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Oxidative Coupling in the Reaction of $\mathrm{Tp^{Me2}Ir}$(2,3-dimethylbutadiene) with Diphenylacetylene

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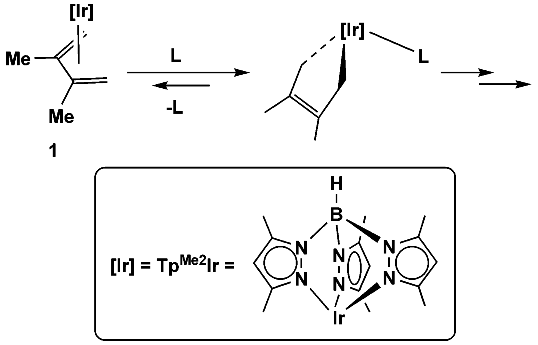
The 2,3-dimethylbutadiene complex $\mathrm{Tp^{Me2}Ir(CH_2{=}C(Me)C(Me){=}CH_2)}$ (**1**) reacts with $\mathrm{PhC{\equiv}CPh}$, in $\mathrm{C_6H_{12}}$ at 60 °C, with coupling of the diene and the alkyne and formation of compound **2a**, which contains an elaborated bicyclic chelating ligand with alkyl and η^3-allyl functionalities. NCMe reacts reversibly with **2a**, giving rise to a mixture of the isomeric iridacyclopentenes $\mathrm{Tp^{Me2}Ir(CH_2C(Me)(CMe{=}CH_2)C(Ph){=}C(Ph))(NCMe)}$ (**3**) and $\mathrm{Tp^{Me2}Ir(CH_2C(Me)(}$*cis*$\mathrm{\text{-}CPh{=}CHPh)C(Me){=}CH)(NCMe)}$ (**4**). Complex **2a** decomposes in $\mathrm{C_6H_{12}}$ at 80 °C to give a complex mixture from which an interesting substituted iridafulvene, **5**, has been isolated by chromatography. All these compounds have been characterized by NMR spectroscopy and X-ray crystallography. Possible reaction mechanisms for the formation of these species are discussed.

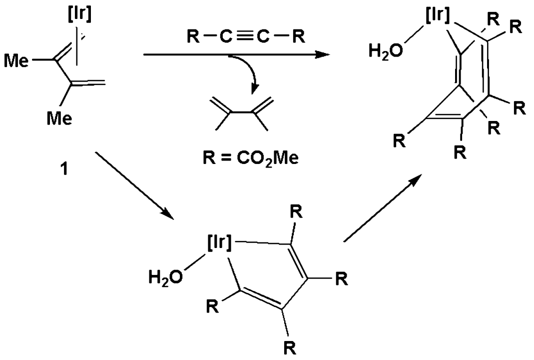
Introduction

The Ir(I)-2,3-dimethylbutadiene complex $\mathrm{Tp^{Me2}Ir(CH_2{=}C(Me)C(Me){=}CH_2)}$ (**1**)[1] ($\mathrm{Tp^{Me2}}$ = hydrotris(3,5-dimethylpyrazolyl)borate)[2] exhibits a rich chemistry toward a variety of Lewis bases (L). These reactions usually take place by formation of an Ir−L bond with concomitant formal oxidative addition of the diene moiety to the metal center and a change of the coordination mode of the hydrocarbyl ligand, from $\eta^4{:}\pi,\pi$ to $\eta^2{:}\sigma,\sigma$ (eq 1).[3] Depending on the nature of the Lewis base, the reaction may be reversible (e.g., with $\mathrm{C_2H_4}$) or proceed further, with formation of products in which the two ligands may couple to form more elaborated coordinated units.[4]



(1)

We have recently reported that the reaction of **1** with dimethyl acetylene dicarboxylate (DMAD)[5] takes place with displacement of the diene and incorporation of three molecules of the alkyne in the form of an iridacycloheptatriene. Metal unsaturation is prevented by coordination of adventitious water (eq 2), the reaction proceeding through intermediacy of an iridacyclopentadiene species, also isolable as the water adduct.[6] Metalacycles of these types are usually proposed as intermediates in the metal-catalyzed cyclotrimerization of alkynes.[7]



(2)

In contrast to DMAD, complex **1** reacts with $\mathrm{Me_3SiC{\equiv}CSiMe_3}$ to form the vinylidene complex $\mathrm{Tp^{Me2}Ir(CH_2C(Me){=}C(Me)CH_2)({=}C{=}C(SiMe_3)_2)}$, i.e., with rearrangement of the alkyne but with no further interaction with the butadiene.[8] In

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Table 1. Crystal Data and Data Collection and Refinement Details for 2a, 3·solv, 4·solv, and 5

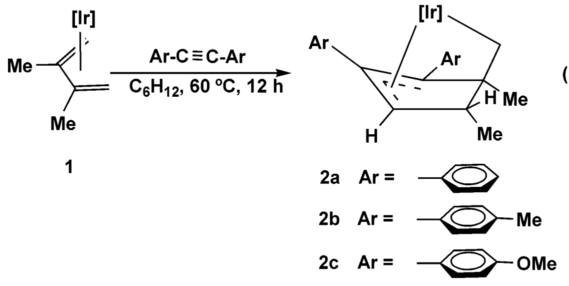
	2a	**3**·solv[c]	**4**·solv[c]	**5**
formula	$C_{35}H_{42}BIrN_6$	$C_{37}H_{45}BIrN_7$	$C_{37}H_{45}BIrN_7$	$C_{35}H_{42}BIrN_6$
mol wt	749.76	790.81	790.81	749.76
color, habit	yellow, plate	colorless, plate	colorless, block	dark, prism
symmetry, space group	monoclinic, $P2_1/c$	triclinic, $P1$	monoclinic, $P2_1/n$	orthorhombic, $P2_12_12_1$
a, Å	8.9245(4)	11.918(6)	12.9261(6)	10.9918(5)
b, Å	34.7658(16)	12.520(19)	14.8923(7)	16.7632(7)
c, Å	10.8015(5)	14.069(14)	18.9635(9)	17.5907(7)
α, deg	90	90.97(2)	90	90
β, deg	110.413(1)	111.84(2)	95.263(1)	90
γ, deg	90	95.65(2)	90	90
V, Å^3	3140.9(2)	1936(4)	3635.1(3)	3241.2(2)
Z	4	2	4	4
D_{calcd}, g cm^{-3}	1.586	1.357	1.445	1.536
μ, mm^{-1}	4.286	3.481	3.708	4.153
θ range, deg	2.3−30.0	2.3−25.0	2.1−30.0	2.2−30.0
temp, K	173(2)	297(2)	173(2)	173(2)
no. of data collected	55 866	24 174	68 663	49 161
no. of unique data	9124 ($R_{int} = 0.055$)	6510 ($R_{int} = 0.125$)	10 241 ($R_{int} = 0.042$)	9453 ($R_{int} = 0.054$)
no. of params/restraints	396/0	424/144	454/143	402/0
$R_1{}^a$ ($F^2 > 2\sigma(F^2)$)	0.0291	0.0663	0.0528	0.0280
$wR_2{}^b$ (all data)	0.0484	0.1842	0.1124	0.0541

