

## Investigations on the Coupling of Ethylene and Alkynes in $[\text{IrTp}^{\text{Me}_2}]$ Compounds: Water as an Effective Trapping Agent

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**Abstract:** The reaction of the bis(ethylene) complex  $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2]$  (**1**) ( $\text{Tp}^{\text{Me}_2}$ : hydrotris(3,5-dimethylpyrazolyl)borate) with two equivalents of dimethyl acetylenedicarboxylate (DMAD) in  $\text{CH}_2\text{Cl}_2$  at 25 °C gives the hydride–alkenyl species  $[\text{Tp}^{\text{Me}_2}\text{IrH}\{\text{C}(\text{R})=\text{C}(\text{R})\text{C}(\text{R})=\text{C}(\text{R})\text{CH}=\text{CH}_2\}]$  (**2**, R:  $\text{CO}_2\text{Me}$ ) in high yield. A careful study of this system has established the active role of a number of intermediates en route to producing **2**. The first of these is the iridium(I) complex  $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)(\text{DMAD})]$  (**4**) formed by substitution of one of the ethylene ligands in **1** by a molecule of DMAD. Complex **4** reacts further with another equivalent of the alkyne to give the unsaturated metallacyclopentadiene  $[\text{Tp}^{\text{Me}_2}\text{Ir}\{\text{C}(\text{R})=\text{C}(\text{R})\text{C}(\text{R})=\text{C}(\text{R})\}]$ ,

which can be trapped by added water to give adduct **7**, or can react with the  $\text{C}_2\text{H}_4$  present in solution generating complex **2**. This last step has been shown to proceed by insertion of ethylene into one of the Ir–C bonds of the metallacyclopentadiene and subsequent  $\beta$ -H elimination. Complex **1** reacts sequentially with one equivalent of DMAD and one equivalent of methyl propiolate (MP) in the presence of water, with regioselective formation of the nonsymmetric iridacyclopentadiene  $[\text{Tp}^{\text{Me}_2}\text{Ir}\{\text{C}(\text{R})=\text{C}(\text{R})\text{C}(\text{H})=\text{C}(\text{R})\}(\text{H}_2\text{O})]$  (**9**). Complex **9** reacts with eth-

ylene giving a hydride–alkenyl complex **10**, related to **2**, in which the  $\text{C}_2\text{H}_4$  has inserted regioselectively into the Ir–C(R) bond that bears the CH functionality. Heating solutions of either **2** or **10** in  $\text{CH}_2\text{Cl}_2$  allows the formation of the allyl species **3** or **11**, respectively, by simple stereoselective migration of the hydride ligand to the  $\alpha$  alkenyl carbon atom and concomitant bond reorganization of the resulting organic chain. All the compounds described herein have been characterized by microanalysis, IR and NMR spectroscopy, and for the case of **3**, **7**, **7**-CO, **8**-NCMe, **9**, **9**-NCMe, and **10**, also by single-crystal X-ray diffraction studies.

**Keywords:** C–C coupling • C–H activation • cyclopentadienyl ligands • insertion • iridium

### Introduction

Metallacyclopentadienes<sup>[1]</sup> are very interesting organometallic species that are involved, as intermediates, in a number

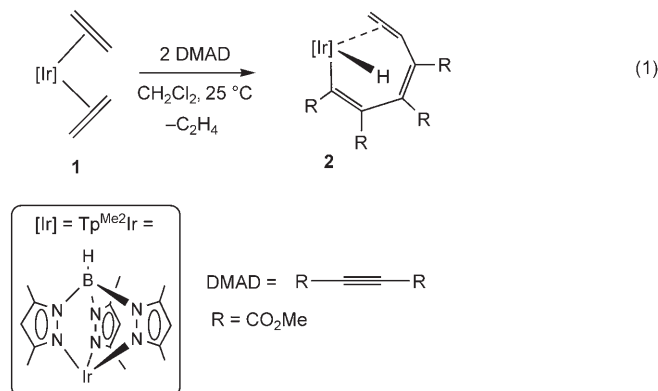
of important catalytic or stoichiometric processes mediated by transition-metal complexes, as in the case of the cyclotrimerization of alkynes (to give benzene derivatives),<sup>[2]</sup> alkyne–nitriles (for the synthesis of pyridines),<sup>[3]</sup> alkyne–olefins (formation of cyclohexadienes),<sup>[3,4]</sup> and so forth.<sup>[1b,5]</sup> In this contribution, we report on the coupling of two molecules of DMAD (dimethyl acetylenedicarboxylate,  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ ) in the  $\text{Tp}^{\text{Me}_2}\text{–Ir}$  system ( $\text{Tp}^{\text{Me}_2}$ : hydrotris(3,5-dimethylpyrazolyl)borate),<sup>[6]</sup> to give an iridacyclopentadiene<sup>[7]</sup> that completes the 18-electron metal count by coordination of a molecule of water. Substitution and insertion reactions of this complex have been investigated, as well as the synthesis and reactivity of a related nonsymmetric iridacyclopentadiene that results from the regioselective coupling of DMAD and MP (MP: methyl propiolate,  $\text{HC}\equiv\text{CCO}_2\text{Me}$ ). Part of this work has been published in preliminary form.<sup>[8]</sup>

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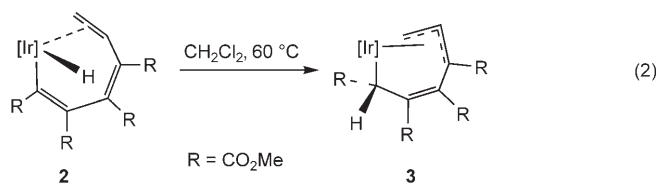
## Results and Discussion

The addition of two equivalents of DMAD to a solution of the bis(ethylene) complex  $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2]$  (**1**)<sup>[9]</sup> in  $\text{CH}_2\text{Cl}_2$  at room temperature produces immediate consumption of **1** and formation of a new compound, **2**, as deduced from the NMR spectra of the reaction mixture [Eq. (1)]. The reaction is stereospecific, and the spectroscopic yield of this species is higher than 85%. The chelating hydrocarbyl–alkene ligand in compound **2** formally results from the C–C coupling of two molecules of DMAD and a vinyl fragment, which is derived from one of the ethylene ligands in **1**.



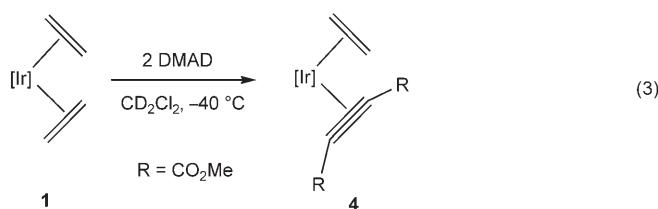
Although compound **2** is the major product in this reaction, attempts to obtain an analytical and spectroscopically pure sample failed due to its slow transformation into a new allyl derivative **3** (see below). Either by crystallization or by column chromatography, species **2** is always isolated as a mixture with **3**. Nevertheless, it survives in solution long enough to be properly characterized by spectroscopy, either in the mixture with **3**, or in the crude product from the reaction. The presence of the hydride ligand is shown by a high-field NMR resonance at  $-16.91$  ppm in the  $^1\text{H}$  NMR spectrum, whereas the  $\pi$ -coordinated vinyl moiety exhibits the pattern of resonances expected for a ligand of this type:<sup>[10]</sup> three multiplets centered at 6.39, 3.63, and 3.07 ppm, with *trans* and *cis*  $^3J(\text{H},\text{H})$  coupling constants of 11.5 and 9.8 Hz, respectively (see Experimental Section for assignments).  $^{13}\text{C}$  NMR data and a full set of two-dimensional experiments are also in agreement with the structure proposed and, in particular, the NOESY spectrum confirms the coordination of the olefin to the metal through the face indicated.

Complex **2** cleanly transforms into the alkyl–allyl **3** when solutions of **2** are warmed at  $60^\circ\text{C}$  [Eq. (2)], and **3** is also obtained, in almost quantitative yield, when the reaction depicted in Equation (1) is performed in  $\text{CH}_2\text{Cl}_2$  at  $60^\circ\text{C}$ .



The formation of **3** is the overall result of the stereospecific transfer of the hydride ligand to the  $\alpha$ -carbon atom of the alkenyl end of the chelating ligand in **2**. Different pathways could in principle be envisaged for this transformation; nevertheless, we propose that it takes place by direct migration of the hydride to the alkenyl carbon atom, with concerted or stepwise bond rearrangement along the chain. Compound **3** exhibits  $^1\text{H}$  NMR resonances due to the  $\pi$ -coordinated allyl moiety<sup>[9]</sup> at 7.07 (CH), 4.09, and 2.94 ppm ( $\text{CH}_2$ ), the corresponding C atoms producing signals in the  $^{13}\text{C}$  NMR spectrum at  $\delta=91.2$  ( $^1J(\text{C},\text{H})=170$  Hz) and 25.2 ppm ( $^1J(\text{C},\text{H})=155$  and 166 Hz), whereas the resonance due to the remaining allylic carbon appears at  $\delta=53.0$  ppm. The Ir-bonded alkyl carbon atom,  $\text{Ir}-\text{C}(\text{H})(\text{CO}_2\text{Me})$ , resonates at  $\delta=12.0$  ppm ( $^1J(\text{C},\text{H})=135$  Hz). This compound has been additionally characterized by an X-ray diffraction structure analysis (see below). As pointed out by a referee, complex **3**, which has interconnected  $\sigma$ -allyl– $\pi$ -allyl functionalities, may be able to adopt a closely related isomeric structure in which the  $\eta^1$  and  $\eta^3$  termini are interchanged, but, due to so far unknown reasons, this is not observed experimentally. The same can be said with respect to complex **11** (see below).

The reaction shown in Equation (1) has been monitored by NMR spectroscopy, at low temperature. When two equivalents of DMAD are added to a solution of **1** in  $\text{CD}_2\text{Cl}_2$  at  $-40^\circ\text{C}$ , the  $^1\text{H}$  NMR spectrum recorded immediately after mixing shows quantitative formation of a new compound, which has been characterized by NMR spectroscopy, at  $0^\circ\text{C}$ , as the Ir<sup>I</sup> adduct  $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)(\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me})]$  (**4**) [Eq. (3)].



The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of this adduct show local  $C_s$  symmetry for the  $\text{Tp}^{\text{Me}_2}$  ligand and all the protons and both carbon nuclei of the ethylene ligand are equivalent, generating a singlet in each spectrum ( $\delta=3.14$  and 51.1 ppm for  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$ , respectively). The  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum shows a singlet at  $\delta=32.5$  ppm, and this value<sup>[11]</sup> compares well with the corresponding chemical shift recorded for complex **1** ( $\delta=32.9$  ppm), which has been shown previously to be an  $18e^-$  species with the  $\text{Tp}^{\text{Me}_2}$  ligand  $\kappa^3$ -coordinated both in the solid state and in solution.<sup>[9]</sup> Compound **4** is generated by substitution of one of the ethylene ligands in **1** by a molecule of DMAD, a process that also occurs when this derivative reacts with one equivalent of soft Lewis bases ( $\text{CO}$  and  $\text{PR}_3$ ;  $\text{R}_3$ :  $\text{Me}_3$ ,  $\text{Me}_2\text{Ph}$ ,  $\text{Et}_3$ ).<sup>[12]</sup> These reactions have been proposed to occur by an

associative mechanism, by means of a change in the coordination mode of the  $\text{Tp}^{\text{Me}_2}$  ligand, from  $\kappa^3$  to  $\kappa^2$ .<sup>[12,13]</sup>

However, and unlike other derivatives of composition  $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)(\text{L})]$  (L: CO,  $\text{PR}_3$ )<sup>[12]</sup> and related Tp species<sup>[13,14]</sup> that adopt a rigid trigonal-bipyramidal structure with the ethylene ligand, which rotates slowly in the NMR timescale, occupying the equatorial position and hence giving rise to an AA'BB' spin system in the  $^1\text{H}$  NMR spectra, compound **4** is fluxional, and its ethylene ligand seems to rotate fast, even at  $-40^\circ\text{C}$ . This difference can be attributed to the fact that the ethylene ligand occupies an axial position in the trigonal bipyramid (Figure 1), in which the  $\pi$

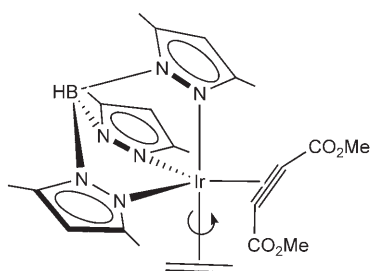


Figure 1. Proposed structure of complex **4**.

back-donation would be weaker than when in the equatorial position.<sup>[15]</sup> The adoption of this structure is also supported by a comparison of the  $^{13}\text{C}$  NMR chemical shift of the ethylene ligand in the series of compounds  $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)(\text{L})]$  (L:  $\text{PMe}_3$ , CO,  $\text{C}_2\text{H}_4$ , and DMAD) (see Table 1). For the

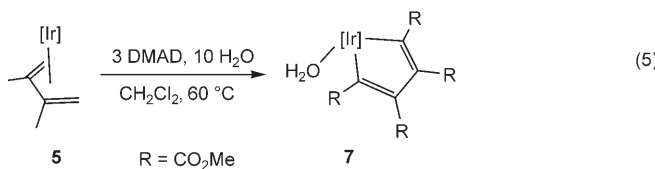
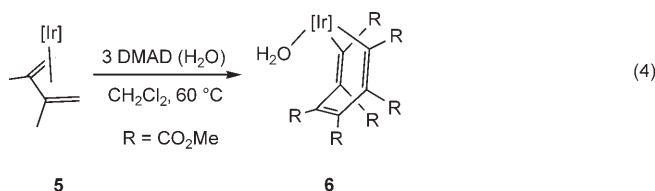
Table 1. Solution chemical shifts for the  $^{13}\text{C}$  nuclei of the ethylene ligands in compounds of composition  $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)(\text{L})]$ .

