Reactivity of the Iridium(I) Alkene/Alkyne Complex $Tp^{Me2}Ir(C_2H_4)(MeO_2CC{\equiv}CCO_2Me)$

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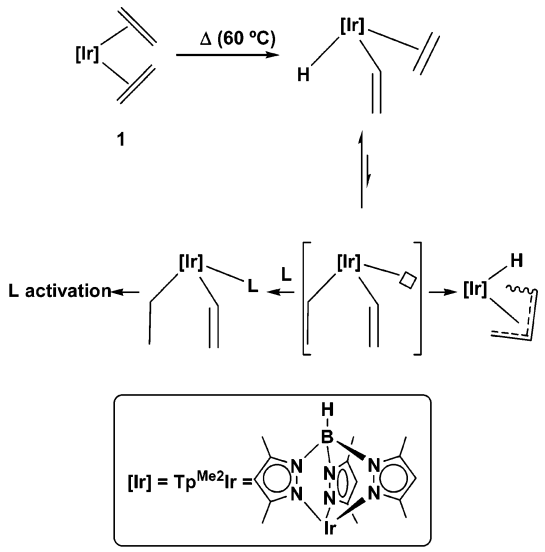
$Tp^{Me2}Ir(C_2H_4)_2$ (**1**; Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate) reacts with 1 equiv of $MeO_2CC{\equiv}CCO_2Me$ (DMAD) at 25 °C, via the intermediacy of the known Ir(I) adduct $Tp^{Me2}Ir(C_2H_4)$(DMAD) (**2**), with formation of the bis(alkenyl) derivative $Tp^{Me2}Ir$(*cis*-C(R)═C(R)H)(CH═CH_2)(C_2H_4) (**3**; R = CO_2Me) in ca. 50% yield. Complex **3** slowly evolves to another alkenyl species, $Tp^{Me2}Ir$(*cis*-C(R)═C(R)H)($CH_2CH_2CH{=}CH_2$) (**4**), which exists as a mixture of two stereoisomers. Interestingly, complex **2** reacts with the hard Lewis base NCMe at −20 °C, giving the Ir(I) adduct Tp^{Me2}-Ir(DMAD)(NCMe) (**5**) the first Ir(I) compound of the $Tp^{Me2}Ir$ system with a hard ligand. The Ir−NCMe bond in **5** is labile, and the acetonitrile is easily interchanged by CO, C_2H_4, and the alkynes $HC{\equiv}CCO_2$-Me (MP) and DMAD. While with CO the reaction stops at the substitution stage with formation of $Tp^{Me2}Ir$(DMAD)(CO) (**8**), with C_2H_4 it gives complex **4** or the bis(alkenyl) species $Tp^{Me2}Ir$(*cis*-C(R)═C(R)H)(CH═CH_2)(NCMe) (**9**), depending on the concentration of NCMe in the reaction medium. With MP the known iridacyclopentadiene $Tp^{Me2}Ir$(C(R)═C(H)C(R)═C(R))(NCMe) (**10**) and the symmetrical iridacycloheptatriene $Tp^{Me2}Ir$(C(R)═C(H)C(R)═C(R)C(H)═C(R)(NCMe) (**11**) can be obtained, while related iridacycles are formed with DMAD. Finally an iridapyrrole with the composition $Tp^{Me2}Ir$(Cl)(C(R)═C(R)C(Me)═NH) (**6**) is the unexpected result of heating complex **5** in a CH_2Cl_2−NCMe mixture at 120 °C. All of the new compounds reported have been characterized by microanalysis and IR and NMR spectroscopy and, in addition, complexes **4** and **6** have been characterized by single-crystal X-ray studies.

Introduction

During the last 15 years, the reactivity of the Ir(I) bis-(ethylene) complex $Tp^{Me2}Ir(C_2H_4)_2$ (**1**; Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate)[1] has been extensively studied by our research group.[2] This compound transforms thermally, by a C−H activation process (Scheme 1), into a reactive unsaturated ethyl−vinyl intermediate which subsequently can interact with molecules L either by forming simple adducts (L = NCMe, py, DMSO, etc.) or by activating them (L = C_6H_6, thiophenes, ethers, etc.). In the context of the present report it is important to highlight that NCMe does not react with the metal center until oxidation to Ir(III) has taken place, and this is not entirely unexpected in view of the hard nature of the N-donor base and the soft nature of the Ir(I) center. In contrast, the reaction of compound **1** with 1 equiv of soft bases proceeds, at low temperature, as depicted in eq 1, i.e., by substitution of one ethylene ligand by the Lewis base, and if the resulting complex is heated at a temperature high enough (depending on the nature of L), the C−H activation of the olefin takes place.

Scheme 1



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(1) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (b) Parkin, G. *Adv. Inorg. Chem.* **1995**, *42*, 291. (c) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 418. (d) Trofimenko, S. *Scorpionates. The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.
(2) (a) Carmona, E.; Paneque, M.; Poveda, M. L. *Dalton Trans.* **2003**, 4022. (b) Carmona, E.; Paneque, M.; Santos, L. L.; Salazar, V. *Coord. Chem. Rev.* **2005**, *294*, 1729.

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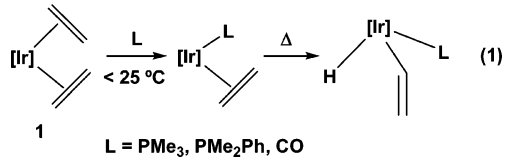
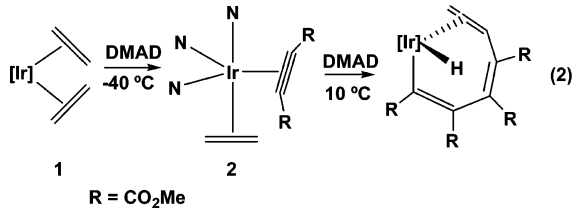


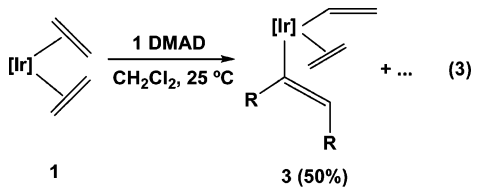
In this paper we report on the different results obtained in the study of the reactivity of the recently described Ir(I) adduct $Tp^{Me2}Ir(C_2H_4)(DMAD)$ (**2**; DMAD = $MeO_2CC{\equiv}CCO_2Me$).[3] This compound is prepared by the low-temperature reaction of compound **1** with DMAD. It is stable up to 10 °C, when it reacts with a second equivalent of the alkyne, as depicted in eq 2. It



is worthwhile to recall that in complex **2**, in contrast with the Ir(I)−olefin species represented in eq 1, the ethylene ligand occupies an axial position of the trigonal-bipyramidal coordination environment about Ir.[3]

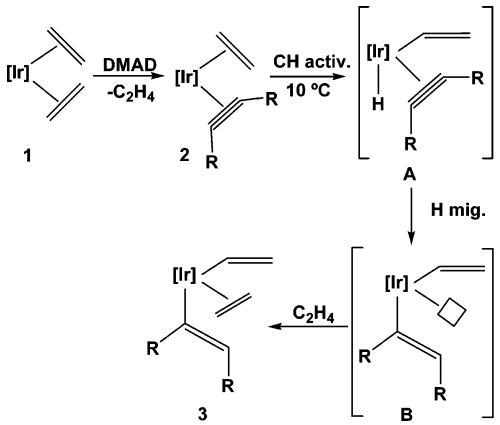
Results and Discussion

Thermal Evolution of $Tp^{Me2}Ir(C_2H_4)(DMAD)$ (2). When $Tp^{Me2}Ir(C_2H_4)_2$ (**1**) is treated with 1 equiv of DMAD in CH_2Cl_2 at room temperature, NMR monitoring of the course of the reaction shows the immediate formation of a mixture of complexes, of which the vinyl−alkenyl species **3**, so far the only identified species, represents approximately 50% of the reaction products (eq 3). Compound **3** evolves in solution (see



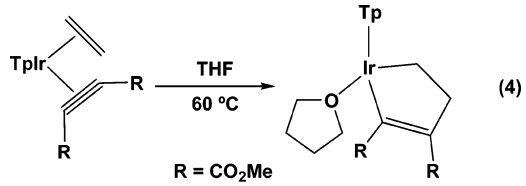
below), and this has prevented its isolation and full characterization. Nevertheless, the spectroscopic data obtained on the mixture are clearly in accord with the proposed structure.[4] Thus, the vinyl ligand generates in the ^1H NMR spectrum a typical pattern of three doublets of doublets at 8.11, 5.33, and 4.21 ppm (see the Experimental Section for coupling constants and assignments), while the ethylene molecule gives rise to two pseudo-doublets (AA′BB′ spin system) at 4.47 and 3.57 ppm, indicating fast rotation, on the NMR time scale, around the Ir−C_2H_4 axis. In addition to those signals, other resonances with the appropriate intensity for two different CO_2Me groups and an olefinic CH (δ 4.75) are observed. These last resonances correspond to an alkenyl ligand, derived from the insertion of a molecule of DMAD into an Ir−H bond, likely with a cis configuration. Compound **3** is also generated if the reaction depicted in eq 3 is carried out stepwise, in a more controlled manner, first at −40 °C, with the generation of compound **2**,

Scheme 2



and then with the temperature raised to 25 °C, but the spectroscopic yield of **3** is not improved by this procedure. However, if the reaction is carried out under 3 bar of C_2H_4, the yield increases substantially to ≥80%.