[a] $R_1(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2(F^2) = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[(w(F_o{}^2)^2]\}^{1/2}$. [c] Solvent squeezed with program PLATON (A. L. Spek, 2005) and not contained in chemical formula and quantities derived thereof.

this contribution we report on the different reaction outcome observed when the alkyne employed is diphenylacetylene.

Results and Discussion

The reaction of Tp^{Me2}Ir(CH$_2$=C(Me)C(Me)=CH$_2$) (**1**) with a slight excess (1.2 equiv) of diphenylacetylene, PhC≡CPh, occurs with formation in high spectroscopic yield (~80%) of a compound, **2a**, that contains the chelating hydrocarbyl ligand depicted in eq 3, which bonds to iridium through alkyl and allyl termini. The reaction can be described formally as a cyclic, nonasymmetrical, coupling of the incoming −C≡C− unit with the butadiene ligand, followed by a stereospecific H-shift.[9] Compound **2a** does not react further with the alkyne under the conditions of eq 3. Other aryl-substituted alkynes react similarly, giving rise to related products, e.g., **2b** and **2c**, as shown in eq 3.



(3)

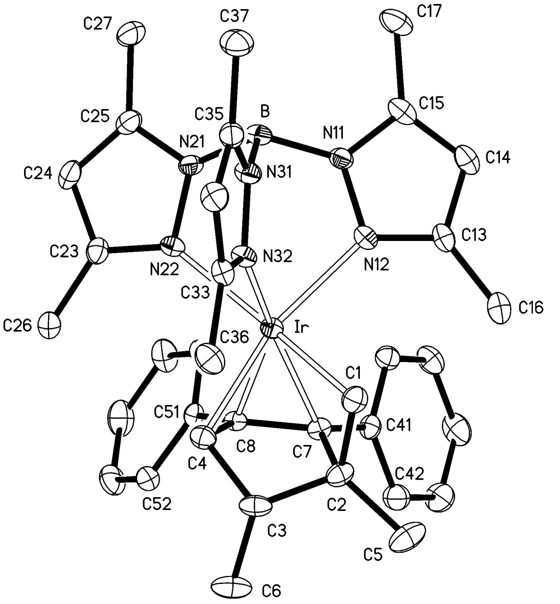
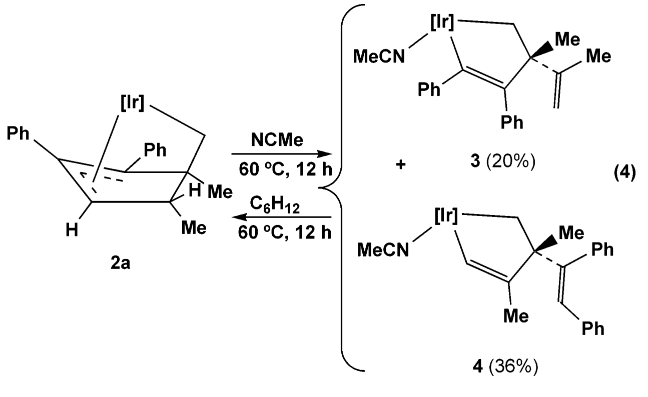


Figure 1. X-ray structure of complex **2a** (thermal ellipsoids drawn at the 40% probability level, hydrogen atoms omitted for clarity).



Compound **2a** has been characterized by microanalysis, NMR spectroscopy, and an X-ray diffraction study. The allyl moiety coordinated to Ir gives rise to ^{13}C NMR signals at 66.4 (terminal *C*Ph), 102.9 (internal *C*Ph), and 28.4 (CH, $^1J_{CH} = 160$ Hz) ppm, while the Ir-bound methylene carbon resonates at −19.1 ppm ($^1J_{CH} = 134$ Hz). In the ^{1}H NMR spectrum, the two diastereotopic IrCH$_2$ protons are found at 2.29 and 0.84 ($^2J_{HH} = 6.4$

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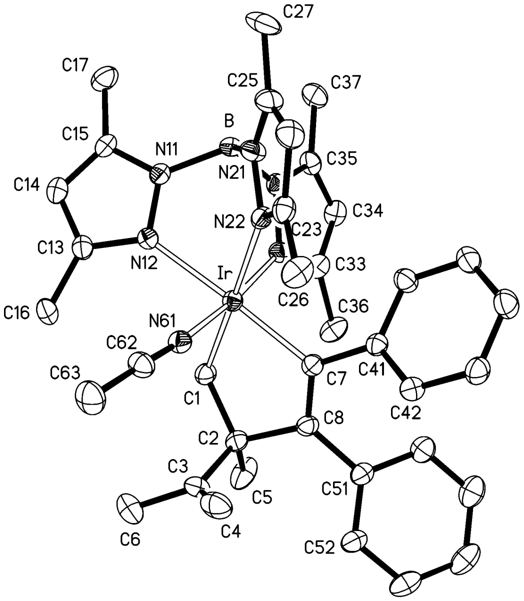

Figure 2. X-ray structure of complex **3** (thermal ellipsoids drawn at the 20% probability level, hydrogen atoms omitted for clarity).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2a

Ir−N(12)	2.195(2)	C(1)−C(2)	1.521(4)
Ir−N(22)	2.291(2)	C(2)−C(3)	1.542(4)
Ir−N(32)	2.103(2)	C(2)−C(7)	1.581(4)
Ir−C(1)	2.064(3)	C(7)−C(8)	1.415(3)
Ir−C(4)	2.139(3)	C(8)−C(4)	1.454(3)
Ir−C(7)	2.215(3)	C(4)−C(3)	1.526(4)
Ir−C(8)	2.122(2)		

