C–C Bond-Forming Reactions of Ir^{III}-Alkenyls and Nitriles or Aldehydes: Generation of Reactive Hydride- and Alkyl-Alkylidene Compounds and Observation of a Reversible 1,2-H Shift in Stable Hydride–Ir^{III} Alkylidene Complexes

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Dedicated to Professor Pascual Royo on the occasion of his 65th birthday

Abstract: Nucleophilic attack of the β-carbon of an Ir^{III}-alkenyl functionality onto the α-carbon of a coordinated nitrile- or aldehyde occurs intramolecularly to yield initially iridacyclic structures. Nitriles give rise to isolable complexes that contain delocalized five-membered rings (iridapyrroles, e.g. **3′**–**8′**) in a reaction catalyzed by H_2O (for some of these syntheses, Ir^{III}-η^3-allyl derivatives may be used as the source of the Ir^{III}-alkenyl moiety). In contrast, the alkenyl-to-aldehyde C–C coupling gives transient iridacycles that evolve by a fast alkyl-to-alkylidene migration and β-H elimination. The end products (**13*** and **14***) contain an elaborated chelating alkoxide–olefin ligand. Addition of $[H(OEt_2)_2][BAr'_4]$ to the iridapyrroles effects stereospecific protonation of the β-ring carbon. Those iridapyrroles which contain an additional metal-alkyl functionality (e.g. **3a***, alkyl = C_2H_5) afford highly reactive cationic alkyl-alkylidene intermediates that evolve instantaneously by migratory insertion/β-H elimination. The end products also contain an elaborated, chelating ligand, although this time with an olefin and imine terminus compared with the previous ligand. Contrary to this result, protonation of the hydride-iridapyrrole complex **8a*** in weakly coordinating solvents permits isolation of two unusual cationic *cis*-hydride-alkylidene compounds **11***, which undergo reversible 1,2-H shifts.

Keywords: aldehydes · C–H activation · carbene ligands · C–C coupling · iridium

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Introduction

The development of synthetic methodologies that allow the selective and efficient formation of carbon–carbon bonds is a fundamental problem in organic synthesis. Whereas discriminating, high yield classical organic routes are scarce, the ability of transition metal compounds to induce stoichiometric or catalytic reactions of this kind has been recognized for many years and has been used extensively in the last decades.[1] A large variety of transformations is available,[2] the majority of which require metal coordination of an unsaturated organic fragment.

Metal carbenes are exceedingly versatile reagents, able to participate in a plethora of carbon–carbon bond forming reactions.[3] Nitriles, imines, aldehydes, ketones and other organic functionalities that comprise multiple carbon–element bonds, become activated upon coordination toward attack by nucleophiles.[1c,d, 4–7] Hence, action of carbon nucleophiles on these species generates new C–C bonds.

Alkenyl complexes of the late transition elements are a relevant group of carbon nucleophiles.[8] They belong to an

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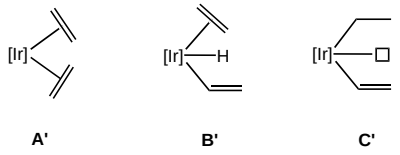
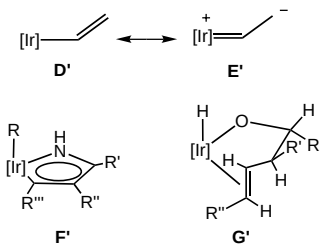
important family of organometallic compounds which finds wide applicability in organic synthesis and are active intermediates in several catalytic processes.[9] Recently we have demonstrated that Ir^{III}-vinyls (and related alkenyls) activate readily a variety of organic substrates.[10] These species can be generated under mild conditions, starting from bis(olefin) complexes (e.g. $[Tp^{Me2}Ir(C_2H_4)_2]$ (**A***)[10b, 11]), and owe their reactivity to the facility with which unsaturated species of type **C′** may be generated by tandem C–H activation (to give **B′**) and migratory insertion reactions. Like other late-transition metal alkenyls[8] they exhibit nucleophilic reactivity



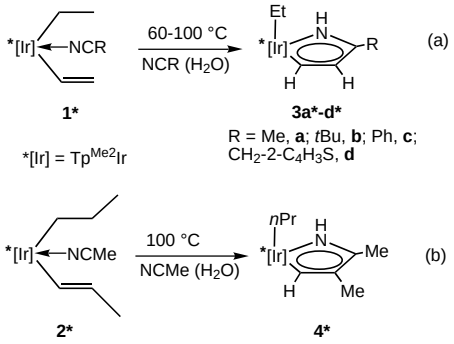
at the β-carbon because of the contribution of canonical form **E′** to the resonance hybrid. It is therefore conceivable that the Ir-alkenyl moiety of **C′** and related fragments acts as a nucleophile toward a coordinated multiple C–O or C–N bond. To verify this hypothesis we have generated unsaturated species of type **C′** in the presence of nitriles and aldehydes as Lewis donors, and studied the ensuing C–C bond forming processes. Herein we report[12] the results of these efforts. Nitriles, active participants in a variety of C–C bond forming reactions,[13, 14] give rise to iridacycles with general structure **F′**, whereas aldehydes, extremely useful syntons for organic synthesis,[14, 15] produce hydride-alkoxide complexes of formulation **G′**. The protonation of these species has also been studied and the results are reported herein.



Abstract in Spanish: *El ataque nucleófilo intramolecular del átomo de carbono β de diversos alquenilos de Ir^{III} sobre el Cα de nitrilos o aldehídos, produce inicialmente complejos metalacíclicos, que en el caso de los nitrilos evolucionan en un proceso catalizado por el agua, para dar estructuras de tipo iridapirrol. Algunos de estos compuestos se pueden obtener también a partir de complejos alílicos de Ir^{III} capaces de originar el fragmento Ir^{III}-alquenilo. Las estructuras cíclicas que se forman merced al acoplamiento C–C entre un aldehído y un alquenilo son de existencia transitoria y experimentan la migración rápida de su grupo Ir-alquilo al átomo de carbono de alquilideno, seguida de la eliminación de un átomo de H en β, dando lugar a productos finales que contienen un ligando quelatante con una terminación de tipo alcóxido y otra de naturaleza olefínica. La adición del ácido $[H(OEt_2)_2]BAr'_4$ a los iridapirroles se traduce en la protonación estereoespecífica del átomo de Cβ del anillo. Si el iridapirrol contiene además un ligando alquilo (por ejemplo **3a***, que posee un grupo etilo), resultan complejos catiónicos de tipo alquilo-alquilideno muy reactivos que evolucionan instantáneamente mediante inserción migratoria y posterior eliminación de Hβ. El ligando bidentado que resulta de este proceso contiene ahora un extremo de olefina y otro de imina. Por lo que respecta al complejo **8a***, su protonación en disolventes con poca tendencia a coordinarse, permite el aislamiento de los derivados catiónicos **11*-syn** y **11*-anti**, de constitución poco común, resultado de la combinación de un ligando hidruro y otro alquilideno en posiciones mutuamente cis. Los dos estereoisómeros experimentan reversiblemente la migración 1,2 del ligando hidruro al átomo de C carbénico.*

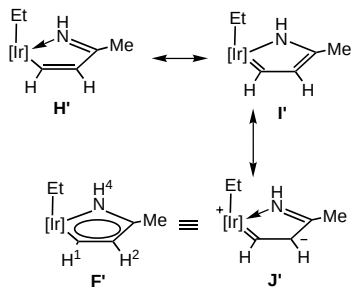
Results

Synthesis and characterization of iridapyrrole complexes: We have already reported[10b] that the complex $[Tp^{Me2}Ir(C_2H_4)_2]$ (**A***) reacts with acetonitrile at 60 °C to give $[Tp^{Me2}Ir(CH{=}CH_2)(C_2H_5)(NCMe)]$ (**1a***) by nitrile trapping of an intermediate of type **C***, formed through the hydride-vinyl complex **B***. Further heating of the colourless solutions of this adduct in acetonitrile produces a pale red solution that affords the red crystalline iridapyrrole **3a*** (Scheme 1 a). The reaction



Scheme 1. Formation of iridapyrrole complexes from Tp^{Me2}Ir-alkenyls.

needs the presence of small amounts of water to occur (see Discussion). Spectroscopic data are consistent with the delocalized iridapyrrole structure shown in the Scheme 1 (see canonical forms **H′**–**J′**).



For example, the iridium-bonded methine unit (CH^1) is responsible for resonances at δ 10.71 and 191.3, in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively. These signals are clearly in a range intermediate between those of metal–carbene and metal–vinyl resonances.[16] Additional support for the proposed aromaticity of **3a*** is provided by the 3 Hz value found for the four-bond H^2-H^4 coupling constant. In the IR the $\tilde{\nu}$(N-H) absorption is observed at 3330 cm^{-1}. Formation of metallapyrrole derivatives, albeit by different synthetic methodologies, is not unprecedented in the literature.[5a, 17]

A single crystal X-ray structure analysis of **3a*** · NCMe has been carried out (Tables 1 and 2). The ORTEP view (Figure 1) shows the expected distorted octahedral geometry around the metal.[10, 11, 18] The three N-Ir-N bond angles within the $Tp^{Me2}Ir$ linkage are close to the ideal 90° value but one of the three Ir–N bonds, namely that *trans* with respect to the ethyl group (2.21(1) Å), is longer than the others, which reflects the high *trans* influence of the alkyl group. The iridacycle is planar, and is characterized by short C1–C2, C2–C3 and N1–C3 bonds. These observations and the also short Ir–C1 separation of 1.88(2) Å, support the notion of extensive electron delocalization within the ring.

Table 1. Crystal data and structure refinement for compound **3a***.

formula	$C_{21}H_{33}BN_7IrNCCH_3$
F_w	627.61
shape (color)	irregular block (orange)
T [K]	298
size [mm]	0.25 × 0.11 × 0.04
crystal system	triclinic
space group	$P\bar{1}$
a [Å]	10.451(6)
b [Å]	15.787(13)
c [Å]	8.200(6)
α [°]	99.50(6)
β [°]	98.88(5)
γ [°]	98.86(5)
V [Å^3]	1295.8(2)
Z	2
F(000)	624.00
ρ_{calcd} [g cm^{-3}]	1.609
radiation	$Mo_{K\alpha}$ (λ = 071073) graphite monochromated
μ ($Mo_{K\alpha}$) [cm^{-1}]	51.78
diffractometer	Rigaku AFC7S
scan type	ω-2θ
scan rate	2.0° per min (in ω)
corrections	Lorentz-polarization absorption (trans. factors: 0.4989–1.0000)
2θ max	50.1
rflns collected	4916
unique rflns	4570
merging factor R(int)	0.206
no. observations	2874($I > 3\sigma(I)$)
R	0.067
Rw	0.192
GOF	1.112
variable parameters	298
max. peak in final diff. map [e$^-$ Å^{-3}]	2.458
min. peak in final diff. map [e$^-$ Å^{-3}]	− 1.908

Table 2. Selected bond lengths [Å] and angles [°] for compound **3a***.