Formation of **3** from **1** can be explained (Scheme 2) by the C−H activation of the coordinated ethylene in **2** to give the unobserved hydrido−vinyl derivative **A**, followed by DMAD insertion with formation of **B** and recoordination of the ethylene initially displaced by the alkyne (the trapping of **B** is more efficient if the reaction is carried out under an atmosphere of C_2H_4, and in this way the evolution of this intermediate by other pathways is avoided). This proposal is not unreasonable, in view of the previous examples known of ethylene C−H activation on compounds of composition $Tp^{Me2}Ir(C_2H_4)(L)$ (L = PR_3, CO, C_2H_4; see Introduction), although all of these processes required temperatures above 60 °C to occur at appreciable rates.[4,5] In the system under consideration, the reaction is much faster and we may propose one explanation for this: i.e., that the Ir−C_2H_4 bond is weaker in this case, since this ligand occupies an axial position in the trigonal bipyramid of compound **2**, while it is in a equatorial position for the other related adducts mentioned. The ease of the vinylic C−H activation observed in **2** may also be contrasted with the behavior found for the Tp derivative related to **2**, which experiences instead a C_2H_4−DMAD coupling to an iridacyclopent-2-ene (eq 4).[6] That



difference may be explained on the basis of steric factors, as we have found that for Tp′Ir derivatives (in general, Tp′ stands for any kind of derivative of the hydrotris(pyrazolyl)borate molecule; for this comparison, Tp′ = Tp, Tp^{Me2}) the more congested the environment, the more facile the C−H activation processes, and this may prevent the oxidative coupling from taking place.

Monitoring the reaction of eq 3 by ^1H NMR in $CDCl_3$ vs time shows the gradual consumption of compound **3** and the concomitant appearance of the new species **4**, resulting from the insertion of the C_2H_4 ligand into the Ir−vinyl bond, as a

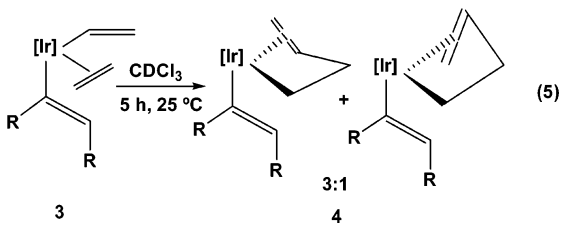
(3) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Álvarez, E.; Mereiter, K., *Chem. Eur. J.*, in press.

(4) For the related $Tp^{Me2}Ir(H)(CH{=}CH_2)(C_2H_4)$ see: Alvarado, Y.; Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Ruiz, C.; Bianchini, C.; Carmona, E. *Chem. Eur. J.* **1997**, *3*, 860.

(5) Gutiérrez Puebla, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Poveda, M. L.; Rey, L.; Ruiz, C.; Carmona, E. *Inorg. Chem.* **1998**, *37*, 4538.

(6) O'Connor, J. M.; Closson, A.; Gantzel, P. *J. Am. Chem. Soc.* **2002**, *124*, 2434.

mixture, probably thermodynamic, of two stereoisomers in a 3:1 ratio (eq 5). Column chromatography allows isolation of



this mixture (without changing the isomer ratio) and the identification of its components by NMR spectroscopy, including NOESY experiments. As can be seen, of the two alkenyl moieties present in **3**, the vinyl ligand is the one that migrates onto the coordinated ethylene, probably due to the lower electronegative character, and hence the highest readiness to migrate, of this fragment. Coordination of the pendant olefin to the metal center allows the 18e configuration with the two isomers originating from the coordination of the opposite faces of the olefin. For the major isomer, the Ir−CH_2 fragment displays a resonance at −50.2 ppm in the $^{13}C\{^1H\}$ NMR spectrum, while the vinyl moiety bonded to the metal gives rise to signals in a zone characteristic for π-coordinated olefins: 66.4 ($^1J_{CH}$ = 163 Hz, CH_2) and 60.9 ppm ($^1J_{CH}$ = 163 Hz, CH). It is worth mentioning that the resonance corresponding to the aliphatic C atom bonded to Ir is shifted to very high field. Although in general alkyl carbon atoms bonded to the metal in the $Tp^{Me2}Ir^{III}$ system resonate at high field, normally between 0 and −20 ppm, in both of the isomers of **4** these resonances are located around −50 ppm. Such remarkable chemical shifts have nevertheless been observed[7] in the cationic Ir(III) complex $Tpm^{Me2}Ir(H)(CH_2CH_2CH{=}CH_2)PF_6$ (Tpm^{Me2} = tris(3,5-dimethylpyrazolyl)methane), which contains an alkyl chain identical with that found in **4**, and therefore it can be concluded that these unusual data are characteristic for these types of derivatives.

The major isomer of **4** has also been characterized by single-crystal X-ray studies. Tables 1 and 2 contain crystal data and bond lengths and angles, respectively, while Figure 1 gives an ORTEP representation of the structure of this compound. As can be observed the two CO_2Me groups on the alkenyl chain are in a cis disposition, supporting the proposed cis formulation of the related ligand in compound **3**. The sp^3 carbon atom bonded to iridium forms an Ir−C(51) bond with a length of 2.08 Å, a value typical of a single bond.[3,8] Interestingly, the olefin bond distance C(53)−C(54) of 1.29 Å corresponds essentially to a C=C double bond (1.34 Å), while the corresponding Ir−C(olefin) bond lengths are comparatively long (2.24 Å, average). These values are in contrast with those found (1.39 and 2.16 Å average, respectively) in a related iridacycle, $Tp^{Me2}Ir(H)(C(R){=}C(R)C(R){=}C(R)CH{=}CH_2)$ (R = CO_2Me), where a longer unsaturated organic chain separates the Ir−C single bond from the Ir π-bonded $CH{=}CH_2$ termini[3] and this points to a relatively weak Ir−olefin bond in **4** and further suggests that its easy isomerization is of a dissociative type. In the cationic Tpm^{Me2} complex mentioned above, which contains an alkyl chain identical with that found in **4**, the Ir-bonded C=C bond distance is also very short (1.30 Å) but the Ir−C(olefin) bond lengths are much shorter than those found in **4** (2.16 Å, average).[7] Finally, the Ir−N(pyrazolyl) bond trans with respect to the olefin ligand in **4** (2.11 Å) is shorter than the other two (ca. 2.17 Å), but this effect is not as pronounced as when the donor ligand has a hard nature.[3]

Table 1. Crystal Data and Data Collection and Refinement Details for $4{\cdot}CH_2Cl_2$ and 6

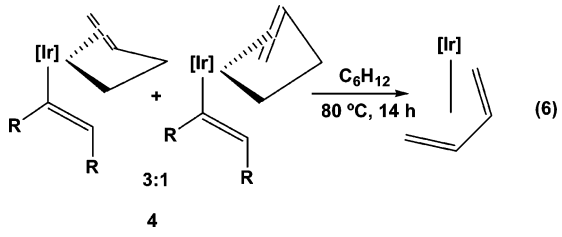
	$4{\cdot}CH_2Cl_2$	**6**
formula	$C_{26}H_{38}BCl_2IrN_6O_4$	$C_{23}H_{32}BClIrN_7O_4$
mol wt	772.53	709.02
color, habit	colorless, plate	red, prism
symmetry, space group	monoclinic, $P2_1/c$	orthorhombic, $P2_12_12_1$
a, Å	8.1996(12)	13.7032(12)
b, Å	24.564(4)	13.9350(12)
c, Å	15.512(2)	15.1568(14)
α, deg	90	90
β, deg	95.884(3)	90
γ, deg	90	90
V, Å^3	3107.9(8)	2894.3(4)
Z	4	4
D_{calcd}, g cm^{-3}	1.651	1.627
μ, mm^{-1}	4.509	4.745
θ range, deg	2.5−30.0	2.1−30.0
temp, K	100(2)	173(2)
no. of data collected	29378	21030
no. of unique data	8739 (*R*(int) = 0.056)	8304 (*R*(int) = 0.059)
no. of params/restraints	369/0	345/0
R1[a] ($F^2 > 2\sigma(F^2)$)	0.0536	0.0381
wR2[b] (all data)	0.1269	0.0680

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $4{\cdot}CH_2Cl_2$

Ir−C(42)	2.046(6)	C(41)−C(42)	1.514(8)
Ir−C(51)	2.082(8)	C(42)−C(43)	1.367(8)
Ir−C(53)	2.250(8)	C(43)−C(44)	1.469(9)
Ir−C(54)	2.225(9)	C(51)−C(52)	1.555(11)
Ir−N(12)	2.168(5)	C(52)−C(53)	1.494(11)
Ir−N(22)	2.184(5)	C(53)−C(54)	1.294(14)
Ir−N(32)	2.110(5)		
N(12)−Ir−N(22)	87.4(2)	C(51)−Ir−C(54)	88.7(3)
N(12)−Ir−N(32)	89.1(2)	Ir−C(42)−C(43)	121.2(4)
N(22)−Ir−N(32)	83.6(2)	Ir−C(51)−C(52)	99.4(5)
C(42)−Ir−C(51)	92.0(3)	Ir−C(53)−C(52)	94.4(5)
C(42)−Ir−C(53)	84.5(3)	Ir−C(53)−C(54)	72.1(6)
C(42)−Ir−C(54)	108.0(3)	C(51)−C(52)−C(53)	100.4(6)
C(51)−Ir−C(53)	65.3(3)	C(52)−C(53)−C(54)	124.9(9)

Compound **4** is thermally not very stable and, when it is heated in solution at 80 °C, it transforms mainly (eq 6) into the known butadiene Ir(I) derivative $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)$.[9] Both stereoisomers of **4** react at the same rate. This



reaction is another example of the exceptions found to our general observation that $Tp^{Me2}Ir^{III}$ derivatives hardly participate in processes which imply a decrease of the oxidation state of the metal. In fact, the first examples

(7) Padilla-Martínez, I. I.; Poveda, M. L.; Carmona, E .; Monge, M. A.; Ruiz-Valero, C. *Organometallics* **2002**, *21*, 93.