L	$\text{PMe}_3$	CO	$\text{C}_2\text{H}_4$	DMAD
$\delta \text{C}_2\text{H}_4$ [ppm]	-8.1	0.6	26.2 <sup>[a]</sup>	51.1

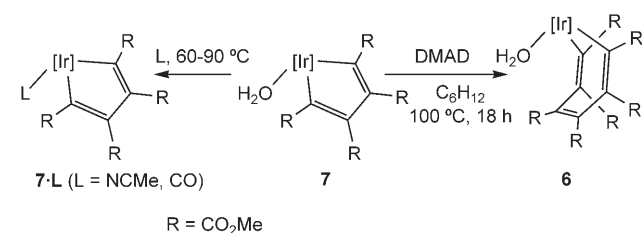
[a] 48 and 5 ppm in the solid state.

case of L being  $\text{C}_2\text{H}_4$ , all the ethylene carbon atoms resonate at  $\delta = 26.2$  ppm. As already reported, this compound is fluxional, and this signal represents the average of the chemical shifts corresponding to the axial and equatorial positions, and thus, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum recorded for **1** in the solid state exhibits two signals for the ethylene ligands, at  $\delta = 48$  and 5 ppm (axial and equatorial, respectively).<sup>[9]</sup> Probably, the preference of the DMAD for the equatorial position in **4** is because it is a better  $\pi$  acceptor than the ethylene ligand. Although it cannot be deduced from the data available, it is proposed that the DMAD ligand does not rotate around the Ir-DMAD axis, due to its strong  $\pi$ -acceptor character. Finally in this respect, the related Tp derivative  $[\text{TpIr}(\text{C}_2\text{H}_4)(\text{DMAD})]$ <sup>[7c]</sup> has also been reported to be fluxional, and the authors suggest a stereochemistry analogous to the one proposed herein for **4**.

Compound **4** is stable up to  $10^\circ\text{C}$ ; above this temperature, and under the conditions of Equation (3), a mixture of species is produced. Monitoring the reaction by  $^1\text{H}$  NMR spectroscopy at  $20^\circ\text{C}$  reveals the formation of **2** together with other unidentified species, although they subsequently disappear, and finally **2** is present in approximately 90% spectroscopic yield. As we were unable to directly characterize any of the intermediate(s) species en route to **2**, and in order to obtain further information about this system, we decided to seek alternative ways to prepare likely intermediates in the formation of **2**. In a recent preliminary communication,<sup>[8a]</sup> we reported that the iridacycloheptatriene **6**, to be described in detail elsewhere, is obtained by the reaction of the Ir-dimethylbutadiene derivative **5** with three equivalents of DMAD in  $\text{CH}_2\text{Cl}_2$  [Eq. (4)]. Interestingly, the presence of a large excess of water (10 equivalents) in the reaction mixture prevents the incorporation of the third equivalent of alkyne, yielding the water-stabilized<sup>[16]</sup> iridacyclopentadiene derivative **7** [Eq. (5)], which is clearly formed by the coupling of two DMAD molecules in the metal coordination sphere.<sup>[7]</sup>



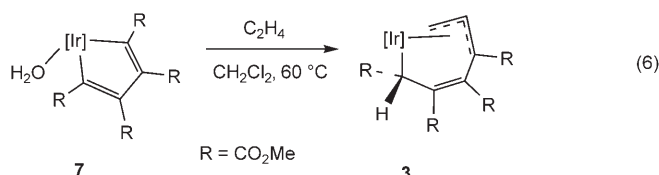
As expected, the water ligand present in **7** is labile, as demonstrated by the substitution reactions carried out with NCMe and CO that yield the corresponding derivatives **7**·NCMe and **7**·CO. With excess of DMAD, an insertion reaction into one of the Ir-C bonds takes place and compound **6** is formed (Scheme 1). All these metallacyclopentadienes have been fully characterized by spectroscopy (see Experimental Section) and in addition, the solid-state struc-



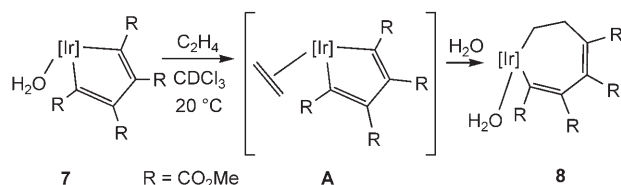
Scheme 1. Synthesis of complex **7** and its reactivity with Lewis bases and DMAD.

tures of **7** and **7**·CO have been determined by X-ray crystallography (see below).

More interesting, in the present context, is the reaction of **7** with ethylene which, at 60 °C, results in the clean formation of the already described compound **3** [Eq. (6)], supporting the intermediacy of an iridacyclopentadiene species in the formation of compound **2** (or **3**) starting from **1** (or **4**).



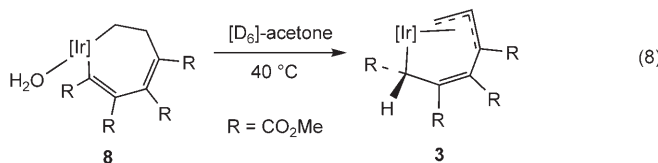
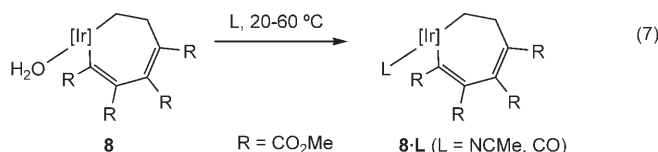
Furthermore, if ethylene is bubbled through a solution of **7** in  $\text{CDCl}_3$ , and the mixture kept at room temperature, NMR monitoring shows the slow formation of a new species **8** (Scheme 2). Compound **8** is stable at room temperature



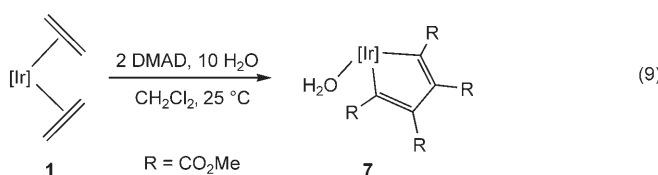
Scheme 2. Formation of the alkyl-allyl derivative **3** and trapping of an intermediate as the water adduct **8**.

and forms metastable solutions in chloroform from which it eventually precipitates and, after dissolution in  $[\text{D}_6]$ acetone, could be appropriately characterized by NMR spectroscopy. The more characteristic signals for this compound are those corresponding to the two adjacent  $\text{CH}_2$  groups: multiplets at  $\delta = 3.37, 2.90$  ( $\text{IrCH}_2\text{CH}_2$ ), and  $2.71, 2.17$  ppm ( $\text{IrCH}_2\text{CH}_2$ ) in the  $^1\text{H}$  NMR spectrum and resonances at  $\delta = 35.5$  ( $\text{IrCH}_2\text{CH}_2$ ) and  $-2.6$  ppm ( $\text{IrCH}_2\text{CH}_2$ ) in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum. Probably, compound **8** is formed through displacement of water by a molecule of ethylene to give **A** (Scheme 2), followed by the insertion of this ligand into one of the equivalent Ir–C bonds. It is worth mentioning the ease with which the ethylene inserts into the Ir–C bond of the presumed intermediate **A**. In the case of the related isolable compound with the unsubstituted Tp ligand,<sup>[7c]</sup> no insertion was observed up to 110 °C. This is in agreement with the known decreased reactivity of the Tp–Ir compounds, as compared with the related  $\text{Tp}^{\text{Me}_2}$ –Ir ones, in activation processes. In the  $\text{Tp}^{\text{Me}_2}$ –Ir system, we have observed cases in which  $\text{C}_2\text{H}_4$  easily inserts into an Ir–C bond, for example in its reaction with  $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_6\text{H}_5)_2(\text{N}_2)]$ ,<sup>[17]</sup> but have also found complexes that are unreactive in this respect, like the iridacyclopentene  $[\text{Tp}^{\text{Me}_2}\text{Ir}\{\overline{\text{CH}_2\text{C}(\text{Me})=\text{C}(\text{Me})\text{CH}_3}\}(\text{C}_2\text{H}_4)]$ , which, upon heating, dissociates the coordinated ethylene.<sup>[18]</sup>

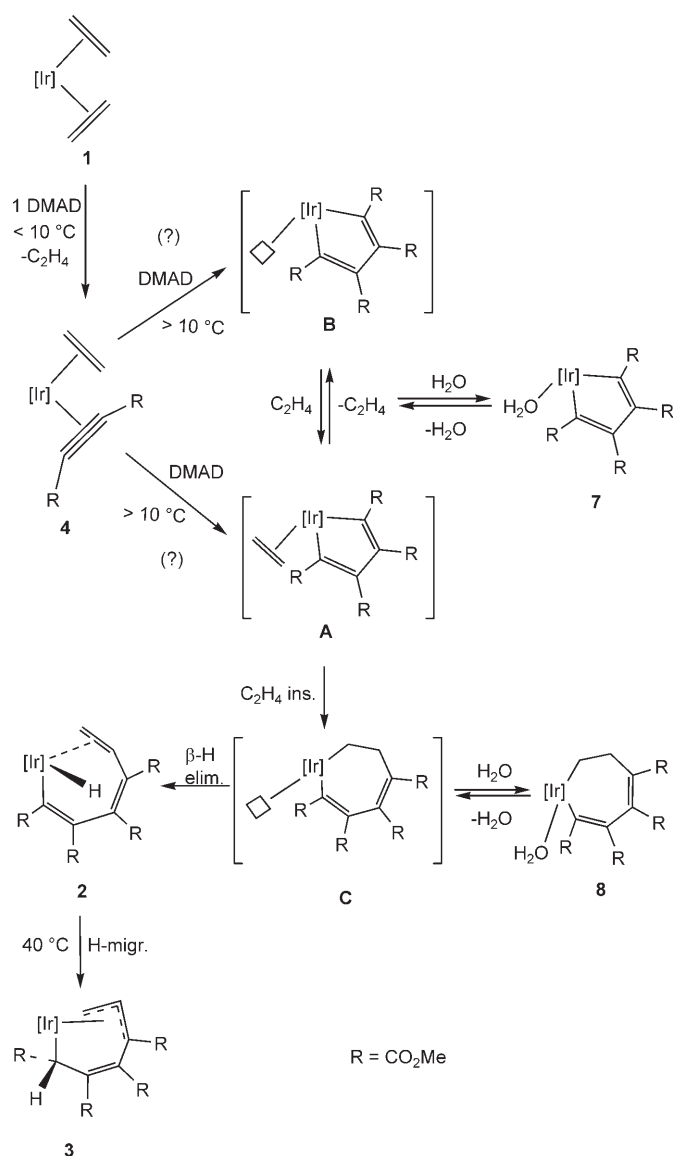
or the very reactive  $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{H})(\text{CH}=\text{CH}_2)(\text{C}_2\text{H}_4)]$ , which has been shown to yield a  $\text{C}_4$  chain by the coupling of the two  $\text{C}_2$  ligands, although by following a mechanistic pathway different from the insertion of ethylene into the Ir–C bond.<sup>[9]</sup> The water ligand in **8** is also labile and the corresponding adducts **8**·NCMe and **8**·CO are easily obtained [Eq. (7)]. These complexes have been fully characterized by spectroscopy and also by an X-ray study carried out with **8**·NCMe (see below). Finally, and as expected, heating solutions of compound **8** at 40 °C promotes its transformation into the allyl derivative **3** [Eq. (8)].



