 40. A solution of compound **38** (0.1 g, 0.16 mmol) in a 2:1 mixture of THF:H_2O (6 mL) was stirred at 90 ºC for 12 h. Then diethyl ether (5 mL) was added and the organic phase separated, extracted with NaCl-saturated water, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude reaction mixture showed the formation of complex **40** which was purified by crystallization from a Et_2O:CH_2Cl_2 (1:2) mixture at -20 ºC to give a white solid. Yield: 63 mg, 0.1 mmol (62%).



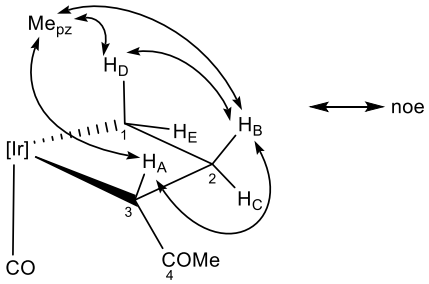
^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.87, 5.83 (s, 1:2, 3 CH_{pz}), 3.38, 2.62 (d, 2 H each, $^2J_{HH}$ = 11.5 Hz, 2 C^1H_2), 2.69, 2.47, 2.35, 2.34 (s, 1:2:1:2, 6 Me_{pz}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 188.3 (C^2), 164.2 (CO), 151.5, 150.5, 143.9, 143.8 (1:2:2:1, C_{qpz}), 109.1, 107.5 (1:2, CH_{pz}), 15.3, 14.2, 12.8, 12.5 (1:2:1:2, Me_{pz}), -3.0 (C^1, $^1J_{CH}$ = 131 Hz); IR (Nujol): ν 2039 (Ir—CO), 1681 cm^{-1} (C=O).

Compound 41. To a cold (0 ºC) solution of compound **30** (0.1 g, 0.17 mmol) in dichloromethane (5 mL), $NaHCO_3$-saturated water (6 mL) was added. To the resulting mixture a solution of *m*-chloroperbenzoic acid (0.12 g, 0.69 mmol) in dichloromethane (5 mL) was added, and stirred at room temperature for 30 min. The organic phase was separated, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude reaction mixture showed formation of **41** which was purified by crystallization as a pale brown solid from a Et_2O:CH_2Cl_2 (1:2) mixture at -20 ºC. Yield: 71 mg, 0.12 mmol (71%). R_f = 0.60 [silica gel, hexane:Et_2O (5:1)].



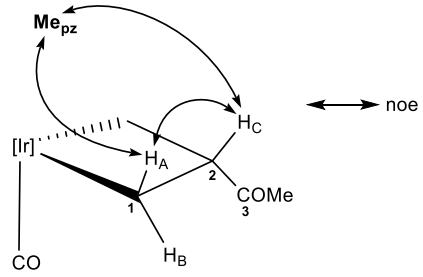
^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.86, 5.77, 5.76 (s, 1 H each, 3 CH_{pz}), 3.53 (s, 1 H, H_E), 2.47 (m, 1 H, H_B), 2.29 (m, 1 H, H_A), 2.52, 2.35, 2.34, 2.32, 2.29 (s, 1:1:1:2:1, 6 Me_{pz}), 2.20 (m, 1 H, H_C), 1.96 (m, 1 H, H_D), 1.55 (s, 3 H, Me); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ = 166.3 (CO), 150.9, 150.6, 144.1, 143.6, 143.5 (1:2:1:1:1, C_{qpz}), 108.3, 106.9, 106.3 (CH_{pz}), 72.2 (C^3), 52.2 (C^4, $^1J_{CH}$ = 167 Hz), 38.2 (C^2, $^1J_{CH}$ = 126 Hz), 22.9 (Me, $^1J_{CH}$ = 124 Hz), 14.3, 14.2, 14.1, 13.0, 12.5, 12.3 (Me_{pz}), -1.2 (C^1, $^1J_{CH}$ = 131 Hz); IR (Nujol): ν 2016 cm^{-1} (Ir—CO).

Compound 42. To a solution of compound **41** (0.03 g, 0.05 mmol) in C_6D_6 (0.5 mL) a few crystals of *p*-toluenesulfonic acid were added and the resulting mixture stirred for 1 h. ^{1}H NMR monitoring, at this point, showed quantitative formation of complex **42**. The solution was then extracted with $NaHCO_3$-saturated water and the organic phase separated, dried with Na_2SO_4 and taken to dryness to give the title compound as a white solid.



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.5, 5.49, 5.30 (s, 1 H each, 3 CH_{pz}), 4.30 (dt, 1 H, $^2J_{CB}$ = 13.2, $^3J_{AB}$ = $^3J_{DB}$ = 7.2 Hz, H_B), 3.89 (dq, 1 H, $^3J_{AC}$ = $^3J_{DC}$ = $^3J_{EC}$ = 10.0 Hz, H_C), 3.54 (dd, 1 H, H_A), 2.43, 2.3, 2.15, 2.08, 2.02, 1.97 (s, 3 H each, 6 Me_{pz}), 2.16 (m, 1 H, H_E), 1.89 (s, 3 H, Me), 1.74 (q, 1 H, $^2J_{ED}$ = 10.3 Hz, H_D), 1.89 (s, 3 H, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 217.4 (C^4), 167.8 (CO), 151.9, 151.3, 150.9, 143.7, 143.4, 142.8 (C_{qpz}), 110.0, 106.9, 106.7 (CH_{pz}), 36.6 (C^2), 30.8 (Me), 13.8, 13.5, 13.4, 12.6, 12.0, 11.9 (Me_{pz}), -1.7 (C^3), -33.1 (C^1); IR (Nujol): ν 2012 (Ir—CO), 1667 cm^{-1} (C=O).