(8) Ilg, K.; Paneque, M.; Poveda, M. L.; Rendón, N.; Santos, L. L.; Carmona, E.; Mereiter, K. *Organometallics* **2006**, *25*, 2230.

(9) Boutry, O.; Poveda, M. L.; Carmona, E. *J. Organomet. Chem.* **1997**, *528*, 143.

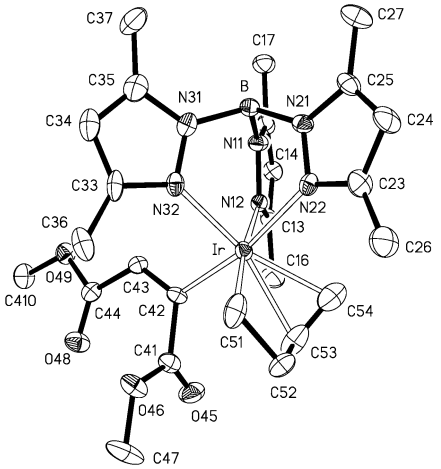
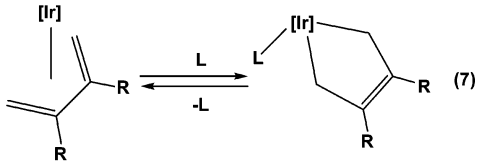


Figure 1. X-ray structure of the major isomer of **4** in crystalline **4**·CH_2Cl_2 (thermal ellipsoids drawn at the 40% probability level, hydrogen atoms omitted for clarity).

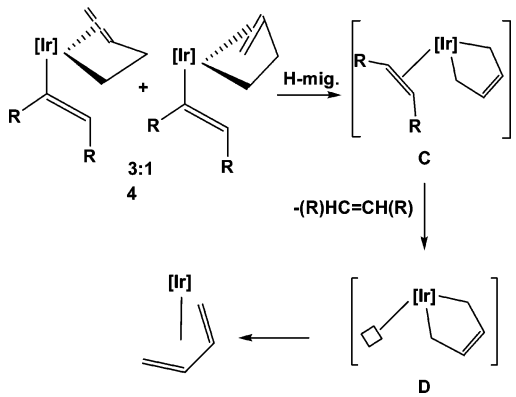
observed involved butadiene-derived species of composition $Tp^{Me2}Ir(CH_2C(R)=C(R)CH_2)(L)$,[10] formed by the reaction of the appropriate Ir(I) precursor $Tp^{Me2}Ir(\eta^4\text{-}CH_2=C(R)C(R)=CH_2)$[9] with a Lewis base L, as they are able to revert to the starting material when the Ir−L bond is not particularly strong, as occurs, among other times, when L = C_2H_4 (eq 7).[10]



Therefore, for the process depicted in eq 6 it can be proposed (Scheme 3) that the transfer of a β-H atom from the alkyl chain to the alkenyl in **4** generates the adduct **C** with a bonded olefin, which is then easily released. It is worth mentioning that the cationic derivative previously quoted, $[Tpm^{Me2}Ir(H)(CH_2CH_2CH=CH_2)]PF_6$, also evolves, albeit in this case by photochemical activation, to the corresponding diene compound $[Tpm^{Me2}Ir(\eta^4\text{-}C_4H_6)]PF_6$.[7]

Reaction of $Tp^{Me2}Ir(C_2H_4)$(DMAD) (2) with NCMe. As addressed in the Introduction, compound **1** reacts, at temperatures <25 °C, with 1 equiv of different soft Lewis bases L by the substitution of one ethylene ligand by L, giving rise to trigonal-bipyramidal structures in which the remaining ethylene

Scheme 3



Scheme 4

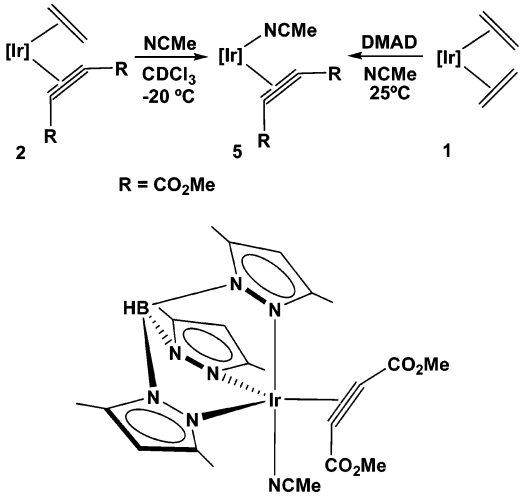
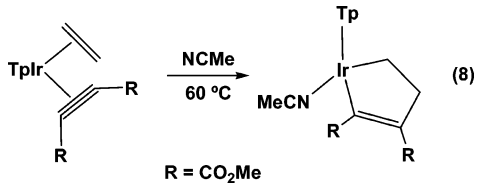


Figure 2. Structure proposed for compound **5**.

unit occupies an equatorial position (with the exception of L = DMAD, which gives **2** with C_2H_4 being axially coordinated).[3,5] Hard bases such as NCMe react through Ir(III) intermediates at much higher temperatures.[4] In contrast, the reaction of compound **2** with NCMe, in CH_2Cl_2 or $CDCl_3$ at −20 °C, takes place with the formation of the Ir(I) adduct $Tp^{Me2}Ir$(DMAD)(NCMe) (**5**) by the displacement of the coordinated ethylene (Scheme 4). The synthesis of **5** can also be performed directly from **1**, by the addition of DMAD to a suspension of it in NCMe at 25 °C. From a series of control experiments it can be concluded that **2** is more reactive toward NCMe than toward DMAD (eq 2). The formation of **5** also strongly contrasts with the reaction between NCMe and the TpIr analogue of **2** (eq 8), where no substitution occurs and the nitrile behaves as THF does in eq 4.[6]



All of the IR and NMR data recorded for **5** are in agreement with this complex having a trigonal-bipyramidal structure, and as the chemical shift corresponding to the $^{13}C_{sp}$ atoms of the DMAD ligand (87.5 ppm) is very similar to that registered for compound **2** (78.6 ppm),[3] we conclude that DMAD also occupies an equatorial position in this adduct (Figure 2). Moreover, the NCMe chemical shift (114.7 ppm) and ν(CN) value (2290 cm^{-1}) are in accord with the acetonitrile ligand being η^1-N bonded, and this is in contrast with a series of NCAr (Ar = aryl) complexes of $(C_5R_5)Ir^I$ (R = H, Me), in which the nitrile has been found to be η^2-N,C coordinated.[11] Compound **5** represents the first example of coordination of NCMe (a hard base) to a $Tp^{Me2}Ir^I$ derivative, and in order to explain the readiness with which this compound is formed and its high thermal stability (see below), it can be invoked that DMAD is a very good electron-withdrawing fragment and facilitates the binding of a hard Lewis base (NCMe) to an, in principle soft,

(10) Gutiérrez-Puebla, E.; Monge, A.; Paneque, M.; Poveda, M. L.; Salazar, V. *Organometalllics* **2000**, *19*, 3120.

(11) (a) Chetcuti, P. A.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1986**, *5*, 1913. (b) Chetcuti, P. A.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1987**, *109*, 942.

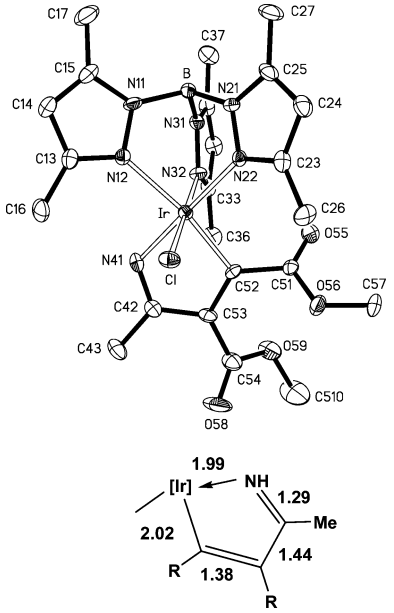
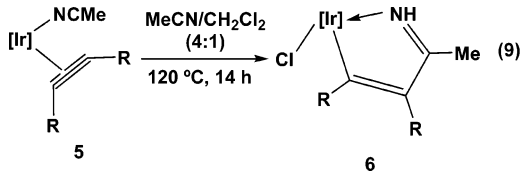


Figure 3. X-ray structure of complex **6** with bond lengths (Å) of the metallacycle on the bottom (thermal ellipsoids drawn at the 40% probability level, hydrogens omitted for clarity).