Compounds **7** or **8** were not detected during the course of the transformation depicted in Equation (1), and this negative evidence is probably due to the absence of enough  $\text{H}_2\text{O}$  in the reaction mixture. In fact, if the reaction is carried out in the presence of an excess of  $\text{H}_2\text{O}$ , compound **7** is formed in almost quantitative spectroscopic yield [Eq. (9)] and, despite the presence of the evolved ethylene in the reaction flask, compound **2** is not observed. The larger amount of water versus ethylene competes effectively for the coordination to iridium preventing the incorporation of the olefin.



Considering all the observations so far, the mechanism depicted in Scheme 3 can be proposed for the formation of compounds **2** and **3**, in which compounds **7** and **8** have also been included. From the experimental data we cannot say which of the intermediates **A** or **B** (**B** is depicted as an unsaturated 16- $e^-$  iridium(III) species rather than an 18- $e^-$  bis-(carbene)–iridium(I) structure<sup>[2c,7b]</sup>) is formed directly from **4** (in both cases we presume that the second molecule of DMAD enters the coordination sphere in an associative process, as is the norm in substitution reactions of Tp–iridium(I) species). If **B** is formed first, then there is a competi-

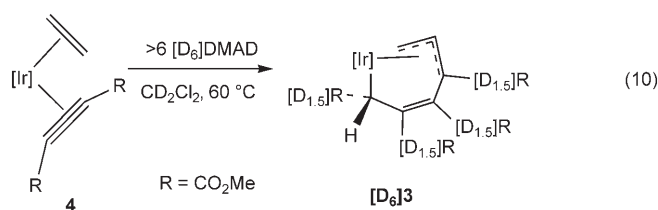


Scheme 3. Mechanism proposed for the formation of complex **3** from the bis(ethylene) derivative **1** and DMAD with inclusion of all the intermediate species isolated.

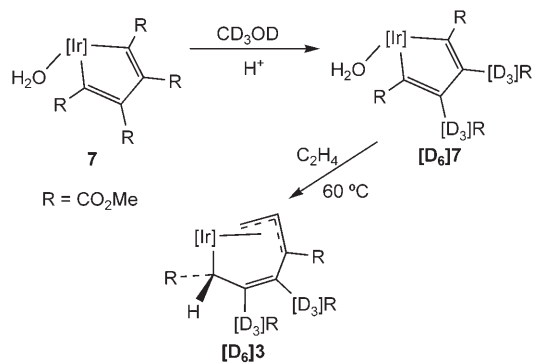
tion for coordination to this intermediate, of the evolved ethylene (to give **A**) and the water present in the reaction mixture (to give **7**). In contrast, if **A** is the favored kinetic species, the coordinated ethylene would be dissociatively exchanged by  $\text{H}_2\text{O}$  under the reaction conditions before  $\text{C}_2\text{H}_4$  insertion into one of the Ir–C bonds of the metallacycle takes place. The ease with which this insertion takes place, and the observation that, under certain conditions, the iridacycloheptatriene **6** is observed in this reaction (see below), and other data obtained in our laboratory in systems related to this one, to be discussed elsewhere, suggest the initial formation of intermediate **B**. Whichever is the first species formed, it is clear that it is the result of the oxidative coupling of two molecules of DMAD bonded simultaneously to iridium, and this process is likely to be governed by the high

tendency of the Tp'-iridium(I) derivatives to oxidize to iridium(III), and more importantly by the mutual *cis* disposition adopted by these ligands in the proposed intermediate that also contains a *fac*-type  $\text{Tp}^{\text{Me}_2}\text{-Ir}$  linkage. This is in agreement with the experimental and theoretical studies carried out with the system  $[\text{Ir}(\text{PR}_3)_3(\text{alkyne})_2]^+$ , which indicate that the phosphines have to occupy a *fac* disposition for the coupling of the two alkynes to take place.<sup>[7b]</sup> Recently, it has been reported that a bis(ethylene)iridium(I) derivative, stabilized by a *mer* tripodal nitrogen donor ligand, reacts with DMAD giving rise to a stable bis(alkyne)iridium(I) complex, even in the presence of NCMe.<sup>[19]</sup>

To complete this study, some deuteration experiments have been carried out. First, we prepared complex **4** at low temperature, by addition of only one equivalent of DMAD to **1**, and then added an excess (6 equivalents) of  $[\text{D}_6]\text{DMAD}$ . After warming at  $60^\circ\text{C}$ , compound  $[\text{D}_6]\text{3}$  was formed and the corresponding  $^1\text{H}$  NMR spectrum exhibited resonances for the four  $\text{CO}_2\text{Me}$  groups of intensity half of that observed in compound **3** [Eq. (10)].

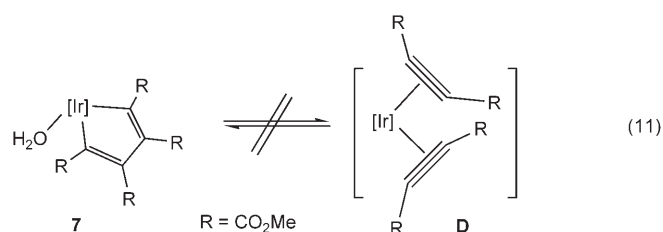


This indicates that **4** does not interchange with free DMAD, and also reflects the symmetry of the intermediates **A** and **B**. Secondly, we have found that two equivalent  $\text{CO}_2\text{Me}$  groups present in **7** can be selectively replaced by  $\text{CO}_2\text{CD}_3$  by a transesterification process in  $\text{CD}_3\text{OD}$ , catalyzed by acid. Although not confirmed, it is highly probable, on steric grounds, that the deuterated positions are those shown in Scheme 4. When  $[\text{D}_6]\text{7}$  is subjected to reaction with  $\text{C}_2\text{H}_4$ , no scrambling of the labels is observed, as two  $\text{CO}_2\text{Me}$  resonances are absent in the  $^1\text{H}$  NMR spectra of compound  $[\text{D}_6]\text{3}$ , probably those shown in Scheme 4. This

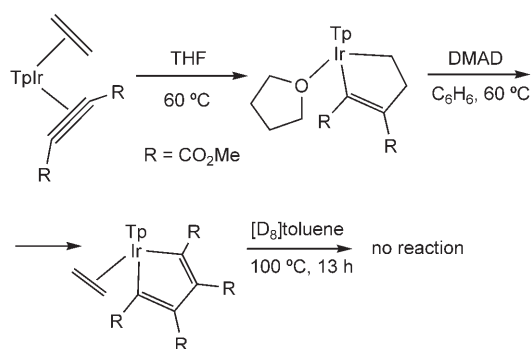


Scheme 4. Partial deuteration of complex **7** by a transesterification reaction in  $\text{CD}_3\text{OD}$ .

experiment rules out any interconversion between the iridacyclopentadiene and a bis(alkyne)Ir<sup>I</sup> species [Eq. (11)] and this is in accord with the findings observed in a related system.<sup>[7a]</sup>



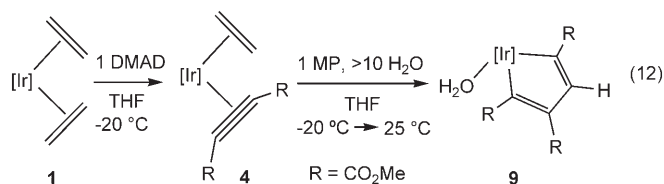
We should mention the different reactivity observed when the reaction of compound **1** is carried out in solution at 60 °C, with three equivalents of DMAD, and for which, under the appropriate conditions, the iridacycloheptatriene **6** is generated. This result is almost independent of the solvent employed (C<sub>6</sub>H<sub>12</sub>, CH<sub>2</sub>Cl<sub>2</sub>, or CHCl<sub>3</sub>), but strongly depends on the conditions of the reaction. Thus, if it is carried out in deuterated chloroform or dichloromethane (in cyclohexane the starting material is not soluble enough), in an NMR tube, compound **3** is formed in almost quantitative spectroscopic yield (>90%). By contrast, if the reaction is performed starting with the same amount of compound and solvent in a much bigger sealed flask (hence with much bigger atmosphere volume), both **3** and **6** are formed, in an approximate 1:1 ratio. This seems to indicate that the iridacyclopentadiene intermediate **B** of Scheme 3 is less reactive towards DMAD than towards ethylene (as mentioned before, the H<sub>2</sub>O adduct **7** reacts with C<sub>2</sub>H<sub>4</sub> at 25 °C, because its reaction with DMAD requires much higher temperatures); this different reactivity may be due to the lesser tendency of the iridium(III) intermediate (already electron deficient) to bind the alkyne, a weaker electron donor than ethylene. At this point it seems appropriate to make another comparison with the related system of the unsubstituted Tp ligand, [TpIr(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>(DMAD)] (Scheme 5).<sup>[7c]</sup> In this case, the first step is also the formation of the iridium(I) adduct [TpIr(C<sub>2</sub>H<sub>4</sub>)(DMAD)], a compound that is stable at room



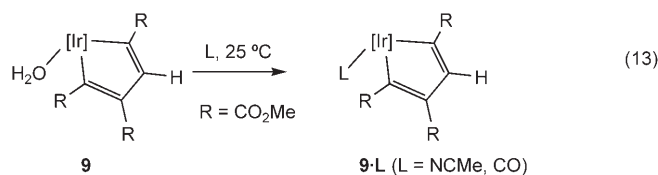
Scheme 5. Formation of an iridacyclopent-2-ene and an iridacyclopentadiene in the system [TpIr(C<sub>2</sub>H<sub>4</sub>)(DMAD)].

temperature, and that when heated in acetonitrile or other solvents, such as THF, forms an iridacyclopent-2-ene, by oxidative coupling of ethylene and DMAD. This coupling is not observed in the case of the corresponding Tp<sup>Me<sub>2</sub></sup> derivative **4**, which, as already mentioned, decomposes at >10 °C in the presence of one equivalent of C<sub>2</sub>H<sub>4</sub> and one equivalent of DMAD to give **2** (in the absence of DMAD, **4** evolves by a vinylic C–H activation process to be reported elsewhere). If DMAD is present, the Tp–iridacyclopentene structure can be transformed, under appropriate conditions, into an iridacyclopentadiene analogous to our proposed intermediate **A**. As already mentioned, this compound is very stable and highly resistant to ethylene insertion into the Ir–C bonds of the metallacycle, no transformation taking place even at 100 °C, this fact highlighting once more the higher reactivity of the Tp<sup>Me<sub>2</sub></sup> derivatives in comparison with the Tp ones.

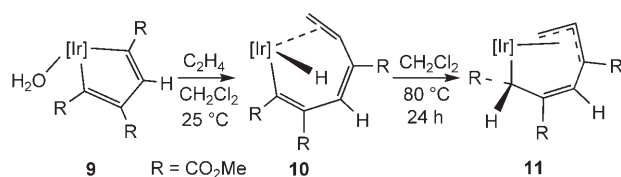
We have also studied the reaction of compound [Tp<sup>Me<sub>2</sub></sup>Ir(C<sub>2</sub>H<sub>4</sub>)(DMAD)] (**4**) with methyl propiolate (MP), a terminal alkyne. In principle, reactivity similar to that observed for DMAD could occur, although the nonsymmetry of MP may give rise to two different coupled regioisomers. Also, the presence of the terminal C–H bond in MP could promote C–H activation reactions.<sup>[20,21]</sup> The sequential addition to **1** of one equivalent each of DMAD and MP in the presence of added water (10 equiv), at low temperature, produces the iridacyclopentadiene **9** [Eq. (12)] selectively upon warming to room temperature: In complex **9** the CH of the MP occupies a β-position in the ring, as deduced by its <sup>1</sup>H NMR chemical shift of δ = 7.75 ppm (in these kinds of Ir complexes an alkenyl CH in α-position would give a signal further downfield, even at δ = 10 ppm).<sup>[20]</sup>



As expected, the water ligand in **9** is labile, and the compounds **9**·NCMe and **9**·CO are readily synthesized by a reaction with an excess of L [Eq. (13)]. The new iridacyclopentadienes have been fully characterized by microanalysis and spectroscopy (IR, <sup>1</sup>H, and <sup>13</sup>C NMR studies) and in addition, the solid-state structures of **9** and **9**·NCMe have been determined by X-ray crystallography (see below).