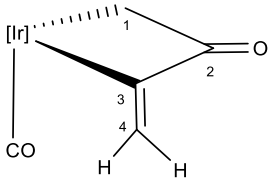
Compound 43. To a solution of compound **13** (0.03 g, 0.05 mmol) in $CDCl_3$ (0.5 mL), a few crystals of *p*-toluenesulfonic acid were added and the resulting mixture stirred for 30 min. ^{1}H NMR monitoring at this point showed formation of **43** in *ca*. 60% spectroscopic yield. The solution was extracted with $NaHCO_3$-saturated water and the organic phase separated, dried with Na_2SO_4 and taken to dryness. Complex **43** was only partially purified by passing this solution through a short silica gel column (white solid).



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.80, 5.73 (s, 1:2, 3 CH_{pz}), 4.85 (tt, 1 H, $^3J_{AC}$ = 9.9, $^3J_{BC}$ = 3.3 Hz, H_C), 2.60, 2.32, 2.31, 2.28 (s, 1:1:2:2, 6 Me_{pz}), 2.19 (s, 3 H, Me), 2.06 (dd, 1 H, $^2J_{AB}$ = 9.9 Hz, H_B), 1.66 (t, 1 H, H_A); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 210.7 (C^3), 167.7 (CO), 150.8, 150.6, 144.2, 143.0 (2:1:1:2, C_{qpz}), 109.2,

106.3 (1:2, CH_{pz}), 62.0 (C^2, $^1J_{CH}$ = 126 Hz), 26.6 (Me, $^1J_{CH}$ = 128 Hz), 14.05, 13.9, 13.4, 13.3 (2:1:1:2, Me_{pz}), -33.9 (C^1, $^1J_{CH}$ = 139 Hz); IR (Nujol): ν 2001 (Ir—CO), 1697 cm^{-1} (C=O).

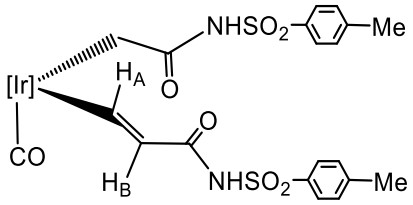
Compound 44. To a cold solution (0 ºC) of compound **35** (0.10 g, 0.16 mmol) in dichloromethane (5 mL), an excess of TsN_3 (0.13 g, 0.66 mmol) and NEt_3 (0.2 mL, 1.4 mmol) were added. The resulting mixture was then stirred at room temperature for 20 h and the solvent evaporated under reduced pressure. ^{1}H NMR spectrum of the crude reaction product showed formation of compound **44** in *ca.* 60% spectroscopic yield which was isolated, in pure form, by column chromatography on silica gel using hexane as eluent. Yield: 42 mg, 0.07 mmol (44%). It was crystallized from hexane:CH_2Cl_2 (1:2) at - 20 ºC. R_f = 0.16 [silica gel, hexane:Et_2O (100:1)].



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 6.48, 5.24 (s, 1 H each, C^4H_2), 5.88, 5.84, 5.68 (s, 1 H each, 3 CH_{pz}), 2.98, 2.72 (d, 1 H each, $^2J_{HH}$ = 14.6 Hz, C^1H_2), 2.38, 2.37, 2.32, 2.27, 2.10 (s, 2:1:1:1:1, 6 Me_{pz}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 214.2 (C^2), 165.2 (CO), 152.1, 151.4, 150.7, 144.1, 144.0 (1:1:1:1:2, C_{qpz}), 130.7 (C^3), 120.3 (C^4, $^1J_{CH}$ = 159 and 156 Hz), 109.5, 106.7, 106.5 (CH_{pz}), 14.4, 14.3, 14.1, 13.1, 12.4, 12.3 (Me_{pz}), 4.0 (C^1, $^1J_{CH}$ = 136 Hz); IR (Nujol): ν 2019 (Ir—CO), 1692 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{20}H_{26}BN_6O_2Ir$: C 41.0, H 4.4, N 14.3; found: C 41.6, H 4.6, N 13.7.