Ir–C1	1.88(2)	Ir–N21	2.13(1)
Ir–N1	2.03(1)	Ir–N31	2.08(1)
Ir–C5	2.12(2)	Ir–N11	2.21(1)
C1–C2	1.37(2)	C2–C3	1.41(2)
N1-Ir-C1	76.7(6)	N1-Ir-C5	92.7(6)

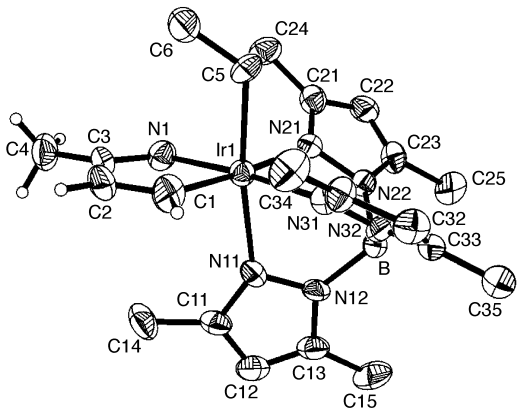


Figure 1. ORTEP representation of the molecules of **3a***.

To ascertain the generality of the alkenyl-to-nitrile coupling on the coordination sphere of Tp′Ir units, a miscellaneous group of Ir-alkenyl fragments and nitriles have been tested, for Tp^{Me2} and Tp as the ancillary ligands. Adducts such as **1a***, and others derived from different nitriles, are readily produced upon reaction of $[Tp^{Me2}Ir(C_2H_4)_2]$ with the corresponding NCR (R = Me,[10b] *t*Bu, Ph, CH_2-2-C_4H_3S). Only the known **1a*** and the *t*Bu analogue **1b*** have been isolated; in the other cases investigated C–C coupling proceeds parallel to adduct formation, hence the reactions were run to complete iridapyrrole formation. [Tp^{Me2}Ir(*trans*-CH=$CHCH_3$)(*n*-C_3H_7)(NCMe)] (**2***) has been generated in a similar manner from [Tp^{Me2}IrH(*trans*-CH=$CHCH_3$)(η^2-C_3H_6)][10b] and NCMe.

Prolonged heating of nitrile solutions of complexes **1*** and **2*** in the presence of minute amounts of water as the catalyst (see below), at temperatures in the range 60–100 °C, affords the iridapyrrole derivatives **3*** and **4*** in the form of red crystalline solids of considerable stability in air (Scheme 1). Metallacycles **3*** are, in general, best obtained by the direct reaction of $[Tp^{Me2}Ir(C_2H_4)_2]$,[10b] NCR and small amounts of H_2O, using the nitrile as the solvent. Spectroscopic properties for the nitrile adducts and the iridapyrroles are listed in the Experimental Section and are in accord with their formulations.

More chemical and structural diversity stems from the study of the related TpIr complexes. Compound **1a**[10b] behaves similarly to **1a*** in the coupling reaction with NCMe (Scheme 2a); however, interaction of the cyclooctenyl derivative [TpIrH(C_8H_{13})(η^2-C_8H_{14})] (**K**)[10b, 19] with both NCMe and NCPh generates a mixture of complexes **5a**–**6a** and **5c**–**6c**, respectively (Scheme 2b).

The unexpected formation of the hydrides **6** probably reflects high steric hindrance in the cyclooctene–cyclooctenyl precursor (**K**, Scheme 3), in which cyclooctene insertion into the Ir–H bond (to give **L**) may compete with olefin elimination (to **M**). The second pathway is responsible for the formation of the allyl [TpIrH(η^3-C_8H_{13})] (**N**) when the cyclooctenyl derivative is heated in C_6H_{12} at 100 °C.[10b]

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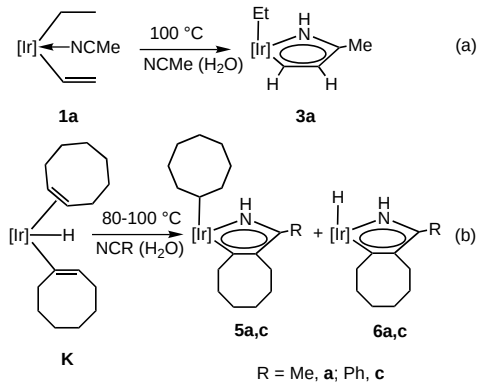
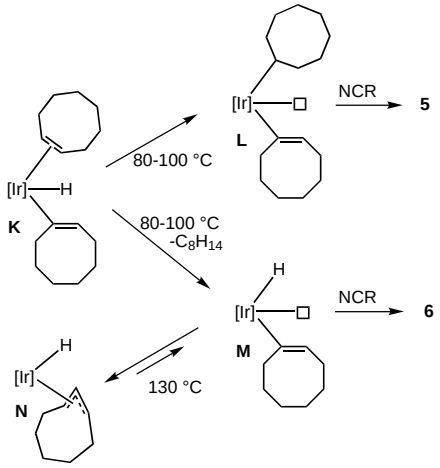


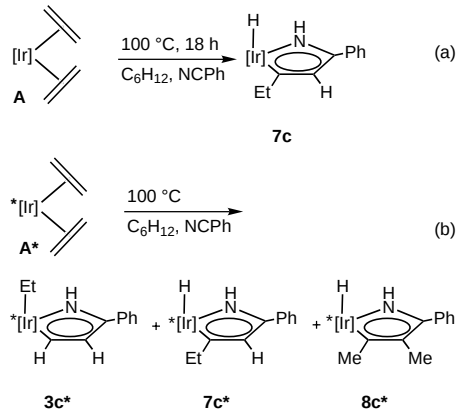
Scheme 2. Formation of iridapyrrole complexes from TpIr-alkenyls.



Scheme 3. Mechanism of formation of iridapyrroles **5** and **6**.

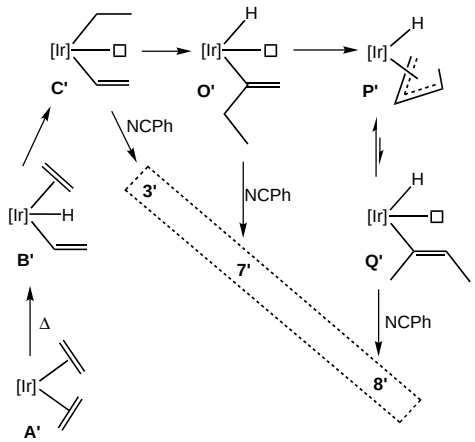
Complexes **6** are also obtained from this allyl and the respective nitrile at 130 °C, indicating that the vinyl-to-allyl transformation is a reversible process.

Yet, another unexpected observation emanated when $[TpIr(C_2H_4)_2]$[19, 20] was heated in cyclohexane in the presence of NCPh (Scheme 4a). Iridapyrrole structures were again generated but, noticeably, in the main compound **7c** a hydride instead of an ethyl group preserves electroneutrality, as the latter becomes part of the ring, substituting its α carbon atom.



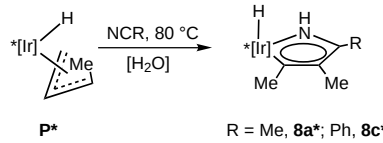
Scheme 4. Iridapyrrole formation in cyclohexane-NCPh as reaction solvent.

The even more complex $[Tp^{Me2}Ir(C_2H_4)_2]$ +NCPh reaction system (C_6H_{12} as solvent) gives rise to the three metallacyclic structures (Scheme 4b; compare with the reaction in neat NCPh, Scheme 1a). It appears that the 16 e$^-$ ethyl–vinyl intermediate **C** is not efficiently trapped by NCPh and can rearrange to **O** (Scheme 5), which then converts into **7c** by



Scheme 5. Mechanism of formation of different iridapyrroles in the reaction of $[Tp'Ir(C_2H_4)_2]$ ($Tp' = Tp$ or Tp^{Me2}) with NCPh in C_6H_{12}.

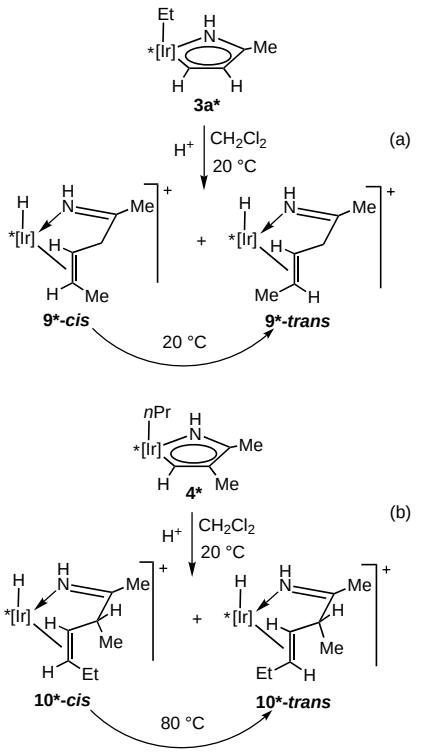
reaction with NCPh. This is in line with our earlier suggestion of **O*** as being an active intermediate in the formation of the allyl $[Tp^{Me2}IrH(\eta^3\text{-}anti\text{-}C_3H_4Me)]$ (**P***) from **C***.[10b] To explain the additional formation of **8c*** we proposed that **O*** can also rearrange to **Q*** through the intermediacy of **P***. Whereas alkenyl-to-allyl transformations similar to **Q*** → **P*** have been reported,[21] in our case it seems to be a reversible reaction; thus, allyl **P*** converts cleanly into **8a*** and **8c*** upon reaction with the corresponding nitrile at 80 °C (Scheme 6). These



Scheme 6. Formation of iridapyrrole complexes from $[Tp^{Me2}IrH(\eta^3\text{-}anti\text{-}C_4H_7)]$ (**P***) and NCR.

results illustrate the complexity of the reactions of $[Tp'Ir(C_2H_4)_2]$ compounds ($Tp' = Tp$, Tp^{Me2}) with the poor nucleophile NCPh, a process obviously very sensitive to the reaction conditions, particularly the temperature and the nitrile concentration, that we have not studied in more detail.

