DOI: 10.1002/chem.200((……))

Investigations on the Coupling of Ethylene and Alkynes in $Tp^{Me2}Ir$ Compounds: Water as an Effective Trapping Agent

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Abstract: The reaction of the bis(ethylene) complex $Tp^{Me2}Ir(C_2H_4)_2$ (**1**) (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate) with 2 equiv. of dimethyl acetylenedicarboxylate, $MeO_2CC{\equiv}CCO_2Me$ (DMAD), in CH_2Cl_2 at 25 ºC gives the hydride-alkenyl species $Tp^{Me2}IrH(C(R)=C(R)C(R)=C(R)CH=CH_2)$ (**2**, R = CO_2Me) in high yield. A careful study of this system has established the active role of a number of intermediates in route to **2**. The first of these is the Ir(I) complex $Tp^{Me2}Ir(C_2H_4)$(DMAD) (**4**) formed by substitution of one of the ethylene ligands in **1** by a molecule of DMAD. **4** reacts further with another equivalent of the alkyne with formation of the unsaturated metallacyclopentadiene "$Tp^{Me2}Ir(C(R)=C(R)C(R)=C(R))$" which can be trapped by added water to give adduct **7**, or react with the C_2H_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 β-H elimination. Complex **1** reacts sequentially with 1 equiv. of DMAD and 1 equiv. of methyl propiolate, $HC{\equiv}CCO_2Me$ (MP), in the presence of water, with regioselective formation of the unsymmetrical iridacyclopentadiene $Tp^{Me2}Ir(C(R)=C(R)C(H)=C(R))(H_2O)$ (**9**). Complex **9** reacts with ethylene giving a hydride-alkenyl complex **10**, related to **2**, in which the C_2H_4 has inserted regiospecifically into the Ir—C(R) bond that bears the CH functionality. Heating CH_2Cl_2 solutions of either **2** or **10** allows the formation of the allyl species **3** or **11**, respectively**,** by simple stereoselective migration of the hydride ligand into the Cα alkenyl carbon 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 · iridacyclopentadienes · C_2H_4 insertion · C-H activation · water complexes

Introduction

Metallacyclopentadienes[1] are very interesting organometallic species which are involved, as intermediates, in a number of important catalytic or stoichiometric processes mediated by transition metal complexes, as is the case of the cyclotrimerization of alkynes (to give benzene derivatives),[2] alkynes-nitriles (for the synthesis of pyridines),[3] alkynes-olefins (formation of cyclohexadienes),[3,4] etc.[1h,5] In this contribution, we report on the coupling of two molecules of DMAD (dimethyl acetylenedicarboxylate, $MeO_2CC{\equiv}CCO_2Me$) in the $Tp^{Me2}Ir$ system (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate),[6] to give an iridacyclopentadiene[7] which 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 unsymmetrical iridacyclopentadiene that results from the regioselective coupling of DMAD and MP (MP = methyl propiolate, $HC{\equiv}CCO_2Me$). Part of this work has been published in preliminary form.[8]

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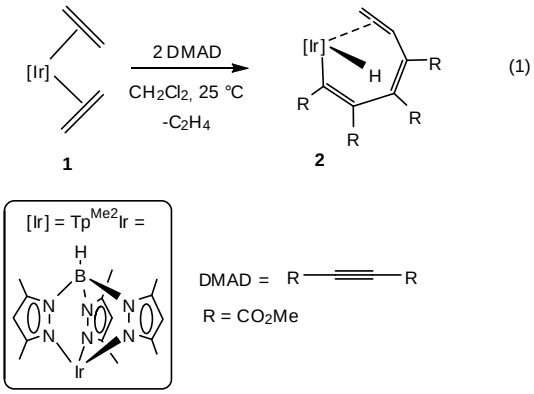
Results and Discussion

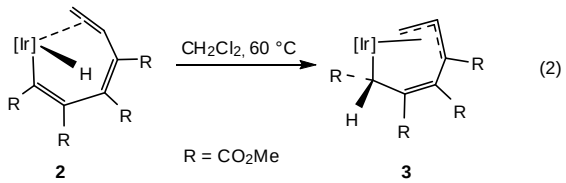
The addition of 2 equiv. of DMAD to a solution of the bis(ethylene) complex $Tp^{Me2}Ir(C_2H_4)_2$ (**1**)[9] in CH_2Cl_2, at room temperature, produces immediate consumption of **1** and formation of a new compound, **2**, as deduced from the NMR spectra of the reaction mixture [Eq. (1)]. The reaction 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 derives itself from one of the ethylene ligands in **1**.

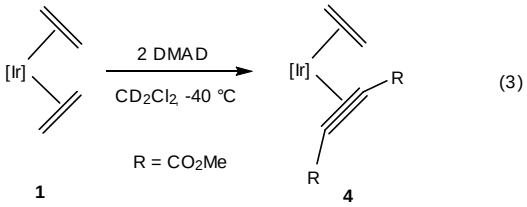


Although compound **2** is the major product in this reaction, attempts to obtain an analytical and spectroscopically pure sample of it failed, due to its slow transformation into a new allyl derivative **3** (see below). Either by crystallization or by column chromatography, species **2** is always isolated as a mixture with **3**. Nevertheless, it survives in solution long enough as 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 resonance at -16.91 ppm in the ^{1}H NMR spectrum, while the π-coordinated vinyl moiety exhibits the pattern of resonances expected for a ligand of this type:[10] three multiplets centered at 6.39, 3.63 and 3.07 ppm, with *trans* and *cis* $^3J_{HH}$ coupling constants of 11.5 and 9.8 Hz, respectively (see Experimental Section for assignments). ^{13}C NMR data and a full set of two-dimension 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 °C [Eq. (2)], and **3** is also obtained, in almost quantitative yield, when the reaction depicted in Eq. (1) is performed in CH_2Cl_2 at 60 °C. The formation of **3** is the neat result of the stereospecific transfer of the hydride ligand to the α-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, with concerted or stepwise bond rearrangement along the chain. Compound **3** exhibits ^{1}H NMR resonances due to the π-coordinated allyl moiety[9] at 7.07 (CH), 4.09 and 2.94 (CH_2) ppm, the corresponding C atoms producing signals in the ^{13}C NMR spectrum at 91.2 ($^1J_{CH}$ = 170 Hz) and 25.2 ppm ($^1J_{CH}$ = 155 and 166 Hz) while the remaining allylic carbon appears at 53.0 ppm. The Ir-bonded alkyl carbon, Ir—*C*(H)(CO_2Me)R resonates at 12.0 ppm ($^1J_{CH}$ = 135 Hz). This compound has been additionally characterized by an X-ray diffraction structure analysis (see below).



The reaction shown in Eq. (1) has been monitored by NMR, at low temperature. When 2 equiv. of DMAD are added to a solution of **1** in CD_2Cl_2 at -40 ºC, the ^{1}H NMR spectrum recorded immediately after mixing shows quantitative formation of a new compound, which has been characterized by NMR, at 0 ºC, as the Ir(I) adduct $Tp^{Me2}Ir(C_2H_4)(MeO_2CC{\equiv}CCO_2Me)$ (**4**) [Eq. (3)]. Its ^{1}H and $^{13}C\{^1H\}$ NMR spectra show local C_s symmetry for the Tp^{Me2} ligand and all the protons and both carbon nuclei of the ethylene ligand are equivalent, generating a singlet in each spectrum (3.14 ppm for ^{1}H and 51.1 ppm for $^{13}C\{^1H\}$). The $^{11}B\{^1H\}$ NMR spectrum shows a singlet at 32.5 ppm, and this value[11] compares well with the corresponding chemical shift recorded for complex **1** (32.9 ppm), which has been shown previously to be a 18-e$^-$ species with the Tp^{Me2} ligand κ^3 coordinated both in the solid state and in solution.[9] 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 (CO and PR_3; R_3 = Me_3, Me_2Ph, Et_3).[12] These reactions have been proposed to occur by an associative mechanism, by means of a change on the coordination mode of the Tp^{Me2} ligand, from κ^3 to κ^2.[12,13]



However, and unlike other derivatives of composition $Tp^{Me2}Ir(C_2H_4)(L)$ (L = CO, PR_3)[12] and related Tp species,[13,14] which adopt a rigid trigonal bipyramidal structure with the, slowly rotating in the NMR time scale, ethylene ligand occupying the equatorial position, and hence giving rise to an AA'BB' spin system in the ^{1}H NMR spectra, compound **4** is fluxional, and its ethylene ligand seems to be fast rotating, even at -40 ºC. This difference can be attributed to the fact that the ethylene ligand is occupying an axial position in the trigonal bipyramid (Fig. 1), where the π back donation would be weaker than when in the equatorial place.[15] The adoption of this structure is also supported by a comparison of the ^{13}C NMR chemical shift of the ethylene ligand in the series of compounds $Tp^{Me2}Ir(C_2H_4)(L)$ (L = PMe_3, CO, C_2H_4 and DMAD) (see Table 1). For the case of L = C_2H_4, all the ethylene carbon atoms resonate at 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 $^{13}C\{^1H\}$ NMR spectrum recorded for **1** in the solid state exhibits two signals for the ethylene ligands, at 48 and 5 ppm (axial and equatorial, respectively).[9] Probably, the preference of the DMAD for the equatorial position in **4** is because it is a better π-acceptor than the ethylene ligand. Although it can not 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 π-acceptor character. Finally on this respect, the related Tp derivative $TpIr(C_2H_4)(DMAD)$[7c] has also been reported to be fluxional, and the authors suggest a stereochemistry analogous to the one proposed herein for **4**.

