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The Synthesis of Iridabenzenes by the Coupling of Iridacyclopentadienes and Olefins

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The iridacyclopentadiene [(Tp^{Me2})Ir{C^1(R)=C(R)C(R)=C^4(R)}(H$_2$O)(*Ir–C*^{4})] (**1**; R = CO$_2$Me) reacts with propene at 60 °C to give the iridabenzene [(Tp^{Me2})Ir{C^1(Et)C(R)C(R)C(R)C^5(R)}(H)(*Ir–C*^{5})] (**6**), which also contains a hydride ligand, as the main product, accompanied by complexes **7** and **8** derived from the insertion of propene into the Ir–C bonds of **1**. In contrast, the closely related metallacycle [(Tp^{Me2})Ir{C^1(R)=C(H)C(R)=C^4(R)}(H$_2$O)(*Ir–C*^{4})] (**1-H**) gives the iridabenzene [(Tp^{Me2})Ir{C^1(Me)C(R)C(H)C(R)C^5(R)}(Me)(*Ir–C*^{5})] (**13**), which contains an iridium-bonded methyl group, upon treatment with propene at 20 °C. The proposed mechanism for the formation of metallabenzenes **6** and **13** postulates Ir–propene → Ir=CHEt or Ir–propene → Ir=CMe$_2$ isomerisations, followed by insertion of the alkylidene ligand into an Ir–C(R) bond (regioselective for **1-H**) and α-H or α-Me elimination from the resulting alkyliridium moiety. At 25 °C, neat acetonitrile induces stereoselective hydride migration onto both the Ir$\overset{\cdots}{-}$C bonds of **6** to give a kinetic mixture (6:1 ratio) of the isomeric adducts [(Tp^{Me2})Ir{C^{1}H(Et)C(R)=C(R)C(R)=C^5(R)}(MeCN)(*Ir–C*^{5})] (**9**) and [(Tp^{Me2})Ir{C^{1}H(R)C(R)=C(R)C(R)=C^5(Et)}(MeCN)(*Ir–C*^{5})] (**10**), with the latter being the thermodynamically preferred product. In contrast, complex **13** is stable in acetonitrile up to 100 °C, where it mainly experiences ring fragmentation to give the iridacyclopentadiene **1-H** as its MeCN adduct. All new compounds have been fully characterised by microanalysis and spectroscopy. Additionally, the solid-state structures of **5**, **6** and **13** have been determined by X-ray crystallography.

Introduction

We have recently reported on the reaction of the iridacyclopentadiene [(Tp^{Me2})Ir{C^1(R)=C(R)C(R)=C^4(R)}(H$_2$O)(*Ir–C*^{4})] [**1**; Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate, R = CO$_2$Me] with ethylene (Scheme 1).[1] The first species formed is the iridacycloheptadiene **2** as the result of the insertion of C$_2$H$_4$ into one of the two identical Ir–C bonds. This species rearranges readily at room temperature to the hydride-alkenyl derivative **3** by extrusion of H$_2$O and β-H elimination, whereas upon heating at 40–60 °C the alkyl-allyl complex **4** is obtained by means of a stereoselective hydride migration. In a parallel study we have observed that (Scheme 1) the iridacyclopentadiene [(Tp^{Me2})Ir{C^1(R)=C(H)C(R)=C^4(R)}(H$_2$O)(*Ir–C*^{4})] (**1-H**) gives rise to related species (**3-H** and **4-H**, respectively) under similar conditions, thereby implying that ethylene inserts regioselectively into the Ir–C bond close to the C–H functionality. In this paper we describe the different and unusual chemistry observed when **1** and **1-H** are treated with propene and 1-butene. Part of the findings reported herein have been briefly communicated.[2]

Results and Discussion

Reaction of Complex 1 with Propene

Bubbling propene through a solution of complex **1** in CH$_2$Cl$_2$ at room temperature leads to partial conversion to the metallacycloheptadiene **5**, as deduced from the NMR spectra of the reaction mixture [Equation (1)], in a spectroscopic yield of about 50%. The yield does not improve upon extending the reaction time. Complex **5** is closely related to species **2**, which forms in the reaction of **1** with ethylene, and is probably formed by the same mechanism, namely temporary displacement of the water ligand by a molecule of propene followed by insertion of the olefin into one of the equivalent Ir–C bonds and subsequent coordination of H$_2$O.[1] Interestingly, this insertion process is highly selective as only one of the four possible stereoisomers is observed.

Complex **5** can be isolated as a pale-yellow, microcrystalline solid by column chromatography on silica gel. The most characteristic ^{1}H NMR signals of this compound are those corresponding to the two diastereotopic protons of the methylene group bonded to the metal, which appear at δ = 3.46 and 2.84 ppm (doublet of doublets and triplet, respectively), while the corresponding carbon atom resonates at δ = 6.5 ppm ($^1J_{C,H}$ = 126 Hz) in the ^{13}C{^{1}H} NMR spectrum. The MeCH group of the metallacycle gives rise

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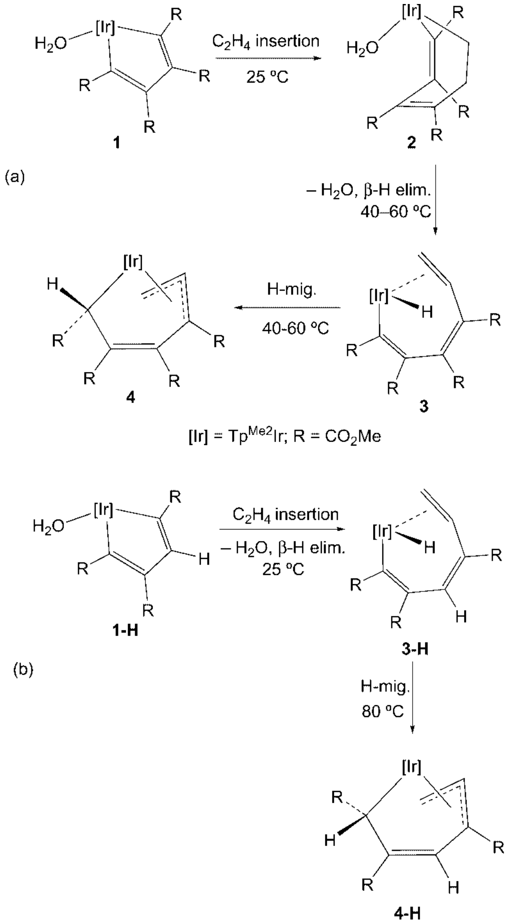
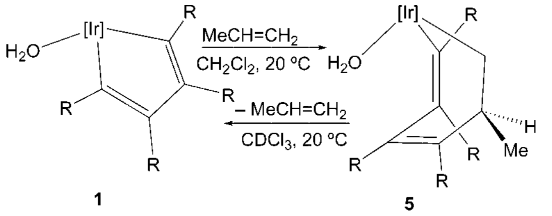


Scheme 1. Reaction of complexes **1** (a) and **1-H** (b) with C_2H_4.



(1)

to ^{1}H NMR resonances at $\delta = 3.22$ (m, CH) and 1.25 ppm (d, *Me*CH) and to $^{13}C\{^1H\}$ NMR signals at $\delta = 38.5$ (*C*HMe) and 19.4 ppm (CH*Me*). The configuration of the CHMe group was derived from an X-ray study, the results of which are shown in Figure 1. The corresponding crystallographic data are collected in the Experimental Section, while selected bond lengths and angles for complex **5** are shown in Table 1. As expected, the Ir–C(sp^3) bond (2.08 Å) is somewhat longer than the Ir–C(sp^2) one (2.02 Å).[3] It should also be noted that, of the three Ir–N bonds, that *trans* to water is appreciably shorter (2.03 Å) than the other two (2.16 Å av.),[1] which are *trans* to the two different Ir–C σ bonds and the Ir–C(sp^3) and the Ir–C(sp^2) bonds (Ir–C16 and Ir–C28, respectively).