Protonation of iridapyrrole complexes—Migratory insertion reactions of Ir-carbene into Ir–H and Ir–C bonds: As canonical form **J′** is expected to contribute to the electronic structure of the iridacycles **3′**–**8′**, nucleophilic reactivity for their β-ring carbon atom may be anticipated.[8, 22] Accordingly, a smooth reaction ensues when complex **3a*** is treated with 1 equiv of $[H(OEt_2)_2][BAr'_4]$ ($Ar' = 3,5\text{-}C_6H_3(CF_3)_2$)[23] at room temperature in CH_2Cl_2 (Scheme 7a) to yield (quantitatively by NMR) the cationic hydride–olefin compound **9*-**

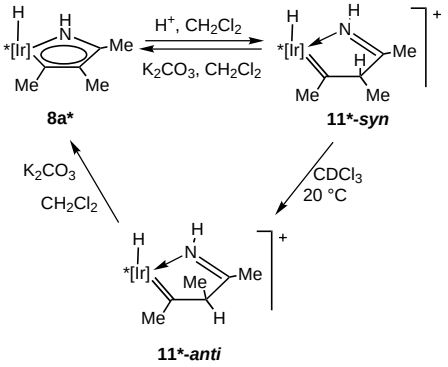


Scheme 7. Protonation of the iridapyrroles **3a*** and **4***.

trans.[24] Under ambient conditions, a kinetic mixture of **9*-*cis*** and **9*-*trans*** (ca 2:1 ratio) is formed first, and then transforms slowly ($t_{1/2} \approx 3$ h) into the thermodynamically more stable isomer **9*-*trans***. Compound **4*** also experiences a similar transformation upon protonation in CH_2Cl_2. As shown in Scheme 7b, a kinetic mixture (ratio ≈1:6) of complexes **10*-*cis*** and **10*-*trans*** is produced first which subsequently converts, although at a much slower rate, into **10*-*trans*** (CH_2Cl_2 at 80 °C, overnight). Interestingly, NMR monitoring of the room temperature reaction shows substantial amounts of two other stereoisomers (see below), which in the course of several hours give rise to the already mentioned 1:6 kinetic mixture of **10*-*cis*** and **10*-*trans***. Complex **10*-*trans*** has high thermal stability and can be recovered even after heating solutions in acetonitrile at 150 °C for several hours. For the sake of clarity, it is worth considering that the protonation of **3a*** and **4*** originates initially transient cationic alkyl–alkylidene intermediates which experience fast, irreversible α-alkyl migration, and reversible β-H elimination reactions (see Discussion).

Compounds **9*** and **10*** have been characterized by 1D and 2D NMR spectroscopy. ^{1}H NMR signals (data for **9*-*trans***) at δ −17.36 and 8.65 (br) are associated with the Ir-H and N-H protons. A NOESY study, along with the observed *trans* coupling of ca. 12 Hz between the olefinic protons of the coordinated olefinic terminus, lead unequivocally to the proposed structure. An X-ray investigation on crystals of **9*-*trans*** · 0.5 Et_2O confirmed the spectroscopic conclusions. Crystals of this compounds are, however, unstable toward loss of the Et_2O molecules of crystallization; moreover the CF_3 groups of the BAr'_4 anion introduce considerable positional disorder. Thus, and despite the fact that the geometry of the molecules of **9*-*trans*** has been unequivocally established, we believe that the poor quality of the X-ray data does not justify its discussion nor the consideration of its bonding parameters.

The analogous protonation of the related iridapyrrole structure **8a*** provides even more interesting results since it allows the isolation of highly unusual cationic *cis*-hydride-alkylidene complexes **11*** (Scheme 8). Compound **11*-*syn***[25] is formed first quantitatively (by NMR). The reaction is



Scheme 8. Formation of cationic hydride-alkylidene compounds.

reversible, as addition of a base to solutions of **11*-*syn*** regenerates the starting hydride-iridapyrrole complex **8a***. Moreover, in $CDCl_3$ **11*-*syn*** rearranges irreversibly into the thermodynamically more stable isomer **11*-*anti***. Treatment of this later compound with K_2CO_3 in CH_2Cl_2 also regenerates complex **8a***. The **11*-*syn*** to **11*-*anti*** isomerization appears to be rather erratic and may be catalyzed by some impurities present in the deuterated solvent.[26] Sunlight should be avoided as other side products are also formed.

In agreement with the proposed formulation, compounds **11*** exhibit characteristic low-field ^{13}C and high-field ^{1}H signals due to the carbene carbon and the hydride proton (ca. δ 325 and −15 ppm, respectively). The stereochemistry of both isomers, **11*-*syn*** and **11*-*anti***, has been deduced from 2D-NOESY spectra, which indicate that the H^+ attack is stereospecific and occured on the face of the ring adjacent to the hydride ligand. To confirm the crystal structure, we carried out an X-ray study of **11*-*syn*** · 0.25 CH_2Cl_2. Nevertheless, crystals of this compound suffer from the same shortcomings as **9*-*trans*** · 0.5 Et_2O, so that the discussion of its structural and bonding parameters seems unwarranted, even if the overall geometry of the molecules can be taken with confidence.[27]

The structural complexity of the molecules of **11*** is only preserved in the very weakly coordinating solvents such as CH_2Cl_2 or $CHCl_3$. The addition of CH_3OH to **11*-*syn*** in $CDCl_3$ induced a 1,2-shift of the hydride atom from iridium to the carbene carbon with formation of the corresponding CH_3OH adduct **12a*-*syn*** (Scheme 9a). The low coordination capacity of methanol caused this rearrangement to be reversible, as the removal of the solvent under vacuum restores, cleanly and quantitatively, the hydride-alkylidene **11*-*syn***. NCMe is a better ligand toward cationic Ir^{III} units, hence it is not unexpected that its reaction with **11*-*syn***

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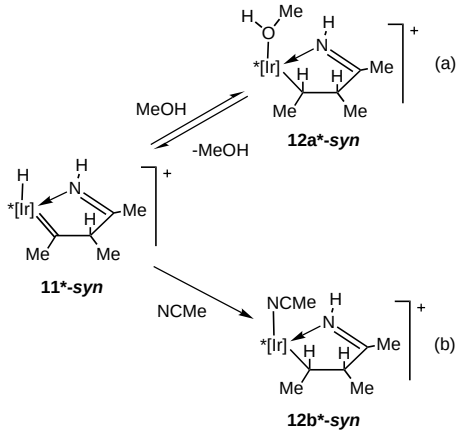
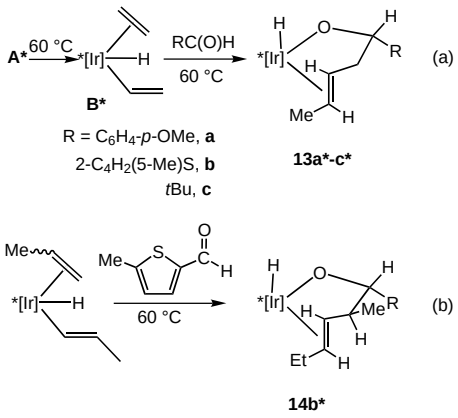


Scheme 9. Solvent-induced hydride-to-carbene migrations in **11*-*syn***.



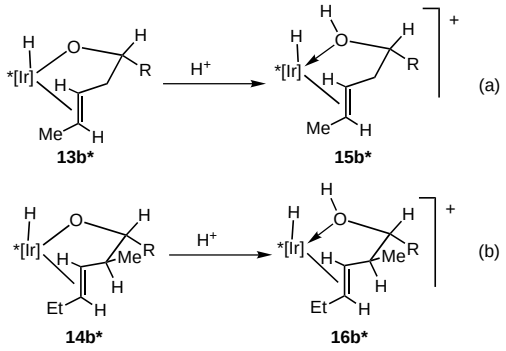
Scheme 10. Alkenyl-to-aldehyde C–C coupling reactions.

produces instantaneously the adduct **12b*-*syn*** (Scheme 9b), which can be isolated as a white microcrystalline solid. An analogous reaction with **11*-*anti*** furnished the corresponding adducts **12a*-*anti*** (reversible) and **12b*-*anti***.

When a mixture of **11*-*syn*** and **11*-*anti*** in $CDCl_3$ was treated with CD_3OD, the complexes **12a*-*syn*** and **12a*-*anti*** were instantaneously produced in the ratio expected. Interestingly, the former, and not the latter, incorporated three deuterium atoms into the two C*H*Me and the NH positions of the ring. The acetonitrile adduct **12b*-*syn*** showed no deuteration upon treatment with CD_3OD. H_2O, however, afforded the similar, though rather labile **12c*-*syn*** and **12c*-*anti*** adducts, with D incorporation in the former, that is **[D$_5$]12c*-*syn*** if D_2O is used. In this case even **[D$_3$]11*-*syn*** (deuterium in IrH, C*H*Me and NH positions) can be observed before the reaction is completed. We can offer no reasonable mechanistic explanation for these observations, although it seems plausible that the incorporation of D occurs in the *syn*-hydride-alkylidene complex. It is worth noting that the water adduct **12c*-*syn*** cleanly converts into **12c*-*anti*** in $CDCl_3$/H_2O mixtures (2–3 d, 20 °C, darkness). Since the latter reverses into **11*-*anti*** by simple exposure to vacuum, this method constitutes a less troublesome method of producing **11*-*anti*** from **11*-*syn***.