Complex **9** reacts with ethylene, at room temperature, with the regio- and stereoselective formation of the hydrido-olefin derivative **10** (Scheme 6). In this case, the formation



Scheme 6. Consecutive formation of complexes **10** and **11** from the iridacyclopentadiene **9** and  $C_2H_4$ .

of this kind of species seems to be very favorable, since the purported intermediate iridacycloheptadiene related to **8** has not been observed, even in the presence of an excess of added water. Sequential addition of DMAD and MP to compound **1**, in the absence of water, at low temperature, followed by stirring at 25 °C for 15 minutes, also yields complex **10**, in almost quantitative yield. Unlike **2**, complex **10** is very stable, can be properly purified, and has been completely characterized, including an X-ray structure determination (see below), which firmly establishes that the insertion of the ethylene has taken place regioselectively into the Ir–C bond of **9** adjacent to the C–H functionality. In accord with the high stability of this derivative, isomerization to the corresponding allyl derivative **11** requires quite forcing conditions (Scheme 6). The NMR data obtained for this compound are in agreement with the structure depicted, but the

compound experiences some kind of fluxional process, probably conformational in origin, which is responsible for the broadening of some of the resonances in both  $^1H$  and  $^{13}C\{^1H\}$  NMR spectra (see Experimental Section).

**X-ray diffraction studies:** Table 2 gives the crystal data and data collection details for all compounds analyzed in this section.

**Complex 3:** Figure 2 shows an ORTEP view of a molecule of **3** and Table 3 gives selected bond lengths and angles. The  $sp^3$  carbon atom bound to iridium forms an iridium–carbon bond with a length of 2.12 Å, a value typical of an Ir–C single bond.<sup>[22]</sup> The  $\eta^3$ -allyl–Ir interaction is characterized by Ir–C bond lengths of Ir–C1 2.16, Ir–C2 2.10, and Ir–C3 2.18 Å, and the C1–C2–C3 angle of 121.4° is clearly in accord with almost pure  $sp^2$  hybridization at the C2 carbon atom.

**Complexes 7 and 7-CO:** In Figures 3 and 4, the molecular structures of complexes **7** and **7-CO** are represented, and Table 4 contains selected bond lengths and angles. The first compound crystallized with about 1.25 molecules of additional water, which form hydrogen bonds with the Ir–OH<sub>2</sub> moiety. The iridacyclopentadiene units in **7** and **7-CO** are almost planar, characterized by the C–Ir–C bite angles of 79.3 and 78.6°, respectively, and all the Ir–C bond lengths fall between 2.00 and 2.06 Å, as expected for  $sp^2$  carbon atoms.<sup>[22]</sup> Interestingly, for complex **7**, the Ir–N(pyrazolyl) bond, *trans* with respect to the hard water ligand, is shorter (2.03 Å) than the other two (2.16 Å average), but this effect is less evident in **7-CO**.

Table 2. Crystal data and data collection and refinement details for **3**, **7**· $\approx 1.25 H_2O$ , [**7-CO**]· $CH_2Cl_2$ , **8**·NCMe, **9**·(Et<sub>2</sub>O, THF), [**9**·NCMe]· $CH_2Cl_2$ , and **10**· $CH_2Cl_2$ .

	<b>3</b>	<b>7</b> · $\approx 1.25 H_2O$	[ <b>7-CO</b> ]· $CH_2Cl_2$	<b>8</b> ·NCMe	<b>9</b> ·(Et <sub>2</sub> O, THF)	[ <b>9</b> ·NCMe]· $CH_2Cl_2$	<b>10</b> · $CH_2Cl_2$
formula	C <sub>29</sub> H <sub>38</sub> BIrN <sub>6</sub> O <sub>8</sub>	C <sub>27</sub> H <sub>38.5</sub> BIrN <sub>6</sub> O <sub>10.25</sub>	C <sub>29</sub> H <sub>36</sub> BCl <sub>2</sub> IrN <sub>6</sub> O <sub>9</sub>	C <sub>31</sub> H <sub>41</sub> BIrN <sub>7</sub> O <sub>8</sub>	C <sub>29</sub> H <sub>43</sub> BIrN <sub>6</sub> O <sub>8</sub>	C <sub>28</sub> H <sub>37</sub> BCl <sub>2</sub> IrN <sub>7</sub> O <sub>6</sub>	C <sub>28</sub> H <sub>38</sub> BCl <sub>2</sub> IrN <sub>6</sub> O <sub>6</sub>
<i>M<sub>r</sub></i>	801.66	813.84	886.55	842.72	806.70	841.56	828.55
color, habit	yellow block	brown prism	brown fragment	yellow plate	yellow prism	yellow prism	yellow prism
symmetry,	triclinic,	orthorhombic,	triclinic,	orthorhombic,	monoclinic,	monoclinic,	monoclinic,
space group	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 1	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> [Å]	10.0964(15)	13.911(1)	10.6366(12)	11.2309(5)	11.2041(7)	14.4962(10)	11.9764(6)
<i>b</i> [Å]	10.9412(16)	14.533(1)	11.1646(12)	16.0105(7)	15.5675(9)	14.5804(10)	19.6942(10)
<i>c</i> [Å]	15.692(2)	16.558(1)	15.8432(16)	19.2018(8)	18.7603(9)	17.1747(12)	14.4471(7)
$\alpha$ [°]	81.541(3)	90	104.610(3)	90	90	90	90
$\beta$ [°]	85.535(3)	90	106.720(3)	90	97.796(2)	114.613(1)	104.229(1)
$\gamma$ [°]	64.231(3)	90	97.060(3)	90	90	90	90
<i>V</i> [Å <sup>3</sup> ]	1543.9(4)	3347.5(4)	1704.4(3)	3452.7(3)	3241.9(3)	3300.2(4)	3303.0(3)
<i>Z</i>	2	4	2	4	4	4	4
$\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ]	1.724	1.615	1.727	1.621	1.653	1.694	1.666
$\mu$ [mm <sup>-1</sup> ]	4.384	4.050	4.134	3.926	4.176	4.259	4.253
$\theta$ range [°]	2.1–30.0	2.3–27.0	2.5–30.0	2.5–27.0	2.8–30.5	2.4–30.0	2.1–30.0
<i>T</i> [K]	123(2)	123(2)	100(2)	298(2)	100(2)	173(2)	173(2)
data collected	27579	30258	31327	42593	36347	35326	60962
unique data	8747	7273	9762	7524	9807	9588	9476
	( <i>R</i> (int) = 0.0187)	( <i>R</i> (int) = 0.0427)	( <i>R</i> (int) = 0.0379)	( <i>R</i> (int) = 0.0581)	( <i>R</i> (int) = 0.0314)	( <i>R</i> (int) = 0.0444)	( <i>R</i> (int) = 0.0235)
parameters/restraints	418/0	432/6	443/0	441/0	451/131	416/0	416/6
<i>R</i> 1 <sup>[a]</sup> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	0.0185	0.0301	0.0372	0.0284	0.0311	0.0417	0.0262
<i>wR</i> 2 <sup>[b]</sup> (all data)	0.0434	0.0723	0.0925	0.0575	0.0777	0.1163	0.0578

[a]  $R1(F) = \sum ||F_o| - |F_c|| / \sum ||F_o|$ . [b]  $wR2(F^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ .

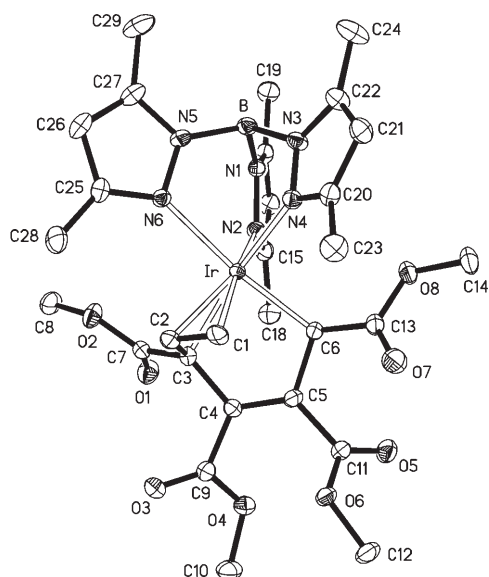


Figure 2. X-ray structure of complex **3** (thermal ellipsoids drawn at the 50% probability level).

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

Ir–N6	2.214(2)	Ir–C2	2.098(2)
Ir–C3	2.181(2)	C5–C6	1.507(3)
Ir–C1	2.164(2)	C3–C4	1.482(3)
Ir–N2	2.139(2)	C2–C3	1.442(3)
Ir–C6	2.118(2)	C1–C2	1.411(3)
Ir–N4	2.106(2)	C4–C5	1.366(3)
N2–Ir–N6	87.61(7)	C1–C2–C3	121.4(2)
N4–Ir–N2	90.68(7)	C2–C3–C4	116.4(2)
N4–Ir–N6	80.62(7)	C5–C4–C3	118.5(2)
C6–Ir–C1	87.48(9)	C4–C5–C6	117.4(2)
C6–Ir–C3	79.86(8)	C5–C6–Ir	110.06(15)
C1–Ir–C3	69.86(9)	C2–C3–Ir	67.21(12)

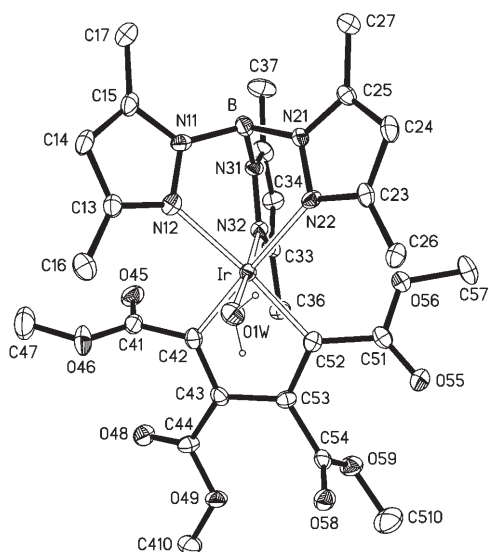


Figure 3. X-ray structure of complex **7** (thermal ellipsoids drawn at the 50% probability level).

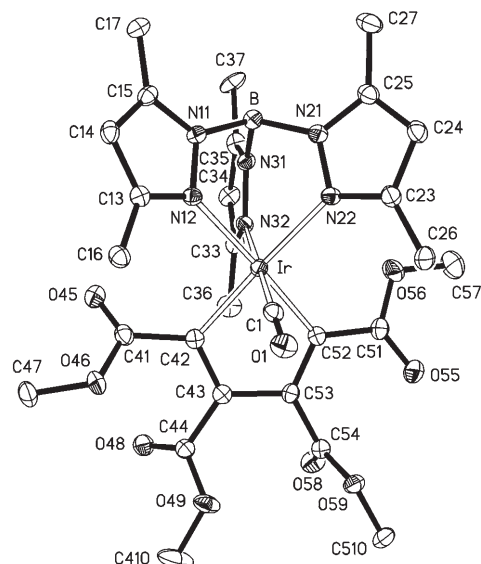


Figure 4. X-ray structure of complex **7-CO** (thermal ellipsoids drawn at the 20% probability level).

Table 4. Selected bond lengths [Å] and angles [°] for complexes **7** and **7-CO**.

	<b>7</b>	<b>7-CO</b>
Ir–N12	2.171(5)	2.151(3)
Ir–N22	2.157(5)	2.128(3)
Ir–N32	2.035(4)	2.111(3)
Ir–C42	2.001(6)	2.055(4)
Ir–C52	2.037(6)	2.067(4)
Ir–L	2.091(3)	1.852(4)
C42–C43	1.368(8)	1.358(6)
C43–C53	1.463(9)	1.463(5)
C52–C53	1.375(8)	1.355(6)
C42–Ir–C52	79.3(2)	78.64(16)
C42–Ir–L	90.19(19)	85.45(17)
C52–Ir–L	87.72(18)	84.99(17)

**Complex 8-NCMe:** Figure 5 shows an ORTEP view of this compound and Table 5 shows selected bond lengths and angles. The Ir–C(alkenyl) distance (2.02 Å) compares well with those mentioned for the iridacyclopentadienes **7** and **7-CO**, but the corresponding Ir–CH<sub>2</sub> bond is longer at 2.09 Å. In turn, this latter bond is slightly shorter than the Ir–C(alkyl) bond present in complex **3** which supports a CO<sub>2</sub>Me substituent. Of the three Ir–N(pyrazolyl) bonds, the one that is *trans* with respect to the NCMe is shorter (2.05 Å) than the other two (2.16 Å average), and in that way the acetonitrile behaves like the H<sub>2</sub>O ligand, another hard donor, in **7**.