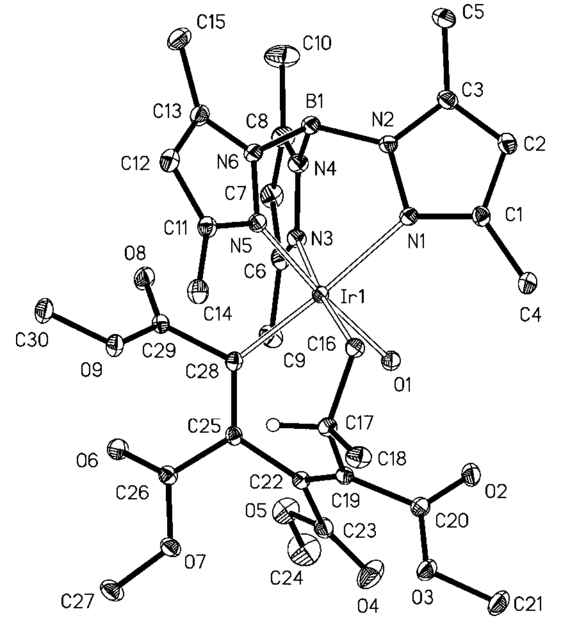


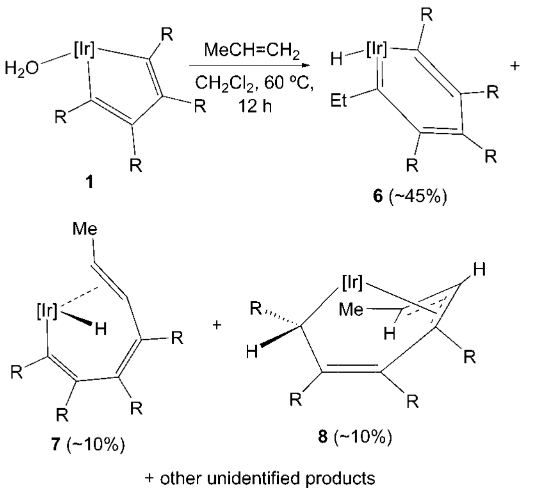
Figure 1. X-ray structure of complex **5**.

Table 1. Selected bond lengths [Å] and angles [°] for **5**.

Ir(1)–N(1)	2.160(2)	C(16)–C(17)	1.549(3)
Ir(1)–N(3)	2.166(2)	C(17)–C(19)	1.516(3)
Ir(1)–N(5)	2.029(2)	C(19)–C(22)	1.346(3)
Ir(1)–C(16)	2.079(2)	C(22)–C(25)	1.479(3)
Ir(1)–C(28)	2.017(2)	C(25)–C(28)	1.366(3)
Ir(1)–O(1)	2.122(2)		
C(28)–Ir(1)–N(5)	91.0(8)	C(16)–Ir(1)–N(1)	90.4(8)
C(28)–Ir(1)–C(16)	94.1(8)	O(1)–Ir(1)–N(1)	88.4(6)
N(5)–Ir(1)–C(16)	92.8(8)	C(28)–Ir(1)–N(3)	90.1(7)
C(28)–Ir(1)–O(1)	92.9(7)	N(5)–Ir(1)–N(3)	91.2(7)
N(5)–Ir(1)–O(1)	174.6(6)	C(16)–Ir(1)–N(3)	174.1(7)
C(16)–Ir(1)–O(1)	90.7(8)	O(1)–Ir(1)–N(3)	85.0(6)
C(28)–Ir(1)–N(1)	175.3(7)	N(1)–Ir(1)–N(3)	85.4(7)
N(5)–Ir(1)–N(1)	87.4(7)		

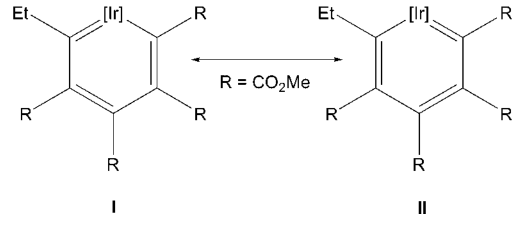
Interestingly, the rearrangement of **1** to **5** shown in Equation (1) does not proceed when thf is used as the reaction solvent, possibly because thf coordination prevents binding of the alkene. We have also found that propene insertion is reversible, at least in $CDCl_3$ and C_6D_6. Thus, upon standing at room temperature for several hours, solutions of **5** in these deuterated solvents revert to **1** and free propene. This occurs even in the presence of added propene, although in these cases the back reaction is naturally slower. In contrast, solutions of **5** in hexane/diethyl ether mixtures remain unchanged for at least 48 h.

Different results are observed when compound **1** is treated with propene in CH_2Cl_2 at 60 °C; this reaction gives the mixture of compounds **6**–**8** shown in Equation (2). Complexes **6** and **7** were isolated as green and dark-yellow microcrystalline solids, respectively, by column chromatography on silica gel, although characterisation of **8** required its direct preparation from **7** (see below). The analytical and spectroscopic data for **6**–**8** support its proposed formulation, which for **6** was confirmed by an X-ray structure determination.



(2)

Compound **6**, which is the major product of Equation (2), has an iridabenzene structure. Its formation from **1** and propene, that is, by coupling of an alkene with a metallacyclopentadiene, constitutes a novel synthetic procedure for this kind of aromatic metallacycle.[4] Its hydride ligand resonates at δ = –21.41 ppm in the ^{1}H NMR spectrum, while the low field resonances at δ = 274.2 and 202.1 ppm found in the $^{13}C\{^{1}H\}$NMR spectrum are due to the Ir–*C*(Et) and Ir–*C*(CO_2Me) carbon nuclei, respectively. Both these values suggest a partial double-bond character of the Ir–C bonds,[4] with a higher carbene character for the carbon atom bonded to the stronger electron-donating alkyl group. In other words, the electronic structure of **6** may be thought of as being intermediate between those of **I** and **II** below, with a larger contribution of the former.



I **II**

This assumption was reinforced by the solid-state structural data obtained by X-ray crystallography[2] (Figure 2 and Table 2). Even though the two Ir–C bond lengths are similar, the Ir–C(Et) bond [1.922(4) Å] is shorter than the Ir–C(CO_2Me) bond [1.979(4) Å]. The iridium atom in **6** deviates appreciably from the mean plane defined by the five ring-carbon atoms (0.57 Å), this deviation being intermediate between values found in the iridabenzene [(Tp^{Me2})Ir{C^{1}(R)C(R)C(R)C(R)C^{5}(R)}(OCOR)(*Ir–C*^{5})], which contains bulkier substituents (0.74 Å),[4f] and in the less congested species [(Tp^{Me2})Ir{C^{1}(H)C(Me)C(Me)C(H)C^{5}(Me)}(H)(*Ir–C*^{5})][3] (0.50 Å).

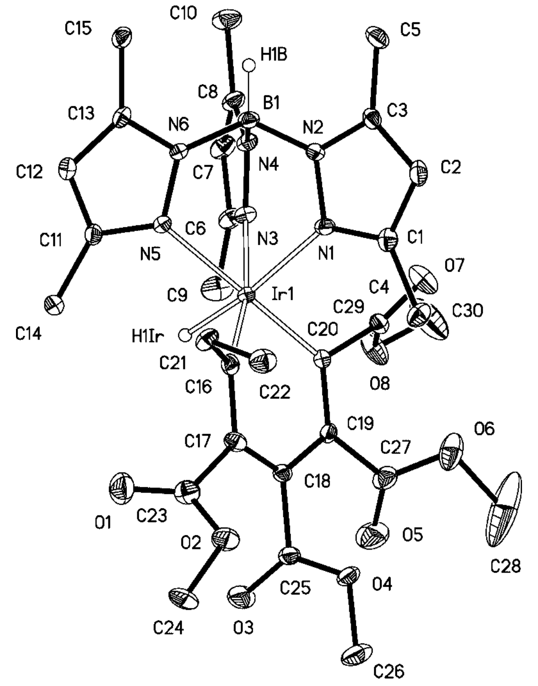


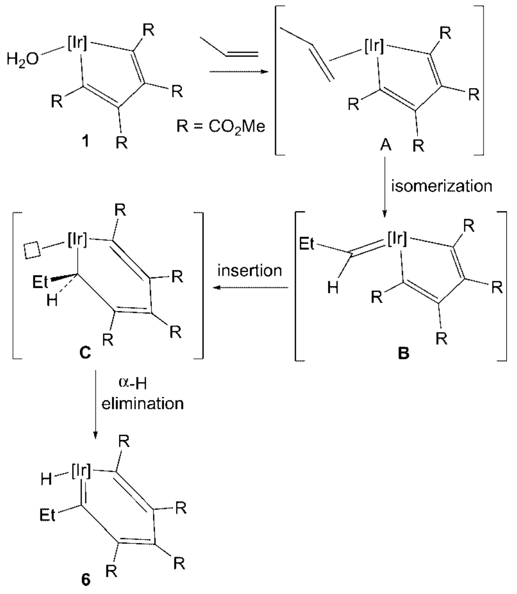
Figure 2. X-ray structure of complex **6**.