C(1)−Ir−N(32)	93.5(1)	N(32)−Ir−C(7)	158.8(1)
C(1)−Ir−C(8)	94.2(1)	C(52)−Ir−C(7)	38.0(1)
N(32)−Ir−C(8)	147.2(1)	C(44)−Ir−C(7)	63.4(1)
C(1)−Ir−C(4)	82.0(1)	N(12)−Ir−C(7)	100.5(1)
N(32)−Ir−C(4)	110.2(1)	C(1)−Ir−N(22)	170.8(1)
C(8)−Ir−C(4)	39.9(1)	N(32)−Ir−N(22)	78.0(1)
C(1)−Ir−N(12)	89.9(1)	C(8)−Ir−N(22)	91.0(1)
N(32)−Ir−N(12)	84.2(1)	C(4)−Ir−N(22)	97.2(1)
C(8)−Ir−N(12)	127.7(1)	N(12)−Ir−N(22)	93.0(1)
C(44)−Ir−N(12)	163.8(1)	C(7)−Ir−N(22)	121.9(1)
C(1)−Ir−C(7)	66.0(1)		

Hz) ppm. The latter signal shows NOE interaction with the C*H*Me proton, in accord with the stereochemistry presented in eq 3. Complexes **2b**,**c** show NMR characteristics very similar to those of **2a**, indicating they adopt closely related structures. Figure 1 shows an ORTEP representation of the molecules of compound **2a**, while Tables 1 and 2 include crystal data and selected bond lengths and angles, respectively. The two C−C distances corresponding to the allyl moiety, C(4)−C(8), 1.454(3) Å, and C(8)−C(7), 1.415(3) Å, are clearly intermediate between a single and a double bond, in agreement with the delocalized structure, with the corresponding three Ir−C distances (Ir−C(4), 2.139(3) Å, Ir−C(8), 2.122(2) Å, and Ir−(7), 2.215(3) Å) being only slightly longer than the single-bond Ir−C(1) distance of 2.064(3) Å. The structural data compare favorably with those found for related functionalities in Tp^{Me2}-Ir(III) species.[5]

The complexity of the chelating ligands present in compounds **2** makes it difficult to propose a reliable mechanistic pathway for their formation, but the reaction of complex **2a** with NCMe, described in the following paragraphs, provides some valuable information and facilitates, at least in part, this task.

When compound **2a** is heated at 60 °C in NCMe for 12 h, it converts mainly into two isomeric acetonitrile adducts, the iridacyclopent-2-ene[10] species **3** and **4** represented in eq 4. Formation of these two adducts is reversible so that heating **3** or **4** in cyclohexane (60 °C) leads to NCMe dissociation and formation of the allyl precursor **2a**. Only one stereoisomer is observed for each structure, and in the two compounds the Me substituent on the C_{sp3} atom points toward the Tp^{Me2} ligand. They have been characterized mainly by NMR spectroscopy and single-crystal X-ray diffraction studies. Figures 2 and 3 show ORTEP views of the molecular structures of compounds **3** and **4**, respectively, while other pertinent data are included in Tables 1, 3, and 4. The two iridacyclopentene species contain localized double bonds, with lengths of 1.367(17) Å for C(7)−C(8) in **3** and 1.387(8) Å for C(3)−C(4) in **4**. In both cases, the Ir−N(32) distance, corresponding to the pyrazolyl ring of the Tp^{Me2} ligand *trans* to the coordinated NCMe, is shorter than the other two Ir−N(pyrazolyl) bond lengths: for **3**, 2.050(10) vs 2.174(10) Å (average of the other two); for **4**, 2.075(4) vs 2.196(5) Å (also average). NMR spectroscopy studies, includingNOESY experiments, collected in the Experimental Section are in accord with the solid-state structures of **3** and **4**.

The molecular complexity of **3** and **4** and their reversible generation from **2a** provide support for the mechanism represented in Scheme 1 for the formation of the latter complex from

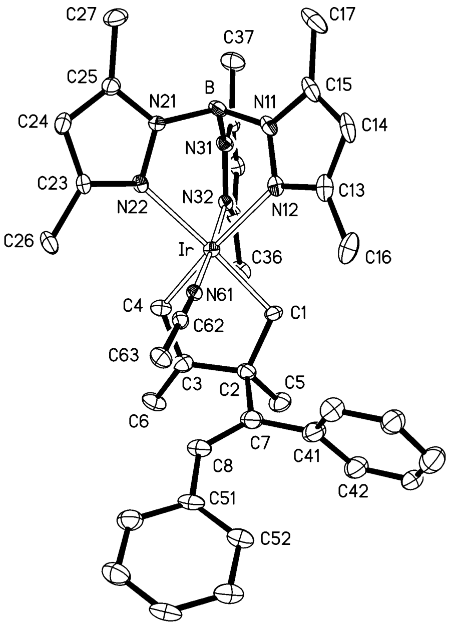

Figure 3. X-ray structure of complex **4** (thermal ellipsoids drawn at the 20% probability level, hydrogen atoms omitted for clarity).

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

Ir−N(12)	2.169(10)	Ir−N(61)	1.894(11)
Ir−N(22)	2.178(10)	C(1)−C(2)	1.552(17)
Ir−N(32)	2.050(10)	C(2)−C(8)	1.570(16)
Ir−C(1)	2.048(12)	C(8)−C(7)	1.367(17)
Ir−C(7)	2.051(12)		

N(61)−Ir−N(32)	174.4(4)	C(1)−Ir−N(12)	94.9(4)
N(61)−Ir−C(1)	90.1(5)	C(7)−Ir−N(12)	174.7(4)
N(32)−Ir−C(1)	92.6(5)	N(61)−Ir−N(22)	88.7(4)
N(61)−Ir−C(7)	93.5(5)	N(32)−Ir−N(22)	88.5(4)
N(32)−Ir−C(7)	91.7(4)	C(1)−Ir−N(22)	178.8(4)
C(1)−Ir−C(7)	80.1(5)	C(7)−Ir−N(22)	100.3(4)
N(61)−Ir−N(12)	88.4(4)	N(12)−Ir−N(22)	84.6(4)
N(32)−Ir−N(12)	86.5(4)		