Ir(I) center. Nevertheless, the Ir^{I}−NCMe bond is kinetically very labile, as deduced from the fast exchange of coordinated NCMe by $NCCD_3$ observed at room temperature. In the adducts of $Tp^{Me2}Ir^{III}$, this exchange is also observed often, but always at high temperatures (≥80 °C).[12]

In spite of the lability of the Ir^{I}−NCMe bond, compound **5** is thermally very stable. In solution, in the presence of NCMe, it stays unaltered at least until 90 °C. Above 100 °C, in a NCMe−CH_2Cl_2 mixture (4:1), an unexpected reaction takes place with formation of the iridapyrrole[12,13] **6** (eq 9), formed



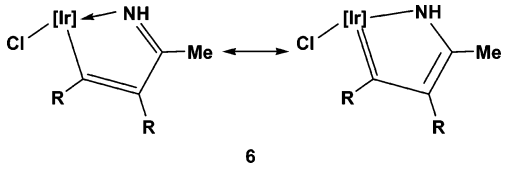
by way of a formal coupling of DMAD, NCMe, and "HCl". Compound **6** has been characterized completely by IR, NMR, and single-crystal X-ray studies. Thus, the IR spectrum exhibits an absorption at 3300 cm^{-1}, corresponding to ν(N−H), while in the $^{13}C\{^1H\}$ NMR spectrum the chemical shift of the C atom bonded to iridium resonates at 187.5 ppm, i.e., a value intermediate between those expected for Ir−C(alkenyl) and Ir−carbene moieties, clearly in agreement with the electronic delocalization along the ring depicted in Scheme 5.[12,13] Figure 3 gives an ORTEP representation for the molecule, while Tables 1 and 3 collect crystallographic data and selected bond lengths

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 6

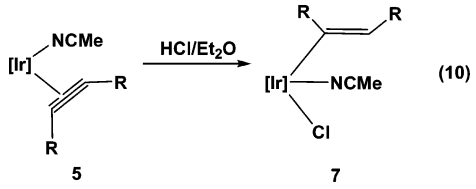
Ir−Cl	2.362(1)	Ir−C(52)	2.023(5)
Ir−N(12)	2.145(5)	N(41)−C(42)	1.294(8)
Ir−N(22)	2.098(4)	C(42)−C(43)	1.508(8)
Ir−N(32)	2.076(4)	C(42)−C(53)	1.439(8)
Ir−N(41)	1.989(4)	C(52)−C(53)	1.377(7)
N(12)−Ir−N(22)	87.6(2)	N(41)−Ir−C(52)	78.0(2)
N(12)−Ir−N(32)	87.9(2)	Ir−N(41)−C(42)	117.4(4)
N(22)−Ir−N(32)	86.9(2)	Ir−C(52)−C(53)	114.4(4)
C(52)−Ir−Cl	87.2(1)	N(41)−C(42)−C(53)	114.9(5)
N(41)−Ir−Cl	86.4(1)	C(42)−C(53)−C(52)	112.9(5)

and angles, respectively. Figure 3 also gives a scheme of the metallacycle with its associated bond lengths. A complex closely related to **6**, with R = H and an ethyl ligand instead of Cl, has been reported by our group previously,[12] and the main structural differences with respect to this compound are a smaller trans influence of the Cl ligand (the Ir−N bond distance trans to Cl is ca. 0.1 Å shorter than the corresponding distance trans to the ethyl ligand) and a longer Ir−C(R) bond distance (2.02 Å for R = CO_2Me vs 1.88 Å for R = H).[12]

Scheme 5



It can be thought that compound **6** is generated in a two-step process: first, complex **5** will react with HCl, which may be present in the solvent or generated from it in some way under the conditions shown in eq 9, forming the alkenyl derivative $Tp^{Me2}IrCl(C(R)=C(R)H)(NCMe)$. Then the iridapyrrole ring will form by the coupling of the alkenyl and NCMe, a process previously observed in our laboratory.[12] In fact, the addition of an excess of HCl (1 M solution in Et_2O) to a solution of **2** (C_6H_{12}, 60 °C) quantitatively produces the purported intermediate (**7**, to be reported elsewhere;[14] eq 10). However, when this



species is heated under the same conditions depicted in eq 9, it stays unaltered and this observation rules out its role as an intermediate in the formation of **6**. We have pursued some additional mechanistic information by means of deuterium labeling experiments. Thus, from the heating of compound **5** in the mixtures $CH_2Cl_2/NCCD_3$, CD_2Cl_2/NCMe, and $CD_2Cl_2/NCCD_3$, it can be deduced that both the proton of the NH and the Me at the β position, as expected, come from the NCMe. Also, we have observed that, once formed, **6** does not exchange its protons either with $NCCD_3$, under the conditions of the reaction, or with D_2O at room temperature (to rule out the possibility of hydrolysis upon manipulation). In spite of all these efforts, we cannot propose a reasonable mechanism for the formation of **6**.

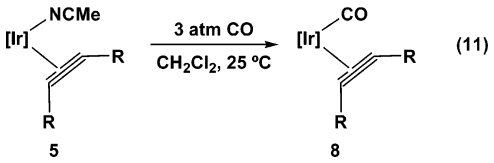
Reactivity of Tp^{Me2}Ir(DMAD)(NCMe) (5) with Unsaturated Molecules. The kinetic lability of the NCMe ligand in compound **5** allows the observation of different substitution

(12) Alías, F. M.; Daff, J. P.; Paneque, M.; Poveda, M. L.; Carmona, E.; Pérez, P. J.; Salazar, V.; Alvarado, Y.; Atencio, R.; Sánchez-Delgado, R. *Chem. Eur. J.* **2002**, *8*, 5132.

(13) (a) Baya, M.; Esteruelas, M. A.; González, A. I.; López, A. M.; Oñate, E. *Organometallics* **2005**, *24*, 1225. (b) Vicente, J.; Arcas, A.; Fernández-Hernández, J. M. *Organometallics* **2005**, *24*, 2516. (c) Legzdins, P.; Lumb, S. A.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 854. (d) Werner, H.; Daniel, T.; Braun, T.; Nürnberg, O. *J. Organomet. Chem.* **1994**, *480*, 145. (e) Martin, G. C.; Boncella, J. M.; Wucherer, E. J. *Organometallics* **1991**, *10*, 2804. (f) Filippou, A. C.; Völkl, C.; Kiprof, P. *J. Organomet. Chem.* **1991**, *415*, 375. (g) Guram, A. S.; Jordan, R. F. *J. Org. Chem.* **1993**, *58*, 5595. (h) For a highly distorted structure see: Curtis, M. D.; Real, J.; Hirpo, W.; Butler, W. H. *Organometallics* **1990**, *9*, 66.

(14) Posadas, C. M. Ph.D. Thesis, University of Seville, 2006.

reactions. Thus, **5** reacts with CO, at room temperature, with formation of the Ir(I) carbonyl compound **8** (eq 11). This



substitution process is retarded by the presence of free NCMe in the solution. Spectroscopic characterization of this compound (^{1}H, ^{13}C{^{1}H}, and ^{11}B{^{1}H} NMR and ν(B−H) in the IR) supports the adoption of a trigonal-bipyramidal structure, with DMAD in the equatorial position and CO in the axial position (Figure 4).[3] In fact, the chemical shift for the $^{13}C_{sp}$ carbon nuclei of the alkyne (86.4 ppm) compares well with that of compound **2** (87.5 ppm), and also the corresponding value for the ^{13}C of the carbonyl ligand (162.1 ppm) is similar to that found for the related $Tp^{Me2}Ir(C_2H_4)(CO)$[5] (165.2 ppm, where the ethylene is located in the equatorial position). In spite of the presence of an excess of CO in the reaction, the DMAD ligand is not displaced to yield the highly water sensitive[5] dicarbonyl adduct $Tp^{Me2}Ir(CO)_2$,[15] as is the case in the reaction of $Tp^{Me2}Ir(C_2H_4)_2$ with CO.[5]

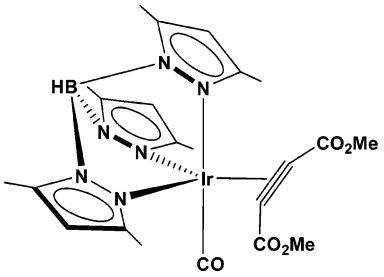
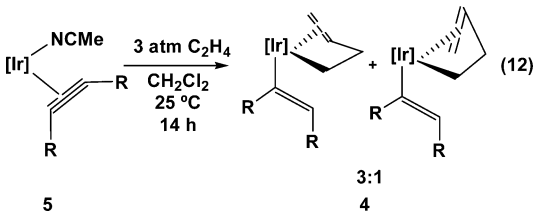
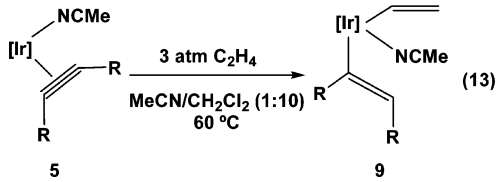


Figure 4. Proposed structure for complex **8**.