C–C Bond-forming reactions involving aldehydes: As an additional test of the capacity of Ir-alkenyl units to act as carbon nucleophiles some of the reactions discussed in the preceeding paragraphs have been investigated employing aldehyde, instead of nitrile, electrophiles. Accordingly, [Tp^{Me2}Ir(C_2H_4)$_2$] was treated at 60 °C in cyclohexane with different aldehydes (Scheme 10a) to give the new compounds **13***. Likewise, [Tp^{Me2}IrH(*trans*-CH=CHMe)(η^2-C_3H_6)] (Scheme 10b) was treated with 5-methyl-2-thiophenecarboxaldehyde to give **14b***. NMR monitoring of the formation of **13a*** shows no detectable intermediates and the generation, besides **13a*** (ca. 70%), of three non-characterized minor by-products. Once again, a combination of 1D and 2D NMR experiments provided unequivocal support for the suggested formulation. As can be seen in Scheme 10, except for differences inherent to the nature of the substrates used (namely aldehydes or nitriles) the structures of **13*** and **14*** show striking resemblance to that of compounds **9*** and **10***; this suggests that the former are also produced as a result of a similar complex reaction pathway (see Discussion).

As shown in Scheme 11, compounds **13b*** and **14b*** can be protonated at the alkoxide oxygen atom to give the corresponding alcohol complexes **15b*** and **16b***. The inertness of the Ir-O(H)R functionality[28] of these compounds towards substitution (e.g. by NCMe) is very likely due to the chelating nature of the organic ligand.

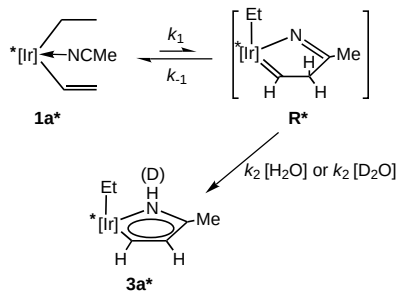


Scheme 11. Protonation of alkoxides **13b*** and **14b***.

Discussion

The results presented in the previous section demonstrate the capacity of Ir^{III}-alkenyls to act as nucleophiles toward nitriles and aldehydes. As stated, this reactivity reflects the importance of resonance form **E** in defining the electronic structure of the Ir-alkenyl unit.

In practice, formation of the iridapyrroles **3′–8′** requires water as a catalyst. Although there is no spectroscopic evidence, a short-lived iridacycle **R*** (Scheme 12, reaction leading to **3a***) may be invoked as a reactive intermediate, trapped subsequently as the thermodynamically favoured iridapyrrole **3a*** by a water-dependent tautomeric process. The formation of **R*** can be regarded as a 1,3-dipolar cycloaddition, a reaction not very commonly encountered in organometallic chemistry.[29] Kinetic data are consistent with this proposal, the graphical representation of k_{obs} versus [D_2O] shows saturation kinetics (Figure 2)[30] and allows



Scheme 12. Proposed mechanism for the H_2O-catalyzed formation of iridapyrroles.

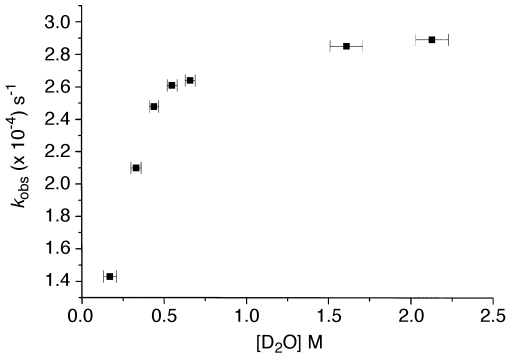


Figure 2. Formation of **3a***: graphical representation of k_{obs} versus $[D_2O]$.

computation of the k_1 and k_{-1}/k_2 values ($[3.2(2)] \times 10^{-4}$ s^{-1} and 0.16(4) M, respectively). The reaction is intramolecular and follows pseudo-first-order kinetics with less than 15% incorporation of $NCCD_3$ when **1a*** is heated with $NCCD_3$ under saturation conditions. When the reaction is monitored by NMR in a $NCCD_3/D_2O$ mixture (saturation conditions), complex **[D_1]3a*** is formed (Scheme 12) but no incorporation of deuterium in the starting material takes place. Under the same conditions there is no significant effect by adding NaOD or CH_3CO_2D, although in the latter case the two β-H atoms of the vinyl ligand of **1a*** become partially deuterated (the extent of the deuteration is proportional to the amount of added acid) in the way to the final product **[D_2]3a*** (see below for the explanation of this additional deuteration).

Further support for the proposed mechanism comes from the measurement of an inverse deuterium kinetic isotope effect (KIE) in the saturation regime when using $[Tp^{Me2}Ir(C_2D_3)(C_2D_5)(NCMe)]$ ($k^H_{obs}/k^D_{obs} = 0.87(2)$, $[D_2O] = 2.1(1)$ M). This measurement shows that no significant C–H bond breaking occurs in the transition state of the rate-determining step. Moreover, it constitutes additional support for the sp^2-to-sp^3 change in hybridization at the nucleophylic β-vinyl carbon implied by this mechanism.[31] The final **R*** → **3a*** water-catalyzed step is irreversible, and very little, if any, deuterium incorporation takes place when **3a*** is heated in CD_3CN/D_2O mixtures at 100 °C for 2 h. The same is true for **8a***.

The vinylic character of the iridapyrrole part of the molecules of **3′–8′**, along with the nucleophilicity of its β-carbon, suggest its protonation could lead to highly reactive, cationic hydride- or alkyl-alkylidene derivatives, depending upon the nature of the starting compound. Species of this type are rare, due to the high tendency of the H^- and R^- groups to migrate onto the carbene carbon. Furthermore, well-defined hydride- and alkyl-carbenes are useful as models for several catalytic processes, notably Fischer–Tropsch synthesis.[9a, 32]

Despite the high reactivity of these compounds, some examples are already known.[33, 34] Jones and co-workers have reported a number of alkyl- and acyl-carbene derivatives of different metals in which the M–C and M=C functionalities are part of a five-membered ring.[35] Ring strain retards the migratory insertion and allows full characterization of the complexes. Werner and co-workers have isolated several stable osmium hydride-alkylidenes which owe their stability to the *trans* distribution of the hydride and carbene ligands.[36] The same group has recently reported on the formation of neutral and cationic *cis*-hydride-alkylidenes of iridium, which do not appear to undergo migratory insertion.[37] In a different publication, alkylation of $[Ru(\eta^5\text{-}C_5H_5)Cl(CAr_2)(PPh_3)]$ gave the products as a result of migration without any of the expected $[Ru(CAr_2)(R)]$ intermediates.[38] Bergman and co-workers reported reversible α-H migration/elimination in cationic complexes of iridium,[39] while we have generated cationic iridium complexes at low temperatures that contain $[Ir(R)(=CHMe)]^+$ fragments (R = H, Et), and studied the comparative migratory aptitudes of H and Et groups.[22a] A most remarkable, reversible α-H elimination, about six orders of magnitude faster than β-H elimination, has been ascertained by Schrock and co-workers for Mo and W complexes of triamidoamine ligands.[40] An interesting intermolecular insertion of [W=C(H)Ar] units into transition metal hydride bonds has been found recently by Fischer and Jungklaus.[41]

The conversion of **3a*** into **9*-*cis*** and **9*-*trans*** by action of $[H(OEt_2)_2]BAr'_4$ can occur as represented in Scheme 13. The cationic intermediate **S*** resulting from the protonation of the β-ring carbon of **3a*** cannot be detected by NMR even at −80 °C (CD_2Cl_2 solution). This is not, however, unexpected, as the Et group has the correct geometry to attack the highly electrophilic carbon of the $Ir^+=C<$ fragment, the Ir–Et bond being aligned parallel to the pπ orbital of the carbene carbon.[32] β-H Elimination to the generated coordination vacancy in the 16-e^- intermediate **T*** should also be extremely facile; this would lead to **U*-*cis*** and **U*-*trans***, the only products observed by ^{1}H NMR at −80 °C. The hydride ligands in **U*** resonate in the NMR spectrum at higher fields than in isomers **9*** (compare $\delta = -18.59$ (**9*-*cis***), −17.36 (**9*-*trans***) vs −21.28 (**U*-*cis***), −23.58 (**U*-*trans***), data in $CDCl_3$ at 25 °C). Notably the elimination of one of the diastereotopic H atoms has an important kinetic preference (the kinetic ratio of **U*-*cis*** to **U*-*trans*** is ca. 4:1). This is due, presumably, to hindered rotation around the C_{ring}–CH_2Me bond of either steric,[42a,b] or electronic (i.e., agostic)[42c] origin. The **U*** mixture is stable up to 0 °C, but at this temperature complexes **9*** start to form at the expenses of **U*** by stereoisomerization of the metal–olefin linkage.[43] **U*-*cis*** and **U*-*trans*** disappear at similar, but no identical, rates. The same is true for the generation of **9*-*cis*** and **9*-*trans***. When the transformation is complete, the ratio of the newly formed species is about 2:1. Hence, it is clear that interconversion of the **U*** isomers takes place under these conditions and that this process competes with the stereoisomerization steps. Finally, **9*-*cis*** converts quantita-

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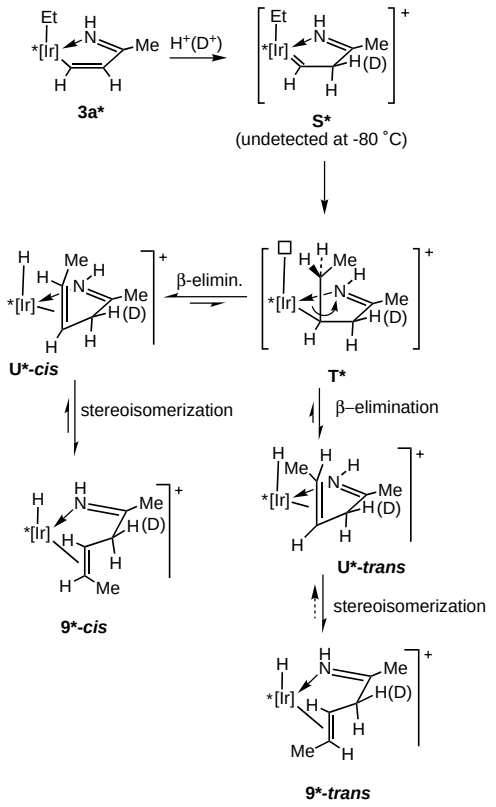
tively into **9*-*trans*** with a half-live of about three hours at 25 °C. The **9*-*cis*** to **9*-*trans*** transformation implies the reversibility of all the individual steps of Scheme 13 except the ethyl migration which leads to **T***. This mechanism is also in agreement with deuteration studies (see Scheme 13 for the



Scheme 13. Mechanism of formation of complexes **9*-*cis*** and **9*-*trans***.

localization of the D in the four olefinic species; in CD_2Cl_2 containing CD_3OD, no deuteration takes place at the NH group), and with NOESY experiments carried out with the species involved and their deuterated counterparts. Thus, we may conclude that the protonation of **3a*** takes place *syn* to the Ir–Et bond. The formation of complexes **10*** involves intermediates similar to **U*** that survive at room temperature for a few hours. They also exhibit distinctive hydride high field ^{1}H NMR signals (**10*-*cis***: $\delta = -18.38$; **10*-*trans***: -17.25. **U***-related stereoisomers: -22.97 and -23.75, data in $CDCl_3$ at 25 °C) and can be proposed to form through a pathway similar to that presented in Scheme 13 for **9***. In this case the transformation of the stereoisomers seems to have higher energy barriers.