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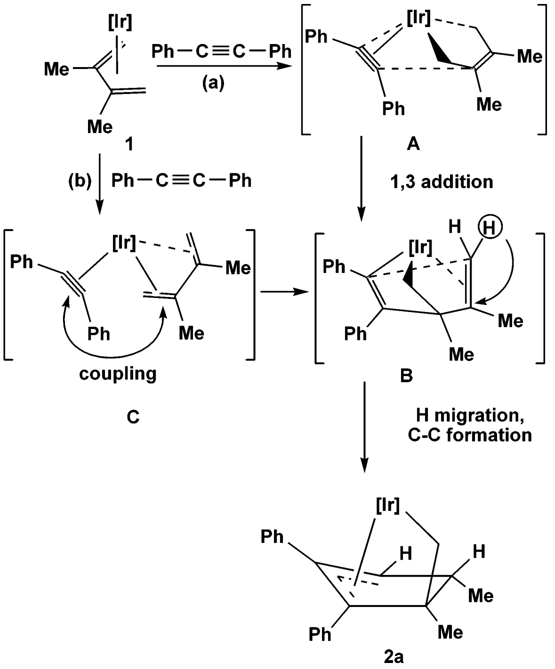
Table 4. Selected Bond Lengths (Å) and Angles (deg) for 4·solv

Ir−N(12)	2.202(5)	Ir−N(61)	1.961(4)
Ir−N(22)	2.190(4)	C(1)−C(2)	1.518(8)
Ir−N(32)	2.075(4)	C(2)−C(3)	1.518(9)
Ir−C(1)	2.063(5)	C(3)−C(4)	1.387(8)
Ir−C(4)	2.016(6)		
N(61)−Ir−C(4)	89.0(2)	C(1)−Ir−N(22)	176.9(2)
N(61)−Ir−C(1)	88.5(2)	N(32)−Ir−N(22)	86.7(2)
C(4)−Ir−C(1)	80.0(2)	N(61)−Ir−N(12)	92.0(2)
N(61)−Ir−N(32)	176.3(2)	C(4)−Ir−N(12)	175.6(2)
C(4)−Ir−N(32)	92.7(2)	C(1)−Ir−N(12)	95.7(2)
C(1)−Ir−N(32)	95.0(2)	N(32)−Ir−N(12)	86.6(2)
N(61)−Ir−N(22)	89.8(2)	N(22)−Ir−N(12)	87.0(2)
C(4)−Ir−N(22)	97.3(2)		

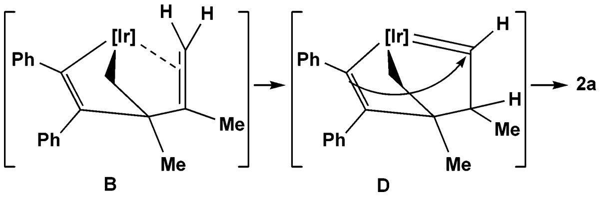
Scheme 1



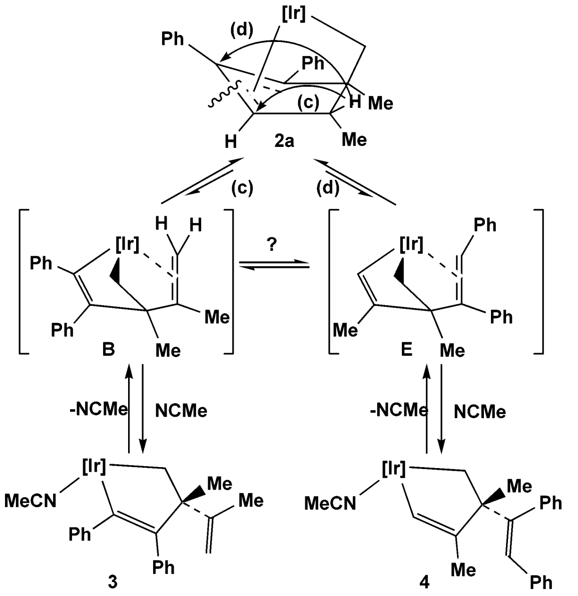
1 and PhC≡CPh. Initial coordination of the alkyne as in path (a) produces the Ir(III) species **A**, an additional example of the well-established η^4:π,π to η^2:σ,σ rearrangement of the butadiene ligand discussed in the Introduction. Intermediate **A** can then experience a 1,3 addition[11] of the alkyne to the metallacycle to form **B**, a bicyclic structure with a coordinated olefinic terminus. Alternatively, path (b) results from initial coordination of the alkyne to an unsaturated Ir(I) intermediate, provided by a coordination change of the Tp^{Me2} ligand from κ^3 to κ^2 similar to the proposed pathway for the reaction of **1** with DMAD.[5,12] This Ir(I) intermediate will give **B** by a [2+2] oxidative coupling and restoration of κ^3−Tp^{Me2} binding. Finally, stereospecific migration of one of the terminal olefinic H atoms of **B** to the adjacent carbon atom and a C−C bond forming process would yield the observed product **2a**. These steps could be concerted or consecutive; in the latter case alkene-to-alkylidene isomerization[13] would be followed by migration of the alkenyl moiety to the carbene (Scheme 2).[13g,14]

It is worth noting that the organometallic skeleton proposed for **B** is identical to that found in the NCMe adduct **3**, so that the pathway proposed in Scheme 1 would imply that the **B** → **2a** transformation is reversible, intermediate **B** being trapped by the Lewis base to give **3**. Accordingly, formation of adducts **3** and **4** from **2a** can be proposed to take place as described in Scheme 3. Path (c) of Scheme 3 summarizes the process already discussed, while the formation of **4** in path (d) would be similar, although in this case the hydrogen atom migrates to the central allylic C(Ph) carbon atom, leading to a new intermediate **E**, which is trapped by NCMe to give **4**. It is possible that **B** could transform directly into **E** or that an equilibrium between the two could be established, but we have no data to distinguish between these mechanistic details.

Scheme 2



Scheme 3



A complex reaction mixture results when a solution of complex **2a** in C_6H_{12} is heated at 80 °C. Following column chromatography, one of the minor products can be isolated and characterized as the benzoannelated metallafulvene complex **5** (eq 5). **5** has been fully characterized by microanalysis, spectroscopy (IR and NMR including NOESY studies), and X-ray crystallography (Figure 4; X-ray data included in Tables 1 and 5). The hydride ligand appears at −14.71 ppm in the ^{1}H NMR spectrum, whereas the iridium-bound carbene carbon resonates at 296.5 ppm in the ^{13}C{^{1}H} NMR spectrum. The Ir−C(1) distance corresponding to the carbene functionality

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[14] (a) Alías, F. M.; Daff, P. J.; 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. (b) Lara, P.; Paneque, M.; Poveda, M. L.; Salazar, V.; Santos, L. L.; Carmona, E. *J. Am. Chem. Soc.* **2006**, *128*, 3512.