Table 2. Selected bond lengths [Å] and angles [°] for **6**.

Ir(1)–N(1)	2.150(3)	Ir(1)–H(1Ir)	1.608
Ir(1)–N(3)	2.150(3)	C(16)–C(17)	1.426(6)
Ir(1)–N(5)	2.144(3)	C(17)–C(18)	1.386(6)
Ir(1)–C(16)	1.922(4)	C(18)–C(19)	1.434(6)
Ir(1)–C(20)	1.979(4)	C(19)–C(20)	1.372(5)
C(16)–Ir(1)–C(20)	90.5(2)	N(5)–Ir(1)–N(3)	80.4(1)
C(16)–Ir(1)–N(5)	92.1(2)	N(1)–Ir(1)–N(3)	87.4(1)
C(20)–Ir(1)–N(5)	176.4(2)	C(16)–Ir(1)–H(1Ir)	89.1
C(16)–Ir(1)–N(1)	98.5(2)	C(20)–Ir(1)–H(1Ir)	90.4
C(20)–Ir(1)–N(1)	93.2(2)	N(5)–Ir(1)–H(1Ir)	87.2
N(5)–Ir(1)–N(1)	88.8(1)	N(1)–Ir(1)–H(1Ir)	171.5
C(16)–Ir(1)–N(3)	170.4(2)	N(3)–Ir(1)–H(1Ir)	84.5
C(20)–Ir(1)–N(3)	96.7(2)		

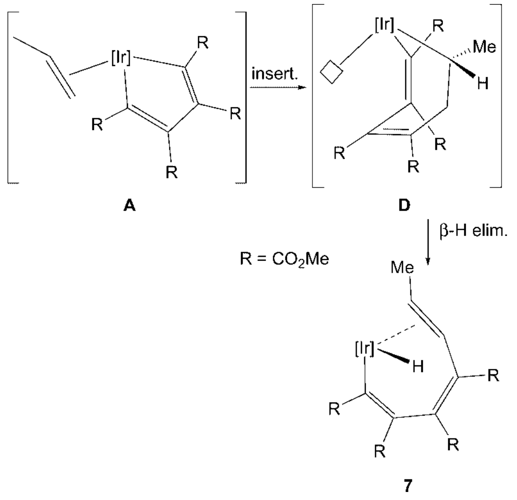
A plausible mechanism for the formation of complex **6** is shown in Scheme 2. Coordination of the olefin after displacement of the molecule of H_2O gives intermediate **A**, which is proposed to undergo alkene isomerisation into a propylidene (to give **B**) and then a stereoselective migratory carbene insertion into one of the Ir–C bonds of the metallacycle. The resulting species **C** converts into the observed iridabenzene by means of an α-hydride elimination. An alkene-to-alkylidene rearrangement is an uncommon process, although there is literature precedent.[5] The migratory insertion of alkylidenes into M–C bonds[6] and the α-hydride elimination are well-known elementary steps.[7] Other mechanistic (also highly speculative) pathways for the formation of **6** can, however, also be envisaged.[8]

The hydride ligand of complex **7** gives rise to a high-field resonance at δ = –16.93 ppm in the ^{1}H NMR spectrum, while the π-coordinated alkene terminus exhibits resonances at δ = 6.01 (d), 4.34 (m) and 1.15 ppm (d) for the C*H*=CHMe, CH=C*H*Me and CH=CH*Me* protons, respectively. The *trans* disposition of the olefinic protons was de-



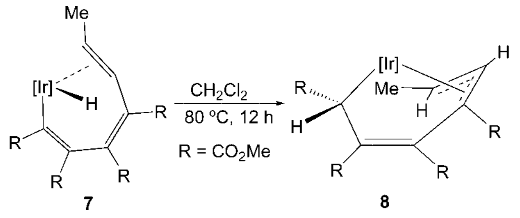
Scheme 2. Proposed mechanism for the formation of **6**.

duced from their $^{3}J_{\mathrm{H,H}}$ coupling constant (11 Hz). The ^{13}C NMR spectroscopic data as well as two-dimensional experiments are also in agreement with the structure proposed. In particular, the NOESY spectrum confirmed the *trans* configuration of the coordinated olefin and also its coordination to the metal through the face displayed in Equation (2). The hydride-alkenyl **7** is related to **3** (see Introduction) and it is important to highlight that only the represented stereoisomer is observed. It probably forms from intermediate **D** by a β-H elimination process (Scheme 3), while, in turn, **D** forms from **A** by an olefin insertion reaction that has a stereoselectivity different to that leading to **5** (note that the configuration of the CHMe group of this complex cannot yield a vinyl compound by β-H elimination).



Scheme 3. Proposed mechanism for the formation of **7**.

Compound **3** is stable in solution for only a short period of time at room temperature as it transforms slowly into the allyl derivative **4**.[1] In contrast, **7** is stable under these conditions, although, upon heating, it also gives rise to an allyl species (**8**) due to the stereospecific transfer of the hydride to the α-carbon atom of the alkenyl ligand of **7** [Equation (3)]. Compound **8** exhibits ^{1}H NMR resonances due to the π-coordinated allyl moiety at δ = 7.11 (d, CH), 3.61 (m, C*H*Me) and 1.47 ppm (d, CH*Me*), while the carbon nuclei of this fragment produce ^{13}C NMR resonances at δ = 93.7 (CH), 38.5 (*C*HMe) and 68.2 ppm (C_q), with these values being similar to those found for the related species **3**.[1] It is interesting to note that **8** contains a catenated η^{1}-allyl-η^{3}-allyl ligand which, in principle, can isomerize by concomitant change of the hapticity of the two allyl moieties. However, as for **4**,[1] only the species with the CO_2Me group on the sp^{3} carbon bonded to the metal is observed.

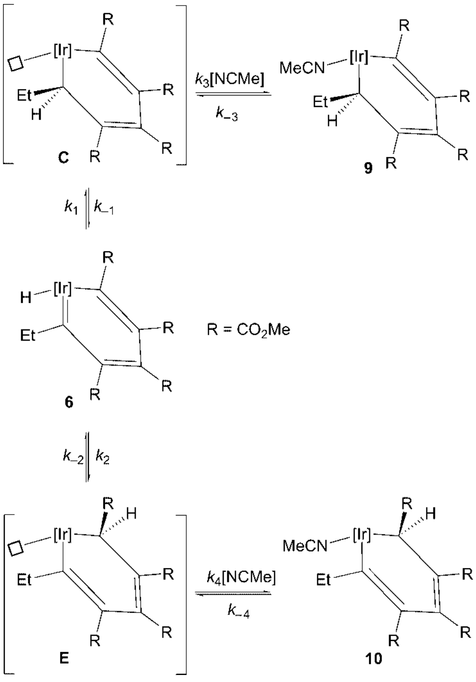


(3)

Reaction of the Iridabenzene 6 with MeCN

As represented in Scheme 4, iridabenzene **6** reacts with neat MeCN at 20 °C to give a 6:1 kinetic mixture of the isomeric metallacyclohexadienes[4c,4h,9] **9** and **10**, which are the products of the stereospecific migration of the hydride ligand onto the two different Ir–C bonds followed by coordination of MeCN. Both complexes can be cleanly separated by chromatography and have been fully characterised by spectroscopic methods. The aliphatic carbon bonded to iridium in complex **9** resonates at δ = 4.8 ppm in the ^{13}C{^{1}H} NMR while the corresponding nucleus of **10** appears at δ = 4.6 ppm. The latter species is the thermodynamic product of the reaction, as **9** transforms cleanly and almost quantitatively into **10** in C_6D_6 at 90 °C ($t_{1/2}$ = 4 h). Interestingly, the kinetic ratio of **9** to **10** in neat MeCN was found to vary with temperature (5 at 30 °C, 4.2 at 40 °C, 2.8 at 60 °C and 2.1 at 80 °C) and a graphic representation of ln[**9**]/[**10**] vs. $1/T$ gives a straight line (Figure 3) from which the values of $\Delta\Delta H^{\neq}$ = 3.75 kcal mol^{-1} and $\Delta\Delta S^{\neq}$ = 5 cal mol^{-1} K^{-1} can be computed (the latter favours the formation of **10** at high temperatures).