In light of the above comments, isolation of the cationic hydride-alkylidene derivatives **11*-*syn*** and **11*-*anti*** might seem a surprise. According to both theoretical arguments[32] and experimental studies by Bercaw and co-workers,[44] hydride migration onto the alkylidene carbon should proceed much faster than alkyl migration. This notion is reinforced by the similar conclusions of related studies on the migration of H and alkyl groups to olefins.[45] However, in the case of $[Tp^{Me2}Ir(R)(=CHMe)(L)]^+$ ($L = PMe_3$,[22a] NCMe[46]) complexes, both R = H and Et appear to migrate with almost the same rate. In complexes **11*-*syn*** and **11*-*anti*** the hydride group is also appropriately positioned to migrate onto the carbene carbon, but contrary to the situation already encountered for the somewhat analogous intermediate **S** of Scheme 13, the resulting 16-electron, 5-coordinate, alkyl intermediate cannot readily rearrange: the H atom on the ring β carbon is too far away from iridium to achieve an accessible transition state, and in similar manner, the Me substituent of the α-carbon stays opposite to the vacant coordination site and cannot be involved in β-H elimination. Hence, in the absence of a Lewis donor that could occupy the vacant coordination site, α-H migration is unproductive, that is its effects are not apparent. This has allowed the isolation of stable cationic, *cis*-hydride-alkylidene complexes of a late transition metal in a high oxidation state. Notwithstanding this, H migration does actually occur reversibly, as demonstrated by the reversible generation of a methanol adduct when **11*-*syn*** is dissolved in CD_3OD (Scheme 9a). These results represent an unusual observation of a *direct* and *reversible* α-H migration onto a well-defined electrophilic alkylidene carbon to give an alkyl ligand.

The aldehyde coupling products **13*** and **14*** (Scheme 10) contain an elaborated, chelating alkoxide-olefin ligand, that results from two C–C coupling reactions. Both the alkene and alkenyl units of the precursor complex, as well as a molecule of the aldehyde, participate in the carbon-carbon bond forming reactions. Scheme 14 gives a mechanistic proposal analogous to that discussed for the formation of complexes **9*** and **10***. In the first C–C coupling, that ultimately leads to **14*** (i.e., that between the β-alkenyl and α-aldehyde carbon atoms), the propenyl methyl group and the aldehyde R substituent (see adducts **V***[7b]) avoid a *syn* configuration to suppress undesirable steric interactions, hence this coupling occurs stereospecifically to give the corresponding alkylidene **W***. This is followed by the second C–C bond forming reaction (i.e., Ir-R migration onto the generated carbene carbon), and then by β-H elimination and stereoisomerization of the alkoxide-olefin complex **X***. The latter step is somewhat more complex than that giving rise to **9*** and **10*** since inversion at the Ir centre is required in this case. This can occur by temporary disengagement of the Ir–olefin bond, a shift of the alkoxide ligand to the vacant position, rotation around the O–CH(R) bond, and reconstruction of the Ir–olefin linkage. Note that at variance with the amido intermediate **R*** of Scheme 12, **W*** cannot undergo H tautomerism to produce an aromatic system related to the iridapyrroles, which makes Et migration much more effective in this case.

As a final question to be addressed before closing, we wonder why intermediate **R*** of Scheme 12 does not show an Et-to-carbene migration similar to that proposed for **W*** in Scheme 14. A combination of concentration and stability effects on the kinetics of the process, arising from the species involved in the respective equilibria, may be responsible for the observed differences. The nitrile adducts are much more stable than the analogous aldehyde adducts (the latter are the proposed **V*** intermediates of Scheme 14 and have not been detected) and, moreover, the nitrile carbon is less electrophilic than the aldehyde carbon. Consequently, much higher

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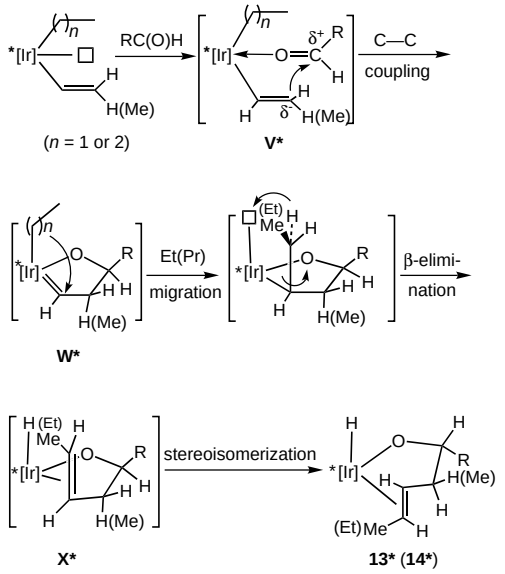
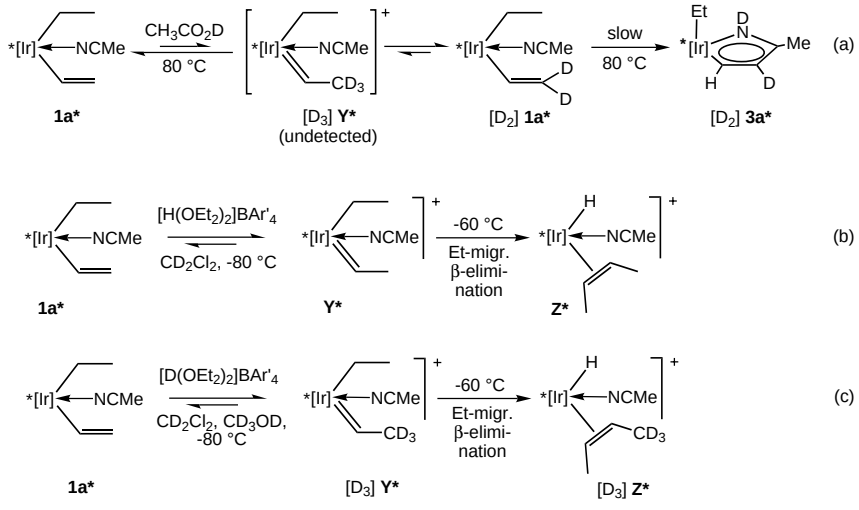


Scheme 14. Mechanism of formation of the alkoxides **13*** and **14***.

temperatures may be needed in order for the Et migration to take place in the nitrile system, whereas trace amounts of water will readily generate the iridapyrroles.

A similar argument could explain the regio specific deuteration of the vinyl ligand in **1a*** when this compound is heated in a mixture of $NCCD_3$, D_2O and CH_3CO_2D (Scheme 15a). The protonation of the β-vinyl carbon is reversible and at low concentrations of D^+ the barrier to Et migration is not overcome, **Y*** converts back into deuterated **1a*** and finally produces **[D$_2$]3a***. In contrast, if **Y*** is generated in high concentration using the strong acid $[H(OEt_2)_2][B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]$, in CD_2Cl_2 at $-80\,^\circ C$, ethyl migration becomes effective and the subsequent β-H elimination leads to compound **Z*** (Scheme 15b). In agreement with these results, the stepwise deuteration specified in Scheme 15c allows firstly the low-temperature characterization of **[D$_3$]Y*** and then the production of **[D$_3$]Z***.[22a, 46]



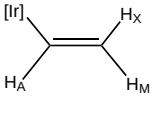
Scheme 15. Fate of the alkylidene species **Y*** depending on the conditions of formation. a) in $NCCD_3$/D_2O/CH_3CO_2D at $80\,^\circ C$ (the rate and hence the amount of deuteration before iridapyrrole formation depends upon the $[D^+]$). b) CD_2Cl_2, 1 equiv $[H(OEt_2)_2]BAr'_4$ at $-80\,^\circ C$. c) CD_2Cl_2, 1 equiv $[D(OEt_2)_2]BAr'_4$, in the presence of CD_3OD at $-80\,^\circ C$.

Conclusion

The β-vinyl carbon of Ir^{III}-alkenyl units behaves as a good nucleophile toward nitriles and aldehydes and participates into carbon–carbon bond forming reactions that generate iridacycles at the early stages of the corresponding processes. Transformations involving nitriles require the participation of water as catalyst, whereas those implicating aldehydes take place under milder conditions, without catalyst participation. The most reasonable explanation for this difference appears to be the higher electrophilicity of the carbonyl carbon, as compared with the nitrile carbon. Nitriles give rise to iridapyrrole structures of considerable thermal stability (accessible also from Ir-η^3-allyls, as source of the Ir-alkenyl reactive fragment). In turn aldehydes provide more complex structures exemplified by those of compounds **13*** and **14***. Protonation of iridapyrroles such as **3a***, that contains also an Ir-alkyl group, give complexes of elaborate imine–olefin ligands, related to the alkoxide-olefin ligands of **13*** and **14*** through the intermediacy of very reactive alkyl-alkylidene species. In either case, the newly formed bidentate ligand incorporates the olefin and alkenyl groups of the precursor complex, plus a molecule of the nitrile or the aldehyde. Contrary to this observation, protonation of the hydride-iridapyrrole **8a*** allows isolation of a highly unusual cationic *cis*-hydride-alkylidene **11*-*syn***. Both this compound and its isomer **11*-*anti*** experience a reversible 1,2-H shift from the metal to the carbene carbon and viceversa.