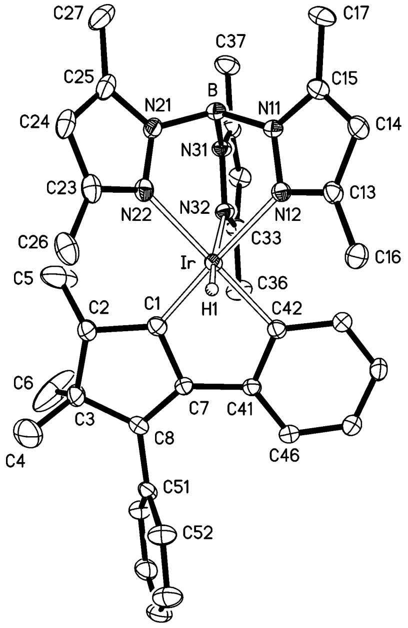
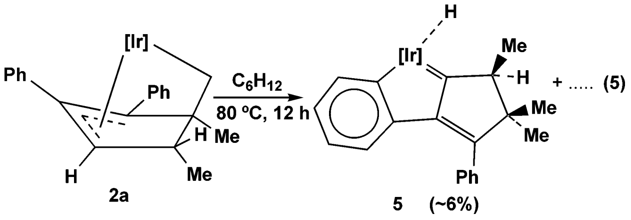


Figure 4. X-ray structure of complex **5** (thermal ellipsoids drawn at the 30% probability level, hydrogen atoms omitted for clarity except the hydride ligand H1).

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 5

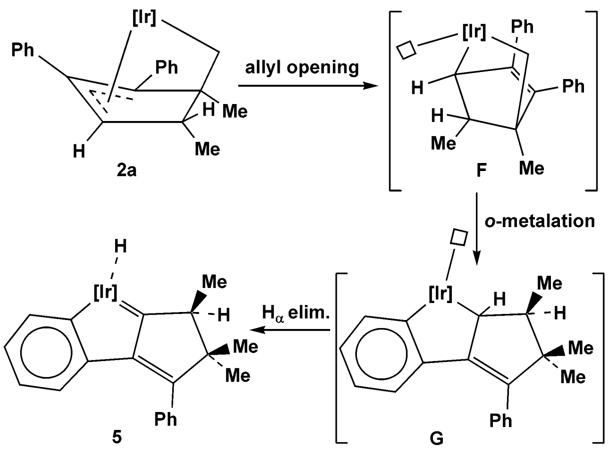
Ir−N(12)	2.170(3)	Ir−H(1)	1.50(4)
Ir−N(22)	2.177(3)	C(1)−C(7)	1.459(5)
Ir−N(32)	2.161(3)	C(7)−C(41)	1.457(5)
Ir−C(1)	1.903(3)	C(41)−C(42)	1.414(5)
Ir−C(42)	2.033(4)	C(7)−C(8)	1.370(5)
C(1)−Ir−C(42)	80.8(1)	N(32)−Ir−N(22)	89.6(1)
C(1)−Ir−N(32)	100.3(1)	N(12)−Ir−N(22)	81.0(1)
C(42)−Ir−N(32)	93.5(1)	C(1)−Ir−H(1)	91.1(15)
C(1)−Ir−N(12)	175.1(1)	C(42)−Ir−H(1)	90.3(16)
C(42)−Ir−N(12)	97.9(1)	N(32)−Ir−H(1)	168.5(15)
N(32)−Ir−N(12)	84.5(1)	N(12)−I−H(1)	84.2(15)
C(1)−Ir−N(2)	100.0(1)	N(22)−Ir−H(1)	86.4(16)
C(42)−Ir−N(22)	176.6(1)		

amounts 1.903(3) Å,[8] significantly shorter than the iridium−C_{aryl} bond, Ir−C(42), of 2.033(4) Å. The latter value compares well with that corresponding to a similar bond in a related iridacycle.[15]



Rearrangement of **2a** into the isomeric hydride-alkylidene structure **5** can be proposed to occur through the reaction pathway represented in Scheme 4. Upon heating, a change in the coordination of the allylic moiety of **2a** from η^3 to η^1 may occur (intermediate **F**), allowing C−H bond activation of a phenyl substituent by *ortho*-metalation and transfer of the corresponding H atom to the Ir−CH_2 carbon atom (**G**). Facile α-H elimination[16] leads to the final product **5**.

Scheme 4



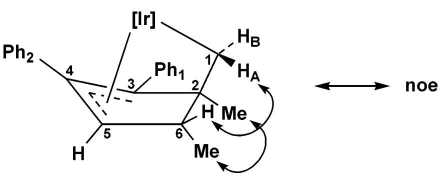
Conclusions

In conclusion, differently from the reactivity of the Ir(I) precursor **1** with DMAD and $Me_3SiC{\equiv}CSiMe_3$, the reaction of this complex with PhC≡CPh produces a chelating alkyl-allyl cyclic derivative, formed by C−H activation and C−C bond forming processes. Complex **2a** shows interesting reactivity, and, in particular, its reaction with NCMe provides useful information that allows the proposal of a reasonable pathway for its formation. Albeit in low yields, an interesting iridafulvene structure has been obtained from **2a**, when its solutions in C_6H_{12} are heated at 80 °C.

Experimental Section

General Procedures. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were obtained from 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 (^1H 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 dinitrogen, following conventional Schlenk techniques. The complex $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$ was obtained by the published procedure.[1] The small amount of product isolated for the case of some of the minor byproducts prevented the recrystallization of the solid samples obtained and hence the registration of better elemental analysis figures.

Compound 2a. A mixture of $Tp^{Me2}Ir(\eta^4\text{-}CH_2{=}C(Me)C(Me){=}CH_2)$ (**1**) (0.3 g, 0.52 mmol) and PhC≡CPh (0.112 g, 0.63 mmol) in cyclohexane (10 mL) was heated at 60 °C for 12 h, during which time it turned dark brown. The solvent was evaporated, and a ~80% spectroscopic yield of **2a** was ascertained by ^1H NMR. This compound was partially purified by adding hexane and filtering the yellow solid obtained. The yield was 0.26 g, ca. 63%. An analytically pure sample of **2a** was obtained after washing several times with cold pentane.