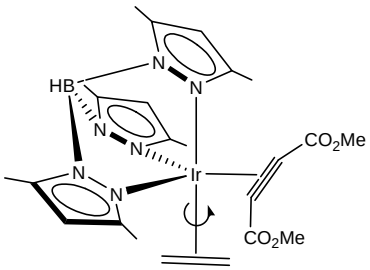


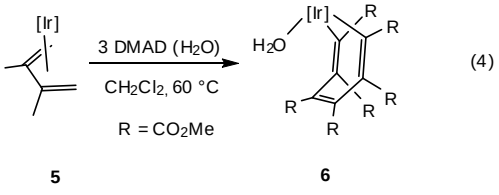
Figure 1. Proposed structure of complex **4**.

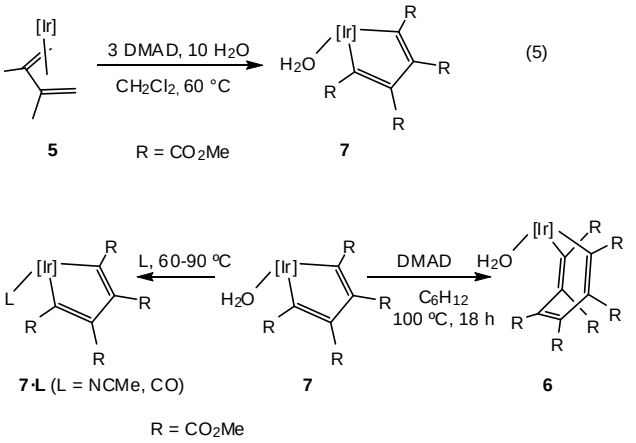
Table 1. Solution Chemical Shifts for the ^{13}C Nuclei of the Ethylene Ligands in Compounds of Composition $Tp^{Me2}Ir(C_2H_4)(L)$.

L	PMe_3	CO	C_2H_4	DMAD
δ C_2H_4 (ppm)	-8.1	0.6	26.2[a]	51.1

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

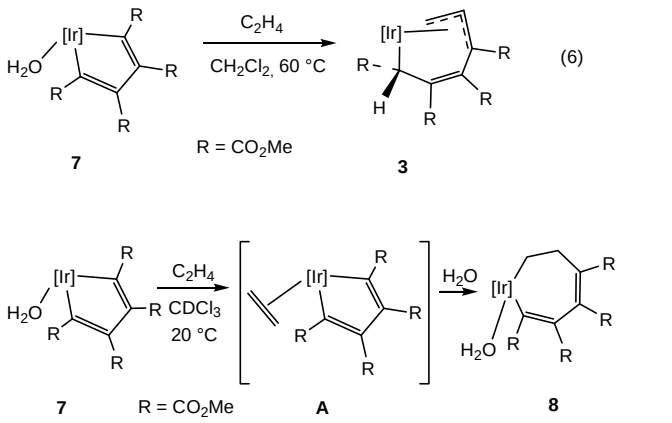
Compound **4** is stable up to 10 °C; above this temperature, and under the conditions of Eq. (3), it evolves to a mixture of species. Monitoring the reaction by ^1H NMR at 20 ºC reveals the formation of **2** together with other unidentified species, although they subsequently disappear, and finally **2** is present in ca. 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,[8a] we have reported that the iridacycloheptatriene **6**, to be described in full detail elsewhere, is obtained by the reaction of the Ir-dimethylbutadiene derivative **5** with 3 equiv. of DMAD in CH_2Cl_2 [Eq. (4)]. Interestingly, the presence of a large excess of water (≥ 10 equiv.) in the reaction mixture prevents the incorporation of the third equivalent of alkyne, yielding the water stabilized[16] iridacyclopentadiene derivative **7** [Eq. (5)], that obviously has been formed by the coupling of two DMAD molecules in the metal coordination sphere.[7] 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 structures of **7** and **7·CO** have been determined by X-ray crystallography (see below).



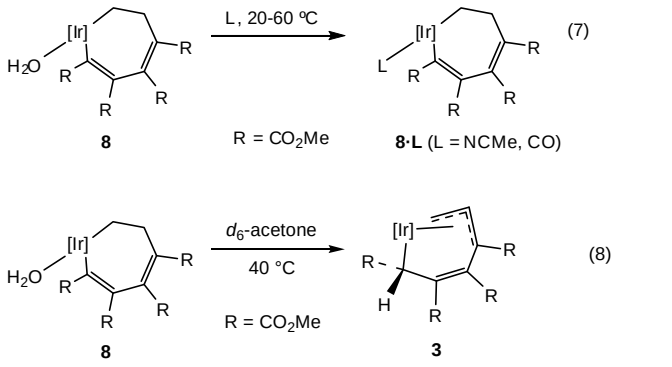


Scheme 1. Synthesis of complex **7** and its reactivity with Lewis bases and DMAD.

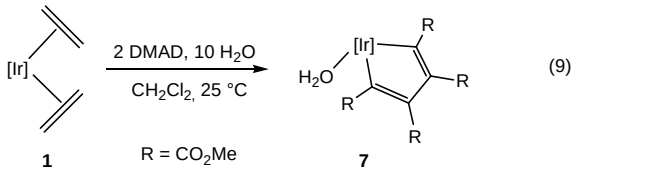
More interesting, in the present context, is the reaction of **7** with ethylene which, at 60 ºC, results in the clean formation of the already described compound **3** [Eq. (6)], supporting the intermediacy of an iridacyclopentadiene species in the formation of compound **2** (or **3**) starting from **1** (or **4**). Furthermore, if ethylene is bubbled through a solution of **7** in $CDCl_3$, 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 and forms metastable solutions in chloroform from where it eventually precipitates and, after dissolution in acetone-d_6, could be appropriately characterized by NMR. The more characteristic signals for this compound are those corresponding to the two adjacent CH_2 groups: multiplets at 3.37, 2.90 ($IrCH_2CH_2$) and 2.71, 2.17 ($IrCH_2CH_2$) ppm in the ^1H NMR spectrum and resonances at 35.5 ($IrCH_2CH_2$) and -2.6 ($IrCH_2CH_2$) ppm in the $^{13}C\{^1H\}$ NMR spectrum. Probably, compound **8** is formed via 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 of mention the facility 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,[7c] no insertion was observed up to 110 ºC. This is in agreement with the known decreased reactivity of the TpIr compounds, as compared with the related $Tp^{Me2}Ir$ ones, in activation processes. In the $Tp^{Me2}Ir$ system we have observed cases in which C_2H_4 easily inserts into an Ir—C bond, for example in its reaction with $Tp^{Me2}Ir(C_6H_5)_2(N_2)$,[17] but also found complexes that are unreactive in this respect, as the iridacyclopentene $Tp^{Me2}Ir(CH_2C(Me)=C(Me)CH_2)(C_2H_4)$ which, upon heating, dissociates the coordinated ethylene;[18] or the very reactive $Tp^{Me2}Ir(H)(CH=CH_2)(C_2H_4)$, which has been shown to yield a C_4 chain by the coupling of the two C_2 ligands, although by following a mechanistic pathway different from the insertion of ethylene into the Ir—C bond.[9] 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, in addition, 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)].



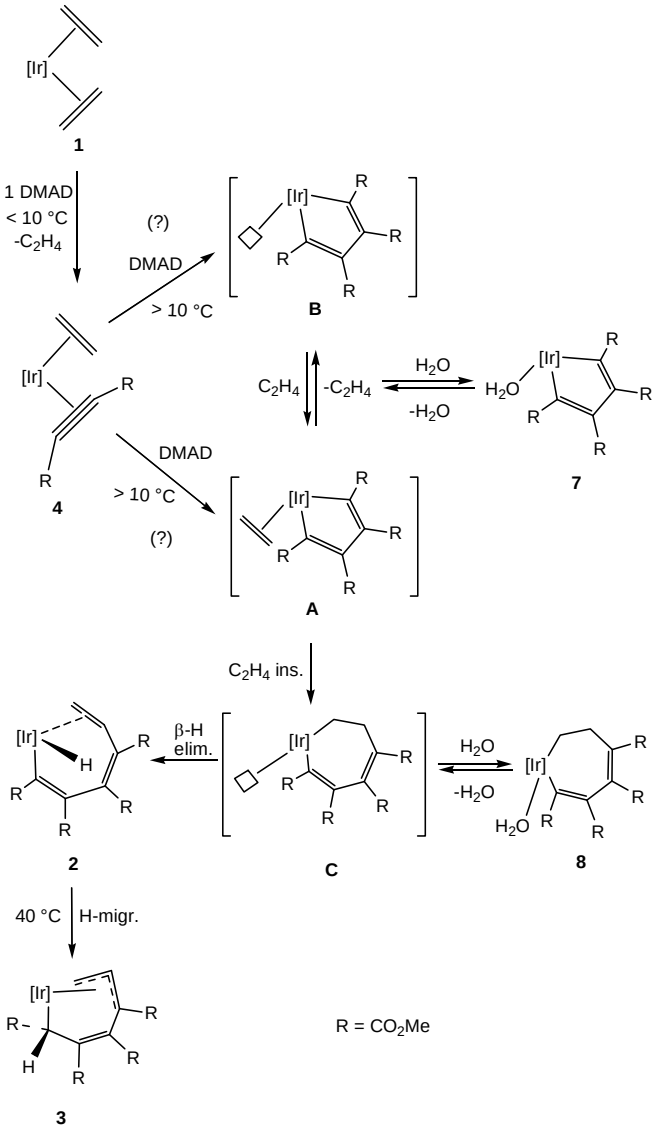
Scheme 2. Formation of the alkyl-allyl derivative **3** and trapping of an intermediate as the water adduct **8**.