**Complex 9:** The structure of this complex is shown in Figure 6 and selected bond lengths and angles are collected in Table 6. Once again the iridacyclopentadiene ring is almost planar and the Ir–N(pyrazolyl) bond *trans* to the H<sub>2</sub>O is shorter (2.04 Å) than the other two (2.15 Å average).



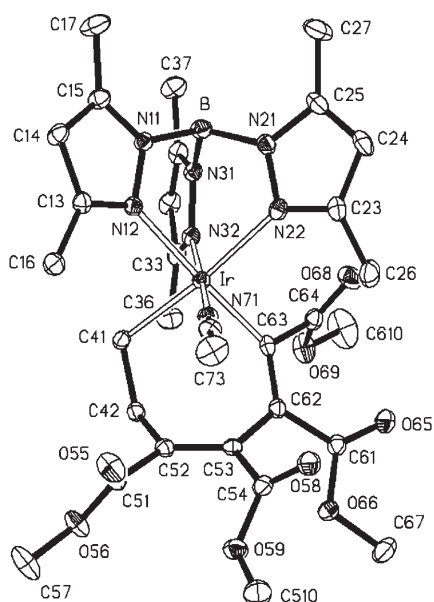


Figure 5. X-ray structure of complex **8-NCMe** (thermal ellipsoids drawn at the 20% probability level).

Table 5. Selected bond lengths [Å] and angles [°] for complex **8-NCMe**.

Ir–N12	2.164(4)	C41–C42	1.545(6)
Ir–N22	2.157(4)	C42–C52	1.496(6)
Ir–N32	2.049(3)	C53–C62	1.477(6)
Ir–C41	2.091(4)	C52–C53	1.368(6)
Ir–C63	2.025(4)	C62–C63	1.354(6)
Ir–N71	1.976(3)	N71–C72	1.133(5)
N22–Ir–N12	84.47(13)	C62–C63–Ir	127.6(3)
N32–Ir–N12	88.30(13)	C42–C41–Ir	117.3(3)
N32–Ir–N22	89.85(16)	C52–C42–C41	110.6(4)
C63–Ir–C41	94.02(17)	C53–C52–C42	121.8(4)
N71–Ir–C41	92.68(18)	C52–C53–C62	122.4(4)
N71–Ir–C63	90.91(16)	C63–C62–C53	124.4(4)

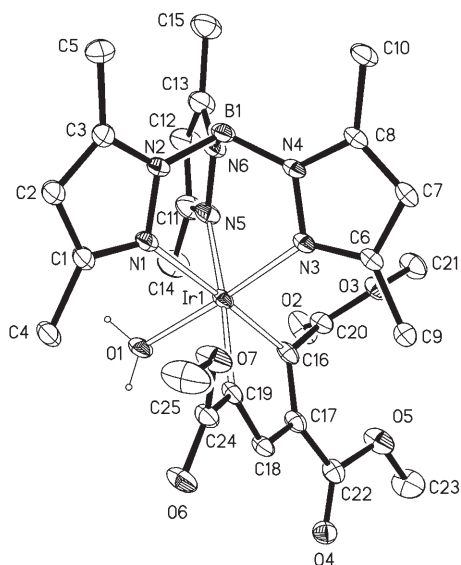


Figure 6. X-ray structure of complex **9** (thermal ellipsoids drawn at the 40% probability level).

Table 6. Selected bond lengths [Å] and angles [°] for complex **9**.

Ir–N1	2.142(3)	Ir–O1	2.103(2)
Ir–N3	2.041(3)	C16–C17	1.363(5)
Ir–N5	2.155(3)	C17–C18	1.464(4)
Ir–C16	2.021(3)	C18–C19	1.357(4)
Ir–C19	2.039(3)		
C16–Ir1–C19	79.45(12)	C16–Ir1–N1	177.72(11)
C16–Ir1–N3	93.49(11)	C19–Ir1–N1	99.04(11)
C19–Ir1–N3	96.87(11)	O1–Ir1–N1	89.46(10)
C16–Ir1–O1	88.74(11)	C16–Ir1–N5	97.52(12)
C19–Ir1–O1	86.28(11)	C19–Ir1–N5	172.68(11)
N3–Ir1–O1	176.43(10)	O1–Ir1–N5	86.99(10)

As mentioned in the Results section, the Ir–C(alkenyl) bond that supports the CH functionality is more reactive towards  $C_2H_4$  insertion than the other similar one present in this molecule. From the corresponding bond lengths, 2.04 as opposed to 2.02 Å, it may be concluded that the first bond is slightly weaker than the second and this may be the reason for the different reactivity. However, we have found that methyl propiolate inserts into the ring of **9** with the opposite regioselectivity.<sup>[23]</sup>

**Complex 9-NCMe:** An ORTEP view of this molecule is shown in Figure 7 and selected bond lengths and angles are collected in Table 7. These are very similar to those found in

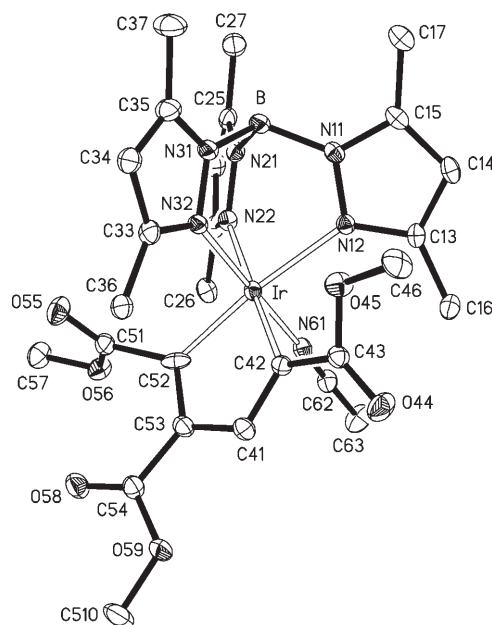


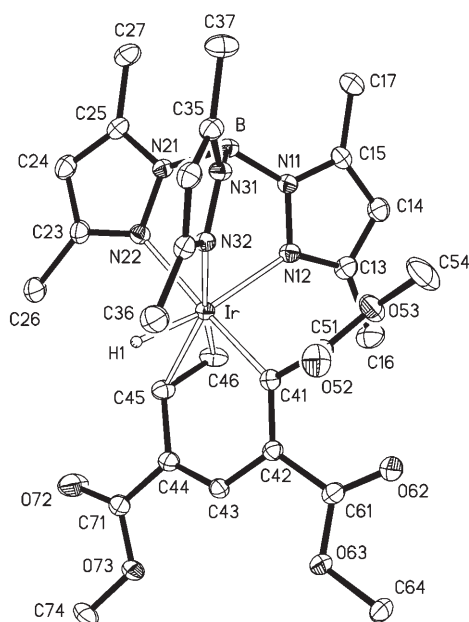
Figure 7. X-ray structure of complex **9-NCMe** (thermal ellipsoids drawn at the 30% probability level).

**9** and will not be commented upon with the exception of the two Ir–C(alkenyl) bond lengths. Interestingly, and compared with **9**, for the carbon atom that supports the CH group, the Ir–C distance is much longer (2.03 Å) than the other one (1.97 Å).

Table 7. Selected bond lengths [Å] and angles [°] for complex **9**-NCMe.

Ir–N22	2.158(5)	Ir–N61	1.991(5)
Ir–N12	2.157(5)	C41–C53	1.410(9)
Ir–N32	2.044(4)	C52–C53	1.364(8)
Ir–C42	2.033(5)	C41–C42	1.351(8)
Ir–C52	1.974(7)	N61–C62	1.144(7)
N12–Ir–N22	82.98(17)	C52–Ir–C42	77.1(2)
N32–Ir–N12	89.91(17)	C53–C52–Ir	118.6(5)
N32–Ir–N22	88.38(18)	C41–C42–Ir	114.6(4)
N61–Ir–C42	87.8(2)	C42–C41–C53	115.8(6)
C52–Ir–N61	87.3(2)	C52–C53–C41	111.5(6)

**Complex 10**: The molecular structure of this compound is shown in Figure 8 and selected bond lengths and angles are collected in Table 8. The Ir–C41 bond length at 2.02 Å is in the expected range for an Ir–C(alkenyl) species, whereas, for the olefin bonded to Ir, the C45–C46 separation of

Figure 8. X-ray structure of complex **10** (thermal ellipsoids drawn at the 40% probability level).Table 8. Selected bond lengths [Å] and angles [°] for complex **10**.

Ir–N12	2.193(2)	Ir–H11	1.600
Ir–C45	2.180(3)	C44–C45	1.495(4)
Ir–N22	2.162(2)	C42–C43	1.460(4)
Ir–C46	2.138(3)	C45–C46	1.391(5)
Ir–N32	2.090(2)	C41–C42	1.363(4)
Ir–C41	2.015(3)	C43–C44	1.343(4)
N22–Ir–N12	87.79(9)	C46–Ir1–C45	37.56(13)
N32–Ir–N12	88.19(9)	C42–C41–Ir	129.1(2)
N32–Ir–N22	82.82(9)	C44–C45–Ir	116.8(2)
C41–Ir–H11	94.7(14)	C41–C42–C43	123.4(3)
C41–Ir–C46	92.93(13)	C44–C43–C42	127.1(3)
C41–Ir–C45	90.64(12)	C43–C44–C45	126.0(3)
C45–Ir–H11	69.5(10)	C46–C45–C44	123.0(3)

1.49 Å is much closer to that corresponding for a single C–C bond (1.54 Å) than for a double bond (1.34 Å), and this probably reflects a quite strong Ir–olefin bond.

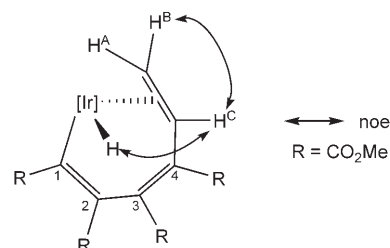
## Conclusion

Two molecules of dimethyl acetylenedicarboxylate, MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me (DMAD), couple in the coordination sphere of Tp<sup>Me2</sup>–Ir<sup>I</sup> systems to give an unsaturated iridacyclopentadiene species that is very effectively trapped by water with formation of the adduct [Tp<sup>Me2</sup>Ir{C(R)=C(R)C(R)=C(R)}(H<sub>2</sub>O)] (R: CO<sub>2</sub>Me). In a related process, reaction with one equivalent each of DMAD and methyl propiolate, HC≡CCO<sub>2</sub>Me (MP), regioselectively gives [Tp<sup>Me2</sup>Ir{C(R)=C(R)C(H)=C(R)}(H<sub>2</sub>O)]. In contrast with the Tp-related system, these species easily react with ethylene, by insertion into an Ir–C(R) bond and subsequent β-H elimination, giving hydride–alkenyl species. Interestingly, the reaction corresponding to the nonsymmetric iridacyclopentadiene is regioselective with the Ir–C(R)=C(H)– arm being the reactive functionality. Finally, very stable allyl species are obtained from these hydride–alkenyl complexes by stereospecific migration of the hydride into the Ir–C(R)=C(R) functionality and concomitant bond reorganization of the resulting organic chain.

## Experimental Section

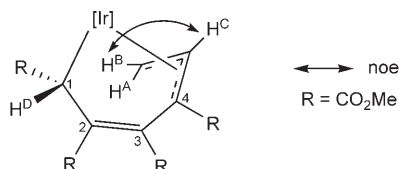
Microanalyses were conducted by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla). Infrared spectra were obtained by using Perkin–Elmer spectrometers, models 577 and 684. The NMR instruments were Bruker DRX-500, DRX-400, and DPX-300 spectrometers. Spectra were referenced to external SiMe<sub>4</sub> (δ = 0 ppm) by using the residual protio solvent peaks as internal standards (<sup>1</sup>H NMR experiments) or the characteristic resonances of the solvent nuclei (<sup>13</sup>C NMR experiments). 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<sup>Me2</sup>Ir(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>] (**1**) and [Tp<sup>Me2</sup>Ir{η<sup>4</sup>-CH<sub>2</sub>=C(Me)C(Me)=CH<sub>2</sub>}] (**5**), were obtained by using published procedures.<sup>19,24</sup> [D<sub>6</sub>]DMAD was obtained by a transesterification reaction with CD<sub>3</sub>OD in acidic media (*p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H).