The lability of the NCMe ligand in compound **5** is also shown by its reaction with ethylene. When compound **5** reacts with this olefin in dichloromethane, complex **4** is obtained (eq 12),

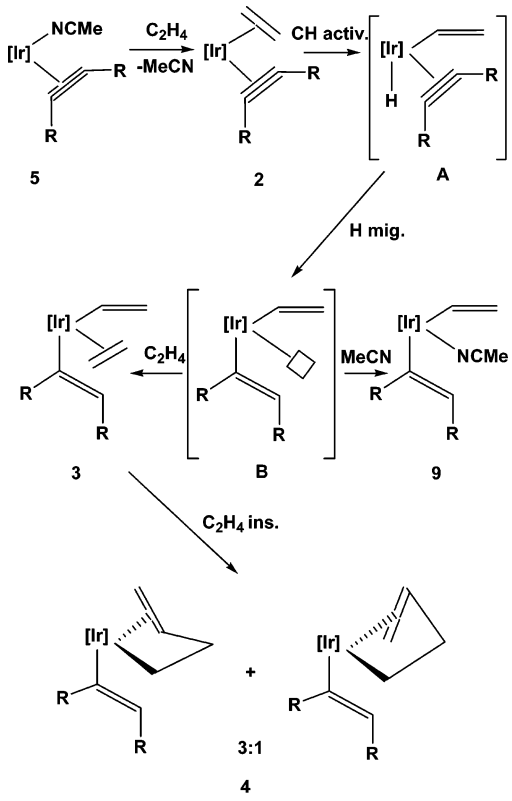


and this reaction provides an alternative method for the preparation of **4**, since the yield is almost quantitative. It is important to mention that this transformation is prevented when NCMe is used as the solvent: even at 60 °C the starting material **5** is recovered unaltered. Nevertheless, appropriate NCMe−CH_2Cl_2 mixtures allow the reaction to proceed and a new compound, the vinyl−alkenyl species **9** (eq 13), results, although



in variable yields depending on the amount of NCMe present in the solvent: with a 10:1 CH_2Cl_2−NCMe mixture, the

Scheme 6



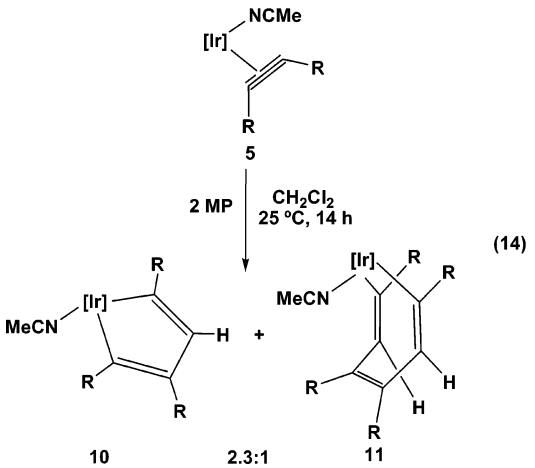
transformation is almost quantitative, albeit slow (40% conversion after 14 h). Complex **9** has been isolated and satisfactorily characterized by spectroscopy (see the Experimental Section for details). For the formation of complexes **4** and **9** starting from **5** and C_2H_4 (eqs 12 and 13), we propose the initial displacement of the coordinated NCMe (Scheme 6), to generate **2**, which would evolve as already depicted in Scheme 2. Once intermediate **B** has been formed, if NCMe is present in sufficient concentration it would react with this intermediate, and this prevents the incorporation of a second molecule of ethylene. In contrast, if the amount of olefin present is much larger than the amount of NCMe, the reaction proceeds preferably toward the formation of isomers **4**.

The studies detailed so far suggest that the substitution of NCMe by C_2H_4 in compound **5** proceeds through a dissociative pathway: i.e., by the generation of the 16e species [Tp^{Me2}Ir(DMAD)] as an intermediate. This is in contrast with the mechanism of substitution proposed in $Tp^{Me2}Ir^I$ derivatives so far: in general, these reactions are believed to proceed by associative mechanisms, assisted by a change in the coordination mode of the Tp^{Me2} ligand, from κ^3 to κ^2.[5,16] Once more, the hard nature of the NCMe ligand probably disfavors its coordination to the Ir(I) center. By extension, we propose that the substitution of NCMe in compound **6** by the other Lewis bases studied ($NCCD_3$, CO, and alkynes, see below) also proceed by dissociative mechanisms.

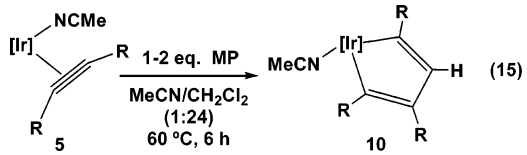
Compound **5** also reacts with alkynes, and we have studied its reaction with DMAD and methyl propiolate (HC≡CCO_2Me, MP). In both cases the results are analogous, although the experimental conditions needed are different. Thus, the addition of 2 equiv of MP to a solution of **5** in CH_2Cl_2 at 25 °C produces a mixture of the two metallacycles, in the form of acetonitrile

(15) Ball, R. G.; Ghosh, C. K.; Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1989**, 341.
(16) Oldham, W. J.; Heinekey, D. M. *Organometallics* **1997**, *16*, 467.

adducts **10** (an iridacyclopentadiene)[3,17] and **11** (an iridacycloheptatriene),[18] shown in eq 14, which can be isolated by column

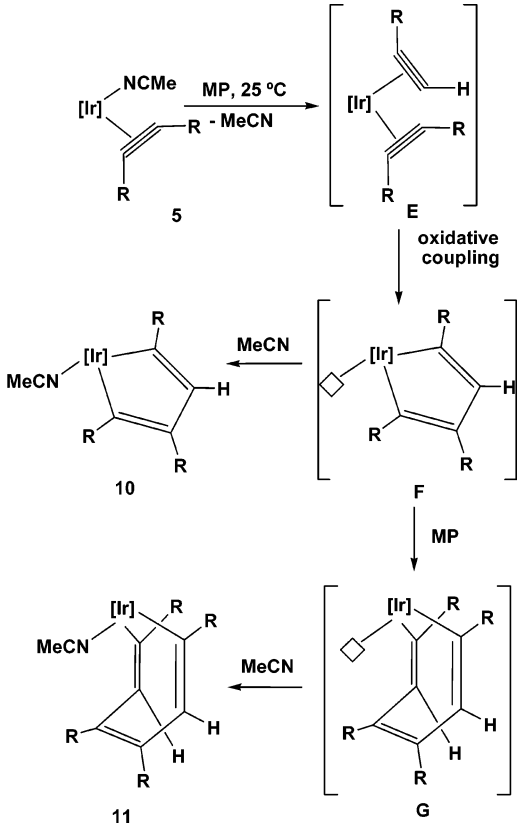


chromatography. Compounds **10** and **11** are respectively the result of the highly regioselective coupling of the originally coordinated DMAD molecule, with 1 or 2 equiv of the incoming methyl propiolate. **10** is a known[3] compound; **11** has been completely characterized by NMR spectroscopy (see the Experimental Section), and because the data obtained closely resemble those described for related complexes[18] we will not comment further. If the reaction of eq 14 is carried out in neat acetonitrile, at 25 °C, only **10** is formed, but part of the starting material remains unaltered; this is also true even if the reaction temperature is increased to 60 °C. However, we have found that this metallacyclopentadiene can be obtained in almost quantitative yield under the conditions depicted in eq 15 using a NCMe−CH_2Cl_2 mixture as solvent (eq 15).



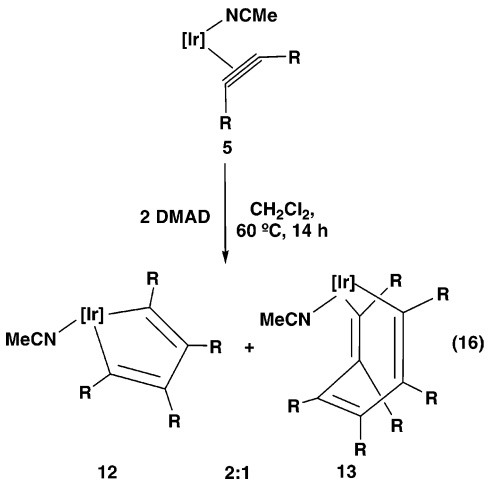
Although it could be proposed that **10** is an intermediate in the formation of **11**, in fact there is no transformation when, once isolated, **10** is heated with an excess of methyl propiolate. In agreement with this, the NCMe ligand of **10** is not substituted by $NCCD_3$ under conditions much harsher (80 °C, 14 h) than those employed in the synthesis of **11**. Scheme 7 shows a reasonable mechanism for the formation of the metallacycles **10** and **11**. The regioselective coupling of DMAD and MP ligands in the $Tp^{Me2}Ir^{I}$ coordination sphere to give intermediate **F** has already been noted. If this intermediate is not trapped by NCMe, it incorporates another molecule of MP (insertion reaction) by a double regioselective process to give the symmetrical iridacycloheptatriene intermediate **G**, which is stabilized by coordination of NCMe. It is worth noting that, in

Scheme 7



contrast with this regioselectivity, the insertion of ethylene in **F** takes place into the Ir−C bond adjacent to the C−H functionality.[3]

The reaction of **5** with DMAD provides similar results, although higher temperatures are required, and this allows the formation of the known metallacycles **12**[3] and **13**[18] (eq 16). If

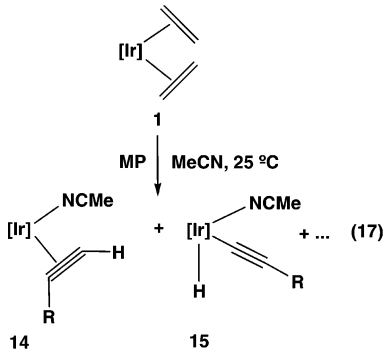


only an equimolar amount of DMAD is added, the reaction provides **12** exclusively. Once more, the addition of NCMe to the reaction retards it, but in this case the formation of **13** is observed even in neat NCMe. When the reactions depicted in eqs 15 and 16 are compared, some interesting differences arise, mainly that the reaction of **5** with DMAD is slower than with methyl propiolate, but also that DMAD is much more effective than methyl propiolate in trapping unsaturated iridacyclopentadiene intermediates, since even in neat NCMe the formation of the iridacycloheptatriene **13** is observed.