The proposed mechanism[9] for the formation of these adducts is also shown in Scheme 4 and implies the competitive transformation of complex **6** into the unsaturated intermediates **C** and **E**, which are then trapped by MeCN. As commented above, complex **9** transforms into the thermodynamically more stable isomer **10** when heated at 90 °C in C_6D_6. In principle, this reaction could be the result of a direct 1,5-suprafacial shift of the hydrogen atom between the two Cα positions.[9] However, several indications appear to be more in agreement with a mechanism in which iridabenzene **6** is a true intermediate of this rearrangement,



Scheme 4. Proposed mechanism for the formation of complexes **9** and **10**.

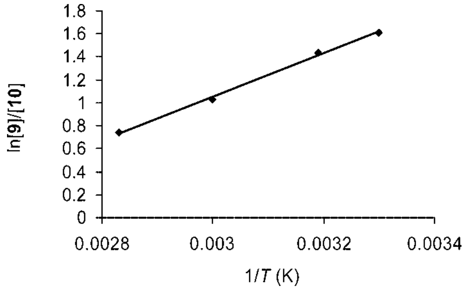
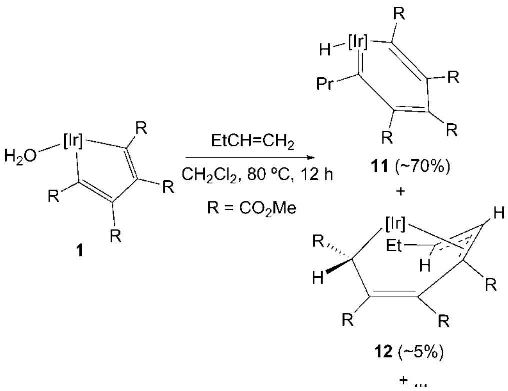


Figure 3. Variation of ln[**9**]/[**10**] with 1/*T*.

which means that, as shown in Scheme 4, all reaction steps are reversible. Thus, under the above conditions (C_6D_6, 90 °C) it is observed that: (i) NMR monitoring of the **9** → **10** rearrangement reveals the formation of observable concentrations of iridabenzene **6**, which is not detected when the reaction is effected in the presence of around 10 equivalents of MeCN or [D_3]MeCN; (ii) the rate of disappearance of **9** does not vary in the presence of 10 equivalents of MeCN (or [D_3]MeCN); (iii) in the presence of [D_3]-MeCN (10 equiv.), **10** contains [D_3]MeCN almost exclusively at 50 % conversion whereas **9** is only partially deuterated (50 %); (iv) **10** exchanges MeCN for [D_3]MeCN (10 equiv. [D_3]MeCN), although the exchange rate is appreciably slower than the transformation of **9** into **10** (around 50 % incorporation after 16 h). All these observations are in agreement with the transformation of **9** into **10** proceeding via iridabenzene **6** (Scheme 4), with the rate-determining step being the dissociation of the acetonitrile ligand of **9** (k_{-3}).

Reaction of Complex 1 with 1-Butene

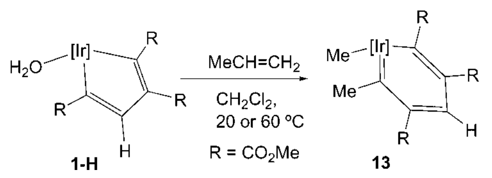
To complete our study of the reactivity of **1** towards olefins, its reaction with 1-butene was also investigated. As expected, the results are similar to those previously discussed for propene, with a mixture of compounds **11** and **12** [Equation (4)] being obtained at 80 °C. Column chromatography of the crude reaction mixture allowed isolation of **11**, and even though the allyl species **12** could not be isolated as a pure solid we were able to characterise it by NMR spectroscopy. Spectroscopic data for these two compounds can be found in the Experimental Section and do not warrant further discussion.



(4)

Reaction of Complex 1-H with Propene

An unexpected redistribution reaction occurs when propene is bubbled through a solution of complex **1-H** in CH_2Cl_2 (25 or 60 °C). Equation (5) shows the nature of the resulting product (iridabenzene **13**), which, quite surprisingly, has a metal-bound methyl group instead of a hydride ligand. This methyl group must proceed from the olefin. Additionally, it is important to note that the coupling process that gives rise to the metallacycle is highly selective, since only the iridabenzene that bears the hydrogen substituent in the *para* position is obtained. Compound **13** was fully characterised by NMR spectroscopy and also by X-ray diffraction studies. Once more, the resonance due to the carbon atom bonded to iridium which supports the Me group, Ir–*C*(Me), appears at lower field than the related Ir–*C*(CO_2Me) (δ = 272.7 and 217.6 ppm, respectively). Another characteristic $^{13}C\{^1H\}$ NMR signal is that of the methyl group bonded to iridium, which appears at high field (δ = –17.6 ppm). The ^1H NMR spectrum shows two singlets at δ = 1.98 and 0.91 ppm for the Me group in the α-position of the metallacycle and for the Me group bonded to iridium, respectively, while the CH of the iridabenzene ring resonates at δ = 9.15 ppm.



(5)

Figure 4 shows an ORTEP view of the molecule of **13**[2] while Table 3 contains selected bond lengths and angles. The Ir atom in this iridacycle deviates by 0.70 Å from the plane defined by the five carbon atoms of the metallacycle. The two Ir–C(ring) distances are different, showing once more the unsymmetrical electronic delocalisation: the Ir–C(Me) bond [1.936(2) Å] is slightly shorter than the Ir–C(CO_2Me) [1.957(2) Å].

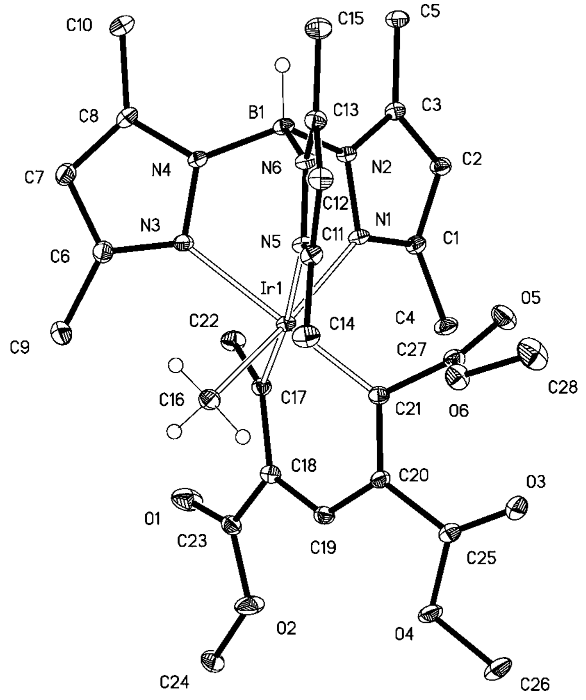
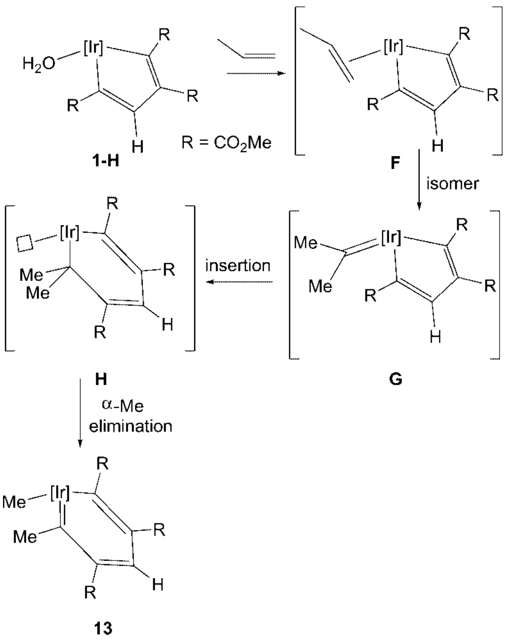


Figure 4. ORTEP view of complex **13**.

Table 3. Selected bond lengths [Å] and angles [°] for **13**.