Compounds **7** or **8** were not detected during the course of the transformation depicted in Eq. (1), and this negative evidence is probably due to the absence of enough H_2O in the reaction mixture. In fact, if the reaction is carried out in the presence of an excess of H_2O, compound **7** is formed in almost quantitative spectroscopic yield [Eq. (9)] and, despite of the presence of the evolved ethylene in the reaction flask, compound **2** is not observed. The larger amount of water *vs*. ethylene competes effectively for the coordination to iridium, preventing the incorporation of the olefin.

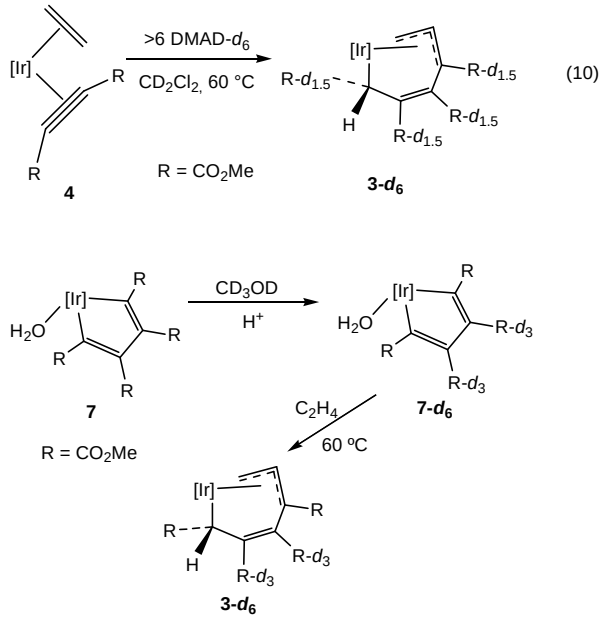


Considering all the observations commented so far, the mechanism depicted in Scheme 3 can be proposed for the formation of compounds **2** and **3**, in which compounds **7** and **8** have also been included. From the experimental data we cannot say which of the intermediates **A** or **B** (**B** is depicted as an unsaturated 16-e$^-$ Ir(III) species rather than as having a 18-e$^-$ bis(carbene) Ir(I) structure[2c,7b]) 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'Ir(I) species). If **B** is formed first, then there is a competence for coordination to this intermediate, of the evolved ethylene (to give **A**) and the water present in the reaction mixture (to give **7**). On the contrary, if **A** is the favored kinetic species, the coordinated ethylene would be dissociatively exchanged by H_2O under the reaction conditions, before C_2H_4 insertion into one of the Ir—C bonds of the metallacycle takes place. The facility 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 governed by the high tendency of the Tp'Ir(I) derivatives to oxidize to Ir(III), and more importantly by the mutually *cis* disposition adopted by these ligands in the purported intermediate that also contains a *fac*-type Tp^{Me2}-Ir linkage. This is in agreement with the experimental and theoretical studies carried out with the system $[Ir(PR_3)_3(alkyne)_2]^+$, which indicate that the phosphines have to occupy a *fac* disposition for the coupling of the two alkynes to take place.[7b] 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.[19]

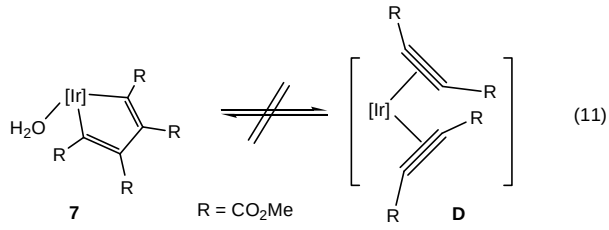


Scheme 3. Mechanism proposed for the formation of complex **3** from the bis(ethylene) derivative **1** and DMAD with inclusion of all the intermediate species isolated.

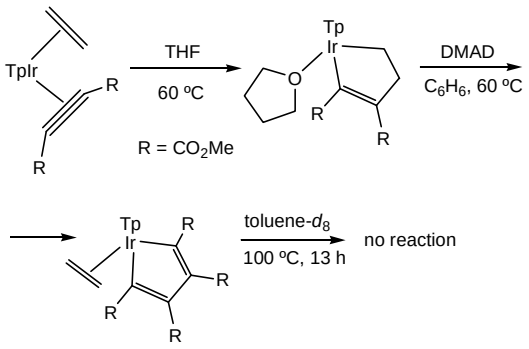
In order to complete this study, some deuteration experiments have been carried out. First, we have prepared, at low temperature, complex **4** by addition to **1** of only one equivalent of DMAD, to add afterwards an excess (≥ 6 equiv.) of DMAD-d_6. After warming at 60 °C, compound **3**-d_6 is formed and the corresponding ^{1}H NMR spectrum exhibits resonances for the four CO_2Me groups of intensity half of the 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 CO_2Me groups present in **7** can be selectively replaced by CO_2CD_3 by a transesterification process in CD_3OD, catalyzed by acid. Although not confirmed, it is highly probable, on steric grounds, that the deuterated positions are those shown in Scheme 4. When **7**-d_6 is subjected to reaction with C_2H_4, no scrambling of the labels is observed, as two CO_2Me resonances are absent in the ^{1}H NMR spectra of compound **3**-d_6, probably those shown in Scheme 4. This experiment rules out any interconversion between the iridacyclopentadiene and a bis(alkyne)Ir(I) species [Eq. (11)] and this is in accord with the findings observed in a related system.[7a]



Scheme 4. Partial deuteration of complex **7** by a transesterification reaction in CD_3OD.



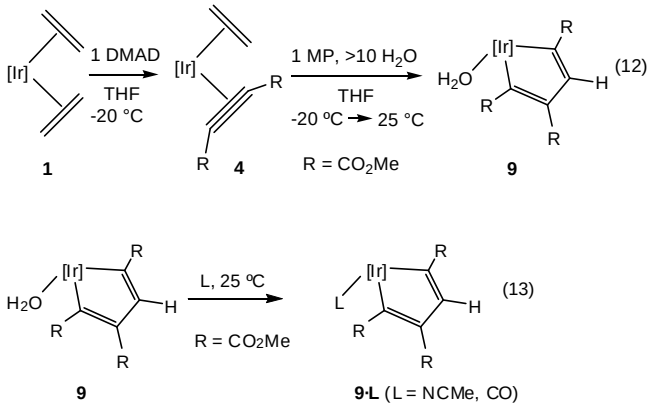
Mention has to be done to the different reactivity observed when the reaction of compound **1** is carried out, in solution at 60 ºC, with 3 equiv. of DMAD, and where, under the appropriate conditions, the iridacycloheptatriene **6** is generated. This result is almost independent on the solvent employed (C_6H_{12}, CH_2Cl_2 or $CHCl_3$), 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 a 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 *ca*. 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_2O adduct **7** reacts with C_2H_4 at 25 ºC, while its reaction with DMAD requires much higher temperatures), and this may be due to the lesser tendency of the Ir(III) intermediate (already electron deficient) to bind the alkyne, less electron-donating than ethylene. At this point it seems appropriate to make another comparison with the related system of the unsubstituted Tp ligand, TpIr(C_2H_4)$_2$-DMAD (Scheme 5).[7c] In this case, the first step is also the formation of the Ir(I) adduct Tp(C_2H_4)(DMAD), a compound that is stable at room temperature, and that when heated in acetonitrile or other solvents like 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^{Me2} derivative **4**, which, as already mentioned, decomposes at >10 ºC in the presence of 1 equiv. of C_2H_4 and 1 equiv. 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 reluctant to experience ethylene insertion into the Ir—C bonds of the metallacycle, no transformation taking place even at 100 ºC, this fact highlighting once more the higher reactivity of the Tp^{Me2} derivatives in comparison with the Tp ones.



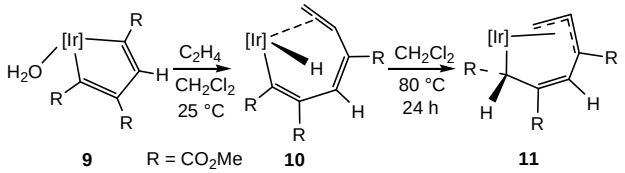
Scheme 5. Formation of an iridacyclopent-2-ene and an iridacyclopentadiene in the system TpIr-C_2H_4-DMAD.

We have also studied the reaction of compound Tp^{Me2}Ir(C_2H_4)(DMAD) (**4**) with methyl propiolate (MP), a terminal alkyne. In principle, a reactivity similar to that observed for DMAD could be advanced, although the asymmetry 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.[20,21] The sequential addition to **1**, at low temperature, of 1 equiv. of DMAD and 1 equiv. of MP in the presence of added water (10 equiv.), produces selectively, upon warming to room temperature, the iridacyclopentadiene **9** [Eq. (12)] in which the CH of the MP occupies a β position in the ring, as deduced by its ^{1}H NMR chemical shift of 7.75 ppm (in this kind of Ir-complexes an alkenyl CH in α position would give a signal further downfield, even at 10 ppm).[20] As expected, the water ligand in **9** is labile, and the compounds **9·NCMe** and **9·CO** are readily synthesized by its

reaction with an excess of L [Eq. (13)]. The new iridacyclopentadienes have been fully characterized by microanalysis and spectroscopy (IR, ^{1}H and ^{13}C NMR studies) and in addition, the solid-state structure 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 of this kind of species seems to be very favorable, since the purported intermediate iridacyclohexadiene related to **8** has not been observed, even in the presence of 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 ºC for 15 min, also yields complex **10**, in almost quantitative yield. Unlike **2**, **10** is very stable, can be properly purified, and it 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 [Eq (15)]. 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 ^{1}H and ^{13}C{^{1}H} NMR spectra (see Experimental Section).



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

X-Ray diffraction studies

Table 2 presents 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** while Table 3 gives selected bond lengths and angles. The sp^3 carbon atom bonded to iridium forms an iridium-carbon bond with a length of 2.12 Å, a value typical of an Ir—C single bond.[22] The η^3-allyl—Ir interaction is characterized by Ir—C bond distances of Ir—C(1), 2.16; Ir—C(2), 2.10 and Ir—C(3), 2.18 Å and the C(1)—C(2)—C(3) angle of 121.4º is clearly in accord with almost pure sp^2 hybridization at the C(2) carbon.