(17) (a) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* **1968**, *7*, 1298. (b) Bianchini, C.; Caulton, K. G.; Chardon, C.; Doublet, M.-L.; Eisenstein, O.; Jackson, T. J.; Meli, A.; Peruzzini, M.; Streib, W. E.; Vacca, A.; Vizza, F. *Organometallics* **1994**, *13*, 2010. (c) Chin, C. S.; Park, Y.; Kim, J.; Lee, B. *J. Chem. Soc., Chem. Commun.* **1995**, 1495. (d) Martín, M.; Sola, E.; Torres, O.; Plou, P.; Oro, L. A. *Organometallics* **2003**, *22*, 5406. See also ref 6.

(18) (a) Álvarez, E.; Gómez, M.; Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Salazar, V.; Santos, L. L.; Rojas-Lima, S.; Mereiter, K.; Ruiz, C. *J. Am. Chem. Soc.* **2003**, *125*, 1478. (b) Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Santos, L. L.; Álvarez, E.; Salazar, V.; Mereiter, K.; Oñate, E. *Organometallics*, in press.

In order to complete the investigations reported in this paper, we have studied the reaction of complex **1** with methyl propiolate, in NCMe as solvent. The reaction takes place at room temperature with the formation of a complex mixture, in which two major compounds have been characterized, namely **14** and **15** (eq 17). Their relative ratio is independent of the amount of

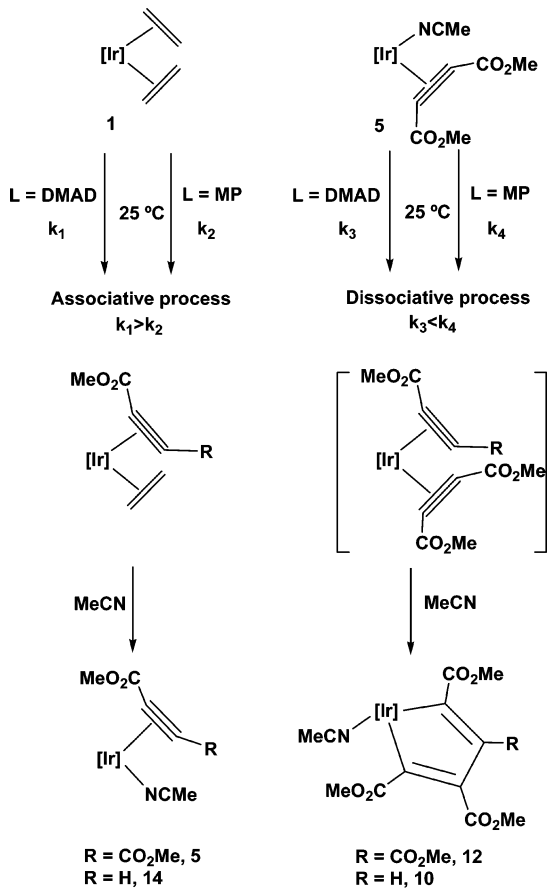


alkyne added but depends on the progress of the reaction. We propose for **14** a structure analogous to that of the corresponding DMAD derivative **5**: i.e., a trigonal bipyramid with the methyl propiolate ligand in an equatorial position. Compound **15** is the result of the formal oxidative addition of the C−H sp bond in **14**.[19]

Monitoring the reaction depicted in eq 17 by NMR spectroscopy shows that it is very slow: after 5 h at 25 °C, both **14** and **15** (ca. 1:1) are present, but the major product is the starting material **1**. After this time, **15** is increasing gradually at the expense of **14**. By extension of the results obtained in the system **1**−DMAD−NCMe, we propose that compound **14** is generated through the slow initial formation of the unobserved adduct [$Tp^{Me2}Ir(C_2H_4)$(MP)], analogous to **2**, which immediately reacts with NCMe to give **14**. As noted above, compound **14** evolves in solution and this has prevented the isolation of pure samples, but it is stable enough to be characterized in the crude solution by NMR spectroscopy (see Experimental Section). Complex **15** is best obtained if the reaction depicted in eq 17 is carried out at 60 °C and has been fully characterized by microanalysis and IR and NMR spectroscopy. The hydride ligand appears at −19.60 ppm in the ^{1}H NMR spectrum, while the two $^{13}C_{sp}$ atoms of the alkynyl ligand resonate very closely to each other in the $^{13}C\{^1H\}$ spectrum (96.8 and 93.2 ppm).

Finally, it is worth highlighting the influence of the electronic characteristics of substrates and reagents on the rate of ligand substitution for the Ir(I) derivatives included in Scheme 8. This scheme gives a qualitative comparison of rate constants and reaction results. In view of these results, it is surprising that the complex $Tp^{Me2}Ir$(MP)(NCMe) (**14**) does not react with an excess of MP to yield a disubstituted iridacyclopentadiene via interchange of coordinated NCMe. This process should be very slow. In contrast, the reaction of $Tp^{Me2}Ir$(DMAD)(NCMe) (**5**) with MP generates an intermediate bis(alkyne) of composition $Tp^{Me2}Ir$(DMAD)(MP) (**E**) (see Scheme 7), which could experience an oxidative addition of the sp C−H bond of MP, but this should be again a slow reaction compared with the oxidative coupling of both alkynes, which is the observed process.

Scheme 8



Conclusions

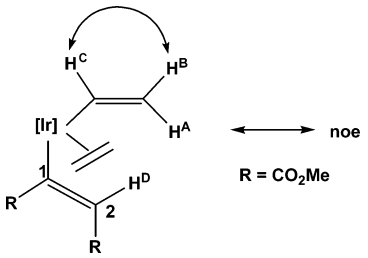
The first $Tp^{Me2}Ir^I$ derivative with a coordinated hard base, namely $Tp^{Me2}Ir$(DMAD)(NCMe), has been prepared and characterized. The lability of the NCMe ligand allows its reaction with unsaturated molecules (CO, MP, DMAD, C_2H_4) to be carried out under mild conditions. While with CO this derivative gives the Ir(I) complex $Tp^{Me2}Ir$(DMAD)(CO), its reactions with the alkynes DMAD and MP afford mixtures of substituted iridacyclopentadienes and iridacycloheptatrienes as acetonitrile adducts. Finally, depending on the reaction conditions, different alkenyl species are obtained with C_2H_4 via vinylic C−H activation.

Experimental Section

General Procedures. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were obtained with a Bruker Vector 22 spectrometer. The NMR instruments were Bruker DRX-500, DRX-400, and DPX-300 spectrometers. Spectra were referenced to external $SiMe_4$ (δ 0 ppm) using the residual protio solvent peaks as internal standards (^{1}H NMR experiments) or the characteristic resonances of the solvent nuclei (^{13}C NMR experiments). Spectral assignments were made by means of routine one- and two-dimensional NMR experiments where appropriate. All manipulations were performed under dry, oxygen-free nitrogen, following conventional Schlenk techniques. The complexes $Tp^{Me2}Ir(C_2H_4)_2$ (**1**) and $Tp^{Me2}Ir(C_2H_4)$(DMAD) (**2**) were obtained by published procedures.[3,4]

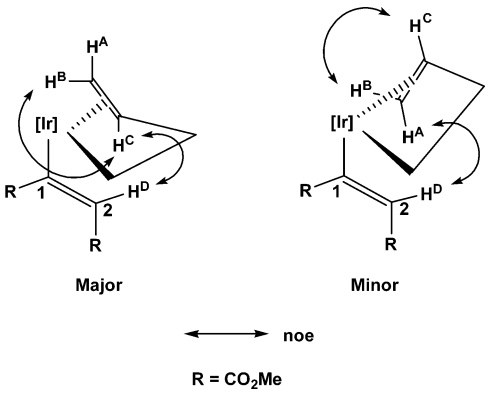
(19) (a) Bianchini, C.; Mealli, C.; Peruzzinni, M.; Vizza, F.; Zanobini, F. *J. Organomet. Chem.* **1988**, *346*, C53. (b) Werner, H.; Meyer, V.; Esteruelas, M. A.; Oro, L. A. *J. Organomet. Chem.* **1989**, *366*, 187. (c) Bianchini, C.; Peruzzini, M.; Vacca, A.; Zanobini, F. *Organometallics* **1991**, *10*, 3697. (d) Yi, C. S.;Liu, N. *Organometallics* **1997**, *16*, 3910. (e) Ríos, I.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529. (f) Esteruelas, M. A.; Herrero, J.; López, A. M.; Oliván, M. *Organometallics* **2001**, *20*, 3202. (g) Asensio, A.; Buil, M. L.; Esteruelas, M. A.; Oñate, E. *Organometallics* **2004**, *23*, 5787. (h) Trujillo, M. Ph.D. Thesis, University of Seville, 1999.

Complex 3. To a solution of **1** (0.100 g, 0.183 mmol) in CD_2Cl_2 (0.5 mL) was added DMAD (0.023 mL, 0.183 mmol), and the resulting mixture was stirred for 1 min at 25 °C. The ^{1}H NMR spectrum obtained at this moment revealed the instantaneous formation of a main compound, **3**, in 50% spectroscopic yield, which could not be isolated due to its high reactivity. The yield was substantially improved (to ca. 80%) if the reaction was carried out under C_2H_4 (2 atm).