**Complex 2**: MeO<sub>2</sub>CC≡CCO<sub>2</sub>Me (0.09 mL, 0.73 mmol) was added to a solution of compound **1** (0.20 g, 0.37 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (6 mL) and the mixture was stirred at RT for 6 h. After this period of time a red solution was observed and the volatiles were removed under reduced pressure. The main compound, **2**, was characterized by NMR spectroscopy, but could not isolated in a pure form due to its easy transformation into **3**.



$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta$  = 6.39 (dd,  $^3J(\text{H}^{\text{C}}, \text{H}^{\text{A}}) = 11.5$ ,  $^3J(\text{H}^{\text{C}}, \text{H}^{\text{B}}) = 9.8$  Hz, 1H;  $\text{H}^{\text{C}}$ ), 5.89, 5.83, 5.59 (s, 1H each;  $3\text{CH}_{\text{pz}}$ ), 3.81, 3.74, 3.51, 3.04 (s, 3H each;  $4\text{CO}_2\text{Me}$ ), 3.63, 3.07 (m, 1H each;  $\text{H}^{\text{A}}$ ,  $\text{H}^{\text{B}}$ , respectively), 2.42, 2.35, 2.27, 2.22 (s, 1:1:2:2;  $6\text{Me}_{\text{pz}}$ ),  $-16.91$  ppm (s, 1H; Ir-H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta$  = 174.8, 169.5, 167.6, 166.9 ( $\text{CO}_2\text{Me}$ ), 156.6, 139.4, 133.4, 126.8 ( $\text{C}^1$ ,  $\text{C}^3$ ,  $\text{C}^2$ ,  $\text{C}^4$ , respectively), 153.7, 152.9, 150.9, 144.8, 144.0, 143.5 ( $\text{C}_{\text{qppz}}$ ), 108.7, 108.6, 106.6 ( $\text{CH}_{\text{pz}}$ ), 57.9 ( $^1J(\text{C}, \text{H}) = 165$  Hz;  $\text{CH}^{\text{C}}$ ), 52.7, 52.5, 52.0, 50.9 ( $\text{CO}_2\text{Me}$ ), 42.0 ( $^1J(\text{C}, \text{H}) = 165$  Hz;  $\text{CH}^{\text{A}}, \text{H}^{\text{B}}$ ), 20.0–10.0 ppm ( $\text{Me}_{\text{pz}}$ ).

**Complex 3:** An excess of  $\text{MeO}_2\text{CC}=\text{CCO}_2\text{Me}$  (0.135 mL, 1.10 mmol) was added to a solution of **1** (0.20 g, 0.37 mmol) in dichloromethane (6 mL) and the resulting mixture was stirred for 6 h at 60°C. After this period,



the solvent was evaporated under vacuo and the solid residue was shown by  $^1\text{H}$  NMR spectroscopy to contain the complex **3**, in almost quantitative yield. Complex **3** was obtained as yellow crystals by the slow diffusion of hexane into a dichloromethane solution at RT.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta$  = 7.07 (dd,  $^3J(\text{H}^{\text{C}}, \text{H}^{\text{A}}) \approx 10.0$  Hz,  $^3J(\text{H}^{\text{C}}, \text{H}^{\text{B}}) \approx 7.5$  Hz, 1H;  $\text{H}^{\text{C}}$ ), 5.90, 5.73, 5.51 (s, 1H each;  $3\text{CH}_{\text{pz}}$ ), 4.84 (s, 1H;  $\text{H}^{\text{D}}$ ), 4.09 (dd,  $^2J(\text{H}^{\text{B}}, \text{H}^{\text{A}}) \approx 2.2$  Hz, 1H;  $\text{H}^{\text{B}}$ ), 3.70, 3.61, 3.43, 3.25 (s, 3H each;  $4\text{CO}_2\text{Me}$ ), 2.94 (dd,  $^2J(\text{H}^{\text{A}}, \text{H}^{\text{B}}) \approx 2.2$  Hz;  $^3J(\text{H}^{\text{A}}, \text{H}^{\text{C}}) \approx 10$  Hz; 1H;  $\text{H}^{\text{A}}$ ), 2.46, 2.42, 2.32, 2.20, 2.19, 2.16 ppm (s, 3H each;  $6\text{Me}_{\text{pz}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta$  = 182.2 (br,  $\text{CH}^{\text{D}}\text{CO}_2\text{Me}$ ), 174.5, 166.7, 166.1 ( $\text{CO}_2\text{Me}$ ), 154.2, 152.8, 151.7, 144.7, 143.6, 143.3 ( $\text{C}_{\text{qppz}}$ ), 148.3, 137.5 ( $\text{C}^3$ ,  $\text{C}^2$ ), 109.8, 108.7, 107.7 ( $\text{CH}_{\text{pz}}$ ), 91.2 ( $^1J(\text{C}, \text{H}) = 170$  Hz;  $\text{CH}^{\text{C}}$ ), 53.0 ( $\text{C}^4$ ), 52.2, 51.9, 51.7, 50.8 ( $\text{CO}_2\text{Me}$ ), 25.2 ( $^1J(\text{C}, \text{H}) = 166$ , 155 Hz;  $\text{CH}^{\text{A}}, \text{H}^{\text{B}}$ ), 16.3, 15.1, 13.6, 13.3, 12.9, 12.7 ( $\text{Me}_{\text{pz}}$ ), 12.0 ppm ( $^1J(\text{C}, \text{H}) = 135$  Hz;  $\text{CH}^{\text{D}}$ ); elemental analysis calcd (%) for  $\text{C}_{29}\text{H}_{38}\text{BIn}_6\text{O}_8$ : C 43.4, H 4.7, N 10.5; found: C 43.1, H 4.8, N 10.2.

**Complex 4:**  $\text{MeO}_2\text{CC}=\text{CCO}_2\text{Me}$  (0.007 mL, 0.055 mmol) was added to a solution of compound **1** (0.03 g, 0.055 mmol) in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) at  $-50^\circ\text{C}$ . The  $^1\text{H}$  NMR spectrum at this temperature showed the instantaneous and quantitative formation of **4**, stable up to  $10^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-10^\circ\text{C}$ ):  $\delta$  = 5.99, 5.48 (s, 2:1;  $3\text{CH}_{\text{pz}}$ ), 3.70 (s, 6H;  $2\text{CO}_2\text{Me}$ ), 3.14 (s, 4H;  $\text{C}_2\text{H}_4$ ), 2.66, 2.39, 2.19, 2.09 ppm (s, 2:2:1:1;  $6\text{Me}_{\text{pz}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-10^\circ\text{C}$ ):  $\delta$  = 160.4 ( $\text{CO}_2\text{Me}$ ), 153.8, 151.7, 145.7, 143.9 (2:1:1:2;  $\text{C}_{\text{qppz}}$ ), 109.2, 108.0 (1:2;  $\text{CH}_{\text{pz}}$ ), 78.6 ( $\text{CCO}_2\text{Me}$ ), 52.3 ( $\text{CO}_2\text{Me}$ ), 51.1 ( $^1J(\text{C}, \text{H}) = 162$  Hz;  $\text{C}_2\text{H}_4$ ), 16.4, 16.1, 13.5, 12.8 ppm (1:2:1:2;  $\text{Me}_{\text{pz}}$ );  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-10^\circ\text{C}$ ):  $\delta$  = 32.5 ppm.

**Complex 7:**  $\text{MeO}_2\text{CC}=\text{CCO}_2\text{Me}$  (0.43 mL, 3.50 mmol) and an excess of water (0.3–0.4 g,  $\geq 10$  equiv) were added to a solution of compound **5** (1 g, 1.75 mmol) in cyclohexane (15 mL), and the mixture was stirred at  $60^\circ\text{C}$  for 12 h. After this time, a dark brown precipitate was observed and the solvent was removed under reduced pressure to obtain complex **7** in almost quantitative yield ( $^1\text{H}$  NMR spectroscopy). The crude product was crystallized from a mixture of hexane/ $\text{CH}_2\text{Cl}_2$  (1:2) at  $-20^\circ\text{C}$  in 94% yield (brown crystals).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta$  = 5.74, 5.49 (s, 2:1;  $3\text{CH}_{\text{pz}}$ ), 3.61, 3.30 (s, 6H each;  $4\text{CO}_2\text{Me}$ ), 2.36, 2.06, 1.91 ppm (s, 3:2:1;  $6\text{Me}_{\text{pz}}$ ); the  $\text{H}_2\text{O}$  resonance was not located;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta$  = 173.6, 168.7 ( $\text{CO}_2\text{Me}$ ), 155.4, 151.4, 143.7, 143.2 (1:2:2:1;  $\text{C}_{\text{qppz}}$ ), 155.0, 150.6 ( $\text{CCO}_2\text{Me}$ ), 107.6, 106.8 (1:2;  $\text{CH}_{\text{pz}}$ ), 52.4, 51.1 ( $\text{CO}_2\text{Me}$ ), 13.5, 13.4, 12.8, 12.2 ppm (2:1:2:1;  $\text{Me}_{\text{pz}}$ ); IR (Nujol):  $\tilde{\nu}(\text{OH}) = 3372$   $\text{cm}^{-1}$  (br); elemental analysis calcd (%) for  $\text{C}_{27}\text{H}_{30}\text{BN}_6\text{O}_9\text{Ir} \cdot 1.25\text{H}_2\text{O}$ : C 39.8, H 4.7, N 10.3; found: C 39.3, H 4.6, N 10.3.

**Complex 7-NCMe:** A solution of compound **7** (0.05 g, 0.06 mmol) in  $\text{CH}_3\text{CN}$  (3 mL) was stirred at  $60^\circ\text{C}$  for 1 h. After this time the solvent was removed under reduced pressure to obtain crude **7-NCMe** in almost quantitative yield. It was purified by crystallization from hexane/ $\text{CH}_2\text{Cl}_2$  (1:1) at  $-20^\circ\text{C}$  (yellow crystals).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta$  = 5.73, 5.52

(s, 2:1;  $3\text{CH}_{\text{pz}}$ ), 3.71, 3.35 (s, 6H each;  $4\text{CO}_2\text{Me}$ ), 2.43 (s, 3H;  $\text{MeCN}$ ), 2.32, 2.14, 2.02 ppm (s, 3:2:1;  $6\text{Me}_{\text{pz}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta$  = 173.1, 167.0 ( $\text{CO}_2\text{Me}$ ), 155.4, 150.7, 143.6, 142.5 (1:2:2:1;  $\text{C}_{\text{qppz}}$ ), 150.1, 148.7 ( $\text{CCO}_2\text{Me}$ ), 116.0 ( $\text{NCMe}$ ), 107.9, 106.6 (1:2;  $\text{CH}_{\text{pz}}$ ), 51.6, 50.7 ( $\text{CO}_2\text{Me}$ ), 14.2, 13.1, 12.5, 12.2 (2:1:2:1;  $\text{Me}_{\text{pz}}$ ), 3.8 ppm ( $\text{NCMe}$ ); IR (Nujol):  $\tilde{\nu}(\text{CN}) = 2246$   $\text{cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{C}_{29}\text{H}_{37}\text{BN}_7\text{O}_8\text{Ir} \cdot \text{CH}_2\text{Cl}_2$ : C 40.1, H 4.3, N 10.9; found: C 40.6, H 4.4, N 11.2.

**Complex 7-CO:** A solution of compound **7** (0.05 g, 0.06 mmol) in  $\text{C}_6\text{H}_{12}$  (3 mL) was placed in a Fischer–Porter vessel. The stirred mixture was heated, under 2 atm of CO, at  $90^\circ\text{C}$  for 12 h. After this period, a pale-brown precipitate was formed and the volatiles were removed under vacuum. The crude **7-CO** was crystallized from hexane/ $\text{CH}_2\text{Cl}_2$  (1:1) at  $-20^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta$  = 5.80, 5.67 (s, 2:1;  $3\text{CH}_{\text{pz}}$ ), 3.74, 3.41 (s, 6H each;  $4\text{CO}_2\text{Me}$ ), 2.35, 2.33, 2.22, 2.17 ppm (s, 1:2:2:1;  $6\text{Me}_{\text{pz}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta$  = 171.3, 166.1 ( $\text{CO}_2\text{Me}$ ), 159.4 ( $\text{CO}$ ), 155.5, 151.4, 144.5, 143.3 (1:2:2:1;  $\text{C}_{\text{qppz}}$ ), 151.6, 138.0 ( $\text{CCO}_2\text{Me}$ ), 109.0, 106.9 (1:2;  $\text{CH}_{\text{pz}}$ ), 51.8, 51.2 ( $\text{CO}_2\text{Me}$ ), 14.8, 13.0, 12.5, 12.4 ppm (2:1:2:1;  $\text{Me}_{\text{pz}}$ ); IR (Nujol):  $\tilde{\nu}(\text{CO}) = 2055$   $\text{cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{C}_{28}\text{H}_{34}\text{BN}_6\text{O}_9\text{Ir} \cdot \text{CH}_2\text{Cl}_2$ : C 39.3, H 4.1, N 9.5; found: C 39.5, H 3.9, N 9.5.