INSERT TABLE 2 HERE

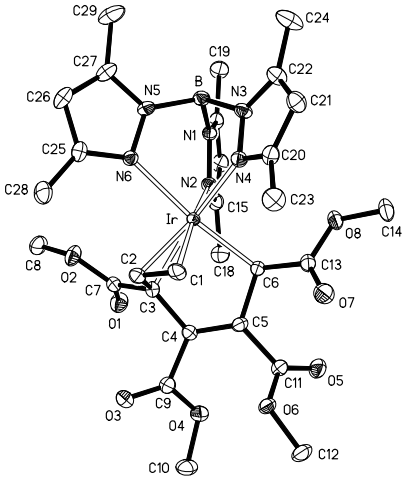


Figure 2. X-ray structure of complex **3** (thermal ellipsoids drawn at the 50% probability level).

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

Ir—N(6)	2.214(2)	Ir—C(2)	2.098(2)
Ir—C(3)	2.181(2)	C(5)—C(6)	1.507(3)
Ir—C(1)	2.164(2)	C(3)—C(4)	1.482(3)
Ir—N(2)	2.139(2)	C(2)—C(3)	1.442(3)
Ir—C(6)	2.118(2)	C(1)—C(2)	1.411(3)
Ir—N(4)	2.106(2)	C(4)—C(5)	1.366(3)
N(2)—Ir—N(6)	87.61(7)	C(1)—C(2)—C(3)	121.4(2)
N(4)—Ir—N(2)	90.68(7)	C(2)—C(3)—C(4)	116.4(2)
N(4)—Ir—N(6)	80.62(7)	C(5)—C(4)—C(3)	118.5(2)
C(6)—Ir—C(1)	87.48(9)	C(4)—C(5)—C(6)	117.4(2)
C(6)—Ir—C(3)	79.86(8)	C(5)—C(6)—Ir	110.06(15)
C(1)—Ir—C(3)	69.86(9)	C(2)—C(3)—Ir	67.21(12)

Complexes 7 and 7·CO: In Figures 3 and 4, the molecular structures of complexes **7** and **7·CO** are represented, while Table 4 collects selected bond lengths and angles. The first compound crystallized with *ca*. 1.25 molecules of additional water which form hydrogen bonds with the Ir—OH_2 moiety. The iridacyclopentadiene units in **7** and **7·CO** are almost planar, characterized by C—Ir—C bite angles of 79.3 and 78.6º, respectively, and all the Ir—C bond distances fall between 2.00 and 2.06 Å as expected for sp^2 carbons.[22] 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 av.) but this effect is rather diminished in **7·CO**.

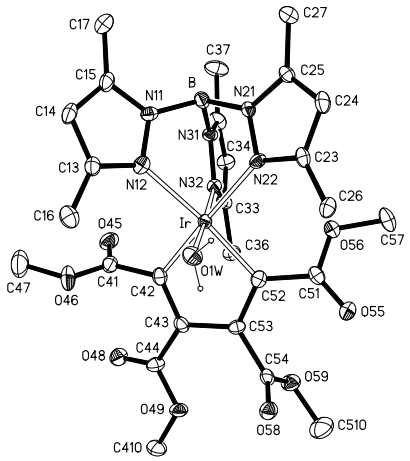


Figure 3. X-Ray structure of complex **7** (thermal ellipsoids drawn at the 50% probability level).

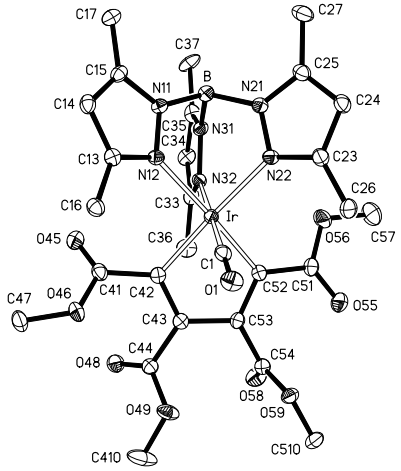


Figure 4. X-Ray structure of complex **7·CO** (thermal ellipsoids drawn at the 20% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complexes **7** and **7·CO**.

	7	**7·CO**
Ir—N(12)	2.171(5)	2.151(3)
Ir—N(22)	2.157(5)	2.128(3)
Ir—N(32)	2.035(4)	2.111(3)
Ir—C(42)	2.001(6)	2.055(4)
Ir—C(52)	2.037(6)	2.067(4)
Ir—L	2.091(3)	1.852(4)
C(42)—C(43)	1.368(8)	1.358(6)
C(43)—C(53)	1.463(9)	1.463(5)
C(52)—C(53)	1.375(8)	1.355(6)
C(42)—Ir—C(52)	79.3(2)	78.64(16)
C(42)—Ir—L	90.19(19)	85.45(17)
C(52)—Ir—L	87.72(18)	84.99(17)

Complex 8·NCMe: Figure 5 shows an ORTEP view of this compound and Table 5 collects selected bond lengths and angles. The Ir—C(alkenyl) distance (2.02 Å) compares well with those commented for the iridacyclopentadienes **7** and **7·CO** while the corresponding Ir—CH_2 is longer at 2.09 Å. In turn, this later bond is slightly shorter than the Ir—C(alkyl) present in complex **3** which supports a CO_2Me substituent. Of the three Ir—N(pyrazolyl) bonds, the one *trans* with respect to the NCMe is shorter (2.05 Å) than the other two (2.16 Å av.), and in that way the acetonitrile behaves like the H_2O ligand, another hard donor, in **7**.

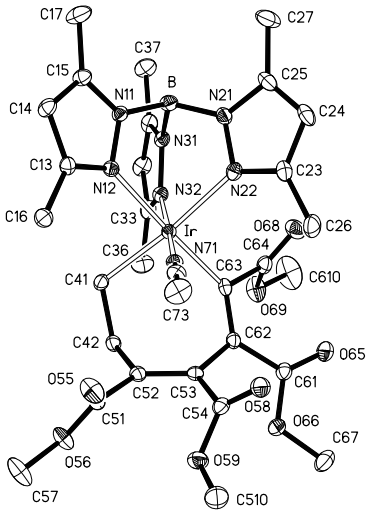


Figure 5. X-Ray structure of complex **8·NCMe** (thermal ellipsoids drawn at the 20% probability level.

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

Ir—N(12)	2.164(4)	C(41)—C(42)	1.545(6)
Ir—N(22)	2.157(4)	C(42)—C(52)	1.496(6)
Ir—N(32)	2.049(3)	C(53)—C(62)	1.477(6)
Ir—C(41)	2.091(4)	C(52)—C(53)	1.368(6)
Ir—C(63)	2.025(4)	C(62)—C(63)	1.354(6)
Ir—N(71)	1.976(3)	N(71)—C(72)	1.133(5)
N(22)—Ir—N(12)	84.47(13)	C(62)—C(63)—Ir	127.6(3)
N(32)—Ir—N(12)	88.30(13)	C(42)—C(41)—Ir	117.3(3)
N(32)—Ir—N(22)	89.85(16)	C(52)—C(42)—C(41)	110.6(4)
C(63)—Ir—C(41)	94.02(17)	C(53)—C(52)—C(42)	121.8(4)
N(71)—Ir—C(41)	92.68(18)	C(52)—C(53)—C(62)	122.4(4)
N(71)—Ir—C(63)	90.91(16)	C(63)—C(62)—C(53)	124.4(4)

Complex 9: The structure of this complex is shown in Figure 6, while 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_2O is shorter (2.04 Å) than the other two (2.15 Å av.). As commented in section Results, the Ir—C(alkenyl) bond that supports the CH functionality is more reactive against C_2H_4 insertion than the other similar one present in this molecule. From the corresponding bond distances, 2.04 *vs*. 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.[23]

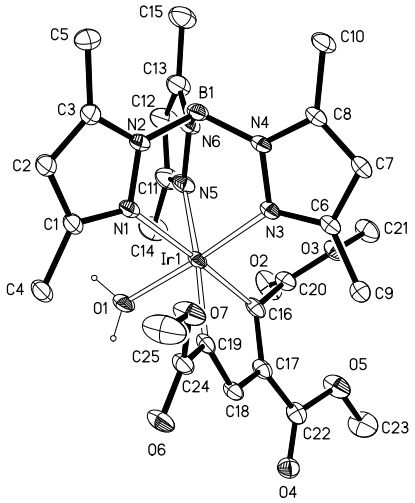


Figure 6. X-Ray structure of complex **9** (thermal ellipsoids drawn at the 40% probability level).

Table 6. Selected Bond Lengths (Å) and Angles (deg) for complex **9**.

Ir—N(1)	2.142(3)	Ir—O(1)	2.103(2)
Ir—N(3)	2.041(3)	C(16)—C(17)	1.363(5)
Ir—N(5)	2.155(3)	C(17)—C(18)	1.464(4)
Ir—C(16)	2.021(3)	C(18)—C(19)	1.357(4)
Ir—C(19)	2.039(3)		
C(16)-Ir(1)-C(19)	79.45(12)	C(16)-Ir(1)-N(1)	177.72(11)
C(16)-Ir(1)-N(3)	93.49(11)	C(19)-Ir(1)-N(1)	99.04(11)
C(19)-Ir(1)-N(3)	96.87(11)	O(1)-Ir(1)-N(1)	89.46(10)
C(16)-Ir(1)-O(1)	88.74(11)	C(16)-Ir(1)-N(5)	97.52(12)
C(19)-Ir(1)-O(1)	86.28(11)	C(19)-Ir(1)-N(5)	172.68(11)
N(3)-Ir(1)-O(1)	176.43(10)	O(1)-Ir(1)-N(5)	86.99(10)

Complex 9·NCMe: An ORTEP view of this molecule is shown in Figure 7 and selected bond length and angles are collected in Table 7. These are very similar to those found in **9** and will not be commented with the exception of the two Ir—C(alkenyl) bond distances. Interestingly, and in comparison with **9**, for the carbon that supports the CH group the Ir—C distance is much longer (2.03 Å) than the other one (1.97 Å).