^{1}H NMR ($CDCl_3$, 25 °C): δ 8.11 (dd, 1 H, $^3J_{CA}$ = 17.3, $^3J_{CB}$ = 9.8 Hz, H^C), 5.79, 5.70, 5.66 (s, 1 H each, 3 CH_{pz}), 5.33, 4.21 (dd, 1 H each, $^2J_{BA}$ = 1.9 Hz, H^B, H^A, respectively), 4.75 (s, 1 H, H^D), 4.47, 3.57 (m, AA′BB′ spin system, 2 H each, C_2H_4), 3.89, 3.50 (s, 3 H each, 2 CO_2Me), 2.50−1.50 (6 Me_{pz}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 177.5, 164.0 (CO_2Me), 151.6 (C^1), 151.0, 150.3, 148.0, 143.5, 143.3, 142.9 (C_{qpz}), 126.7 (C^2, $^1J_{CH}$ = 166 Hz), 125.6 (CH^C, $^1J_{CH}$ = 155 Hz), 117.8 (CH^AH^B, $^1J_{CH}$ = 155 Hz), 110−106 (CH_{pz}), 64.2 (C_2H_4, $^1J_{CH}$ = 164 Hz), 50.8, 50.7 (CO_2Me), 20−10 (Me_{pz}).

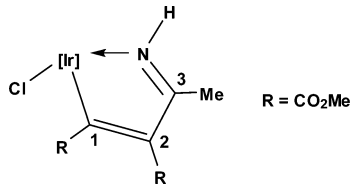
Compound 4. (a) If the reaction described above is carried out under 2 atm of C_2H_4, for 12 h, complex **4** is obtained in ca. 80% spectroscopic yield. (b) Compound **5** (0.2 g, 0.3 mmol) was dissolved in CH_2Cl_2 (12 mL) and the solution placed in a Fischer−Porter vessel which was pressurized with C_2H_4 (3 atm). The resulting mixture was stirred at 60 °C for 14 h, and thereafter the volatiles were removed under reduced pressure. The ^{1}H NMR spectrum of the crude product of the reaction showed the formation of complex **4**, as a mixture of isomers in a 3:1 ratio and in a spectroscopic yield higher than 80%. **5** was isolated by column chromatography on silica gel using a 1:3 of Et_2O−hexane mixture as eluent (yield 0.08 g, 38%; isomer ratio 3:1). An analytically pure sample was obtained by crystallization from CH_2Cl_2−pentane at −20 °C (colorless crystals).



Major isomer: ^{1}H NMR (C_6D_6, 25 °C) δ 5.62, 5.52, 5.40 (s, 1 H each, 3 CH_{pz}), 5.33 (m, 1 H, H^C), 4.87 (br s, 1 H, H^D), 4.67, 2.96 (d, 1 H each, $^3J_{AC}$ = 12.9, $^3J_{BC}$ = 8.3 Hz, H^A, H^B, respectively), 3.98, 3.20 (br s, s, 3 H each, 2 CO_2Me), 3.49, 3.30 (m, 1 H each, $IrCH_2CH_2$), 2.60, 1.18 (m, ddd, J_{HH} = 11.8, 8.3, 4.3 Hz, $IrCH_2CH_2$), 2.56, 2.18, 2.15, 2.12, 1.99, 1.37 (s, 3 H each, 6 Me_{pz}); $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C) δ 178.0, 163.7 (CO_2Me), 152.3, 150.6, 149.7, 143.6, 143.3, 142.5 (C_{qpz}), 157.8 (C^1), 127.8 (C^2, $^1J_{CH}$ = 170 Hz), 108.9, 108.6, 107.2 (CH_{pz}), 66.4 (CH^AH^B, $^1J_{CH}$ = 163 Hz), 60.9 (br, detected by HETCOR, CH^C, $^1J_{CH}$ = 163 Hz), 51.0, 49.7 (CO_2Me), 28.2 ($IrCH_2CH_2$, $^1J_{CH}$ = 126 Hz), 14.8, 13.6, 13.2, 12.6, 12.5, 12.0 (Me_{pz}), −50.2 ($IrCH_2CH_2$, $^1J_{CH}$ = 138 Hz). **Minor isomer**: ^{1}H NMR ($CDCl_3$, 25 °C) δ 5.76, 5.64 (s, 2:1, 3 CH_{pz}), 5.35 (m, 1 H, H^C), 5.18, 2.69 (d, 1 H each, $^3J_{AC}$ = 12.5, $^3J_{BC}$ = 8.9 Hz, H^A, H^B, respectively), 4.77 (brs, 1 H, H^D), 3.90, 2.17 (m, 1 H each, $IrCH_2CH_2$), 3.85, 3.53 (s, 3 H each, 2 CO_2Me), 1.90, 1.10 (dd, ddd, $^2J_{HH}$ = $^3J_{HH}$ = 9.8 Hz, $IrCH_2CH_2$), Tp^{Me2} signals were not assigned; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ 178.0, 163.9 (CO_2Me), 157.8 (C^1), 125.9 (C^2, $^1J_{CH}$ = 167 Hz), 65.8 (CH^AH^B, $^1J_{CH}$ = 133 Hz), 60.9 (CH^C, $^1J_{CH}$ = 164 Hz), 51.2, 51.2 (CO_2Me), 29.2 ($IrCH_2CH_2$, $^1J_{CH}$ = 131 Hz), −49.3 ($IrCH_2CH_2$, $^1J_{CH}$ = 134 Hz), Tp^{Me2} signals were not assigned. Anal. Calcd for $C_{25}H_{36}BN_6O_4Ir$: C, 43.7; H, 5.2; N, 12.2. Found: C, 43.3; H, 5.2; N, 11.7.

Complex 5. To a solution of **1** (0.40 g, 0.73 mmol) in acetonitrile (10 mL) was added DMAD (0.09 mL, 0.73 mmol), and the mixture was stirred at room temperature for 10 min. After this period of time, a dark yellow solution was observed, the solvent was evaporated under vacuum, and quantitative conversion into compound **5** was ascertained by ^{1}H NMR spectroscopy (dark yellow crystals). IR (Nujol): ν(BH) 2525, (CN) 2290 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ 5.88, 5.38 (s, 2:1, 3 CH_{pz}), 3.80 (s, 6 H, 2 CO_2Me), 2.49, 2.39, 2.20, 1.94 (s, 2:2:1:1, 6 Me_{pz}), 2.35 (s, 3 H, MeCN). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 161.1 (CO_2Me), 152.7, 151.0, 143.5, 143.4 (1:2:2:1, C_{qpz}), 113.8 (Me*C*N), 108.8, 106.0 (1:2, CH_{pz}), 87.5 (CCO_2Me), 51.5 (CO_2Me), 16.8, 14.5, 13.3, 12.2 (1:2:1:2, Me_{pz}), 3.8 (*Me*CN). $^{11}B\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 32.4. Anal. Calcd for $C_{23}H_{31}BN_7O_4Ir$: C, 41.1; H, 4.6; N, 14.6. Found: C, 41.0; H, 4.5; N, 14.1.

Complex 6. A solution of **5** (0.2 g, 0.3 mmol) in a mixture of acetonitrile (5 mL) and CH_2Cl_2 (1 mL) was stirred at 120 °C for 14 h. Then a bright red solution was observed and the solvent was removed under reduced pressure. Almost quantitative conversion into compound **6** was ascertained by ^{1}H NMR spectroscopy. An analytically pure sample was obtained by slow solvent evaporation, at room temperature, of a solution of **6** in CH_2Cl_2. Yield: 0.12 g, 47% (dark red crystals). IR (Nujol): ν(NH) 3309 cm^{-1}.

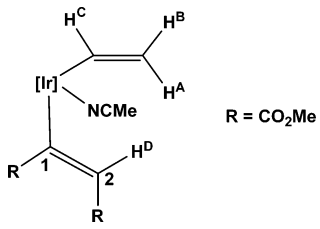


^{1}H NMR (CD_2Cl_2, 25 °C): δ 9.15 (br s, 1 H, NH), 5.94, 5.86, 5.62 (s, 1 H each, 3 CH_{pz}), 3.80, 3.61 (s, 3 H each, C^2CO_2Me, C^1CO_2Me, respectively), 2.89 (s, 3 H, C^3Me), 2.63, 2.44, 2.42, 2.38, 2.32, 1.81 (s, 3 H each, 6 Me_{pz}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 191.4 (C^3), 187.2 (C^1), 175.4, 164.9 (C^1CO_2Me, C^2CO_2Me, respectively), 154.2, 154.2, 152.4, 144.7, 144.2, 144.2 (C_{qpz}), 141.2 (C^2), 108.7, 108.7, 108.1 (CH_{pz}), 52.0, 51.3 (C^2CO_2Me, C^1CO_2Me, respectively), 24.8 (C^3Me), 14.9, 13.8, 12.9, 12.9, 12.3, 12.2 (Me_{pz}). Anal. Calcd for $C_{23}H_{32}BClN_7O_4Ir$: C, 39.0; H, 4.5; N, 13.8. Found: C, 38.9; H, 4.5; N, 13.4.

Complex 8. Compound **5** (0.15 g, 0.22 mmol) was dissolved in CH_2Cl_2 (10 mL) and the solution placed in a Fischer−Porter vessel which was pressurized with CO (3 atm). The resulting mixture was stirred at room temperature for 1 h, and a pale yellow solution was observed. The volatiles were removed under vacuum (pale yellow crystals), and quantitative conversion into compound **8** was ascertained by ^{1}H NMR. IR (Nujol): ν(BH) 2533, (CO) 2017 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ 5.91, 5.49 (s, 2:1, 3 CH_{pz}), 3.83 (s, 6 H, 2 CO_2Me), 2.52, 2.38, 2.25, 2.10 (s, 2:2:1:1, 6 Me_{pz}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 162.1 (CO), 159.9 (CO_2Me), 152.4, 151.7, 144.2, 143.7 (1:2:2:1, C_{qpz}), 109.3, 106.3 (1:2, CH_{pz}), 86.4 (CCO_2Me), 52.1 (CO_2Me), 16.4, 15.2, 13.1, 12.3 (1:2:1:2, Me_{pz}). ^{11}B-

{^{1}H} NMR ($CDCl_3$, 25 °C): δ 32.5. Anal. Calcd for $C_{22}H_{28}BN_6O_5Ir$: C, 40.1; H, 4.2; N, 12.7. Found: C, 40.1; H, 4.2; N, 12.3.