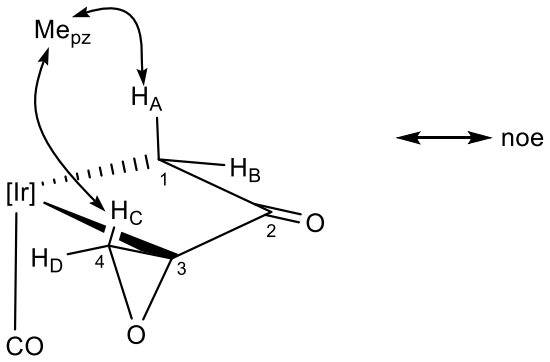
Compound 45. This compound was obtained in *ca.* 12% yield (20 mg, 0.02 mmol) as an insoluble byproduct in the synthesis of compound **44**. Due to its low solubility in common solvents its purification was easy (including chromatography). R_f = 0.20 [silica gel, Et_2O:AcOEt (1:1)]. Crystallization by slow

evaporation of a solution of compound **45** in a mixture of Et_2O:$CHCl_3$ (1:1) provided good quality crystals for X-ray studies.



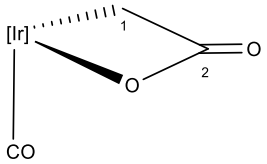
^{1}H NMR ($CDCl_3$, 25 ºC): δ = 9.16 (d, 1 H, $^2J_{BA}$ = 16.6 Hz, H_A), 8.70 (br s, 1 H, NH), 7.99, 7.32, 7.25 (m, 2:1:1, 8 CH_{ar}), 7.68 (br s, 1 H, NH), 6.19 (d, 1 H_B), 5.83, 5.78, 5.69 (s, 1 H each, 3 CH_{pz}), 3.06, 2.02 (d, 1 H each, $^2J_{HH}$ = 11.5 Hz, $IrCH_2$), 2.43, 2.39, 2.34, 2.33, 2.29, 2.00 (s, 3 H each, 6 Me_{pz}), 2.35, 2.03 (s, 3 H each, 2 Me); IR (Nujol): ν 2054 (Ir—CO), 1746 and 1692 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{35}H_{42}BN_8O_7S_2Ir \cdot ½\ Et_2O$: C 42.4, H 4.6, N 11.0; found: C 42.6, H 4.2, N 10.9.

Compound 46. To a cold solution (0 ºC) of compound **44** (0.10 g, 0.17 mmol) in dichloromethane (5 mL), a solution of *m*-chloroperbenzoic acid (0.13 g, 0.75 mmol) in the same solvent was added, the resulting mixture stirred at room temperature for 3 h and extracted with $NaHCO_3$-saturated water. The organic phase was then separated, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR of the crude reaction product showed the formation of compound **46** in *ca.* 95% spectroscopic yield which was purified by column chromatography on silica gel using a mixture of hexane:Et_2O (2:1) as eluent. Yield: 58 mg, 0.1 mmol (59%). R_f = 0.30 [silica gel, hexane:Et_2O (1:2)].



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.85, 5.79, 5.76 (s, 1 H each, 3 CH_{pz}), 3.10 (d, 1 H, $^2J_{BA}$ = 14.6 Hz, H_A), 3.05 (d, 1 H, $^2J_{DC}$ = 6.6 Hz, H_C), 2.86 (d, 1 H, H_D), 2.82 (d, 1 H, H_B), 2.37, 2.36, 2.35, 2.30, 2.28, 2.16 (s, 3 H each, 6 Me_{pz}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 217.2 (C^2), 164.4 (CO), 152.2, 151.2, 144.4, 143.9 (1:2:1:2, C_{qpz}), 109.7, 106.8, 106.7 (CH_{pz}), 53.3 (C^4, $^1J_{CH}$ = 177, 174 Hz), 41.0 (C^3), 14.5, 14.0, 13.1, 13.0, 12.4, 12.3 (Me_{pz}), 1.0 (C^1, $^1J_{CH}$ = 139 Hz); IR (Nujol): ν 2023 (Ir—CO), 1714 cm^{-1} (C=O).

Compound 47. In a two-necks round bottom flask O_3 was passed during 10 min through a solution of compound **44** (0.10 g, 0.17 mmol) in dichloromethane (20 mL) at -78 ºC. Then, Me_2S (0.05 mL) was added, the cooling bath removed, and the resulting mixture stirred at room temperature for 3 h. Water (10 mL) was then added, the mixture shaken vigorously and the organic layer separated, dried with Na_2SO_4 and taken to dryness. ^{1}H NMR analysis of the crude reaction showed the formation of the title compound which was purified by column chromatography on silica gel using a mixture of hexane:Et_2O (10:1) as eluent. Yield: 52 mg, 0.09 mmol (53%). R_f = 0.30 [silica gel, hexane:Et_2O (10:1)].



^{1}H NMR ($CDCl_3$, 25 ºC): δ = 5.89, 5.83, 5.72 (s, 1 H each, 3 CH_{pz}), 2.73, 2.71 (AB spin system, 2 H, $^2J_{HH}$ = 14.0 Hz, C^1H_2), 2.41, 2.39, 2.37, 2.33, 2.32, 2.23 (s, 3 H each, 6 Me_{pz}); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ = 188.6 (C^2), 160.5 (CO), 152.5, 152.1, 151.5, 144.9, 144.3, 144.1 (C_{qpz}), 109.6, 107.4, 106.5 (CH_{pz}), 14.9, 13.5, 12.9, 12.7, 12.6, 12.0 (Me_{pz}), -6.1 (C^1, $^1J_{CH}$ = 140 Hz); IR (Nujol): ν 2033 (Ir—CO), 1710 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{20}H_{26}BN_6O_2Ir\cdot C_6H_{14}$: C 43.6, H 4.7, N 12.7; found: C 43.3, H 4.4, N 12.6.