Experimental Section

All preparations and manipulations were carried out under oxygen-free nitrogen following conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. The light petroleum used had a b.p. 40–60 °C. The complexes $[TpIr(C_2H_4)_2]$,[19, 20] $[Tp^{Me2}Ir(C_2H_4)_2]$,[10b] $[Tp^{Me2}IrH(CH{=}CHMe)(\eta^2\text{-}C_3H_6)]$,[10b] **1a**,[10b] **1a***,[10b] **K**,[10b] **N**,[10b] **P***,[10b] and $[H(OEt_2)_2]BAr'_4$[23] were prepared according to literature procedures. Microanalyses were by the Microanalytical Services of the Instituto de Investigaciones Químicas (Sevilla). In series of analogous compounds, only some selected representatives were analyzed. Infrared spectra were recorded on Perkin–Elmer model 1710 and Bruker Vector 22 spectrometers; NMR spectra on Bruker AMX-300, 400 and 500 MHz spectrometers. The ^1H and $^{13}C\{^1H\}$ resonances of the solvent were used as internal standard, but the chemical shifts are reported with respect to TMS. Most of the NMR assignements are based on extensive ^1H–^1H decoupling experiments, and homo- and heteronuclear two-dimensional spectra. No NMR data are reported for the BAr'_4 anion.



[Tp^{Me2}Ir(CH=CH$_2$)(C$_2$H$_5$)(NCCMe$_3$)] (1b*): A solution of complex $[Tp^{Me2}Ir(C_2H_4)_2]$ (0.1 g) in pivalonitrile (2.5 mL) was heated in a sealed glass ampoule at 60 °C for 18 h. The volatiles were evaporated and the residue dried under vacuo at 60 °C for 2 h. Yield: 109 mg, >95 %; ^1H NMR

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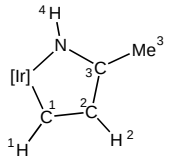
($CDCl_3$, 25 °C; see above for atom labels): $\delta = 8.27$ (dd, 1H, $^3J(A,M) = 10$, $^3J(A,X) = 17.8$ Hz, H_A), 5.76, 5.69, 5.66 (s, 1H each, 3CHpz), 5.55 (dd, 1H, $^2J(M,X) = 3.7$ Hz, H_M), 4.70 (dd, 1H, H_X), 2.37, 2.36, 2.33, 2.24, 2.21 (s, 1:1:2:1:1 ratio, 6Mepz), 2.01 (m, 2H, $IrCH_2$), 1.42 (s, 9H, CMe_3), 0.45 (t, 3H, $^3J(H,H) = 7.7$ Hz, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = 151.6$, 150.0, 142.7, 142.5, 142.4 (1:2:1:1:1 ratio, Cqpz), 138.4 ($IrCH{=}CH_2$), 121.4 (NCR), 113.6 ($IrCH{=}CH_2$), 107.1, 106.2, 106.0 (CHpz), 30.2 (CMe_3), 28.6 (CMe_3), 15.4 ($IrCH_2CH_3$), 13.5, 13.1, 12.9, 12.6, 12.4 (2:1:1:1:1 ratio, Mepz), −11.4 ($IrCH_2$); IR (nujol): $\tilde{\nu} = 2262$ cm^{-1} (C-N); elemental analysis calcd (%) for: $C_{24}H_{39}BN_7Ir$ (628): C 45.9, H 6.2, N 15.6; found: C 46.0, H 6.4, N 15.2.

The complex $[Tp^{Me2}Ir(CH{=}CH_2)(C_2H_5)(NCPh)]$ (**1c***) was observed as an intermediate in the formation of the corresponding iridapyrrole from $[Tp^{Me2}Ir(C_2H_4)_2]$ in NCPh at 60 °C, but was not isolated. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 8.33$ (dd, 1H, $^3J(A,M) = 8$, $^3J(A,X) = 16$ Hz, H_A), 5.62 (dd, 1H, $^2J(M,X) = 3.8$ Hz, H_M), 4.89 (dd, 1H, H_X), 1.45 (m, 2H, $IrCH_2$), 0.53 (t, 3H, $^3J(H,H) = 7.5$ Hz, CH_2CH_3).

$[Tp^{Me2}Ir(trans\text{-}CH{=}CHCH_3)(CH_2CH_2CH_3)(NCMe)]$ (2*): Complex $[Tp^{Me2}IrH(CH{=}CHCH_3)(\eta^2\text{-}C_3H_6)]$ (0.1 g) was heated in NCMe (5 mL) at 60 °C for 18 h. The resulting solution was evaporated to dryness to give complex **2*** as a white microcrystalline powder in almost quantitative yield. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 7.32$ (dq, 1H, $^3J(H,H) = 15.5$, $^4J(H,H) = 1.1$ Hz, $IrCH{=}CHMe$), 5.75, 5.68, 5.64 (s, 1H each, 3CHpz), 4.83 (dq, 1H, $^3J(H,H) = 6$ Hz, $IrCH{=}CHMe$), 2.46 (s, 3H, NCMe), 2.36, 2.33, 2.29, 2.19, 2.18 (s, 1:2:1:1:1 ratio, 6Mepz), 2.01 (m, 2H, $IrCH_2$), 0.87 (m, 3H, CH_2CH_3), 0.50 (m, 2H, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = 151.6$, 149.7, 149.6, 142.7, 142.5, 142.3 (Cqpz), 124.8, 122.8 (-CH=CH-, $^1J(C,H) = 135$, 143 Hz, respectively), 111.5 (NCMe), 107.1, 106.3, 106.1 (CHpz), 24.2 (CH_2CH_3), 22.7 (=CH*Me*), 17.7 (CH_2CH_3), 13.3, 13.2, 12.7, 12.6, 12.3 (1:2:1:1:1 ratio, 6Mepz), 4.0 (NC*Me*), −0.6 ($IrCH_2$).

$[Tp^{Me2}Ir(\overline{CHCHC(Me)NH})(CH_2CH_3)]$ (3a*): The adduct **1a*** (0.1 g) was heated (100 °C) in wet acetonitrile (5 mL plus a drop of water) during 18 h. The resulting dark red solution was concentrated in vacuo and cooled at −20 °C. Red crystalline **3a*** was obtained in 90% yield (90 mg). This complex can be obtained directly from $[Tp^{Me2}Ir(C_2H_4)_2]$ in wet acetonitrile without isolating the intermediate adduct **1a***. ^1H NMR ($CDCl_3$, 25 °C; see above for atom labels): $\delta = 10.71$ (d, 1H, $^3J(1,2) = 7$ Hz, H^1), 8.18 (br, 1H, H^4), 6.82 (dd, 1H, $^4J(2,4) = 3$ Hz, H^2), 5.81, 5.79, 5.49 (s, 1H each, 3CHpz), 2.55 (s, 3H, Me^3), 2.40, 2.39, 2.37, 2.36, 2.26, 1.72 (s, 3H each, 6Mepz), 1.23, 1.12 (dq, 1H each, $^2J(H,H) = 11$, $^3J(H,Me) = 8$ Hz, CH_2CH_3), 0.06 (t, 3H, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = 191.3$ (C^1), 185.9 (C^3), 152.0, 151.8, 150.1, 143.1, 143.0, 142.4 (Cqpz), 131.4 (C^2), 107.2, 106.5 (1:2 ratio, CHpz), 21.9 (Me^3), 14.1, 13.5, 13.1, 12.6, 12.5, 11.1 (2:1:1:1:1 ratio, Mepz and CH_2CH_3), −16.9 ($IrCH_2$); IR (nujol): $\tilde{\nu} = 3330$ cm^{-1} (N-H); elemental analysis calcd (%) for $C_{21}H_{33}BN_7Ir$ (586): C 43.0, H 5.6, N 16.7; found: C 43.1, H 5.7, N 16.9.



$[Tp^{Me2}Ir(\overline{CHCHC(Me_3)NH})(CH_2CH_3)]$ (3b*): This compound was obtained as described above for complex **3a***, although prolonged heating of the adduct **1b*** (48 h) at 100 °C in $NCCMe_3$ is necessary for complete conversion. Yield: >95%. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 10.61$ (d, 1H, $^3J(1,2) = 7.6$ Hz, H^1), 8.55 (br, 1H, H^4), 7.04 (dd, 1H, $^4J(2,4) = 3.4$ Hz, H^2), 5.83, 5.79, 5.50 (s, 1H each, 3CHpz), 2.42, 2.38, 2.37, 2.36, 2.27, 1.71 (s, 3H each, 6Mepz), 1.31 (s, 9H, CMe_3), 1.24 (m, 2H, $IrCH_2$), 0.07 (t, 3H, $^3J(H,H) = 8$ Hz, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = 195.9$ (C^1), 188.9 (C^3), 152.3, 151.8, 149.9, 143.0, 142.9, 142.4 (Cqpz), 128.3 (C^2), 107.1, 106.6, 106.3 (CHpz), 36.6 (CMe_3), 28.8 (CMe_3), 14.2, 14.0, 13.3, 13.1, 12.5, 12.4, 11.5 (Mepz and CH_2CH_3), −15.9 ($IrCH_2$); IR (nujol): $\tilde{\nu} = 3385$ cm^{-1} (N-H); elemental analysis calcd (%) for $C_{24}H_{39}BN_7Ir$ (628): C 45.9, H 6.2, N 15.6; found: C 46.0, H 6.3, N 15.9.

$[Tp^{Me2}Ir(\overline{CHCHC(Ph)NH})(CH_2CH_3)]$ (3c*): Following the general method, this complex was obtained from $[Tp^{Me2}Ir(C_2H_4)_2]$ and neat NCPh in 85% yield as a dark red microcrystalline solid from NCPh/petroleum ether at −20 °C. In this particular case the formation of the iridapyrrole needed only heating at 60 °C for 24 h. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 11.01$ (d, 1H, $^3J(1,2) = 7.6$ Hz, H^1), 8.92 (br, 1H, H^4), 7.56 (dd, 1H, $^4J(2,4) = 3$ Hz, H^2), 5.83, 5.75, 5.49 (s, 1H each, 3CHpz), 2.59, 2.53, 2.40, 2.21, 1.70 (s, 1:1:2:1:1 ratio, 6Mepz), 1.31 (m, 2H, $IrCH_2$), 0.10 (t, 3H, $^3J(H,H) = 7.6$ Hz, CH_2CH_3). C_6H_5 protons not assigned; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = 192.7$ (C^1), 184.5 (C^3), 152.1, 151.9, 150.2, 143.2, 142.5 (1:1:1:2:1 ratio, 6 Cqpz), 136.0 (Cqar), 129.9 (C^2), 129.3, 128.8, 126.6 (1:2:2 ratio, CHar), 107.3, 106.7, 106.6 (CHpz), 14.3, 14.0, 13.6, 13.1, 12.5, 12.4, 11.1 (Mepz and CH_2CH_3), −16.0 ($IrCH_2$); IR (nujol): $\tilde{\nu} = 3350$ cm^{-1} (N-H); elemental analysis calcd (%) for: $C_{26}H_{35}BN_7Ir$ (648): C 48.1, H 5.4, N 15.1; found: C 48.3, H 5.3, N 15.6.