**Reaction of 7 with DMAD:**  $\text{MeO}_2\text{CC}=\text{CCO}_2\text{Me}$  (0.014 mL, 0.114 mmol) was added to a solution of **7** (0.03 g, 0.038 mmol) in cyclohexane (3 mL) and the mixture was stirred at  $100^\circ\text{C}$  for 18 h. After removing the volatiles under reduced pressure, quantitative conversion into the known complex **6**<sup>[8a]</sup> was ascertained by  $^1\text{H}$  NMR spectroscopy.

**Complex 8:** Compound **7** (0.30 g, 0.38 mmol) was dissolved in  $\text{CHCl}_3$  (9 mL, passed previously through a silica column to remove the ethanol stabilizer) and  $\text{C}_2\text{H}_4$  was bubbled through the solution for 10 min. The resulting solution was maintained, without stirring, under ethylene in a closed vessel for 14 h at RT. After this period of time a pale-yellow precipitate of **8** was separated from the dark-brown mother liquor and dried under vacuo (yield: 0.14 g, ca. 45%). It was crystallized from a mixture of  $\text{CHCl}_3$ /acetone (1:1) at  $-20^\circ\text{C}$  (pale-yellow crystals).  $^1\text{H}$  NMR ( $[\text{D}_6]$ acetone, 25°C):  $\delta$  = 5.75, 5.73, 5.70 (s, 1H each;  $3\text{CH}_{\text{pz}}$ ), 3.88, 3.64, 3.50, 2.91 (s, 3H each;  $4\text{CO}_2\text{Me}$ ), 3.37, 2.90 (dt, m,  $^2J(\text{H}, \text{H}) = 11.9$  Hz,  $^3J(\text{H}, \text{H}) = 3.7$  Hz, 1H each;  $\text{IrCH}_2\text{CH}_2$ ), 2.80 (brs, 2H;  $\text{H}_2\text{O}$ ), 2.71, 2.17 (ddd, dt,  $^3J(\text{H}, \text{H}) = 14.2$  Hz,  $^2J(\text{H}, \text{H}) = 10.7$  Hz, 1H each;  $\text{IrCH}_2\text{CH}_2$ ), 2.42, 2.39, 2.35, 2.30, 2.14, 2.09 ppm (s, 3H each;  $6\text{Me}_{\text{pz}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $[\text{D}_6]$ acetone, 25°C):  $\delta$  = 178.2, 175.3, 170.1, 166.2 ( $\text{CO}_2\text{Me}$ ), 164.4, 140.8, 135.6, 130.8 ( $\text{CCO}_2\text{Me}$ ), 154.6, 152.7, 151.2, 144.9, 144.3, 142.7 ( $\text{C}_{\text{qppz}}$ ), 108.8, 108.4, 107.0 ( $\text{CH}_{\text{pz}}$ ), 53.1, 52.0, 51.0, 50.1 ( $\text{CO}_2\text{Me}$ ), 35.3 ( $^1J(\text{C}, \text{H}) = 129$  Hz;  $\text{IrCH}_2\text{CH}_2$ ), 15.5, 14.2, 13.4, 13.3, 12.5, 12.3 ( $\text{Me}_{\text{pz}}$ ),  $-2.6$  ppm ( $^1J(\text{C}, \text{H}) = 123$  Hz;  $\text{IrCH}_2\text{CH}_2$ ); IR (Nujol):  $\tilde{\nu}(\text{OH}) = 3370$   $\text{cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{C}_{29}\text{H}_{40}\text{BN}_6\text{O}_9\text{Ir} \cdot 0.5\text{CHCl}_3$ : C 41.7, H 4.5, N 9.9; found: C 41.5, H 4.5, N 9.7.

**Complex 8-NCMe:** A solution of compound **8** (0.015 g, 0.018 mmol) in  $\text{CH}_3\text{CN}$  (6 mL) was stirred at RT for 14 h. After this time the solvent was removed under reduced pressure and the crude product was purified by crystallization from hexane/ $\text{CH}_2\text{Cl}_2$  at  $-20^\circ\text{C}$  (pale-yellow crystals).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta$  = 5.77, 5.68 (s, 1:2;  $3\text{CH}_{\text{pz}}$ ), 3.83, 3.68, 3.58, 3.04 (s, 3H each;  $4\text{CO}_2\text{Me}$ ), 2.78, 2.70 (dt, td,  $^2J(\text{H}, \text{H}) = 12.7$  Hz,  $^3J(\text{H}, \text{H}) = 3.2$  Hz, 1H each;  $\text{IrCH}_2\text{CH}_2$ ), 2.64, 2.33 (2td,  $^2J(\text{H}, \text{H}) = 3J(\text{H}, \text{H}) = 12.5$  Hz, 1H each;  $\text{IrCH}_2\text{CH}_2$ ), 2.38 (s, 3H;  $\text{MeCN}$ ), 2.36, 2.34, 2.32, 2.29, 2.24, 2.15 ppm (s, 3H each;  $6\text{Me}_{\text{pz}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta$  = 177.1, 171.9, 165.9, 163.4 ( $\text{CO}_2\text{Me}$ ), 170.0, 140.6, 135.9, 130.8 ( $\text{CCO}_2\text{Me}$ ), 152.8, 151.2, 150.0, 143.8, 143.4, 142.0 ( $\text{C}_{\text{qppz}}$ ), 119.3 ( $\text{MeCN}$ ), 108.2, 107.9, 106.4 ( $\text{CH}_{\text{pz}}$ ), 52.1, 51.9, 51.3, 50.4 ( $\text{CO}_2\text{Me}$ ), 35.3 ( $\text{IrCH}_2\text{CH}_2$ ), 15.4, 14.1, 13.8, 13.3, 12.6, 12.5 ( $\text{Me}_{\text{pz}}$ ), 4.5 ( $\text{MeCN}$ ),  $-1.7$  ppm ( $\text{IrCH}_2\text{CH}_2$ ); IR (Nujol):  $\tilde{\nu}(\text{CN}) = 2360$   $\text{cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{C}_{31}\text{H}_{41}\text{BN}_7\text{O}_8\text{Ir}$ : C 44.2, H 4.9, N 11.6; found: C 44.0, H 4.7, N 11.3.

**Complex 8-CO:** A solution of compound **8** (0.015 g, 0.020 mmol) in  $\text{C}_6\text{H}_{12}$  (2 mL) was placed in a Fischer–Porter vessel. The stirred mixture was heated, under 2 atm of CO, at  $60^\circ\text{C}$  for 14 h. After this period of time, the volatiles were removed in vacuum and the crude product was crystallized from hexane/ $\text{CH}_2\text{Cl}_2$  (1:1) at  $-20^\circ\text{C}$  (white crystals).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta$  = 5.82, 5.81, 5.76 (s, 1H each;  $3\text{CH}_{\text{pz}}$ ), 3.88, 3.70, 3.61, 3.10 (s, 3H each;  $4\text{CO}_2\text{Me}$ ), 2.86, 2.79 (m, 1H each;  $\text{IrCH}_2\text{CH}_2$ ), 2.35,

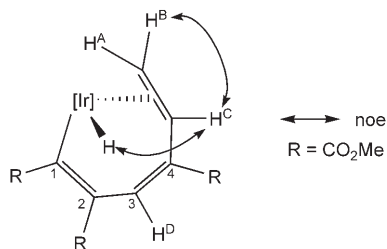
2.28 (m, 1H each;  $\text{IrCH}_2\text{CH}_2$ ), 2.40, 2.35, 2.30, 2.28 ppm (s, 1:2:1:2;  $6\text{Me}_{\text{pz}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta=173.9$ , 171.1, 167.1, 165.8 ( $\text{CO}_2\text{Me}$ ), 164.6 (CO), 152.5, 152.2, 151.0, 144.5, 144.4, 142.8 ( $\text{C}_{\text{qppz}}$ ), 150.4, 147.0, 134.0, 133.8 ( $\text{CCO}_2\text{Me}$ ), 108.4, 108.0, 106.8 ( $\text{CH}_{\text{pz}}$ ), 52.2, 52.0, 51.7, 50.9 ( $\text{CO}_2\text{Me}$ ), 35.1 ( $\text{IrCH}_2\text{CH}_2$ ), 15.5, 14.4, 14.3, 13.1, 12.7, 12.5 ( $\text{Me}_{\text{pz}}$ ), 5.2 ppm ( $\text{IrCH}_2\text{CH}_2$ ); IR (Nujol):  $\tilde{\nu}(\text{CO})=2035\text{ cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{C}_{30}\text{H}_{38}\text{BN}_6\text{O}_6\text{Ir}$ : C 40.7, H 4.4, N 9.2; found: C 40.6, H 4.3, N 9.0.

**Complex 9:** A solution of **1** (0.5 g, 0.92 mmol) in THF (15 mL) was cooled at  $-20^\circ\text{C}$  and  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  (0.11 mL, 0.92 mmol) was added. The mixture was stirred at  $-20^\circ\text{C}$  for 5 min and then some water ( $\approx 10$  equiv) and  $\text{MeO}_2\text{CC}\equiv\text{CH}$  (0.08 mL, 0.92 mmol) were added. After 10 min of stirring at  $-20^\circ\text{C}$  the resulting solution was allowed to stir at RT for 1 h. After this period, the volatiles were removed under reduced pressure and the crude product was purified by crystallization from  $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$  (3:1) at  $-20^\circ\text{C}$  in 47% yield (pale-brown crystals).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta=7.75$  (s, 1H; CH), 5.66, 5.57, 5.45 (s, 1H each;  $3\text{CH}_{\text{pz}}$ ), 3.56, 3.05 (s, 1:2;  $3\text{CO}_2\text{Me}$ ), 2.33, 2.32, 2.30, 1.76, 1.75, 1.50 ppm (s, 3H each;  $6\text{Me}_{\text{pz}}$ ); the coordinated  $\text{H}_2\text{O}$  was not located;  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta=176.1$ , 172.1, 164.9 ( $\text{CO}_2\text{Me}$ ), 170.3, 146.6, 140.2 (br,  $\text{CCO}_2\text{Me}$ ), 155.1, 151.7, 151.0, 143.7, 143.5, 143.0 ( $\text{C}_{\text{qppz}}$ ), 153.3 (br,  $^1J(\text{C,H})=159\text{ Hz}$ , CH), 106.9, 106.5, 105.8 ( $\text{CH}_{\text{pz}}$ ), 51.1, 50.3, 50.2 ( $\text{CO}_2\text{Me}$ ), 13.0, 12.9, 12.3, 12.3 ppm (1:1:1:3;  $\text{Me}_{\text{pz}}$ ); IR (Nujol):  $\tilde{\nu}(\text{OH})=3400\text{ cm}^{-1}$  (br); elemental analysis calcd (%) for  $\text{C}_{25}\text{H}_{34}\text{BN}_6\text{O}_6\text{Ir}$ : C 40.9, H 4.6, N 11.4; found: C 40.7, H 4.5, N 10.9.

**Complex 9-NCMe:** A solution of compound **9** (0.015 g, 0.020 mmol) in  $\text{CH}_3\text{CN}$  (2 mL) was stirred at  $50^\circ\text{C}$  for 5 h. After this time, the solvent was removed under reduced pressure and the crude product crystallized by pentane diffusion into a  $\text{CH}_2\text{Cl}_2$  solution (dark-yellow crystals).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta=7.82$  (s, 1H; CH), 5.75, 5.74, 5.50 (s, 1H each;  $3\text{CH}_{\text{pz}}$ ), 3.65, 3.42, 3.36 (s, 3H each;  $3\text{CO}_2\text{Me}$ ), 2.36 (s, 3H; MeCN), 2.34, 2.32, 2.22, 2.02, 1.91 ppm (s, 2:1:1:1:1;  $6\text{Me}_{\text{pz}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta=175.6$ , 172.1, 164.5 ( $\text{CO}_2\text{Me}$ ), 164.2, 146.3, 134.9 ( $\text{CCO}_2\text{Me}$ ), 155.0, 151.0, 150.2, 143.7, 143.2, 142.6 ( $\text{C}_{\text{qppz}}$ ), 152.7 ( $^1J(\text{C,H})=159\text{ Hz}$ , CH), 115.4 (MeCN), 107.7, 106.7, 106.1 ( $\text{CH}_{\text{pz}}$ ), 51.1, 50.8, 50.6 ( $\text{CO}_2\text{Me}$ ), 14.3, 13.8, 13.2, 12.5, 12.5, 12.4 ( $\text{Me}_{\text{pz}}$ ), 3.8 ppm (MeCN); IR (Nujol):  $\tilde{\nu}(\text{CN})=2248\text{ cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{C}_{27}\text{H}_{35}\text{BN}_6\text{O}_6\text{Ir}\cdot 0.5\text{CH}_2\text{Cl}_2$ : C 41.4, H 4.5, N 12.3; found: C 41.8, H 4.5, N 12.1.