Ir(1)–N(1)	2.152(2)	Ir(1)–C(21)	1.957(2)
Ir(1)–N(3)	2.156(2)	C(17)–C(18)	1.428(3)
Ir(1)–N(5)	2.194(2)	C(18)–C(19)	1.392(3)
Ir(1)–C(16)	2.095(2)	C(19)–C(20)	1.415(3)
Ir(1)–C(17)	1.936(2)	C(20)–C(21)	1.396(3)
C(17)–Ir(1)–C(21)	90.9(9)	C(16)–Ir(1)–N(3)	88.6(8)
C(17)–Ir(1)–C(16)	90.6(1)	N(1)–Ir(1)–N(3)	87.5(7)
C(21)–Ir(1)–C(16)	90.0(9)	C(17)–Ir(1)–N(5)	174.5(8)
C(17)–Ir(1)–N(1)	92.2(8)	C(21)–Ir(1)–N(5)	94.7(8)
C(21)–Ir(1)–N(1)	93.8(8)	C(16)–Ir(1)–N(5)	89.0(9)
C(16)–Ir(1)–N(1)	175.2(8)	N(1)–Ir(1)–N(5)	87.8(7)
C(17)–Ir(1)–N(3)	92.1(8)	N(3)–Ir(1)–N(5)	82.4(7)
C(21)–Ir(1)–N(3)	176.8(8)		

Scheme 5 shows a possible mechanism for the formation of **13**. Once again, it is proposed that an alkylidene, **G**, resulting from the isomerisation of the propene ligand in **F** is a key intermediate, although for reasons that are difficult to explain a dimethylcarbene unit, $=CMe_2$, appears to be favoured over the linear propylidene, $=C(H)Et$. This isomerisation would be followed by a regioselective migration of the alkenyl carbon atom adjacent to the CH group onto the alkylidene, to give **H**, and finally by an α-Me elimination. This last process, namely the α-elimination of alkyl or aryl groups, is unusual, although some examples are known.[10] Clearly other mechanistic possibilities can be envisaged for the formation of complex **13** but, once again, they include highly speculative assumptions.[8]

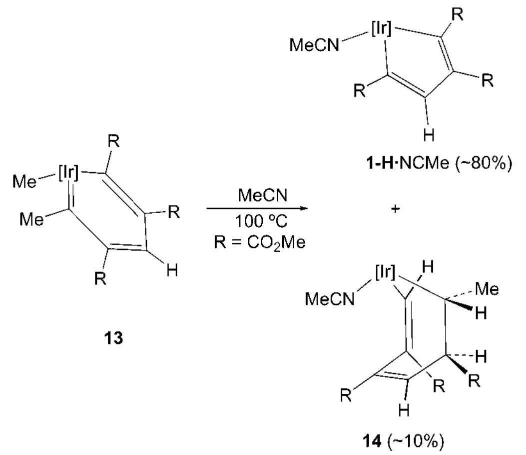


Scheme 5. Proposed mechanism for the formation of **13**.

Reaction of the Iridabenzene 13 with MeCN

Preliminary studies on the reactivity of the iridabenzene **13** reveal interesting differences with respect to the behaviour observed for **6**. Thus, **13** does not react with neat acetonitrile at 20 °C, and at 100 °C it mainly reverts to iridacycle **1-H**, which was isolated in the form of the known MeCN adduct **1-H·MeCN** [Equation (6)], a complex that has already been reported as resulting from the reaction of **1-H** with MeCN.[1] This clearly demonstrates that, despite requiring C–C bond formation and cleavage, the reaction of **1-H** with propene is a reversible process. Furthermore, Equation (6) represents an unusual fragmentation of a metallabenzene species.

Compound **1-H·MeCN** is not the only compound formed in the reaction of **13** and MeCN at 100 °C (approx. 80% spectroscopic yield) as the ^1H NMR spectrum of the crude product mixture shows the presence of a second species – the new compound **14** (approx. 10% spectroscopic yield, separated by column chromatography) – for which the structure shown in Equation (6) can be tentatively suggested on the basis of NMR spectroscopic studies. It is pro-

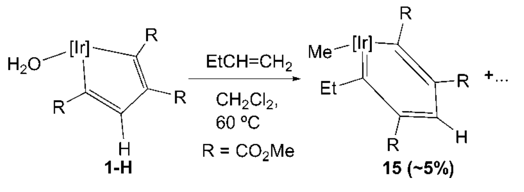


(6)

posed that the three carbon atoms of the original molecule of propene become incorporated into the metallacycle skeleton of **14**, although the complexity of the structure and the absence of mechanistic information advise against a discussion of possible reaction routes, which at this stage would be highly speculative.

Reaction of Complex 1-H with 1-Butene

Finally, reaction of **1** with EtCH=CH$_2$ at 60 °C takes place with formation of a complex reaction mixture from which only complex **15** (approx. 5% spectroscopic yield, separated by column chromatography) has been unequivocally identified [Equation (7)]. The major product (approx. 20% spectroscopic yield) is an isolable compound following chromatographic procedures but an unambiguous formulation cannot be proposed with the available data. It seems clear, however, that it is structurally related to other compounds that are generated in very small amounts during the reactions of **1** and **1-H** with propene and 1-butene.



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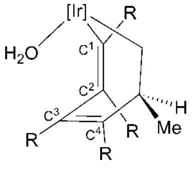
Conclusions

Iridabenzene complexes that also contain metal-bound hydride or methyl groups have been obtained by a new synthetic method that consists of the coupling of iridacyclopentadienes with olefins in a process that is proposed to occur by an olefin-to-alkylidene isomerisation in the metal coordination sphere. Interestingly, the reaction outcome depends strongly on the substitution pattern of the five-membered metallacycle and the nature of the olefin (propene being very efficient as a metallabenzene generator while ethylene gives only products derived from the insertion of the olefin into the Ir–C bonds). The reactivity of these iridabenzenes with acetonitrile has been studied and it has been found that the hydride ligand migrates easily and reversibly onto the Ir–C bonds of the metallacycle. Finally, a very unusual thermal fragmentation of a metallabenzene has also been observed.

Experimental Section

General Procedures: Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla). Infrared spectra were obtained with Perkin–Elmer 577 and 684 spectrometers. NMR spectra were recorded with Bruker DRX-500, DRX-400 and DPX-300 spectrometers. Spectra are referenced to external SiMe$_4$ (δ = 0 ppm) using the residual protio solvent peaks (^{1}H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments) as internal standards. Spectral assignments were made by means of routine one- and two-dimensional NMR experiments where appropriate. Manipulations were performed either in air or under oxygen-free dinitrogen, following conventional Schlenk techniques. The complexes [(Tp^{Me2})-Ir{C^1(R)=C(R)C(R)=C^4(R)}(H$_2$O)(*Ir–C^4*)] (**1**) and [(Tp^{Me2})-Ir{C^1(R)=C(H)C(R)=C^4(R)}(H$_2$O)(*Ir–C^4*)] (**1-H**) were obtained by published procedures.[1]

Complex 5: MeCH=CH$_2$ was bubbled through a solution of **1** in CH$_2$Cl$_2$ (0.2 g, 0.25 mmol; 7 mL) for 7 min. The resulting mixture was stirred under propene in a sealed vessel at room temperature for 12 h, and the solvent was then removed under reduced pressure. The ^{1}H NMR spectrum of the residue showed it to consist of a mixture of **1** and **5** in a 1:1 ratio. Complex **1** was isolated by column chromatography on silica gel, with a mixture of hexane and Et$_2$O (1:1) as eluent, in 32% yield. An analytically pure sample was obtained by crystallisation from a mixture of hexane and Et$_2$O (1:1) at –20 °C (pale-yellow crystals). R_f = 0.18 [silica gel, hexane/Et$_2$O (1:5)]. IR (Nujol): ν(OH) = 3381 cm^{-1} (br). ^{1}H NMR (CDCl$_3$, 25 °C): δ = 5.77, 5.71, 5.66 (s, 1 H each, 3 CH$_{pz}$), 3.95, 3.65, 3.58, 3.05 (s, 3 H each, 4 CO$_2$Me), 3.46, 2.84 (dd+t, $^2J_{H,H}$ = 12.4, $^3J_{H,H}$ = 3.7 Hz, 1 H each, IrCH$_2$), 3.22 (m, 1 H, C*H*Me), 2.37, 2.36, 2.36, 2.31, 2.16, 2.13 (s, 3 H each, 6 Me$_{pz}$), 1.25 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH*Me*) ppm; the coordinated molecule of H$_2$O could not be located. ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ = 178.2, 175.8, 169.9, 164.9 (*C*O$_2$Me), 164.0 (C^1), 153.6, 151.2, 149.9, 144.2, 143.6, 142.3 (C$_{qpz}$), 145.6 (C^4), 132.1, 129.2 (C^3, C^4), 108.4, 107.8, 106.5 (CH$_{pz}$), 52.8, 52.0, 51.2, 50.4 (CO$_2$*Me*), 38.5 ($^1J_{C,H}$ = 133 Hz, *C*HMe), 19.4 (CH*Me*), 14.8, 14.2, 13.4, 12.9, 12.6, 12.4 (Me$_{pz}$), 6.5 ($^1J_{C,H}$ = 126 Hz, CH$_2$) ppm. C$_{30}$H$_{42}$BIrN$_6$O$_9$·0.5Et$_2$O (870.03): calcd. C 44.2, H 5.4, N 9.6; found C 44.4, H 5.4, N 9.2.