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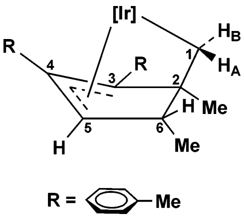
[15] Santos, L. L.; Mereiter, K.; Paneque, M.; Slugovc, C.; Carmona, E. *New J. Chem.* **2003**, *27*, 107.

[16] Carmona, E.; Paneque, M.; Poveda, M. L. *Dalton Trans.* **2003**, 4022.

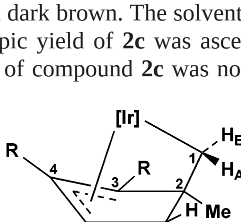
^{1}H NMR (CDCl$_3$, 65 °C): δ 7.19 (br d, 2 H, $^3J_{HH}$ = 7.7 Hz, *o,o′*-CH$_{ar}$(Ph$_1$)), 7.12 (br m, 2 H, *o, o′*-CH$_{ar}$(Ph$_2$)), 6.93 (br t, 1 H, $^3J_{HH}$ = 7.3 Hz, *p*-CH$_{ar}$(Ph$_1$)), 6.88 (m, 3 H, *m,m′*-CH$_{ar}$(Ph$_1$) + *p*-CH$_{ar}$(Ph$_2$)), 6.79 (br t, 2 H, $^3J_{HH}$ = 7.1 Hz, *m,m′*-CH$_{ar}$(Ph$_2$)), 5.91, 5.66, 5.28 (s, 1 H each, 3 CH$_{pz}$), 4.38 (s, 1 H, C^{5}H), 2.54, 2.47, 2.35, 2.22, 2.17, 0.96 (s, 3 H each, 6 Me$_{pz}$), 2.29 (detected by the HETCOR spectrum), 0.84 (d, 1 H each, $^2J_{HH}$ = 6.4 Hz, H$_B$, H$_A$, respectively), 1.82 (q, 1 H, $^3J_{HH}$ = 6.3 Hz, C^{6}H), 1.45 (d, 3 H, C^{6}Me), 1.01 (s, 3 H, C^{2}Me). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 153.6, 152.2, 149.9, 145.6, 143.5, 143.0 (C$_{qpz}$), 139.5, 136.2 (C$_{qar}$(Ph$_1$), C$_{qar}$(Ph$_2$), respectively), 132.0, 131.6 (*o,o′*-CH$_{ar}$(Ph$_2$), *o,o′*-CH$_{ar}$ (Ph$_1$), respectively), 126.2 (*m,m′*-CH$_{ar}$(Ph$_2$)), 125.8 (*m,m′*-CH$_{ar}$(Ph$_1$), *p*-CH$_{ar}$(Ph$_2$)), 125.1 (*p*-CH$_{ar}$(Ph$_1$)), 108.9, 107.6, 105.8 (CH$_{pz}$), 102.9 (C^4), 66.4 (C^3), 60.0 (C^2), 49.9 (C^6, $^1J_{CH}$ = 135 Hz), 28.4 (C^5, $^1J_{CH}$ = 160 Hz), 24.7 (C^2*Me*, $^1J_{CH}$ = 123 Hz), 18.4 (C^6*Me*, $^1J_{CH}$ = 123 Hz), 18.4, 15.5, 14.0, 13.0, 12.9, 12.7 (Me$_{pz}$), −19.1 (C^1, $^1J_{CH}$ = 134 Hz). Anal. Calcd for $C_{35}H_{42}BN_6Ir$: C, 56.1; H, 5.6; N, 11.2. Found: C, 55.8; H, 5.7; N, 10.9.

Compound 2b. A mixture of Tp^{Me2}Ir(η^4-CH$_2$=C(Me)C(Me)=CH$_2$) (**1**) (0.2 g, 0.35 mmol) and *p,p′*-dimethyltolane (0.086 g, 0.42 mmol) in cyclohexane (8 mL) was heated at 60 °C for 12 h, during which time it turned dark brown. The solvent was evaporated and a ~80% spectroscopic yield of **2b** was ascertained by ^{1}H NMR. Further purification of compound **2b** was not pursued.



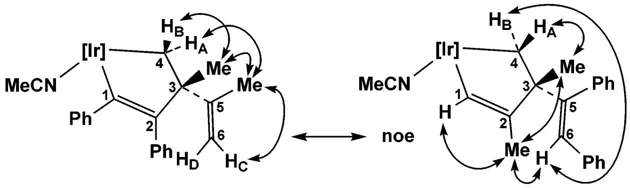
^{1}H NMR (CDCl$_3$, 25 °C): δ 7.05 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, 2 CH$_{ar}$), 6.69 (d, 2 H, $^3J_{HH}$ = 7.3 Hz, 2 CH$_{ar}$), the other aromatic H's appear as broad signals, and it is not possible to distinguish them in the baseline, 5.89, 5.65, 5.28 (s, 1 H each, 3 CH$_{pz}$), 4.30 (s, 1 H, C^{5}H), 2.52, 2.43, 2.32, 2.19, 2.12, 0.88 (s, 3 H each, 6 Me$_{pz}$), 2.20 (detected by the HETCOR spectrum), 0.78 (d, 1 H each, $^2J_{HH}$ = 6.1 Hz, H$_B$, H$_A$, respectively), 2.10, 1.41 (s, 3 H each, 2 C$_6$H$_4$*Me*), 1.74 (q, 1 H, $^3J_{HH}$ = 6.4 Hz, C^{6}H), 1.39 (d, 3 H, C^{6}Me), 0.96 (s, 3 H, C^{2}Me). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 153.6, 152.1, 149.9, 145.5, 143.4, 143.0 (C$_{qpz}$), 136.5, 135.2, 134.2, 133.2 (C$_{qar}$), 131.4, 129.7, 127.0, 126.7 (CH$_{ar}$), 108.9, 107.5, 105.8 (CH$_{pz}$), 102.9 (C^4), 66.0 (C^3), 59.7 (C^2), 49.6 (C^6, $^1J_{CH}$ = 131 Hz), 28.3 (C^5, $^1J_{CH}$ = 160 Hz), 24.9 (C^2*Me*), 21.1, 12.9 (C$_6$H$_4$*Me*), 21.0, 18.5, 15.7, 14.1, 13.3, 13.2 (Me$_{pz}$), 18.7 (C^6*Me*), −19.3 (C^1, $^1J_{CH}$ = 134 Hz).