**Complex 9-CO:** A solution of compound **9** (0.20 g, 0.27 mmol) in  $\text{C}_6\text{H}_{12}$  (3 mL) was placed in a Fischer–Porter vessel. The stirred mixture was heated, under 2 atm of CO, at RT for 14 h. After this period of time, the volatiles were removed in vacuum and the crude product was crystallized from hexane/ $\text{Et}_2\text{O}$  (1:1) at  $-20^\circ\text{C}$  (0.12 g, yield: 60%, white crystals).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta=7.88$  (s, 1H; CH), 5.80, 5.63 (s, 2:1;  $3\text{CH}_{\text{pz}}$ ), 3.73, 3.49, 3.45 (s, 3H each;  $3\text{CO}_2\text{Me}$ ), 2.33, 2.30, 2.09, 2.05 ppm (s, 3:1:1:1;  $6\text{Me}_{\text{pz}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta=173.4$ , 170.4, 164.0 ( $\text{CO}_2\text{Me}$ ), 160.0 (CO), 154.9, 151.8, 150.5, 144.6, 144.0, 143.2 ( $\text{C}_{\text{qppz}}$ ), 153.9 ( $^1J(\text{C,H})=162\text{ Hz}$ ; CH), 151.0, 148.2, 127.3 ( $\text{CCO}_2\text{Me}$ ), 108.7, 107.0, 106.5 ( $\text{CH}_{\text{pz}}$ ), 51.6, 51.2, 51.2 ( $\text{CO}_2\text{Me}$ ), 14.8, 14.7, 13.0, 12.7, 12.6, 12.6 ppm ( $\text{Me}_{\text{pz}}$ ); IR (Nujol):  $\tilde{\nu}(\text{CO})=2047\text{ cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{C}_{26}\text{H}_{32}\text{BN}_6\text{O}_7\text{Ir}$ : C 42.0, H 4.3, N 11.3; found: C 41.5, H 4.2, N 10.8.

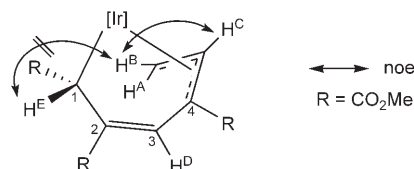
**Complex 10—Method A:** A solution of compound **1** (0.20 g, 0.37 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) was cooled at  $-20^\circ\text{C}$  and  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  (0.045 mL, 0.37 mmol) was added. After stirring 10 min at this temperature,  $\text{MeO}_2\text{C}\equiv\text{CH}$  (0.03 mL, 0.37 mmol) was added and the resulting solu-



tion was stirred at RT for 1 h. The volatiles were removed under vacuo and complex **10** was isolated by column chromatography on silica gel, by using a 5:1 mixture of hexane/ $\text{Et}_2\text{O}$  as eluent. Yield: 0.18 g (70%). An analytically pure sample was obtained by crystallization from pentane/ $\text{CH}_2\text{Cl}_2$  (1:1) at  $-20^\circ\text{C}$  (dark-yellow crystals).

**Method B:**  $\text{C}_2\text{H}_4$  was bubbled for 10 min through a solution of complex **9** (0.03 g, 0.04 mmol) in  $\text{CHCl}_3$  (9 mL, passed previously through a column on silica gel to eliminate the ethanol stabilizer) and the resulting solution was left, without stirring, under  $\text{C}_2\text{H}_4$  in a sealed ampoule for 14 h at RT. The solvent was removed under reduced pressure and quantitative conversion into compound **10** was ascertained by  $^1\text{H}$  NMR.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta=7.50$  (s, 1H;  $\text{H}^{\text{D}}$ ), 6.73 (dd,  $^3J(\text{H}^{\text{C}},\text{H}^{\text{A}})=11.2\text{ Hz}$ ,  $^3J(\text{H}^{\text{C}},\text{H}^{\text{B}})=9.7\text{ Hz}$ , 1H;  $\text{H}^{\text{C}}$ ), 5.92, 5.79, 5.58 (s, 1H each;  $3\text{CH}_{\text{pz}}$ ), 3.84, 3.62, 3.06 (s, 3H each;  $3\text{CO}_2\text{Me}$ ), 3.66, 3.01 (d,  $^3J(\text{H}^{\text{A}},\text{H}^{\text{C}})=11.2\text{ Hz}$ ;  $^3J(\text{H}^{\text{B}},\text{H}^{\text{C}})=9.7\text{ Hz}$ ;  $\text{H}^{\text{A}}$ ,  $\text{H}^{\text{B}}$ , respectively), 2.43, 2.32, 2.31, 2.26, 2.24, 2.13 (s, 3H each;  $6\text{Me}_{\text{pz}}$ ),  $-16.91$  ppm (s, 1H; Ir-H);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta=175.3$ , 167.6, 165.6 ( $\text{CO}_2\text{Me}$ ), 162.0 ( $\text{C}^1$ ), 153.8, 152.3, 150.9, 144.4, 143.8, 143.4 ( $\text{C}_{\text{qppz}}$ ), 137.3 ( $^1J(\text{C,H})=161\text{ Hz}$ ;  $\text{C}^3$ ), 130.2 ( $\text{C}^2$ ), 123.8 ( $\text{C}^4$ ), 108.7, 108.6, 106.6 ( $\text{CH}_{\text{pz}}$ ), 60.9 ( $^1J(\text{C,H})=165\text{ Hz}$ ;  $\text{CH}^{\text{C}}$ ), 52.0, 51.7, 50.6 ( $\text{C}^4\text{CO}_2\text{Me}$ ,  $\text{C}^2\text{CO}_2\text{Me}$ ,  $\text{C}^1\text{CO}_2\text{Me}$ , respectively), 43.0 ( $^1J(\text{C,H})=162\text{ Hz}$ ;  $\text{CH}^{\text{A}}\text{H}^{\text{B}}$ ), 16.6, 16.3, 15.7, 12.9, 12.8, 12.8 ppm ( $\text{Me}_{\text{pz}}$ ); IR (Nujol):  $\tilde{\nu}(\text{Ir-H})=2199\text{ cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{C}_{27}\text{H}_{33}\text{BN}_6\text{O}_6\text{Ir}$ : C 40.6, H 4.6, N 10.1; found: C 40.8, H 4.5, N 10.3.

**Complex 11—Method A:** A solution of compound **1** (0.20 g, 0.37 mmol) in  $\text{CH}_2\text{Cl}_2$  (8 mL) was cooled at  $-20^\circ\text{C}$  and  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  was added (0.045 mL, 0.37 mmol). After stirring 10 min at this temperature,



$\text{MeO}_2\text{CC}\equiv\text{CH}$  (0.03 mL, 0.37 mmol) was added and the resulting solution was stirred at  $80^\circ\text{C}$  for 24 h. After this period of time, the solvent was evaporated under reduced pressure and the crude product crystallized from pentane/ $\text{CH}_2\text{Cl}_2$  (1:1) at  $-20^\circ\text{C}$  (pale-yellow crystals).

**Method B:** A solution of compound **10** (0.03 g, 0.04 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was stirred at  $80^\circ\text{C}$  for 24 h. The volatiles were removed under reduced pressure and quantitative conversion into compound **11** was ascertained by  $^1\text{H}$  NMR spectroscopy.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta=7.10$  (dd,  $^3J(\text{H}^{\text{C}},\text{H}^{\text{A}})=10.1\text{ Hz}$ ,  $^3J(\text{H}^{\text{C}},\text{H}^{\text{B}})=7.8\text{ Hz}$ , 1H;  $\text{H}^{\text{C}}$ ), 6.77 (s, 1H;  $\text{H}^{\text{D}}$ ), 5.86, 5.74, 5.50 (s, 1H each;  $3\text{CH}_{\text{pz}}$ ), 4.26 (brs, 1H;  $\text{H}^{\text{E}}$ ), 4.07, 3.10 (s, brs, 1H each;  $\text{H}^{\text{B}}$ ,  $\text{H}^{\text{A}}$ , respectively), 3.62, 3.56, 3.32 (s, s, brs, 3H each;  $3\text{CO}_2\text{Me}$ ), 2.47, 2.42, 2.34, 2.20, 2.05 ppm (s, 1:1:1:2:1;  $6\text{Me}_{\text{pz}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 25°C):  $\delta=175.5$  ( $\text{CO}_2\text{Me}$ ), 174.8, 167.7 (br,  $\text{CO}_2\text{Me}$ ), 155.2 (br,  $\text{C}_{\text{qppz}}$ ), 152.5, 151.6, 144.8, 143.4, 143.2 ( $\text{C}_{\text{qppz}}$ ), 140.3 (br,  $^1J(\text{C,H})=160\text{ Hz}$ ;  $\text{C}^3$ ), 109.7, 108.5, 107.8 ( $\text{CH}_{\text{pz}}$ ), 91.9 ( $^1J(\text{C,H})=167\text{ Hz}$ ;  $\text{CH}^{\text{C}}$ ), 53.7 (br;  $\text{C}^4$ ), 51.9, 51.6 ( $\text{CO}_2\text{Me}$ ), 50.7 (br;  $\text{CO}_2\text{Me}$ ), 23.9 (br;  $\text{CH}^{\text{A}}\text{H}^{\text{B}}$ ), 16.3, 15.2 (br;  $\text{Me}_{\text{pz}}$ ), 14.0, 13.3, 13.0, 12.7 ( $\text{Me}_{\text{pz}}$ ), 12.0 ppm (br;  $\text{C}^1$ ); the broad signals were assigned with the help of the long-range HETCOR spectrum;  $\text{C}^2$  was not located; elemental analysis calcd (%) for  $\text{C}_{27}\text{H}_{36}\text{BN}_6\text{O}_6\text{Ir}$ : C 43.6, H 4.8, N 11.3; found: C 43.3, H 4.7, N 11.0.

**X-ray structure determinations:** X-ray data were collected by using a Bruker Smart APEX CCD system or a Bruker–Nonius X8kappa APEX II CCD system (for **9**) by using graphite-monochromated  $\text{MoK}_{\alpha}$  radiation ( $\lambda=0.71073\text{ \AA}$ ) and  $0.3^\circ$   $\omega$ -scan frames covering complete spheres of the reciprocal space with  $\theta_{\text{max}}=27\text{--}30^\circ$ . After data integration with program SAINT, corrections for absorption,  $\lambda/2$  effects, and crystal decay were applied with SADABS.<sup>[25]</sup> The structures were solved by direct methods by using the program SHELXS97. Structure refinement on  $F^2$  was carried out with the program SHELXL97.<sup>[26]</sup> All non-hydrogen atoms were refined anisotropically. Most hydrogen atoms were placed in calculated positions and thereafter treated as riding. A torsional param-

ter was refined for each pyrazole-bound methyl group. The hydride hydrogen atom in  $10\text{-CH}_2\text{Cl}_2$  was refined in  $x,y,z$  by using an Ir–H distance restraint of 1.60 Å. Moderate disorder encountered in  $7\cdot\approx 1.25\text{H}_2\text{O}$  (one water molecule with partial occupancy),  $9\cdot(\text{Et}_2\text{O}, \text{THF})$  (mixed occupation of a solvent cavity by tetrahydrofuran and diethyl ether in 1:1 ratio, both solvents hydrogen bonded to the water molecule of the Ir complex) and  $10\text{-CH}_2\text{Cl}_2$  (two pseudo-mirror related orientations of C45–C46 in 9:1 ratio) was taken into account. Crystal data and experimental details are given in Table 2.

CCDC204945, 232726, and 624619–624623 contain 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](http://www.ccdc.cam.ac.uk/data_request/cif).

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