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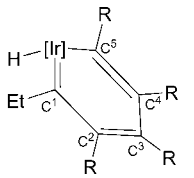
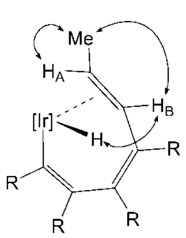
Complexes 6–8: Compound **1** was dissolved in CH$_2$Cl$_2$ (0.5 g, 0.63 mmol; 12 mL), then MeCH=CH$_2$ was bubbled through the solution for 7 min and the stirring was continued under propene, in a closed vessel, for 12 h at 60 °C. After this period the solvent was removed under reduced pressure and the formation of a mixture of complexes **6** (approx. 45%), **7** (approx. 10%) and **8** (approx. 10%), along with other by-products, was ascertained by ^{1}H NMR spectroscopy. Complexes **6**–**8** were separated by column chromatography (silica gel) with hexane/Et$_2$O (1:1) as eluent. Complex **6** (34% yield) was purified by crystallisation from a mixture of pentane and CH$_2$Cl$_2$ (1:1) at –20 °C (dark-green crystals). Complex **7** (10% yield) was obtained analytically pure by crystallisation from a mixture of hexane and CH$_2$Cl$_2$ (1:1) at –20 °C (dark-yellow solid). Complex **8** could not be obtained as a pure solid by this method, but it could be alternatively and satisfactorily obtained as follows: Compound **7** was dissolved in CH$_2$Cl$_2$ (0.020 g, 0.02 mmol; 2 mL) and the solution stirred at 80 °C for 12 h. After this period of time the solvent was removed under vacuum and ^{1}H NMR monitoring of the crude reaction showed quantitative transformation of **7** into **8**. This compound could be purified by crystallisation from a mixture of hexane and CH$_2$Cl$_2$ (1:1) at –20 °C (yellow solid).

6: R_f = 0.47 [silica gel, hexane/Et$_2$O (1:3)]. IR (Nujol): ν(Ir–H) = 2162 cm^{-1}. ^{1}H NMR (CDCl$_3$, 25 °C): δ = 5.80, 5.72, 5.69 (s, 1 H each, 3 CH$_{pz}$), 3.85, 3.80, 3.70, 3.18 (s, 3 H each, 4 CO$_2$Me), 3.13, 2.38 (dq, $^2J_{H,H}$ = 15.8, $^3J_{H,H}$ = 7.7 Hz, 1 H each, CH$_3$CH_2), 2.47, 2.42, 2.37, 2.06, 2.03, 1.17 (s, 3 H each, 6 Me$_{pz}$), 0.74 (t, 3 H, CH_3CH$_2$), –21.41 (s, 1 H, Ir-H) ppm; the signal at δ = 2.38 ppm is obscured by the resonances of the Me$_{pz}$ and was detected in the COSY spectrum. ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ = 274.2 (C^1), 202.1 (C^5), 179.0, 170.8, 168.2, 167.0 (CO$_2$Me), 154.0, 152.0, 150.3, 146.1, 145.4, 143.2 (C$_{qpz}$), 151.7 (C^3), 140.1 (C^2), 131.1 (C^4), 106.6, 106.5, 105.3 (CH$_{pz}$), 52.9, 52.7, 52.6, 51.2 (CO$_2$$Me$), 51.3 ($^1J_{C,H}$ = 130 Hz, CH$_3$$CH_2$), 16.3, 16.2, 13.9, 13.0, 12.9 (1:1:1:2:1, Me$_{pz}$), 11.4 (CH$_3$CH$_2$) ppm. C$_{30}$H$_{40}$BIrN$_6$O$_8$ (815.03): calcd. C 44.2, H 4.9, N 10.3; found C 43.9, H 4.8, N 10.0.



6

7: R_f = 0.39 [silica gel, hexane/Et$_2$O (1:8)]. IR (Nujol): ν(Ir–H) = 2194 cm^{-1}. ^{1}H NMR (CDCl$_3$, 25 °C): δ = 6.01 (d, $^3J_{B,A}$ = 11 Hz, 1 H, H$_B$), 5.92, 5.76, 5.62 (s, 1 H each, 3 CH$_{pz}$), 4.34 (m, 1 H, H$_A$), 3.83, 3.75, 3.52, 3.06 (s, 3 H each, 4 CO$_2$Me), 2.43, 2.30, 2.29, 2.28, 2.26, 2.18 (s, 3 H each, 6 Me$_{pz}$), 1.15 (d, $^3J_{H,H}$ = 6.0 Hz, 3 H, CH$_A$$Me$), –16.93 (s, 1 H, Ir-H) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ = 174.6, 169.5, 167.6, 166.9 (CO$_2$Me), 152.4, 152.3, 150.5, 144.8, 143.5, 143.5 (C$_{qpz}$), 138.3, 133.8, 128.8, 126.7 (CCO$_2$Me), 108.5, 107.9, 106.1 (CH$_{pz}$), 61.1 (CH$_B$), 56.4 (CH$_A$), 52.5, 52.3, 51.8, 50.7 (CO$_2$$Me$), 17.8 (CH$_A$$Me$), 16.5, 16.5, 15.9, 12.9, 12.9, 12.7 (Me$_{pz}$) ppm. C$_{30}$H$_{40}$BIrN$_6$O$_8$·1.25CH$_2$Cl$_2$ (921.28): calcd. C 40.7, H 4.6, N 9.1; found C 40.7, H 4.8, N 8.6.



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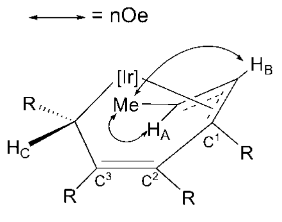
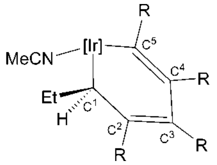


8

8: ^{1}H NMR (CDCl$_3$, 25 °C): δ = 7.11 (d, $^3J_{B,A}$ = 10.3 Hz, 1 H, H$_B$), 5.86, 5.80, 5.59 (s, 1 H each, 3 CH$_{pz}$), 5.06 (s, 1 H, H$_C$), 3.72, 3.64, 3.45, 3.35 (br) (s, 3 H each, 4 CO$_2$Me), 3.61 (m, 1 H, H$_A$), 2.70, 2.41, 2.36, 2.28, 2.24, 2.17 (s, 3 H each, 6 Me$_{pz}$), 1.47 (d, $^3J_{H,H}$ = 5.7 Hz, 3 H, CH$_A$$Me$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ = 175.0, 166.8 (2:2, CO$_2$Me), 152.5, 151.8, 144.5, 143.4 (1:2:1:2, C$_{qpz}$), 130.9, 128.8 (C^2, C^3), 110.6, 108.7, 107.2 (CH$_{pz}$), 93.7 ($^1J_{C,H}$ = 161 Hz, CH$_B$), 68.2 (C^1), 52.2, 51.9, 51.6, 50.9 (CO$_2$$Me$), 38.5 (CH$_A$), 19.2 (CH$_A$$Me$), 17.8, 15.7, 13.6, 13.5, 13.1, 12.8 (Me$_{pz}$), 9.9 ($^1J_{C,H}$ = 134 Hz, CH$_C$) ppm. C$_{30}$H$_{40}$BIrN$_6$O$_8$ (815.03): calcd. C 44.2, H 4.9, N 10.3; found C 44.5, H 4.9, N 10.1.