Compound 2c. A mixture of Tp^{Me2}Ir(η^4-CH$_2$=C(Me)C(Me)=CH$_2$) (**1**) (0.2 g, 0.35 mmol) and *p,p′*-dimethoxytolane (0.1 g, 0.42 mmol) in cyclohexane (8 mL) was heated at 60 °C for 12 h, during which time it turned dark brown. The solvent was evaporated, and a ~80% spectroscopic yield of **2c** was ascertained by ^{1}H NMR. Further purification of compound **2c** was not pursued.



^{1}H NMR (CDCl$_3$, 25 °C): δ 7.08 (d, 2 H, $^3J_{HH}$ = 8.2. Hz, 2 CH$_{ar}$), 6.46 (d, 2 H, $^3J_{HH}$ = 8.2 Hz, 2 CH$_{ar}$), the other aromatic H's appear as broad signals, and it is not possible to distinguish them in the baseline, 5.90, 5.66, 5.28 (s, 1 H each, 3 CH$_{pz}$), 4.30 (s, 1 H, C^{5}H), 3.65, 3.62 (s, 3 H each, 2 C$_6$H$_4$O*Me*), 2.51, 2.44, 2.32, 2.20, 2.15, 0.95 (s, 3 H each, 6 Me$_{pz}$), 2.33 (detected by the HETCOR spectrum), 0.74 (d, 1 H each, $^2J_{HH}$ = 6.6 Hz, H$_B$, H$_A$, respectively), 1.72 (q, 1 H, $^3J_{HH}$ = 6.6 Hz, C^{6}H), 1.38 (d, 3 H, C^{6}Me), 0.96 (s, 3 H, C^{2}Me). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 157.7, 157.0 (C$_{qar}$OMe), 153.4, 152.0, 149.8, 145.4, 143.4, 142.9 (C$_{qpz}$), 132.3, 128.7 (*o, o′*-CH$_{ar}$), 111.6, 111.3 (*m, m′*-CH$_{ar}$), the other C$_{ar}$ could not be detected, 108.8, 107.5, 105.7 (CH$_{pz}$), 102.4 (C^4), 65.3 (C^3), 59.3 (C^2), 55.2, 54.9 (C$_6$H$_4$O*Me*), 49.4 (C^6), 28.4 (C^5), 24.8 (C^2*Me*), 18.7 (C^6*Me*), 18.2, 15.6, 14.1, 13.2, 13.1, 12.9 (Me$_{pz}$), −19.4 (C^1).

Compounds 3 and 4. Compound **2a** (0.35 g, 0.47 mmol) was dissolved in NCMe (20 mL). The solution was stirred at 60 °C for 12 h, and the volatiles were evaporated under vacuo. NMR monitoring of the crude product revealed a mixture of compounds **3** and **4** with yields of 20 and 36%, respectively, together with other unidentified byproducts. Separation in pure form of these two compounds was accomplished by column chromatography on silica gel, using hexane−Et$_2$O (1:1) as eluent.



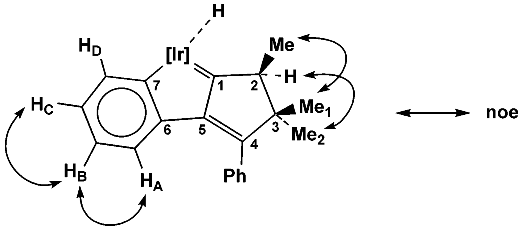
3 **4**

Compound 3. ^{1}H NMR (CDCl$_3$, 25 °C): δ 7.76 (br d, 1 H, 1 CH$_{ar}$), 7.15 (br m, 1 H, 1 CH$_{ar}$), 6.87 (t, 1 H, $^3J_{HH}$ ≈ 7 Hz, 1 CH$_{ar}$), 6.76 (br m, 1 H, 1 CH$_{ar}$), 6.74 (t, 1 H, $^3J_{HH}$ ≈ 7 Hz, 1 CH$_{ar}$), 6.66 (br m, 1 H, 1 CH$_{ar}$), 6.63 (t, 2 H, $^3J_{HH}$ ≈ 7 Hz, 2 CH$_{ar}$), 6.49 (br, 2 H, 2 CH$_{ar}$), 5.74, 5.71, 5.43 (s, 1 H each, 3 CH$_{pz}$), 5.51 (d, 1 H, $^2J_{DC}$ = 3.5 Hz, H$_D$), 5.07 (br d, 1 H, H$_C$), 3.17 (d, 1 H, $^2J_{BA}$ = 11.0 Hz, H$_B$), 2.99 (d, 1 H, H$_A$), 2.61, 2.44, 2.42, 2.33, 2.32, 1.19 (s, 3 H each, 6 Me$_{pz}$), 2.20 (s, 3 H, MeCN), 2.08 (s, 3 H, C^{5}Me), 1.09 (s, 3 H, C^{3}Me). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 158.9 (C^5), 152.4, 149.7, 149.5, 143.7, 142.8, 142.4 (C$_{qpz}$), 151.8 (C^2), 134.0, 130.1, 129.7, 126.5, 126.0, 125.9, 123.3, 122.4 (CH$_{ar}$), 116.5 (Me*C*N), 111.0 (C^6, $^1J_{CH}$ = 153 Hz), 107.0, 105.8, 105.5 (CH$_{pz}$), 61.0 (C^3), 27.2 (C^3*Me*), 20.1 (C^5*Me*), 15.0, 14.1, 13.8, 12.7, 12.4, 12.2 (Me$_{pz}$), 7.3 (C^4, $^1J_{CH}$ = 126 Hz), 4.3 (*Me*CN). C^1 and C$_{qar}$ have not been located. IR (Nujol): ν(CN) 2287 cm^{-1}. Anal. Calcd for $C_{37}H_{45}BN_7Ir$: C, 56.2; H, 5.7; N, 12.4. Found: C, 55.6; H, 5.8; N, 11.6.