II X-RAY STRUCTURE ANALYSIS

Crystals suitable for X-ray diffraction analysis were coated with dry perfluoropolyether, mounted on glass fibers, and fixed in a cold nitrogen stream (except for **7**) to the goniometer head. Data collections were performed on a Bruker-Nonius X8 Apex-II CCD diffractometer (**5, 10, 19, 25, 33** and **45**) or a Bruker Smart Apex CCD diffractometer (**7, 12** and **15**) using graphite monochromated Mo radiation (λ(Mo Kα) = 0.71073 Å) and fine-sliced ω and φ scans (scan widths 0.30° to 0.50°). The data were reduced (SAINT)[2] and corrected for absorption effects by the multiscan method (SADABS). [2] The structures were solved by direct methods (SIR2002, [3] SHELXS[4]) and refined against all F^2 data by full-matrix least-squares techniques (*SHELXTL-6.12*) minimizing $w[F_o^2\text{-}F_c^2]^2$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions and allowed to ride on their carrier atoms with the isotropic temperature factors U_{iso} fixed at 1.2 times (1.5 times for methyl groups) of the U_{eq} values of the respective carrier atoms. Some geometric restraints (SADI and DFIX shelxl instructions), the ADP restraint SIMU and the rigid bond restraint (DELU and ISOR) were used to make the geometric and ADP values of the disordered atoms more reasonable. As examples: positional disorder: **10** and **33**, structural disorder: **25**, and disordered $CHCl_3$ solvent molecules in **45**. CCDC 1565331 (**5**), 1565332 (**7**), 1565333 (**10**), 1565334 (**12**), 1565335 (**15**), 1565336 (**19**), 1565337 (**25**), 1565338 (**33**) and 1565339 (**45**) contain the supplementary crystallographic data for this paper.

Figure S1: ORTEP drawing of **5** at 30% ellipsoids probability, most of hydrogen atoms are omitted for clarity.

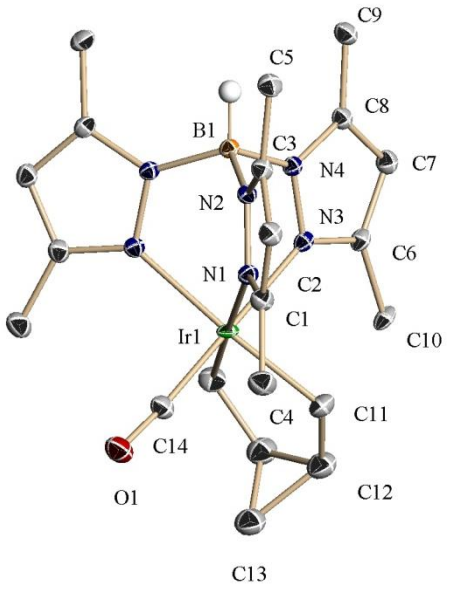


Table S1: Crystal data and structure refining for **5**:

Empirical formula	$C_{21}H_{30}BIrN_6O$	
Formula weight	585.52	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/m	
Unit cell dimensions	a = 7.8986(5) Å	α= 90°.
	b = 13.2259(9) Å	β= 105.185(2)°.
	c = 11.0710(7) Å	γ = 90°.
Volume	1116.16(13) $Å^3$	
Z	2	
Density (calculated)	1.742 Mg/m^3	
Absorption coefficient	6.006 mm^{-1}	
F(000)	576	
Crystal size	0.27 x 0.26 x 0.18 mm^3	
Theta range for data collection	1.91 to 25.25°.	
Index ranges	-8<=h<=9, -15<=k<=15, -13<=l<=13	
Reflections collected	11339	
Independent reflections	2114 [R(int) = 0.0284]	
Completeness to theta = 25.25°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4111 and 0.2939	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2114 / 299 / 154	
Goodness-of-fit on F^2	1.275	
Final R indices [I>2sigma(I)]	R1 = 0.0421, wR2 = 0.1207	
R indices (all data)	R1 = 0.0433, wR2 = 0.1224	
Largest diff. peak and hole	2.740 and -1.184 e.$Å^{-3}$	

Figure S2: ORTEP drawing of **7** at 30% ellipsoids probability, most of hydrogen atoms are omitted for clarity.