Complex 9: Compound **6** was dissolved in MeCN (0.01 g, 0.01 mmol; 2 mL) and the mixture was stirred at room temperature for 12 h. After this period of time the solvent was removed under reduced pressure and the formation of a mixture of **9** and **10** in a 6:1 ratio was ascertained by ^{1}H NMR spectroscopy. Compound **9** (dark-yellow crystals) could be separated by column chromatography on silica gel with diethyl ether as eluent. R_f = 0.57 [silica gel, Et$_2$O]. IR (Nujol): ν(CN) = 2303 cm^{-1}. ^{1}H NMR (CDCl$_3$, 25 °C): δ = 5.70, 5.69, 5.65 (s, 1 H each, 3 CH$_{pz}$), 4.21 (t, $^3J_{H,H}$ = 6.6 Hz, 1 H, C^{1}H), 3.74, 3.71, 3.59, 3.09 (s, 3 H each, 4 CO$_2$Me), 2.52 (s, 3 H, MeCN), 2.47, 2.38, 2.33, 2.29, 2.23, 2.12 (s, 3 H each, 6 Me$_{pz}$), 1.06 (m, 2 H, CH$_3$CH_2), 0.16 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3CH$_2$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ = 176.0, 171.0, 170.5, 167.3 (CO$_2$Me), 167.8 (C^5), 153.6, 150.1, 149.9, 143.2, 143.2, 142.7 (C$_{qpz}$), 142.3, 134.1 (C^2, C^3), 131.0 (C^4), 116.3 (MeCN), 108.0, 107.5, 106.2 (CH$_{pz}$), 51.9, 51.8, 51.6, 50.2 (CO$_2$$Me$), 31.5 ($^1J_{C,H}$ = 128 Hz, CH$_3$$CH_2$), 16.6, 14.3, 14.3, 13.3, 12.7, 12.5 (Me$_{pz}$), 13.7 (CH$_3$CH$_2$), 4.8 ($^1J_{C,H}$ = 123 Hz, C^1), 3.6 (MeCN) ppm. C$_{32}$H$_{43}$BIrN$_7$O$_8$ (856.03): calcd. C 44.9, H 5.0, N 11.4; found C 44.8, H 5.0, N 11.3.



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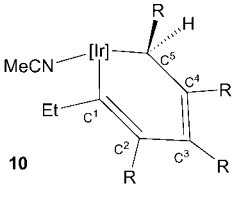
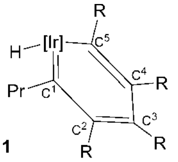
Complex 10: Compound **9** or a mixture of **9** and **10** (obtained as described above) was heated in cyclohexane with a drop of MeCN at 90 °C for 48 h and the solvent was then removed under reduced pressure. ^{1}H NMR analysis of the dark-yellow residue showed almost quantitative formation of **10**. IR (Nujol): ν(CN) = 2243 cm^{-1}. ^{1}H NMR (CDCl$_3$, 25 °C): δ = 5.73, 5.65 (s, 2:1, 3 CH$_{pz}$), 5.58 (s, 1 H, C^{1}H), 3.73, 3.67, 3.66, 2.97 (s, 3 H each, 4 CO$_2$Me), 2.54 (s, 3 H, MeCN), 2.40, 2.38, 2.36, 2.35, 2.10, 2.08 (s, 3 H each, 6 Me$_{pz}$), 2.29, 2.18 (m, 1 H each, CH$_3$CH_2), 0.66 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_3CH$_2$) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ = 183.5, 171.5, 169.7, 169.3 (CO$_2$Me), 165.5 (C^5), 153.3, 149.9, 149.3, 143.5, 143.3, 142.6 (C$_{qpz}$), 144.1, 127.4 (C^2, C^3), 129.9 (C^4), 116.9 (MeCN), 107.5, 107.1, 106.7 (CH$_{pz}$), 51.9, 51.8, 51.3, 50.3 (CO$_2$$Me$), 36.4 ($^1J_{C,H}$ = 125 Hz, CH$_3$$CH_2$), 15.6, 14.8, 14.1, 13.8, 13.2, 12.6 (Me$_{pz}$), 14.0 (CH$_3$CH$_2$), 4.6 ($^1J_{C,H}$ = 123 Hz, C^1), 3.6 (MeCN) ppm. C$_{32}$H$_{43}$BIrN$_7$O$_8$ (856.03): calcd. C 44.9, H 5.0, N 11.4; found C 44.8, H 4.9, N 11.4.



10

Complexes 11 and 12: Compound **1** was dissolved in CH$_2$Cl$_2$ (0.2 g, 0.25 mmol; 7 mL), and EtCH=CH$_2$ was bubbled through the solution for 5 min. The resulting solution was stirred under 1-butene in a closed vessel for 12 h at 80 °C. After this period of time the solvent was removed under vacuum and the formation of a mixture of complexes **11** (approx. 70%) and **12** (approx. 5%), along with other by-products, was ascertained by ^{1}H NMR spectroscopy. Complexes **11** and **12** were separated by column chromatography (silica gel) with hexane/Et_2O (1:1) as eluent. Complex **11** (38% yield) could be purified by crystallisation from a mixture of pentane and CH_2Cl_2 (1:1) at –20 °C (pale brown crystals). Complex **12** could not be separated by column chromatography and was characterised by NMR spectroscopy of the crude mixture.

11: R_f = 0.38 [silica gel, hexane/Et_2O (1:3)]. IR (Nujol): ν(Ir–H) = 2157 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 5.79, 5.72, 5.68 (s, 1 H each, 3 CH_{pz}), 3.84, 3.80, 3.69, 3.17 (s, 3 H each, 4 CO_2Me), 3.04, 2.34 (dt + m, $^2J_{H,H}$ = 13.5, $^3J_{H,H}$ = 5 Hz, $CH_3CH_2CH_2$, 1 H each), 2.48, 2.42, 2.37, 2.06, 2.03, 1.16 (s, 3 H each, 6 Me_{pz}), 1.33, 1.12 (m, m, 1 H each, $CH_3CH_2CH_2$), 0.61 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, $CH_3CH_2CH_2$), –21.41 (s, 1 H, Ir-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 272.8 (C^1), 201.5 (C^5), 178.8, 170.5, 168.0, 166.8 (CO_2Me), 153.8, 151.7, 150.0, 145.8, 145.1, 143.0 (C_{qpz}), 151.1 (C^3), 140.3 (C^2), 130.8 (C^4), 106.3, 106.3, 105.0 (CH_{pz}), 60.6 ($CH_3CH_2CH_2$), 52.6, 52.4, 52.3, 50.9 (CO_2Me), 20.5 ($CH_3CH_2CH_2$), 16.0, 16.0, 13.6, 12.8, 12.7, 12.7 (Me_{pz}), 15.0 ($CH_3CH_2CH_2$) ppm. $C_{31}H_{42}BIrN_6O_8$ (829.74): calcd. C 44.9, H 5.1, N 10.1; found C 44.5, H 5.2, N 9.8.



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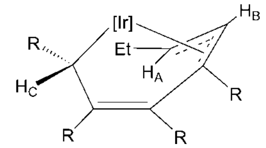
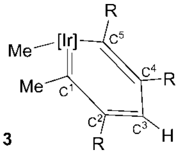


12

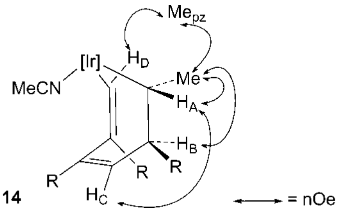
12: R_f = 0.30 [silica gel, hexane/Et_2O (1:3)]. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 7.05 (d, $^3J_{B,A}$ = 10.0 Hz, 1 H, H_B), 5.86, 5.79, 5.59 (s, 1 H each, 3 CH_{pz}), 5.09 (s, 1 H, H_C), 3.74, 3.72, 3.45, 2.69 (s, 3 H each, 4 CO_2Me), 3.58 (this signal is obscured by the CO_2Me resonances and was detected by a COSY spectrum, 1 H, H_A), 2.40, 2.35, 2.27, 2.25, 2.18, 1.41 (s, 3 H each, 6 Me_{pz}), 1.90, 1.54 (signals detected by a COSY spectrum, 1 H each, CH_2CH_3), 1.27 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 92.8 ($^1J_{C,H}$ = 162 Hz, CH_B), 46.9 ($^1J_{C,H}$ = 166 Hz, CH_A), 26.9 ($^1J_{C,H}$ = 126 Hz, CH_2CH_3), 9.4 ($^1J_{C,H}$ = 135 Hz, CH_C) ppm.