Complex 9. Compound **5** (0.14 g, 0.21 mmol) was dissolved in a mixture of CH_2Cl_2 (10 mL) and acetonitrile (1 mL) and the solution placed in a Fischer−Porter vessel which was pressurized with C_2H_4 (3 atm). The resulting mixture was stirred at 60 °C for 14 h, and then the solvent was removed under reduced pressure. Almost quantitative conversion into compound **9** was ascertained by ^{1}H NMR. This compound was purified by crystallization from a CH_2Cl_2−pentane mixture at −20 °C in 60% yield (brown crystals). IR (Nujol): ν(CN) 2307 cm^{-1}.



^{1}H NMR ($CDCl_3$, 25 °C): δ 7.66 (dd, 1 H, $^3J_{CA}$ = 17.8, $^3J_{CB}$ = 10.3 Hz, H^C), 5.75, 5.71 (s, 1:2, 3 CH_{pz}), 5.46, 4.62 (dd, 1 H each, $^2J_{BA}$ = 2.9 Hz, H^B, H^A, respectively), 4.80 (s, 1 H, H^D), 3.82, 3.51 (s, 3 H each, 2 CO_2Me), 2.52 (s, 3 H, MeCN), 2.36, 2.34, 2.25, 2.15, 1.97 (s, 2:1:1:1:1, 6 Me_{pz}). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 178.7, 164.4 (*C*O_2Me), 159.0 (C^1), 151.7, 151.1, 150.1, 143.3, 143.1, 143.0 (C_{qpz}), 128.6 (CH^C, $^1J_{CH}$ = 143 Hz), 124.5 (C^2, $^1J_{CH}$ = 166 Hz), 118.2 (CH^{A}H^B, $^1J_{CH}$ = 153 Hz), 114.7 (Me*C*N), 107.7, 107.2, 106.8 (CH_{pz}), 50.8, 50.7 (CO_2*Me*), 16.0, 14.5, 14.2, 13.0, 12.5, 12.3 (Me_{pz}), 3.8 (*Me*CN). Anal. Calcd for $C_{23}H_{31}BN_7O_4Ir\cdot 0.5CH_2Cl_2$: C, 41.2; H, 4.8; N, 13.2. Found: C, 40.7; H, 4.7; N, 13.2.

Complexes 10 and 11. To a solution of compound **5** (0.30 g, 0.45 mmol) in CH_2Cl_2 (15 mL) was added $MeO_2CC{\equiv}CH$ (0.08 mL, 0.90 mmol), and the mixture was stirred at room temperature for 14 h. The solvent was removed under reduced pressure, and the residue was shown by ^{1}H NMR to be a mixture of the known **10**[3] and **11** in 57% and 24% spectroscopic yields, respectively, along with other unidentified byproducts. Both species could be isolated by column chromatography on silica gel using a diethyl ether−hexane (1:1) mixture → ethyl acetate as eluent. Yield: 0.15 g, 46% for **10**; 0.08 g, 22% for **11** (orange crystals). **11**: R_f = 0.54 (silica gel, Et_2O−hexane (6:1)); IR (Nujol) ν(CN) 2248 cm^{-1}; ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.26 (s, 2 H, 2 CH), 5.70, 5.56 (s, 2:1, 3 CH_{pz}), 3.78, 3.04 (s, 6 H each, 4 CO_2Me), 2.54 (s, 3 H, MeCN), 2.36, 2.13, 2.00 (s, 3:2:1, 6 Me_{pz}); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) δ 174.7, 170.2 (*C*O_2Me), 151.4, 150.5, 142.5, 142.5 (1:2:1:2, C_{qpz}), 137.4 (CH, $^1J_{CH}$ = 156 Hz), 136.4, 134.6 (*C*CO_2Me), 121.0 (Me*C*N), 106.5, 106.1 (1:2, CH_{pz}), 52.2, 51.0 (CO_2*Me*), 15.4, 13.2, 13.2, 12.5 (1:2:1:2, Me_{pz}), 3.8 (*Me*CN). Anal. Calcd for $C_{31}H_{39}BN_7O_6Ir\cdot(CH_3CH_2)_2O$: C, 45.2; H, 5.0; N, 11.2. Found: C, 45.2; H, 4.6; N, 11.3.

Complexes 12 and 13. To a solution of **5** (0.14 g, 0.26 mmol) in CH_2Cl_2 (5 mL) was added DMAD (0.064 mL, 0.420 mmol), and the resulting mixture was stirred at 60 °C for 6 h. Then the volatiles were removed under reduced pressure and the ^{1}H NMR spectrum of the crude product showed the presence of the known compounds **12**[3] and **13**[18] in 60% and 30% spectroscopic yields, respectively, along with other unidentified byproducts. Complexes **12** and **13** were isolated by column chromatography on silica gel using a diethyl ether−hexane (1:1) mixture → AcOEt as eluent. Yield: 0.11 g, 52% for **12**; 0.06 g, 25% for **13**.

Complex 14. Compound **1** (0.20 g, 0.37 mmol) was suspended in acetonitrile (12 mL), and $MeO_2CC{\equiv}CH$ (0.033 mL, 0.370 mmol) was added. The resulting mixture was stirred at room temperature for 14 h, and after this period of time the solution turned yellow. The solvent was removed under reduced pressure, and the ^{1}H NMR spectrum of the crude product showed the formation of compounds **14** and **15** in a 1:1.3 ratio, along with other unidentified byproducts. **14** could not be isolated as a pure sample, due to its easy transformation into complex **15**. ^{1}H NMR ($CDCl_3$, 25 °C): δ 6.22 (s, 1 H, CH), 5.89, 5.78, 5.74 (s, 1 H each, 3 CH_{pz}), 3.78 (s, 3 H, CO_2Me), 2.44 (s, 3 H, MeCN), 2.6−1.5 (6 Me_{pz}). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 158.7 (*C*O_2Me), 155−140 (C_{qpz}), 114.4 (Me*C*N), 110−105 (CH_{pz}), 97.0 (CH, $^1J_{CH}$ = 192 Hz), 71.0 (*C*CO_2Me), 51.1 (CO_2*Me*), 20.0−10.0 (Me_{pz}), 4.0 (*Me*CN).

Complex 15. Compound **1** (0.20 g, 0.37 mmol) was suspended in acetonitrile (12 mL), and $MeO_2CC{\equiv}CH$ (0.033 mL, 0.370 mmol) was added. The resulting mixture was stirred at 60 °C for 14 h, and then a yellow solution was observed. The solvent was removed under reduced pressure, and the ^{1}H NMR spectrum of the crude product showed the formation of compound **15** in 80% spectroscopic yield, along with other unidentified byproducts. **15** was isolated by column chromatography on silica gel using an AcOEt−hexane (1:2) mixture → AcOEt−hexane (2:1) mixture as eluent. Yield: 0.07 g, 30% (white crystals). R_f = 0.57 (silica gel, ethyl acetate−hexane (2:1)). IR (Nujol): ν(CN) 2174, ν(IrH) 2104 cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ 5.81, 5.77, 5.68 (s, 1 H each, 3 CH_{pz}), 3.60 (s, 3 H, CO_2Me), 2.51, 2.39, 2.36, 2.33, 2.28, 2.23 (s, 3 H each, 6 Me_{pz}), 2.47 (s, 3 H, MeCN), −19.60 (s, 1 H, Ir−H). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): δ 155.4 (*C*O_2Me), 152.7, 151.3, 150.3, 143.7, 143.4, 143.4 (C_{qpz}), 115.7 (Me*C*N), 106.5, 106.3, 105.8 (CH_{pz}), 96.8, 93.2 (IrC≡C), 51.4 (CO_2*Me*), 16.2, 14.7, 13.9, 12.8, 12.4, 12.2 (Me_{pz}), 3.9 (*Me*CN). Anal. Calcd for $C_{21}H_{29}BN_7O_2Ir$: C, 41.0; H, 4.7; N, 15.9. Found: C, 40.7; H, 4.6; N, 15.3.

X-ray Structure Determination. X-ray data of complexes **4** (as the solvate **4**·CH_2Cl_2) and **6** were collected on a Bruker Smart APEX CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and 0.3° ω-scan frames covering hemispheres of the reciprocal space with θ_{max} = 30°. After data integration with the program SAINT+, corrections for absorption, λ/2 effects, and crystal decay were applied with the program SADABS.[20] The structures were solved by direct methods, expanded with Fourier syntheses, and refined on F^2 with the program suite SHELX97.[21] 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. Crystal data and experimental details are given in Table 1, the molecular structures are shown in Figures 1 and 3, and selected geometric data are presented in Tables 2 and 3.

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Supporting Information Available: CIF files giving complete crystallographic data and technical details for compounds **4**·CH_2Cl_2 and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM061056Q

(20) Bruker programs: SMART, version 5.629; SAINT+, version 6.45; SADABS, version 2.10; SHELXTL, version 6.14 (Bruker AXS Inc., Madison, WI, 2003).

(21) Sheldrick, G. M. SHELX97: Program System for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1997.