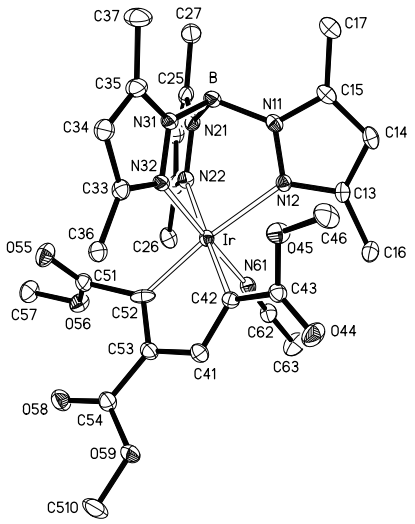


Figure 7. X-Ray structure of complex **9·NCMe** (thermal ellipsoids drawn at the 30% probability level).

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

Ir—N(22)	2.158(5)	Ir—N(61)	1.991(5)
Ir—N(12)	2.157(5)	C(41)—C(53)	1.410(9)
Ir—N(32)	2.044(4)	C(52)—C(53)	1.364(8)
Ir—C(42)	2.033(5)	C(41)—C(42)	1.351(8)
Ir—C(52)	1.974(7)	N(61)—C(62)	1.144(7)
N(12)-Ir-N(22)	82.98(17)	C(52)-Ir-C(42)	77.1(2)
N(32)-Ir-N(12)	89.91(17)	C(53)-C(52)-Ir	118.6(5)
N(32)-Ir-N(22)	88.38(18)	C(41)-C(42)-Ir	114.6(4)
N(61)-Ir-C(42)	87.8(2)	C(42)-C(41)-C(53)	115.8(6)
C(52)-Ir-N(61)	87.3(2)	C(52)-C(53)-C(41)	111.5(6)

Complex 10: The molecular structure of this compound is shown in Figure 8, while selected bond length and angles are collected in Table 8. The Ir—C(41) bond distance at 2.02 Å is in the expected range for an Ir—C(alkenyl) species while, for the olefin bonded to Ir, the C(45)—C(46) separation of 1.49 Å is much closer to the corresponding for a single C—C bond (1.54 Å) than for a double one (1.34 Å), and this probably reflects a quite strong Ir-olefin bond.

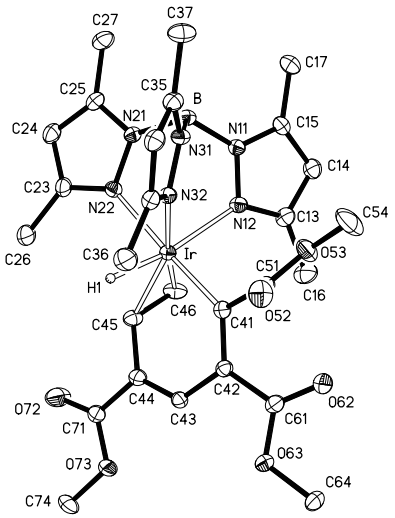


Figure 8. X-Ray structure of complex **10** (thermal ellipsoids drawn at the 40% probability level).

Table 8. Selected Bond Lengths (Å) and Angles (deg) for complex **10**

Ir—N(12)	2.193(2)	Ir—H(1I)	1.600
Ir—C(45)	2.180(3)	C(44)—C(45)	1.495(4)
Ir—N(22)	2.162(2)	C(42)—C(43)	1.460(4)
Ir—C(46)	2.138(3)	C(45)—C(46)	1.391(5)
Ir—N(32)	2.090(2)	C(41)—C(42)	1.363(4)
Ir—C(41)	2.015(3)	C(43)—C(44)	1.343(4)
N(22)-Ir-N(12)	87.79(9)	C(46)-Ir(1)-C(45)	37.56(13)
N(32)-Ir-N(12)	88.19(9)	C(42)-C(41)-Ir	129.1(2)
N(32)-Ir-N(22)	82.82(9)	C(44)-(45)-Ir	116.8(2)
C(41)-Ir-H(1I)	94.7(14)	C(41)-C(42)-C(43)	123.4(3)
C(41)-Ir-C(46)	92.93(13)	C(44)-C(43)-C(42)	127.1(3)
C(41)-Ir-C(45)	90.64(12)	C(43)-C(44)-C(45)	126.0(3)
C(45)-Ir-H(1H)	69.5(10)	C(46)-C(45)-C(44)	123.0(3)

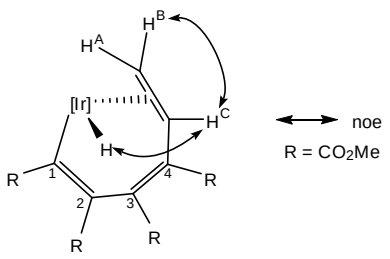
Conclusion

Two molecules of dimethyl acetylendicarboxylate, $MeO_2CC{\equiv}CCO_2Me$ (DMAD) couple in the coordination sphere of $Tp^{Me2}Ir(I)$ to give an unsaturated iridacyclopentadiene species which is very effectively trapped by water with formation of the adduct $Tp^{Me2}Ir(C(R)=C(R)C(R)=C(R))(H_2O)$ (R = CO_2Me). In a related process, 1 equiv. each of DMAD and methyl propiolate, $HC{\equiv}CCO_2Me$ (MP) give regioselectively $Tp^{Me2}Ir(C(R)=C(R)C(H)=C(R))(H_2O)$. 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 unsymmetrical 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-alkenyls by stereospecific migration of the hydride into the Ir-*C*(R)=C(R) functionality and concomitant bond reorganization of the resulting organic chain.

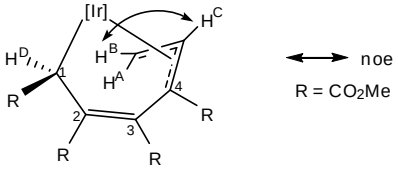
Experimental Section

General Procedures: Microanalyses were by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla). Infrarred spectra were obtained from 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 $SiMe_4$ (δ = 0 ppm) using the residual protio solvent peaks as internal standards (^{1}H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). Spectral assignments were made by means of routine one- and two-dimensional NMR experiments where appropriate. Manipulations were performed either in air or under oxygen-free dinitrogen, following conventional Schlenk techniques. The complexes $Tp^{Me2}Ir(C_2H_4)_2$ (**1**) and $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$ (**5**), were obtained by published procedures.[9,24] DMAD-d_6 was obtained by a transesterification reaction with CD_3OD in acidic media (*p*-$MeC_6H_4SO_3H$).

Complex 2: To a solution of compound **1** in CH_2Cl_2 (0.20 g, 0.37 mmol; 6 mL) $MeO_2CC{\equiv}CCO_2Me$ (0.09 mL, 0.73 mmol) was added and the mixture stirred at room temperature for 6 h. After this period of time a red solution is observed and the volatiles were removed under reduced pressure. The main compound, **2**, was characterized by NMR but it was not isolated pure due to its easy transformation into **3**. ^{1}H NMR ($CDCl_3$, 25 ºC): δ 6.39 (dd, 1 H, $^3J_{CA}$ = 11.5, $^3J_{CB}$ = 9.8 Hz, H^C), 5.89, 5.83, 5.59 (s, 1 H each, 3 CH_{pz}), 3.81, 3.74, 3.51, 3.04 (s, 3 H each, 4 CO_2Me), 3.63, 3.07 (m, 1 H each, H^A, H^B, resp.), 2.42, 2.35, 2.27, 2.22 (s, 1:1:2:2, 6 Me_{pz}), -16.91 (s, 1 H, Ir–H).^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ 174.8, 169.5, 167.6, 166.9 (*C*O_2Me), 156.6, 139.4, 133.4, 126.8 (C^1, C^3, C^2, C^4, resp.), 153.7, 152.9, 150.9, 144.8, 144.0, 143.5 (C_{qpz}), 108.7, 108.6, 106.6 (CH_{pz}), 57.9 (CH^C, $^1J_{CH}$ = 165 Hz), 52.7, 52.5, 52.0, 50.9 (CO_2*Me*), 42.0 (CH^AH^B, $^1J_{CH}$ = 165 Hz), 20.0-10.0 (Me_{pz}).