Compound 4. ^{1}H NMR (CDCl$_3$, 25 °C): δ ~7.5 (br, 2 H, 2 *o*-CH$_{ar}$), 7.35 (m, 3 H, 2 *m*-CH$_{ar}$ + 1 *p*-CH$_{ar}$), 7.05 (q, 1 H, $^3J_{HH}$ = 1.0 Hz, C^{1}H), 6.98 (m, 3 H, 2 *m*-CH$_{ar}$ + 1 *p*-CH$_{ar}$), 6.87 (s, 1 H, C^{6}H), 6.75 (m, 2 H, 2 *o*-CH$_{ar}$), 5.81, 5.77, 5.55 (s, 1 H each, 3 CH$_{pz}$), 3.41 (d, 1 H, $^2J_{BA}$ = 11.4 Hz, H$_B$), 2.77 (d, 1 H, H$_A$), 2.57, 2.44, 2.42, 2.36, 2.29 (s, 1:1:1:2:1, 6 Me$_{pz}$), 1.91 (br s, 3 H, C^2-Me), 1.65 (s, 3 H, MeCN), 1.13 (s, 3 H, C^{3}Me). ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ 154.9 (C^5), 151.7, 149.9, 149.4, 143.3, 143.0, 142.5 (C$_{qpz}$), 149.1 (C^2), 143.0, 139.2 (C$_{qar}$), ~130 (br, *o*-CH$_{ar}$), 128.9 (*o*-CH$_{ar}$), 128.0, 128.0 (*m*-CH$_{ar}$), 126.1 (*p*-CH$_{ar}$), 125.4 (*p*-CH$_{ar}$ + C^6, $^1J_{CH}$ = 154 Hz), 121.5 (C^1, $^1J_{CH}$ = 139 Hz), 116.1 (Me*C*N), 108.5, 106.7, 106.1 (CH$_{pz}$), 59.5 (C^3), 27.4 (C^3*Me*), 20.6 (C^2*Me*), 15.5, 14.5, 13.5, 13.2, 12.6, 12.4 (Me$_{pz}$), 5.1 (C^4, $^1J_{CH}$ = 126 Hz), 3.8 (*Me*CN). IR (Nujol): ν(CN) 2280 cm^{-1}. Anal. Calcd for $C_{37}H_{45}BN_7Ir$: C, 56.2; H, 5.7; N, 12.4. Found: C, 56.1; H, 5.8; N, 11.8.

Compound 5. Compound **2a** was dissolved in C$_6$H$_{12}$ (0.01 g, 0.013 mmol; 2 mL) and the resulting solution heated at 80 °C for 12 h. The volatiles were removed under vacuum, and ^{1}H NMR analysis of the crude product revealed the presence of **5** in ca. 6% yield. This compound was separated by column chromatography on silica gel using hexane as eluent.

^{1}H NMR (CDCl$_3$, 25 °C): δ 7.5−7.3 (m, 5 H, CH$_{ar}$(Ph)), 7.05 (d, 1 H, $^3J_{HH}$ = 7.3 Hz, H$_A$), 6.66 (td, 1 H, J_{HH} = 1.5 Hz, H$_B$), 6.5



(m, 2 H, H_C, H_D), 5.84, 5.82, 5.57 (s, 1 H each, 3 CH_{pz}), 2.50 (q, 1 H, $^3J_{HH} = 7.7$ Hz, C^2H), 2.45, 2.44, 2.39, 2.29, 2.21, 1.11 (s, 3 H each, 6 Me_{pz}), 1.26 (s, 3 H, Me_2), 1.01 (s, 3 H, Me_1), 0.79 (d, 3 H, C^2Me), −14.71 (s, 1 H, Ir−H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ 296.5 (C^1), 152.1, 150.6, 150.1, 144.1, 143.9, 142.8 (C_{qpz}), 149.5, 144.3 (C^7, C^6, C^5, one of them has not been located), 148.4 (C^4), 138.8 (C_qPh), 137.8 (CH_A), 128.1 (*m*-CH_{ar}(Ph)), 127.7 (*p*-CH_{ar}(Ph)), 126.1 (CH_B), 124.4 (*o*-CH_{ar}(Ph)), 121.9 (CH_C), 121.5 (CH_D), 106.5, 105.9, 105.5 (CH_{pz}), 69.2 (C^2,$^1J_{CH} = 123$ Hz), 58.1 (C^3), 24.6 (Me_2), 19.9 (Me_1), 16.0, 15.7, 12.9, 12.7, 12.3 (1:1:1:2:1, Me_{pz}), 11.2 (C^2Me). Anal. Calcd for $C_{35}H_{42}BN_6Ir$: C, 56.0; H, 5.6; N, 11.2. Found: C, 55.3; H, 6.0; N, 11.6.

X-ray Structure Determination. X-ray data of complexes **2a**, **3**, **4**, and **5** (**3** and **4** as solvates **3**·solv and **4**·solv crystallized from dichloromethane−hexane) were collected on a Bruker Smart APEX CCD area detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and 0.3° ω-scan frames covering complete spheres of the reciprocal space with $\theta_{max} = 25-30°$. After data integration with the program SAINT+, corrections for absorption, $\lambda/2$ effects, and crystal decay were applied with the program SADABS.[17] The structures were solved by direct methods, expanded by Fourier syntheses, and refined on F^2 with the program suite SHELX97.[18] 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 **5** was refined in x,y,z and U_{iso} without restraints. The disordered solvents in **3**·solv and **4**·solv were squeezed with the program PLATON.[19] Crystal data and experimental details are given in Table 1, the molecular structures are shown in Figures 1−4, and selected geometric data are reported in Tables 2−5.

Acknowledgment. Financial support from the Spanish Ministerio de Educación y Ciencia (MEC) (projects CTQ2004-00409/BQU, FEDER support, and HU2003-039) and from the Junta de Andalucía is gratefully acknowledged. C.M.P. and N.R. thank the Junta de Andalucía and the MEC for research grants. Dr. V. Salazar is thanked for some experimental help.

Supporting Information Available: Complete crystallographic data and technical details in CIF format for compounds **2a**, **3**·solv, **4**·solv, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] Bruker programs: *SMART*, version 5.629; *SAINT+*, version 6.45; *SADABS*, version 2.10; *SHELXTL*, version 6.14; Bruker AXS Inc.: Madison, WI, 2003.

[18] Sheldrick, G. M. *SHELX97*: Program System for Crystal Structure Determination; Bruker AXS Inc.: Madison, WI, 1997.

[19] Spek, A. L. PLATON: A Multipurpose Crystallographic Tool; University of Utrecht: Utrecht, The Netherlands, 2005.