$[Tp^{Me2}Ir(\overline{CHCHC(CH_2\text{-}2\text{-}C_4H_3S)NH})(CH_2CH_3)]$ (3d*): The reaction of $[Tp^{Me}Ir(C_2H_4)_2]$ (0.2 g) with $NCCH_2\text{-}2\text{-}C_4H_3S$ (0.05 mL) in C_6H_{12} (2 mL) (12 h, 60 °C) furnished compound **3d*** in 60% yield (150 mg) after crystallization from Et_2O/petroleum ether 1:1. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 10.81$ (d, 1H, $^3J(1,2) = 7.3$ Hz, H^1), 8.32 (br, 1H, H^4), 6.97 (dd, 1H, $^4J(2,4) = 2.9$ Hz, H^2), 7.25, 7.01 (d, m, 1:2 ratio, $^3J(H,H) = 5.4$ Hz, 3CHth), 5.81, 5.76, 5.50 (s, 1H each, 3CHpz), 4.49, 4.39 (AB spin system, 1H each, $^2J(H,H) = 18.0$ Hz, CH_2C^3), 2.42, 2.38, 2.36, 2.26, 2.16, 1.72 (s, 3H each, 6Mepz), 1.24, 1.04 (dq, 1H each, $^2J(H,H) = 12.1$, $^3J(H,Me) = 7.5$ Hz, $IrCH_2$), 0.07 (t, 3H, CH_2CH_3); $^{13}C\{^1H\}$NMR ($CDCl_3$, 25 °C): 191.8 (C_1, $^1J(C,H) = 142$ Hz), 185.7 (C_3), 152.1, 151.9, 150.2, 143.1, 143.1, 142.5 (Cqpz), 137.5 (Cqth), 130.2 (C^2, $^1J(C,H) = 160$ Hz), 127.6, 127.5, 125.4 (CHth), 107.3, 106.7, 106.6 (CHpz), 34.8 (CH_2C^3, $^1J(C,H) = 129$ Hz), 14.3, 14.2, 13.2, 12.6, 12.5, 11.2 (Mepz), 13.2 (CH_2CH_3), −16.3 ($IrCH_2$, $^1J(C,H) = 125$ Hz); IR (nujol): $\tilde{\nu} = 3328$ cm^{-1} (N-H); elemental analysis calcd (%) for $C_{25}H_{35}BN_7SIr$ (668): C 44.8, H 5.2, N 15.6; found: C 44.0, H 5.0, N 14.1.

$[TpIr(\overline{CHCHC(Me)NH})(CH_2CH_3)]$ (3a): Following the general method and starting from $[TpIr(C_2H_4)_2]$ or $[TpIr(CH{=}CH_2)(Et)(NCMe)]$ (**1a**), in acetonitrile at 100 °C, complex **3a** was obtained in ≈95% yield. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 10.07$ (d, 1H, $^3J(1,2) = 7.1$ Hz, H^1), 7.95 (br, 1H, H^4), 7.82, 7.74, 7.68, 7.65, 7.53, 6.77, 6.25, 6.22, 6.01 (6d, 3t, 1H each, 9CHpz), 6.92 (dd, 1H, $^4J(2,4) = 3$ Hz, H^2), 2.58 (s, 3H, Me^3), 1.17, 1.04 (dq, 1H each, $^2J(H,H) = 11$, $^3J(H,Me) = 8$ Hz, $IrCH_2$), 0.06 (t, 3H, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = 194.0$ (C^1), 187.0 (C^3), 140.2, 139.4, 137.4, 134.6 (intens. 2), 134.0, 105.6, 105.4, 104.5 (CHpz), 131.1 (C^2), 22.0 (Me^3), 16.2 (CH_2CH_3), −11.5 ($IrCH_2$); IR (nujol): $\tilde{\nu} = 3340$ cm^{-1} (N-H); elemental analysis calcd (%) for: $C_{15}H_{21}BN_7Ir$ (502): C 35.9, H 4.2, N 19.5; found: C 36.0, H 4.1, N 20.0.

$[Tp^{Me2}Ir(\overline{CHC(Me)C(Me)NH})(CH_2CH_2CH_3)]$ (4*): This complex was obtained from complex **2*** in almost quantitative yield upon heating its solutions in wet acetonitrile for 12 h at 100 °C. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 10.01$ (s, 1H, H^1), 8.35 (br, 1H, H^4), 5.83, 5.79, 5.50 (s, 1H each, 3CHpz), 2.43, 2.42, 2.38, 2.37, 2.36, 2.27, 2.02, 1.71 (6Mepz, Me^2 and Me^3), 1.21, 1.03 (m, 1H each, $IrCH_2$), 0.45 (m, 2H, CH_2CH_3), 0.68 (t, 3H, $^3J(H,H) = 7$ Hz, CH_2CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = 192.1$ (C^1), 185.3 (C^3), 151.9, 151.4, 150.0, 142.9, 142.3 (1:1:1:2:1 ratio, Cqpz), 135.9 (C^2), 107.1, 106.6, 106.4 (CHpz), 22.8, 22.6 (Me^2 and Me^3), 19.6 (CH_2CH_3), 17.0 (CH_2CH_3), 14.1, 13.3, 13.1, 12.5, 12.4, 11.0 (Mepz), −5.7 ($IrCH_2$); IR (Nujol): $\tilde{\nu} = 3345$ cm^{-1} (N-H).

$[TpIr(\overline{C_8H_{12}C(Me)NH})(C_8H_{15})]$ (5a): Complex $[TpIrH(C_8H_{13})(\eta^2\text{-}C_8H_{14})]$ was dissolved in acetonitrile and heated at 80 °C for 24 h. The volatiles were removed in vacuo and the residue purified by cromatography (silica gel, petroleum ether/Et_2O 9:1). Two red bands were pooled. From the first the title compound was obtained, as an orange crystalline solid, in 75% yield. The second band afforded the red complex **6a** in 15% yield. ^1H NMR ($CDCl_3$, 25 °C): $\delta = 7.97$, 7.79, 7.68, 7.64, 7.51, 6.68, 6.21, 6.21, 5.94, (6d, 3t, 1H each, $^3J(H,H) = 2$ Hz, 9CHpz), 7.80 (br, 1H, H^4), 2.7–0.38 (m, 26H, $13CH_2$), 2.61 (m, 1H, IrCH), 2.40 (s, 3H, Me^3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta = 198.6$ (C^1), 184.1 (C^3), 140.4, 140.1, 137.1, 134.8, 133.9, 133.8, 105.3, 105.1, 104.1 (CHpz), 136.9 (C^2), 36.7, 36.2, 35.6, 30.6, 30.5, 29.4, 27.5, 27.4, 27.0, 26.3, 26.1, 26.0 (CH_2), 22.9 (Me^3), 2.47 (IrCH; $^1J(C,H) = 127$ Hz); IR (nujol): $\tilde{\nu} = 3335$ cm^{-1} (N-H); elemental analysis calcd (%) for: $C_{19}H_{27}BN_7Ir$ (556): C 41.0, H 4.9, N 17.6; found: C 41.2, H 5.0, N 18.0.

$[TpIr(\overline{C_8H_{12}C(Me)NH})(H)]$ (6a): Although this complex was obtained as a by-product in the synthesis of the previous compound, it was best obtained from the hydride $[TpIrH(\eta^3\text{-}C_8H_{13})]$ and acetonitrile (130 °C, 1 h). ^1H NMR ($CDCl_3$, 25 °C): $\delta = 7.92$, 7.84, 7.67, 7.64, 7.62, 6.87, 6.21, 6.14, 6.05 (6d, 3t, 1H each, $^3J(H,H) = 1.8$ Hz, 9CHpz), 7.77 (br, 1H, H^4), 2.80–1.20 (m, 12H,

6 CH_2), 2.46 (s, 3H, Me^3), −20.5 (s, 1H, IrH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 198.7 (C^1), 186.6 (C^3), 145.2, 142.8, 136.9, 134.1, 105.9, 105.7, 104.4 (1:1:1:2:2:1:1 ratio, CHpz), 134.5 (C^2), 36.2, 30.5, 29.8, 26.9, 26.4, 26.2 (CH_2), 22.5 (Me^3); IR (nujol): $\tilde{\nu}$ = 3335 (N-H), 2100 (Ir-H) cm^{-1}.

[TpIr(C$_8$H$_{12}$C(Ph)NH)(R)] (R = C$_8$H$_{15}$ (5c), H (6c)): These complexes were obtained from [TpIrH(C_8H_{13})(η^2-C_8H_{14})] and NCPh/C_6H_{12} (1:15) at 80 °C for 72 h. Two red bands evolved by cromatography on silica gel (petroleum ether/Et_2O 9:1). From the first, orange crystalline **5c** was obtained in 45% yield. The second one afforded complex **6c** in 45% yield. Data for **5c**: ^1H NMR ($CDCl_3$, 25 °C): δ = 8.09, 7.81, 7.72, 7.68, 7.55, 6.83, 6.28, 6.22, 6.01 (6d, 3t, 1H each, ^3J(H,H) = 2 Hz, 9CHpz), 8.07 (br, 1H, H^4), 7.41 (br, 5H, C_6H_5), 2.60 (m, 1H, IrCH), 2.09–0.4 (m, 26H, 13 CH_2); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 203.3 (C^1), 187.4 (C^3), 140.5 (Cqar), 140.5, 140.2, 137.0, 135.0, 133.9, 133.8, 105.4, 105.2, 104.3 (Cqpz), 137.4 (C2), 128.7, 128.3, 127.4 (1:2:2 ratio, CHar), 36.8, 36.2, 31.9, 30.5, 29.3, 29.1, 27.5, 27.0, 26.9, 26.6, 26.4, 26.3, 26.0 (CH2), 3.9 (IrCH); IR (nujol): $\tilde{\nu}$ = 3340 cm^{-1}-(N-H); elemental analysis calcd (%) for $C_{32}H_{43}BN_7Ir$ (728): C 52.7, H 5.9, N 13.5; found: C 53.0, H 5.9, N 13.7.