Complex 3: To a solution of **1** (0.20 g, 0.37 mmol) in dichlorometane (6 mL) was added an excess of $MeO_2CC{\equiv}CCO_2Me$ (0.135 mL, 1.10 mmol) and the resulting mixture stirred for 6 h at 60 ºC. After this period, the solvent was evaporated under vacuo and the solid residue was shown by ^{1}H NMR to contain the title compound, in almost quantitative yield. Complex **3** was obtained, as yellow crystals, by the slow diffusion of hexane into a dichlorometane solution at room temperature. ^{1}H NMR ($CDCl_3$, 25 ºC) δ: 7.07 (dd, 1 H, $^3J_{CA}$ ≈ 10.0, $^3J_{CB}$ ≈ 7.5 Hz, H^C), 5.90, 5.73, 5.51 (s, 1 H each, 3 CH_{pz}), 4.84 (s, 1 H, H^D), 4.09 (dd, 1 H, $^2J_{BA}$ ≈ 2.2 Hz, H^B), 3.70, 3.61, 3.43, 3.25 (s, 3 H each, 4 CO_2Me), 2.94 (dd, 1 H, H^A), 2.46, 2.42, 2.32, 2.20, 2.19, 2.16 (s, 3 H each, 6 Me_{pz}). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC) δ: 182.2 (br, CH^DCO_2Me), 174.5, 166.7, 166.1 (*C*O_2Me), 154.2, 152.8, 151.7, 144.7, 143.6, 143.3 (C_{qpz}), 148.3, 137.5 (C^3, C^2), 109.8, 108.7, 107.7 (CH_{pz}), 91.2 (CH^C, $^1J_{CH}$ = 170 Hz), 53.0 (C^4), 52.2, 51.9, 51.7, 50.8 (CO_2*Me*), 25.2 (CH^AH^B $^1J_{CH}$ = 166 and 155 Hz), 16.3, 15.1, 13.6, 13.3, 12.9, 12.7 (Me_{pz}), 12.0 (CH^D, $^1J_{CH}$ = 135 Hz). Anal. Calc. for $C_{29}H_{38}BIrN_6O_8$: C, 43.4; H, 4.7; N, 10.5. Found: C, 43.1; H, 4.8; N, 10.2.



Complex 4: To a solution of compound **1** in CD_2Cl_2 at -50 ºC (0.03 g, 0.055 mmol; 0.5 mL) $MeO_2CC{\equiv}CCO_2Me$ (0.007 mL, 0.055 mmol) was added. The ^{1}H NMR spectrum at this temperature showed the instantaneous and quantitative formation of **4**, stable up to 10 ºC. ^{1}H NMR (CD_2Cl_2, -10 ºC): δ 5.99, 5.48 (s, 2:1, 3 CH_{pz}), 3.70 (s, 6 H, 2 CO_2Me), 3.14 (s, 4 H, C_2H_4), 2.66, 2.39, 2.19, 2.09 (s, 2:2:1:1, 6 Me_{pz}). ^{13}C{^{1}H} NMR (CD_2Cl_2, -10 ºC): δ 160.4 (*C*O_2Me), 153.8, 151.7, 145.7, 143.9 (2:1:1:2, C_{qpz}), 109.2, 108.0 (1:2, CH_{pz}), 78.6 (*C*CO_2Me), 52.3 (CO_2*Me*), 51.1 (C_2H_4, $^1J_{CH}$ = 162 Hz), 16.4, 16.1, 13.5, 12.8 (1:2:1:2, Me_{pz}). ^{11}B{^{1}H} NMR (CD_2Cl_2, -10 ºC): δ 32.5.

Complex 7: To a solution of compound **5** in cyclohexane (1 g, 1.75 mmol; 15 mL), $MeO_2CC{\equiv}CCO_2Me$ (0.43 mL, 3.50 mmol) and an excess of water (0.3-0.4 g, ≥10 equiv.) were added and the mixture stirred at 60 ºC 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}H NMR). The crude product was crystallized from a mixture of hexane:CH_2Cl_2 (1:2) at -20 ºC in 94% yield (brown crystals). IR (Nujol): ν(OH) 3372 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 ºC): δ 5.74, 5.49 (s, 2:1, 3 CH_{pz}), 3.61, 3.30 (s, 6 H each, 4 CO_2Me), 2.36, 2.06, 1.91 (s, 3:2:1, 6 Me_{pz}). The H_2O resonance has not been located. ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ 173.6, 168.7 (*C*O_2Me), 155.4, 151.4, 143.7, 143.2 (1:2:2:1, C_{qpz}), 155.0, 150.6 (*C*CO_2Me), 107.6, 106.8 (1:2, CH_{pz}), 52.4, 51.1 (CO_2*Me*), 13.5, 13.4, 12.8, 12.2 (2:1:2:1, Me_{pz}). Anal. Calc. for $C_{27}H_{36}BN_6O_9Ir{\cdot}1.25\ H_2O$: C, 39.8; H, 4.7; N, 10.3. Exp.: C, 39.3; H, 4.6; N, 10.3.

Complex 7·NCMe: A solution of compound **7** in CH_3CN (0.05 g, 0.06 mmol; 3 mL) was stirred at 60 ºC 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:CH_2Cl_2 (1:1) at -20 ºC (yellow crystals). IR (Nujol): ν(CN) 2246 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 ºC): δ 5.73, 5.52 (s, 2:1, 3 CH_{pz}), 3.71, 3.35 (s, 6 H each, 4 CO_2Me), 2.43 (s, 3 H, MeCN), 2.32, 2.14, 2.02 (s, 3:2:1, 6 Me_{pz}). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ 173.1, 167.0 (*C*O_2Me), 155.4, 150.7, 143.6, 142.5 (1:2:2:1, C_{qpz}), 150.1, 148.7 (*C*CO_2Me), 116.0 (N*C*Me), 107.9, 106.6 (1:2, CH_{pz}), 51.6, 50.7 (CO_2*Me*), 14.2, 13.1, 12.5, 12.2 (2:1:2:1, Me_{pz}), 3.8 (NC*Me*). Anal. Calc. for $C_{29}H_{37}BN_7O_8Ir{\cdot}\ CH_2Cl_2$: 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** in C_6H_{12} (0.05 g, 0.06 mmol; 3 mL) was placed in a Fischer-Porter vessel. The stirred mixture was heated, under 2 atm. of CO, at 90 ºC for 12 h. After this period of time a pale brown precipitate was formed and the volatiles were removed in vacuum. This crude **7·CO** was crystallized from hexane:CH_2Cl_2 (1:1) at -20 ºC. IR (Nujol): ν(CO) 2055 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 ºC): δ 5.80, 5.67 (s, 2:1, 3 CH_{pz}), 3.74, 3.41 (s, 6 H each, 4 CO_2Me), 2.35, 2.33, 2.22, 2.17 (s, 1:2:2:1, 6 Me_{pz}). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 ºC): δ 171.3, 166.1 (*C*O_2Me), 159.4 (CO), 155.5, 151.4, 144.5, 143.3 (1:2:2:1, C_{qpz}), 151.6, 138.0 (*C*CO_2Me), 109.0, 106.9 (1:2, CH_{pz}), 51.8, 51.2 (CO_2*Me*), 14.8, 13.0, 12.5, 12.4 (2:1:2:1, Me_{pz}). Anal. Calc. for $C_{28}H_{34}BN_6O_9Ir{\cdot}\ CH_2Cl_2$: C, 39.3; H, 4.1; N, 9.5. Found: C, 39.5; H, 3.9; N, 9.5.

Reaction of 7 with DMAD: To a solution of **7** in cyclohexane (0.03 g, 0.038 mmol; 3 mL) $MeO_2CC{\equiv}CCO_2Me$ (0.014 mL, 0.114 mmol) was added and the mixture stirred at 100 ºC for 18 h. After removing the volatiles under reduced pressure, quantitative conversion into the known complex **6**[8a] was ascertained by ^{1}H NMR.

Complex 8: Compound **7** (0.30 g, 0.38 mmol) was dissolved in $CHCl_3$ (9 mL, passed previously through a silica column to remove the ethanol stabilizer) and C_2H_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 room temperature. After this period of time a pale yellow precipitate of **8** was separated from the dark brown mother liquor and dried inder vacuo (yield: 0.14 g, *ca.* 45%). It was crystallized from a mixture of $CHCl_3$:acetone (1:1) at -20 ºC (pale yellow crystals). IR (Nujol): ν(OH) 3370 cm^{-1}. ^{1}H NMR (acetone-d_6, 25 ºC): δ 5.75, 5.73, 5.70 (s, 1 H each, 3 CH_{pz}), 3.88, 3.64, 3.50, 2.91 (s, 3 H each, 4 CO_2Me), 3.37, 2.90 (dt, m, 1 H each, $^2J_{HH}$ = 11.9, $^3J_{HH}$ = 3.7 Hz,

IrC*H*$_2$CH$_2$), 2.80 (br s, 2 H, H_2O), 2.71, 2.17 (ddd, dt, 1 H each, $^3J_{HH}$ = 14.2, $^2J_{HH}$ = 10.7 Hz, IrCH$_2$C*H*$_2$), 2.42, 2.39, 2.35, 2.30, 2.14, 2.09 (s, 3 H each, 6 Me$_{pz}$). $^{13}C\{^1H\}$ NMR (acetone-d_6, 25 ºC): δ 178.2, 175.3, 170.1, 166.2 (*C*O_2Me), 164.4, 140.8, 135.6, 130.8 (*C*O_2Me), 154.6, 152.7, 151.2, 144.9, 144.3, 142.7 (C$_{qpz}$), 108.8, 108.4, 107.0 (CH$_{pz}$), 53.1, 52.0, 51.0, 50.1 (O_2*Me*), 35.3 (IrCH$_2$*C*H$_2$, $^1J_{CH}$ = 129 Hz), 15.5, 14.2, 13.4, 13.3, 12.5, 12.3 (Me$_{pz}$), -2.6 (Ir*C*H$_2$CH$_2$, $^1J_{CH}$ = 123 Hz). Anal. Calc. for $C_{29}H_{40}BN_6O_9Ir\cdot0.5\ CHCl_3$**:** C, 41.7; H, 4.5; N, 9.9. Exp.: C, 41.5; H, 4.5; N, 9.7.