Complex 13: MeCH=CH_2 was bubbled through a solution of **1-H** in CH_2Cl_2 (0.32 g, 0.44 mmol; 10 mL) for 5 min. The resulting mixture was stirred under propene at room temperature for 15 h, and after this period of time the solution had turned from dark yellow to green. The solvent was removed under reduced pressure and formation of compound **13** in 80% spectroscopic yield was determined by ^{1}H NMR spectroscopy. Complex **13** could be purified by column chromatography on silica gel with a mixture of hexane and Et_2O (2:1) as eluent (54% yield). It could be crystallised from a mixture of hexane and Et_2O (2:1) at –20 °C as thin, dark-green needles. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 9.15 (s, 1 H, C^3H), 5.84, 5.80, 5.65 (s, 1 H each, 3 CH_{pz}), 3.87, 3.79, 3.25 (s, 3 H each, 3 CO_2Me), 2.43, 2.41, 2.19, 2.07, 0.99 (s, 2:1:1:1:1, 6 Me_{pz}), 1.98 (s, 3 H, C^1Me), 0.91 (s, 3 H, IrMe) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 272.7 (C^1), 217.6 (C^5), 179.9, 166.0, 165.4 (CO_2Me), 154.5, 151.8, 148.8, 144.6, 144.5, 142.5 (C_{qpz}), 153.7 ($^1J_{C,H}$ = 158 Hz, C^3), 139.5 (C^2), 132.0 (C^4), 108.1, 107.9, 105.5 (CH_{pz}), 52.1, 51.9, 50.7 (CO_2Me), 44.9 ($^1J_{C,H}$ = 128 Hz, C^1Me), 15.4, 14.9, 13.1, 13.0, 12.9, 12.6 (Me_{pz}), –17.6 ($^1J_{C,H}$ = 130 Hz, IrMe) ppm. $C_{28}H_{38}BIrN_6O_6{\cdot}Et_2O$ (831.03): calcd. C 46.2, H 5.8, N 10.1; found C 46.0, H 5.6, N 10.3.



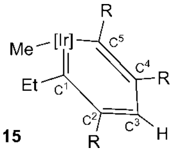
13

Complex 14: Two or three drops of MeCN were added to a solution of compound **13** in cyclohexane (0.03 g, 0.04 mmol; 2 mL) and the mixture was stirred at 100 °C for 15 h. After this period of time the solvent was removed under reduced pressure and the ^{1}H NMR spectrum of the crude reaction mixture showed the presence of complex **14** in 12% spectroscopic yield. It could be isolated by column chromatography on silica gel, with a mixture of hexane and Et_2O (1:3) as eluent, in 7% yield (dark yellow crystals). ^{1}H NMR ($CDCl_3$, 25 °C): δ = 10.76 (s, 1 H, H_D), 6.87 (d, $^3J_{H,H}$ = 7.1 Hz, 1 H, H_C), 5.76, 5.71, 5.69 (s, 1 H each, 3 CH_{pz}), 3.72, 3.65, 3.63 (s, 3 H each, 3 CO_2Me), 3.46 (m, 1 H, H_B), 3.39 (m, 1 H, H_A), 2.38, 2.36, 2.32, 2.14, 2.09 (s, 1:1:2:1:1, 6 Me_{pz}), 0.40 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_AMe), 2.29 (s, 3 H, MeCN) ppm. In C_6D_6 H_C resonates at δ = 7.47 ppm (d, $^3J_{C,B}$ = 8.1 Hz) while H_B appears at δ = 3.99 ppm (dd, $^3J_{B,A}$ = 11.6 Hz) and H_A at δ = 3.80 ppm (dq, $^3J_{A,Me}$ = 7.3 Hz). The NOESY connections shown above were obtained in this solvent. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 176.8, 170.4, 166.4 (CO_2Me), 163.1 ($^1J_{C,H}$ = 139 Hz, CH_D), 151.5, 150.3, 150.2, 143.8, 143.4, 143.0 (C_{qpz}), 137.1 ($^1J_{C,H}$ = 161 Hz, CH_C), 134.1, 128.9 (C_qCO_2Me), 116.8 (MeCN), 108.2, 108.0, 106.8 (CH_{pz}), 55.5 ($^1J_{C,H}$ = 136 Hz, CH_B), 51.5, 51.0, 50.9 (CO_2Me), 21.6 (CH_AMe), 15.8, 14.0, 13.4, 12.7, 12.4 (1:1:1:2:1, Me_{pz}), 9.1 ($^1J_{C,H}$ = 128 Hz, CH_A), 3.5 (MeCN) ppm. $C_{30}H_{41}BIrN_7O_6$ (798.03): calcd. C 45.1, H 5.2, N 12.3; found C 44.6, H 5.8, N 12.2.



14

Complex 15: EtCH=CH_2 was bubbled through a solution of **1-H** in CH_2Cl_2 (0.4 g, 0.54 mmol; 12 mL) for 5 min. The resulting mixture was stirred under 1-butene at 60 °C for 15 h, and after this period of time the solvent was removed under reduced pressure. The ^{1}H NMR spectrum of the crude reaction mixture showed the formation of compound **15** (6%) along with other by-products. It was separated by column chromatography on silica gel, with a mixture of hexane and Et_2O (5:1) as eluent, in 5% yield (dark-green crystals). R_f = 0.23 [silica gel, hexane/Et_2O (1:1)]. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 8.95 (s, 1 H, C^3H), 5.82, 5.76, 5.65 (s, 1 H each, 3 CH_{pz}), 3.87, 3.78, 3.25 (s, 3 H each, 3 CO_2Me), 2.95, 2.15 (m, 1 H each, CH_2CH_3), 2.44, 2.43, 2.39, 2.17, 2.13, 1.09 (s, 3 H each, 6 Me_{pz}), 0.90 (s, 3 H, IrMe), 0.81 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 283.4 (C^1), 210.7 (C^5), 179.2, 166.5, 165.5 (CO_2Me), 154.2, 151.7, 149.4, 144.8, 144.3, 142.4 (C_{qpz}), 152.8 ($^1J_{C,H}$ = 159 Hz, C^3), 139.9 (C^2), 131.0 (C^4), 108.1, 107.9, 105.3 (CH_{pz}), 52.1, 52.0, 50.8 (CO_2Me), 50.8 (CH_2CH_3), 15.1, 13.7, 13.0, 12.8, 12.6 (2:1:2:1:1, Me_{pz}, CH_2CH_3), –18.4 ($^1J_{C,H}$ = 128 Hz, IrMe) ppm. $C_{29}H_{40}BIrN_6O_6{\cdot}Et_2O$ (845.03): calcd. C 46.9, H 5.9, N 9.9; found C 46.6, H 5.9, N 9.8.



15

X-ray Crystallography: The X-ray structures of complexes **6** and **13** were reported in a preliminary communication.[2] Data for compound **5** were collected with a Bruker-Nonius X8APEX-II CCD diffractometer by using ω and ϕ scans with a scan width of 0.3° (in the range $5.60° < 2\theta < 61.16°$) and a 20-s exposure time with a crystal-to-detector distance of 37.5 mm. The data were reduced (SAINT)[11] and corrected for Lorentz polarisation effects and absorption by a multiscan method with SADABS.[12] The structure was solved by direct methods (SIR-2002)[13] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12).[14] All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included in calculated positions and refined as riding on their respective carbon atoms with isotropic displacement parameters. $C_{35}H_{54}BIrN_6O_9$ [$C_{30}H_{54}BIrN_6O_9 \cdot C_5H_{12}$], M_r = 905.85, yellow prism crystal ($0.24 \times 0.22 \times 0.19$ mm) from pentane/diethyl ether; triclinic, space group $P\bar{1}$ (no. 2), a = 10.7973(3), b = 11.2238(3), c = 16.5423(4) Å, α = 102.7200(10)°, β = 90.3650(10)°, γ = 101.6970(10)°, V = 1912.16(9) Å^3, Z = 2, $\rho_{\text{calcd.}}$ = 1.573 g cm^{-3}, $\lambda(\text{Mo-}K_\alpha)$ = 0.71073 Å, $F(000)$ = 920, μ = 3.551 mm^{-1}, T = 100(2) K. 39188 Measured reflections, of which 11594 were unique (R_{int} = 0.0257); 469 refined parameters, final R_1 = 0.0226 for reflections with $I > 2\sigma(I)$, wR_2 = 0.0619 (all data), GOF = 1.095.

CCDC-631538 (for **5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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