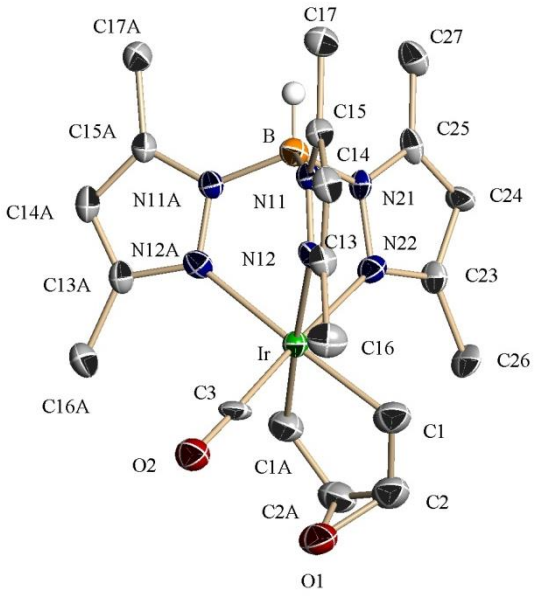


Table S2: Crystal data and structure refining for **7**:

Empirical formula	$C_{20}H_{28}BIrN_6O_2$	
Formula weight	587.49	
Temperature	299(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/m$	
Unit cell dimensions	a = 7.983(2) Å	α= 90°.
	b = 13.312(3) Å	β= 108.450(10)°.
	c = 11.005(2) Å	γ = 90°.
Volume	1109.4(4) $Å^3$	
Z	2	
Density (calculated)	1.759 Mg/m^3	
Absorption coefficient	6.046 mm^{-1}	
F(000)	576	
Crystal size	0.60 x 0.20 x 0.02 mm^3	
Theta range for data collection	2.48 to 25.05°.	
Index ranges	-9<=h<=9, -15<=k<=15, -13<=l<=13	
Reflections collected	10662	
Independent reflections	2046 [R(int) = 0.1020]	
Completeness to theta = 25.05°	98.8 %	
Absorption correction	Analytical	
Max. and min. transmission	0.92 and 0.36	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2046 / 0 / 154	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0780, wR2 = 0.1778	
R indices (all data)	R1 = 0.0971, wR2 = 0.1869	
Largest diff. peak and hole	5.265 and -2.018 $e.Å^{-3}$	

Figure S3: ORTEP drawing of **10** at 30% ellipsoids probability, most of hydrogen atoms are omitted for clarity.

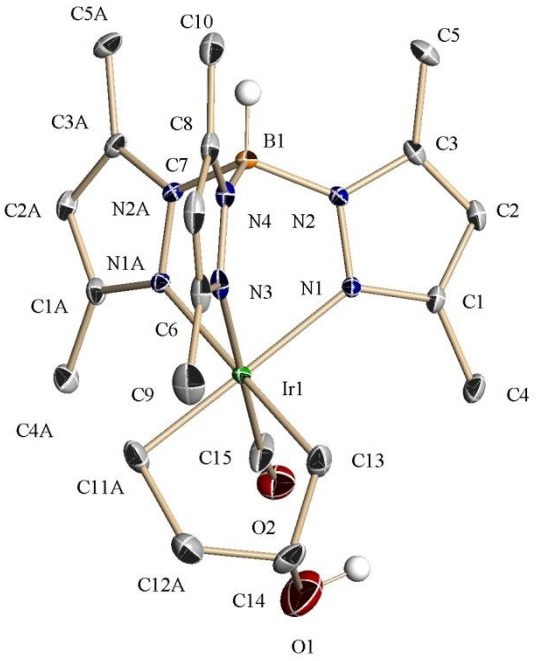


Table S3: Crystal data and structure refining for **10**:

Empirical formula	$C_{20}H_{31}BIrN_6O_2$	
Formula weight	590.51	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/m	
Unit cell dimensions	a = 7.9367(8) Å	α= 90°.
	b = 13.1619(13) Å	β= 105.384(2)°.
	c = 10.9680(10) Å	γ = 90°.
Volume	1104.69(19) $Å^3$	
Z	2	
Density (calculated)	1.775 Mg/m^3	
Absorption coefficient	6.072 mm^{-1}	
F(000)	582	
Crystal size	0.39 x 0.09 x 0.09 mm^3	
Theta range for data collection	3.08 to 25.24°.	
Index ranges	-9<=h<=9, -15<=k<=15, -12<=l<=13	
Reflections collected	16605	
Independent reflections	2088 [R(int) = 0.0308]	
Completeness to theta = 25.24°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6110 and 0.2005	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2088 / 56 / 169	
Goodness-of-fit on F^2	1.280	
Final R indices [I>2sigma(I)]	R1 = 0.0300, wR2 = 0.0811	
R indices (all data)	R1 = 0.0302, wR2 = 0.0812	
Largest diff. peak and hole	2.085 and -1.380 e.$Å^{-3}$	

Figure S4: ORTEP drawing of **12** at 30% ellipsoids probability, most of hydrogen atoms are omitted for clarity.

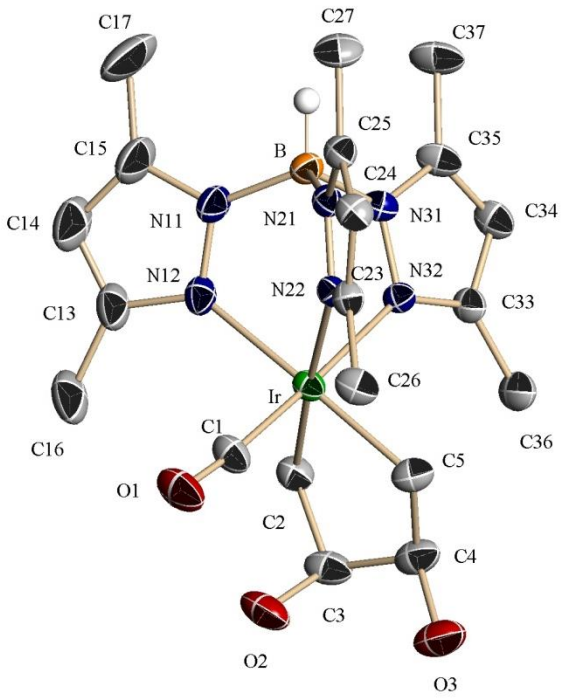


Table S4: Crystal data and structure refining for **12**:

Empirical formula	$C_{43}H_{66}B_2Ir_2N_{12}O_6$	
	$[2(C_{20}H_{30}BIrN_6O_3), 0.5(C_6H_{12})]$	
Formula weight	1253.10	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 16.3066(6) Å	α= 90°.
	b = 18.1340(7) Å	β= 104.459(2)°.
	c = 17.1839(7) Å	γ = 90°.
Volume	4920.4(3) $Å^3$	
Z	4	
Density (calculated)	1.692 Mg/m^3	
Absorption coefficient	5.461 mm^{-1}	
F(000)	2480	
Crystal size	0.36 x 0.14 x 0.12 mm^3	
Theta range for data collection	2.28 to 27.00°.	
Index ranges	-20<=h<=20, -23<=k<=23, -21<=l<=21	
Reflections collected	59327	
Independent reflections	10670 [R(int) = 0.0484]	
Completeness to theta = 27.00°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.586	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10670 / 0 / 598	
Goodness-of-fit on F^2	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0364, wR2 = 0.0814	
R indices (all data)	R1 = 0.0538, wR2 = 0.0892	
Largest diff. peak and hole	1.547 and -1.544 $e.Å^{-3}$	

Figure S5: ORTEP drawing of **15** at 30% ellipsoids probability, most of hydrogen atoms are omitted for clarity.

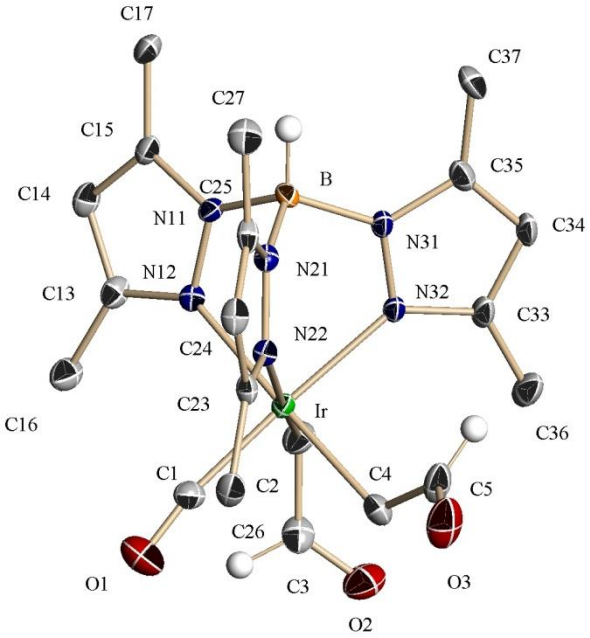


Table S5: Crystal data and structure refining for **15**:

Empirical formula	$C_{20}H_{28}BIrN_6O_3$	
Formula weight	603.49	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.1542(4) Å	α= 90°.
	b = 14.0169(7) Å	β= 100.022(1)°.
	c = 19.7781(9) Å	γ = 90°.
Volume	2226.08(19) $Å^3$	
Z	4	
Density (calculated)	1.801 Mg/m^3	
Absorption coefficient	6.032 mm^{-1}	
F(000)	1184	
Crystal size	0.38 x 0.17 x 0.08 mm^3	
Theta range for data collection	2.55 to 30.00°.	
Index ranges	-11<=h<=11, -19<=k<=19, -27<=l<=27	
Reflections collected	33627	
Independent reflections	6013 [R(int) = 0.0270]	
Completeness to theta = 30.00°	92.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.585	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6013 / 0 / 286	
Goodness-of-fit on F^2	1.186	
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0736	
R indices (all data)	R1 = 0.0411, wR2 = 0.0748	
Largest diff. peak and hole	1.347 and -1.986 $e.Å^{-3}$	

Figure S6: ORTEP drawing of **19** at 30% ellipsoids probability, most of hydrogen atoms are omitted for clarity.

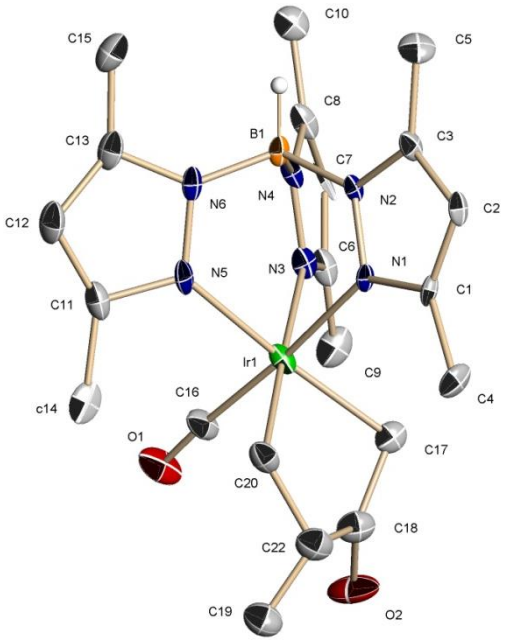


Table S6: Crystal data and structure refining for **19**:

Empirical formula	$C_{21}H_{30}BIrN_6O_2$	
Formula weight	601.52	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P $2_{1/}$n	
Unit cell dimensions	a = 7.9799(19) Å	α= 90°.
	b = 14.319(3) Å	β= 97.007(5)°.
	c = 20.100(4) Å	γ = 90°.
Volume	2279.5(9) $Å^3$	
Z	4	
Density (calculated)	1.753 Mg/m^3	
Absorption coefficient	5.887 mm^{-1}	
F(000)	1184	
Crystal size	0.18 x 0.17 x 0.16 mm^3	
Theta range for data collection	2.85 to 30.41°.	
Index ranges	-11<=h<=11, -20<=k<=20, -28<=l<=19	
Reflections collected	26449	
Independent reflections	6484 [R(int) = 0.0698]	
Completeness to theta = 30.41°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4527 and 0.4171	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6484 / 286 / 262	
Goodness-of-fit on F^2	1.103	
Final R indices [I>2sigma(I)]	R1 = 0.0928, wR2 = 0.1860	
R indices (all data)	R1 = 0.1245, wR2 = 0.2265	
Largest diff. peak and hole	3.679 and -2.141 e.$Å^{-3}$	

Figure S7: ORTEP drawing of **25** at 30% ellipsoids probability, most of hydrogen atoms are omitted for clarity.

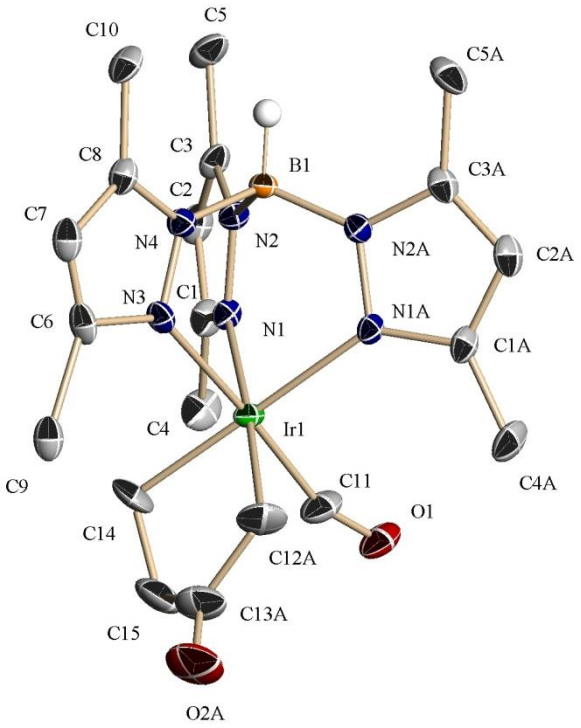


Table S7: Crystal data and structure refining for **25**:

Empirical formula	$C_{20}H_{28}BIrN_6O_2$	
Formula weight	587.49	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/m	
Unit cell dimensions	a = 7.9819(12) Å	α= 90°.
	b = 13.3275(19) Å	β= 103.661(4)°.
	c = 10.7750(16) Å	γ = 90°.
Volume	1113.8(3) $Å^3$	
Z	2	
Density (calculated)	1.752 Mg/m^3	
Absorption coefficient	6.022 mm^{-1}	
F(000)	576	
Crystal size	0.16 x 0.11 x 0.10 mm^3	
Theta range for data collection	1.95 to 30.59°.	
Index ranges	-11<=h<=10, -15<=k<=19, -15<=l<=11	
Reflections collected	8426	
Independent reflections	3536 [R(int) = 0.0480]	
Completeness to theta = 30.59°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5842 and 0.4458	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3536 / 222 / 175	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0812, wR2 = 0.1558	
R indices (all data)	R1 = 0.1023, wR2 = 0.2121	
Largest diff. peak and hole	5.610 and -5.010 e.$Å^{-3}$	

Figure S8: ORTEP drawing of **33** at 30% ellipsoids probability, most of hydrogen atoms are omitted for clarity.

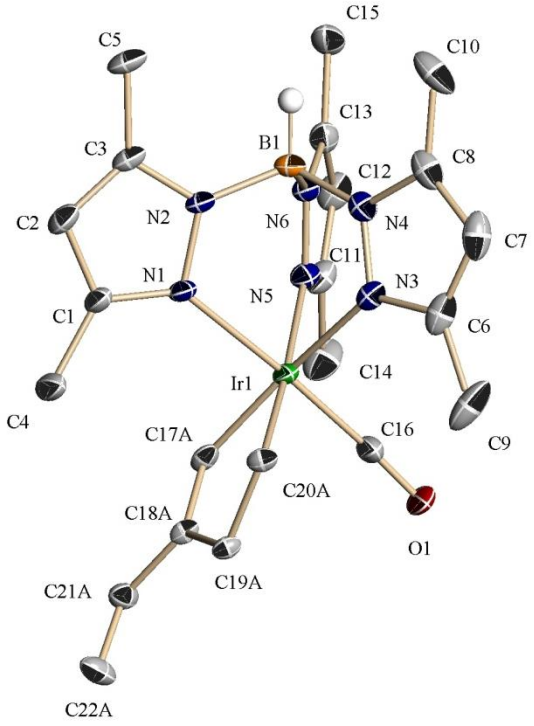


Table S8: Crystal data and structure refining for **33**:

Empirical formula	$C_{22}H_{30}BIrN_6O$	
Formula weight	597.53	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P $\bar{1}$	
Unit cell dimensions	a = 10.0761(7) Å	α= 115.898(2)°.
	b = 11.5751(8) Å	β= 93.773(2)°.
	c = 12.2502(9) Å	γ = 112.071(2)°.
Volume	1144.89(14) $Å^3$	
Z	2	
Density (calculated)	1.733 Mg/m^3	
Absorption coefficient	5.857 mm^{-1}	
F(000)	588	
Crystal size	0.17 x 0.14 x 0.09 mm^3	
Theta range for data collection	3.31 to 25.25°.	
Index ranges	-12<=h<=11, -13<=k<=13, -14<=l<=14	
Reflections collected	13246	
Independent reflections	4000 [R(int) = 0.0210]	
Completeness to theta = 25.25°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6207 and 0.4359	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4000 / 0 / 340	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0194, wR2 = 0.0464	
R indices (all data)	R1 = 0.0227, wR2 = 0.0476	
Largest diff. peak and hole	0.854 and -1.384 e.$Å^{-3}$	

Figure S9: ORTEP drawing of **45** at 30% ellipsoids probability, most of hydrogen atoms and $CHCl_3$ solvent molecules are omitted for clarity.

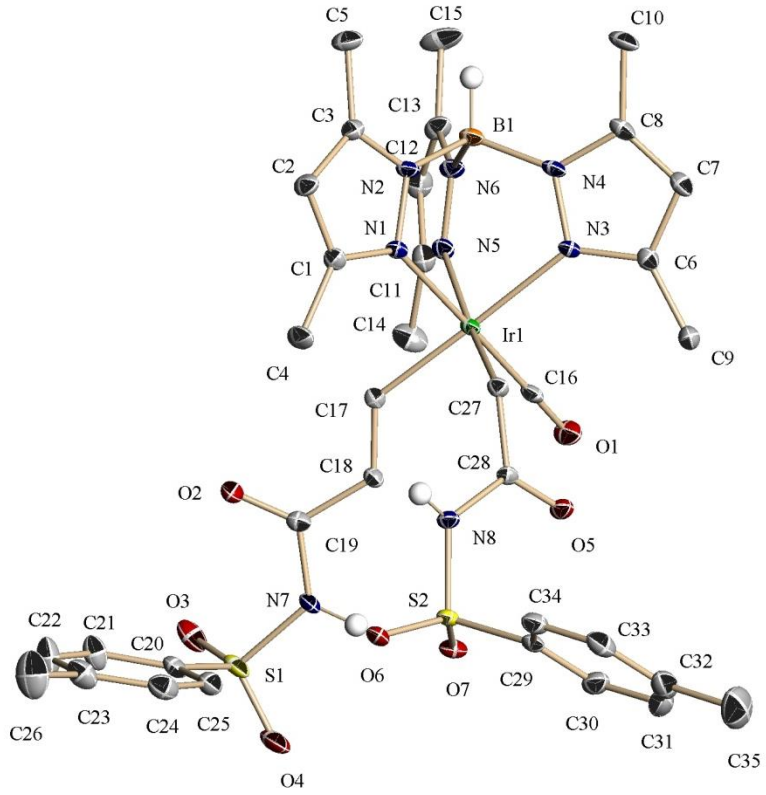


Table S9: Crystal data and structure refining for **45**:

Empirical formula	$C_{40}H_{47}BCl_{15}IrN_8O_7S_2$	
	$[C_{35}H_{42}BIrN_8O_7S_2, 5(CHCl_3)]$	
Formula weight	1550.74	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.5792(6) Å	α= 90°.
	b = 31.0920(13) Å	β= 107.1790(10)°.
	c = 16.4342(6) Å	γ = 90°.
Volume	6140.9(4) $Å^3$	
Z	4	
Density (calculated)	1.677 Mg/m^3	
Absorption coefficient	2.945 mm^{-1}	
F(000)	3072	
Crystal size	0.37 x 0.28 x 0.17 mm^3	
Theta range for data collection	1.45 to 25.25°.	
Index ranges	-15<=h<=15, -37<=k<=36, -19<=l<=19	
Reflections collected	54334	
Independent reflections	11090 [R(int) = 0.0308]	
Completeness to theta = 25.25°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6344 and 0.4087	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11090 / 182 / 709	
Goodness-of-fit on F^2	1.122	
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.1137	
R indices (all data)	R1 = 0.0510, wR2 = 0.1166	
Largest diff. peak and hole	1.999 and -1.411 $e.Å^{-3}$	

III REFERENCES

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