Complex 8·NCMe: A solution of compound **8** in CH_3CN (0.015 g, 0.018 mmol; 6 mL) was stirred at room temperature for 14 h. After this time the solvent was removed under reduced pressure and the crude product was purified by crystallization from hexane:CH_2Cl_2 at -20 ºC (pale yellow crystals). IR (Nujol): υ(CN) 2360 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 ºC): δ 5.77, 5.68 (s, 1:2, 3 CH$_{pz}$), 3.83, 3.68, 3.58, 3.04 (s, 3 H each, 4 CO_2Me), 2.78, 2.70 (dt, td, 1 H each, $^2J_{HH}$ = 12.7, $^3J_{HH}$ = 3.2 Hz, IrC*H*$_2$CH$_2$), 2.64, 2.33 (td, 1 H each, $^2J_{HH}$ = $^3J_{HH}$ = 12.5 Hz, IrCH$_2$C*H*$_2$), 2.38 (s, 3 H, MeCN), 2.36, 2.34, 2.32, 2.29, 2.24, 2.15 (s, 3 H each, 6 Me$_{pz}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ 177.1, 171.9, 165.9, 163.4 (*C*O_2Me), 170.0, 140.6, 135.9, 130.8 (*C*O_2Me), 152.8, 151.2, 150.0, 143.8, 143.4, 142.0 (C$_{qpz}$), 119.3 (Me*C*N), 108.2, 107.9, 106.4 (CH$_{pz}$), 52.1, 51.9, 51.3, 50.4 (O_2*Me*), 35.3 (IrCH$_2$*C*H$_2$), 15.4, 14.1, 13.8, 13.3, 12.6, 12.5 (Me$_{pz}$), 4.5 (*Me*CN), -1.7 (Ir*C*H$_2$CH$_2$). Anal. Calc. for $C_{31}H_{41}BN_7O_8Ir$**:** C, 44.2; H, 4.9; N, 11.6. Found: C, 44.0; H, 4.7; N, 11.3.

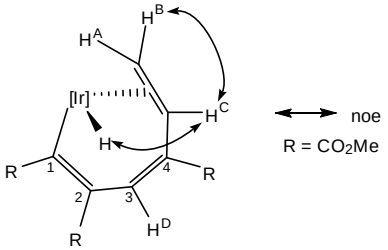
Complex 8·CO: A solution of compound **8** in C_6H_{12} (0.015 g, 0.020 mmol; 2 mL) was placed in a Fischer-Porter vessel. The stirred mixture was heated, under 2 atm. of CO, at 60 ºC for 14 h. After this period of time, the volatiles were removed in vacuum and the crude product was crystallized from hexane:CH_2Cl_2 (1:1) at -20 ºC (white crystals). IR (Nujol): υ(CO) 2035 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 ºC): δ 5.82, 5.81, 5.76 (s, 1 H each, 3 CH$_{pz}$), 3.88, 3.70, 3.61, 3.10 (s, 3 H each, 4 CO_2Me), 2.86, 2.79 (m, 1 H each, IrC*H*$_2$CH$_2$), 2.35, 2.28 (m, 1 H each, IrCH$_2$C*H*$_2$), 2.40, 2.35, 2.30, 2.28 (s, 1:2:1:2, 6 Me$_{pz}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ 173.9, 171.1, 167.1, 165.8 (*C*O_2Me), 164.6 (CO), 152.5, 152.2, 151.0, 144.5, 144.4, 142.8 (C$_{qpz}$), 150.4, 147.0, 134.0, 133.8 (*C*O_2Me), 108.4, 108.0, 106.8 (CH$_{pz}$), 52.2, 52.0, 51.7, 50.9 (O_2*Me*), 35.1 (IrCH$_2$*C*H$_2$), 15.5, 14.4, 14.3, 13.1, 12.7, 12.5 (Me$_{pz}$), 5.2 (Ir*C*H$_2$CH$_2$). Anal. Calc. for $C_{30}H_{38}BN_6O_9Ir$**:** 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 ºC and $MeO_2CC{\equiv}CCO_2Me$ (0.11 mL, 0.92 mmol) was added. The mixture was stirred at -20 ºC for 5 min. and then some water (≈ 10 equiv.) and $MeO_2CC{\equiv}CH$ (0.08 mL, 0.92 mmol) were added. After 10 min. of stirring at -20 ºC the resulting solution was allowed to stir at room temperature for 1 h. After this period, the volatiles were removed under reduced pressure and the crude product was purified by crystallization from Et_2O:CH_2Cl_2 (3:1) at -20 ºC in 47% yield (pale brown crystals). IR (Nujol): ν(OH) 3400 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 ºC): δ 7.75 (s, 1 H, CH), 5.66, 5.57, 5.45 (s, 1 H each, 3 CH$_{pz}$), 3.56, 3.05 (s, 1:2, 3 CO_2Me), 2.33, 2.32, 2.30, 1.76, 1.75, 1.50 (s, 3 H each, 6 Me$_{pz}$). The coordinated H_2O has not been located. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ 176.1, 172.1, 164.9 (*C*O_2Me), 170.3, 146.6, 140.2 (br, *C*CO_2Me), 155.1, 151.7, 151.0, 143.7, 143.5, 143.0 (C$_{qpz}$), 153.3 (br, CH, $^1J_{CH}$ = 159 Hz), 106.9, 106.5, 105.8 (CH$_{pz}$), 51.1, 50.3, 50.2 (CO_2*Me*), 13.0, 12.9, 12.3, 12.3 (1:1:1:3, Me$_{pz}$). Anal. Calc. for $C_{25}H_{34}BN_6IrO_7$: C, 40.9; H, 4.6; N, 11.4. Found: C, 40.7; H, 4.5; N, 10.9.

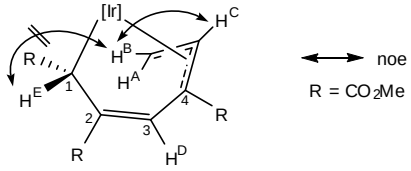
Complex 9·NCMe: A solution of compound **9** in CH_3CN (0.015 g, 0.020 mmol; 2 mL) was stirred at 50 ºC for 5 h. After this time, the solvent was removed under reduced pressure and the crude product crystallized by pentane diffusion into a CH_2Cl_2 solution (dark yellow crystals). IR (Nujol): υ(CN) 2248 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 ºC): δ 7.82 (s, 1 H, CH), 5.75, 5.74, 5.50 (s, 1 H each, 3 CH$_{pz}$), 3.65, 3.42, 3.36 (s, 3 H each, 3 CO_2Me), 2.36 (s, 3 H, MeCN), 2.34, 2.32, 2.22, 2.02, 1.91 (s, 2:1:1:1:1, 6 Me$_{pz}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ 175.6, 172.1, 164.5 (*C*O_2Me), 164.2, 146.3, 134.9 (*C*CO_2Me), 155.0, 151.0, 150.2, 143.7, 143.2, 142.6 (C$_{qpz}$), 152.7 (CH, $^1J_{CH}$ = 159 Hz), 115.4 (Me*C*N), 107.7, 106.7, 106.1 (CH$_{pz}$), 51.1, 50.8, 50.6 (CO_2*Me*), 14.3, 13.8, 13.2, 12.5, 12.5, 12.4 (Me$_{pz}$), 3.8 (*Me*CN). Anal. Calc. for $C_{27}H_{35}BN_7O_6Ir\cdot0.5\ CH_2Cl_2$**:** 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** in C_6H_{12} (0.20 g, 0.27 mmol; 3 mL) was placed in a Fischer-Porter vessel. The stirred mixture was heated, under 2 atm. of CO, at room temperature for 14 h. After this period of time, the volatiles were removed in vacuum and the crude product was crystallized from hexane:Et_2O (1:1) at -20 ºC (0.12 g, yield: 60%, white crystals). IR (Nujol): υ(CO) 2047 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 ºC): δ 7.88 (s, 1 H, CH), 5.80, 5.63 (s, 2:1, 3 CH$_{pz}$), 3.73, 3.49, 3.45 (s, 3 H each, 3 CO_2Me), 2.33, 2.30, 2.09, 2.05 (s, 3:1:1:1, 6 Me$_{pz}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ 173.4, 170.4, 164.0 (*C*O_2Me), 160.0 (CO), 154.9, 151.8, 150.5, 144.6, 144.0, 143.2 (C$_{qpz}$), 153.9 (CH, $^1J_{CH}$ = 162 Hz), 151.0, 148.2, 127.3 (*C*CO_2Me), 108.7, 107.0, 106.5 (CH$_{pz}$), 51.6, 51.2, 51.2 (CO_2*Me*), 14.8, 14.7, 13.0, 12.7, 12.6, 12.6 (Me$_{pz}$). Anal. Calc. for $C_{26}H_{32}BN_6O_7Ir$**:** C, 42.0; H, 4.3; N, 11.3. Found: C, 41.5; H, 4.2; N, 10.8.

Complex 10: (**a**) A solution of compound **1** in CH_2Cl_2 (0.20 g, 0.37 mmol; 8 mL) was cooled at -20 ºC and $MeO_2CC{\equiv}CCO_2Me$ was added (0.045 mL, 0.37 mmol). After stirring 10 min. at this temperature, $MeO_2C{\equiv}CH$ (0.03 mL, 0.37 mmol) was added and the resulting solution was stirred at room temperature for 1 hour. The volatiles were removed under vacuo and complex **10** was isolated by column chromatography on silica gel, using a 5:1 mixture of hexane:Et_2O as eluent. Yield: 0.18 g (70%). An analytically pure sample was obtained by crystallization from pentane:CH_2Cl_2 (1:1) at -20 ºC (dark yellow crystals). (**b**) Through a solution of complex **9** in $CHCl_3$ (0.03 g, 0.04 mmol; 9 mL passed previously through a column on silica gel to eliminate the ethanol stabilizer) C_2H_4 was bubbled for 10 min. and the resulting solution was left, without stirring, under C_2H_4 in a sealed ampoule for 14 hours at room temperature. The solvent was removed under reduced pressure and quantitative conversion into compound **10** was ascertained by ^{1}H NMR. IR (Nujol): ν(Ir–H) 2199 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 ºC): δ 7.50 (s, 1 H, H^D), 6.73 (dd, 1 H, $^3J_{CA}$ = 11.2, $^3J_{CB}$ = 9.7 Hz, H^C), 5.92, 5.79, 5.58 (s, 1 H each, 3 CH$_{pz}$), 3.84, 3.62, 3.06 (s, 3 H each, 3 CO_2Me), 3.66, 3.01 (d, 1 H each, H^A, H^B, resp.), 2.43, 2.32, 2.31, 2.26, 2.24, 2.13 (s, 3 H each, 6 Me$_{pz}$), -16.91 (s, 1 H, Ir–H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ 175.3, 167.6, 165.6 (*C*O_2Me), 162.0 (C^1), 153.8, 152.3, 150.9, 144.4, 143.8, 143.4 (C$_{qpz}$), 137.3 (C^3, $^1J_{CH}$ = 161 Hz), 130.2 (C^2), 123.8 (C^4), 108.7, 108.6, 106.6 (CH$_{pz}$), 60.9 (CH^C, $^1J_{CH}$ = 165 Hz), 52.0, 51.7, 50.6 (C$^4CO_2$*Me*, C$^2CO_2$*Me*, C$^1CO_2$*Me*, resp.), 43.0 (CH^{A}H^B, $^1J_{CH}$ = 162 Hz), 16.6, 16.3, 15.7, 12.9, 12.8, 12.8 (Me$_{pz}$). Anal. Calc. for $C_{27}H_{33}BN_6O_6Ir$**:** C, 40.6; H, 4.6; N, 10.1. Exp.: C, 40.8; H, 4.5; N, 10.3.



Complex 11: (**a**) A solution of compound **1** in CH_2Cl_2 (0.20 g, 0.37 mmol; 8 mL) was cooled at -20 ºC and $MeO_2CC{\equiv}CCO_2Me$ was added (0.045 mL, 0.37 mmol). After stirring 10 minutes at this temperature, $MeO_2C{\equiv}CH$ (0.03 mL, 0.37 mmol) was added and the resulting solution was stirred at 80 ºC for 24 h. After this period of time, the solvent was evaporated under reduced pressure and the crude product cystallized from pentane:CH_2Cl_2 (1:1) at -20 ºC (pale yellow crystals). (**b**) A solution of compound **10** in CH_2Cl_2 (0.03 g, 0.04 mmol; 2 mL) was stirred at 80 ºC for 24 h. The volatiles were removed under reduced pressure and quantitative conversion into compound **11** was ascertained by ^{1}H NMR. ^{1}H NMR ($CDCl_3$, 25 ºC): δ 7.10 (dd, 1 H, $^3J_{CA}$ = 10.1, $^3J_{CB}$ = 7.8 Hz, H^C), 6.77 (s, 1 H, H^D), 5.86, 5.74, 5.50 (s, 1 H each, 3 CH$_{pz}$), 4.26 (br s, 1 H, H^E), 4.07, 3.10 (s, br s, 1 H each, H^B, H^A, resp.), 3.62, 3.56, 3.32 (s, s, br s, 3 H each, 3 CO_2Me), 2.47, 2.42, 2.34, 2.20, 2.05 (s, 1:1:1:2:1, 6 Me$_{pz}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 ºC): δ 175.5 (*C*O_2Me), 174.8, 167.7 (br, *C*O_2Me), 155.2 (br, C$_{qpz}$), 152.5, 151.6, 144.8, 143.4, 143.2 (C$_{qpz}$), 140.3 (br, C^3, $^1J_{CH}$ = 160 Hz), 109.7, 108.5, 107.8 (CH$_{pz}$), 91.9 (CH^C, $^1J_{CH}$ = 167 Hz), 53.7 (br, C^4), 51.9, 51.6 (CO_2*Me*), 50.7 (br, CO_2*Me*), 23.9 (br, CH^{A}H^B), 16.3, 15.2 (br, Me$_{pz}$), 14.0, 13.3, 13.0, 12.7 (Me$_{pz}$), 12.0 (br, C^1). The broad signals have been assigned with the help of the long range HETCOR spectrum. C^2 has not been located. Anal. Calc. for $C_{27}H_{36}BN_6O_6Ir$**:** 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 on Bruker Smart APEX CCD system or a Bruker-Nonius X8kappa APEX II CCD system (for **9**) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and 0.3° ω-scan frames covering complete spheres of the reciprocal space with θ_{max} = 27-30°. After data integration with program SAINT corrections for absorption, $\lambda/2$ effects, and crystal decay were applied with SADABS.[25] The structures were solved by direct methods using the program SHELXS97. Structure refinement on F^2 was carried out with the program SHELXL97.[26] All non-hydrogen atoms were refined anisotropically. Most H atoms were placed in calculated positions and thereafter treated as riding. A torsional parameter was refined for each pyrazole bound methyl group. The hydride H-atom in **10**·CH_2Cl_2 was refined in x,y,z using a Ir-H distance restraint of 1.60 Å. Moderate disorder encountered in **7**·~1.25H_2O (one water molecule with partial occupancy), **9**·(Et_2O, THF) (mixed occupation of a solvent cavity by tetrahydrofuran and diethylether in 1:1 ratio, both solvents hydrogen bonded to the water molecule of the Ir complex) and **10**·CH_2Cl_2 (two pseudo-mirror related orientations of C(45)-C(46) in 9:1 ratio) was taken into account. Crystal data and experimental details are given in Table 2.

CCDC 204945, 232726, and 624619 to 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**.

Acknowledgements

Financial support from the Spanish Ministry of Science (Projects CTQ2004-00409, FEDER support, and HU2003-039) and the Junta de Andalucía is gratefully acknowledged. N.R. thanks the MEC for a research grant.

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Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

Table 2. Crystal Data and Data collection and Refinement Details for **3**, **7·~1.25H$_2$O**, **[7·CO]**·CH_2Cl_2, **8·NCMe**, **9**·(Et_2O, THF), [**9·NCMe**]·CH_2Cl_2 and **10·CH$_2$Cl$_2$**.

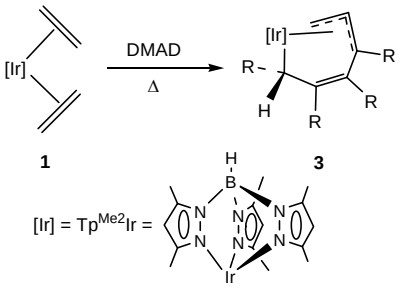
	3	**7**·~1.25H_2O	**[7·CO]**·CH_2Cl_2	**8·NCMe**	**9**·(Et_2O, THF)	**[9·NCMe]**·CH_2Cl_2	**10**·CH_2Cl_2
formula	$C_{29}H_{38}BIrN_6O_8$	$C_{27}H_{38.5}BIrN_6O_{10.25}$	$C_{29}H_{36}BCl_2IrN_6O_9$	$C_{31}H_{41}BIrN_7O_8$	$C_{29}H_{43}BIrN_6O_8$	$C_{28}H_{37}BCl_2IrN_7O_6$	$C_{28}H_{38}BCl_2IrN_6O_6$
mol wt	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, space group	Triclinic, *P*-1	Orthorhombic, $P2_12_12_1$	Triclinic, *P*-1	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1$/n	Monoclinic, $P2_1$/c	Monoclinic, $P2_1$/n
a, Å	10.0964(15)	13.911(1)	10.6366(12)	11.2309(5)	11.2041(7)	14.4962(10)	11.9764(6)
b, Å	10.9412(16)	14.533(1)	11.1646(12)	16.0105(7)	15.5675(9)	14.5804(10)	19.6942(10)
c, Å	15.692(2)	16.558(1)	15.8432(16)	19.2018(8)	18.7603(9)	17.1747(12)	14.4471(7)
α, deg	81.541(3)	90	104.610(3)	90	90	90	90
β, deg	85.535(3)	90	106.720(3)	90	97.796(2)	114.613(1)	104.229(1)
γ deg	64.231(3)	90	97.060(3)	90	90	90	90
V, Å^3	1543.9(4)	3347.5(4)	1704.4(3)	3452.7(3)	3241.9(3)	3300.2(4)	3303.0(3)
Z	2	4	2	4	4	4	4
D_{calcd}, g cm^{-3}	1.724	1.615	1.727	1.621	1.653	1.694	1.666
μ, mm^{-1}	4.384	4.050	4.134	3.926	4.176	4.259	4.253
θ range, deg	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
temp, K	123(2)	123(2)	100(2)	298(2)	100(2)	173(2)	173(2)
no. of data collected	27579	30258	31327	42593	36347	35326	60962
no. of unique data	8747 [*R*(int) = 0.0187]	7273 [R(int) = 0.0427]	9762 [R(int) = 0.0379]	7524 [R(int) = 0.0581]	9807 [R(int) = 0.0314]	9588 [R(int) = 0.0444]	9476 [R(int) = 0.0235]
no. of params/restraints	418/0	432/6	443/0	441/0	451/131	416/0	416/6
R1[a] ($F^2 > 2\sigma(F^2)$)	0.0185	0.0301	0.0372	0.0284	0.0311	0.0417	0.0262
wR2[b] (all data)	0.0434	0.0723	0.0925	0.0575	0.0777	0.1163	0.0578

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

Ir-mediated C-C coupling

Eleuterio Álvarez, Margarita Paneque, Cristina M. Posadas, Manuel L. Poveda,* Nuria Rendón, and Kurt Mereiter*

Investigations on the Coupling of Ethylene and Alkynes in $Tp^{Me2}Ir$ Compounds: Water as an Effective Trapping Agent



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

Unrevealing coupling mechanism: The bis(ethylene) complex **1** reacts with $MeO_2CC{\equiv}CCO_2Me$ to give the alkyl-allyl derivative **3** as the result of the coupling of one ethylene ligand and two alkyne molecules. A detailed study has shown the intermediacy of at least four organometallic species *en route* to **3**.