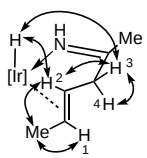
Data for **6c**: ^1H NMR ($CDCl_3$, 25 °C): δ = 8.02 (br, 1H, H^4), 8.01, 7.82, 7.68, 7.63, 6.98, 6.19, 6.09 (2d, m, 2d, m, t, 1:1:2:1:1:2:1 ratio, ^3J(H,H) = 2 Hz, 9CHpz), 7.42 (m, 5H, C_6H_5), 3.1–1.2 (m, 12H, 6 CH_2), −20.30 (s, 1H, IrH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 203.0 (C^1), 189.7 (C^3), 145.2, 142.8, 136.9, 134.7, 134.1, 105.9, 105.7, 104.5 (1:1:1:2:2:1:1 ratio, CHpz), 139.5 (Cqar), 137.3 (C^2), 128.9, 128.3, 127.6 (1:2:2 ratio, CHar), 36.1, 31.9, 29.7, 26.9, 26.4, 26.3 (CH_2); IR (nujol): $\tilde{\nu}$ = 3345 (N-H), 2115 (Ir-H) cm^{-1}; elemental analysis calcd (%) for $C_{24}H_{29}BN_7Ir$ (618): C 46.6, H 4.7, N 15.9; found: C 46.8, H 4.8, N 16.0. This complex can be obtained as the sole product upon reaction of [TpIrH(η^3-C_8H_{13})] with NCPh.

[TpIr(C(Et)CHC(Ph)NH)(H)] (7c): The bis(ethylene) complex [TpIr(C_2H_4)$_2$] (0.06 g, 0.13 mmol) was heated in C_6H_{12} (15 mL) containing NCPh (0.5 mL), at 100 °C for 18 h. The resulting mixture was filtered and evaporated, and the residue extracted with CH_2Cl_2. After filtration through celite, petroleum ether was added and the solution cooled at −20 °C. Red **7c** was obtained in 50% yield (37 mg). ^1H NMR ($CDCl_3$, 25 °C): δ = 8.5 (br, 1H, H^4), 7.97, 7.92, 7.67, 7.63, 7.19, 6.82, 6.26, 6.18, 6.03 (6d, 3t, 1H each, ^3J(H,H) = 2.1 Hz, 9CHpz), 7.71 (br s, 1H, H^2), 7.71, 7.43 (m, 2:3 ratio, C_6H_5), 2.93 (m, 2H, CH_2CH$_3$), 0.86 (t, 3H, ^3J(H,H) = 8 Hz, CH$_2$CH_3), −20.10 (s, 1H, IrH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 209.0 (C^1), 185.7 (C^3), 145.8, 143.0, 137.5, 134.7, 134.4, 134.1, 106.0, 105.8, 104.7 (CHpz), 135.4, 130.2, 128.6 (CHar), 124.4 (C^2, ^1J(C,H) = 168 Hz), 36.8 (CH_2CH_3), 13.3 (CH_2CH_3); IR (nujol): $\tilde{\nu}$ = 3350 (N-H), 2115 (Ir-H) cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{23}BN_7Ir$ (564): C 42.6, H 4.1, N 17.4; found: C 42.7, H 4.1, N 17.1.

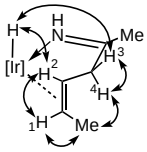
[Tp^{Me2}Ir(C(Me)C(Me)C(Me)NH)(H)] (8a*): Following the general method and starting from the allylic species [Tp^{Me2}IrH(η^3-*anti*-C_3H_4Me)] (acetonitrile, 100 °C, 12 h) the title compound was obtained as an orange solid after crystallization from acetonitrile in 80% yield. ^1H NMR ($CDCl_3$, 25 °C): δ = 8.01 (br, 1H, H^4), 5.81, 5.80, 5.58 (s, 1H each, 3CHpz), 2.38, 2.36, 2.35, 2.20, 1.97, 1.84, 1.62 (1:2:2:1:1:1:1 ratio, 6Mepz, Me^1, Me^2 and Me^3), −23.0 (s, 1H, IrH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 195.5 (C^1), 185.7 (C^3), 152.1, 151.0, 150.3, 143.4, 142.7 (Cqpz), 132.3 (C^2), 106.7, 105.8, 105.4 (CHpz), 27.0, 22.6 (Me^2 and Me^3), 17.0 (Me^1), 14.7, 13.4, 13.0, 12.5, 12.3, 10.4 (Mepz); IR (nujol): $\tilde{\nu}$ = 3330 (N-H), 2130 (Ir-H) cm^{-1}; elemental analysis calcd (%) for: $C_{21}H_{33}BN_7Ir$ (586): C 43.0, H 5.6, N 16.7; found: C 42.9, H 5.2, N 17.0. This compound can be deuterated in the N-H position with CD_3OD in the presence of trace amounts of [H(OEt_2)$_2$]BAr′$_4$.

[Tp^{Me2}Ir(C(Me)C(Me)C(Ph)NH)(H)] (8c*): Synthesized as the previous compound but in benzonitrile. Crystallization was achieved from mixtures of Et_2O/petroleum ether. Yield: 75%. ^1H NMR ($CDCl_3$, 25 °C): δ = 8.31 (br, 1H, H^4), 7.45 (m, 5H, C_6H_5), 5.84, 5.80, 5.59 (s, 1H each, 3CHpz), 2.48, 2.38, 2.37, 2.35, 2.34, 2.26, 1.93, 1.68 (s, 3H each, 6Mepz, Me^1 and Me^2), −22.64 (s, 1H, IrH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 200.6 (C^1), 187.0 (C^3), 152.3, 151.1, 150.4, 143.5, 142.8 (Cqpz), 139.3 (Cqar), 131.6 (C^2), 128.8, 128.3, 127.7 (1:2:2 ratio, CHar), 106.6, 105.9, 105.4 (CHpz), 27.8 (Me^2), 17.1 (Me^1), 14.8, 14.4, 13.0, 12.5, 12.3, 10.6 (Mepz); IR (Nujol): $\tilde{\nu}$ = 3360 (N-H), 2130 (Ir-H) cm^{-1}; elemental analysis calcd (%) for: $C_{26}H_{35}BN_7Ir$ (602): C 48.1, H 5.4, N 15.1; found: C 47.9, H 5.6, N 15.4.

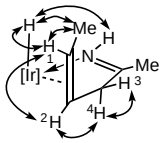
[Tp^{Me2}IrN(H)=C(Me)CH$_2$-*trans*-CH=CHMe)(H)]BAr′$_4$ (9*-*trans*): A mixture of compound **3a*** (0.06 g, 0.10 mmol) and [H(OEt_2)$_2$][B(C_6H_3-3,5-(CF_3)$_2$)$_4$] (0.10 g, 0.10 mmol) was dissolved in CH_2Cl_2 (10 mL), at room temperature, to form a colorless solution. Following overnight stirring, the solvent was eliminated under vacuo and the residue extracted with a mixture of Et_2O/petroleum ether (10 mL, 1:1). After filtration, concentration under reduced pressure and cooling to −20 °C, the title compound was isolated as a white microcrystalline solid (0.09 g, 60%, yield). ^1H NMR ($CDCl_3$, 25 °C; see above for atom labels and NOEs): δ = 8.65 (br, 1H, NH), 5.94, 5.84, 5.73 (s, 1H each, 3CHpz), 5.37 (dd, 1H, ^3J(2,1) = 11.7, ^3J(2,3) 5.6 Hz, H^2), 4.15 (dq, 1H, ^3J(1,Me) = 6.1 Hz, H^1), 3.30, 3.24 (ABX spin system, 1H each, ^2J(3,4) = 20.1 Hz, a 1.4 Hz coupling with NH is also observed for H^3, H^4 and H^3), 2.46, 2.36, 2.32, 2.13, 2.08, 2.03 (s, 3H each, Mepz), 2.17 (d, 3H, ^4J(Me,NH) = 1.0 Hz, C(*Me*)=NH), 0.94 (d, 3H, *Me*CH), −17.36 (s, 1H, IrH); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): δ = 194.5 (s, C=N), 151.1, 151.0, 149.6, 146.0, 145.7, 145.5 (Cqpz), 109.4, 108.2, 107.0 (CHpz), 68.0, 69.1 (-CH=CH-, ^1J(C,H) = 162, 168 Hz, resp.), 44.0 (CH_2, ^1J(C,H) = 130 Hz), 23.9 (*Me*C=N), 16.1, 15.7, 14.1, 14.0, 12.5, 12.2, 12.1 (Mepz and *Me*CH^1); IR (nujol): $\tilde{\nu}$ = 3185 (N-H), 2200 (Ir-H) cm^{-1}; elemental analysis calcd (%) for $C_{53}H_{46}B_2F_{24}N_7Ir \cdot \frac{1}{2}Et_2O$ (1487): C 44.4, H 3.4, N 6.6; found: C 44.9, H 3.6, N 6.2. When the reaction is carried out in $CDCl_3$ or CD_2Cl_2, at −80 °C and then warmed to room temperature, an initial 2:1 mixture of **9*-*cis*** and **9*-*trans*** is observed; compound **9*-*cis*** rearranges in solution to the isolated **9*-*trans*** ($t_{1/2}$ ca 3 h at room temperature).



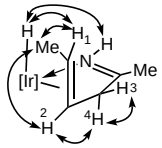
NOE



Data for **9*-*cis***: ^1H NMR ($CDCl_3$, 25 °C; see above for atom labels and NOEs): δ = 8.43 (br, 1H, NH), 6.15 (td, 1H, ^3J(2,1) = ^3J(2,3) = 8.8, ^3J(2,4) = 3.3 Hz, H^2), 5.92, 5.83, 5.75 (s, 1H each, CHpz), 4.16 (dq, 1H, H^1, ^3J(1,Me) = 6.6 Hz), 3.47 (dd, 1H, ^2J(3,4) = 20.7, ^4J(3,NH) = 1.4 Hz, H^3), 2.94 (dd, 1H, H^4), 2.46, 2.40, 2.30, 2.11, 1.95, 1.88 (s, 3H each, Mepz), 1.54 (d, 3H, MeCH), −18.59 (s, 1H, IrH); C(Me)=NH not assigned.



When the reaction is carried out in CD_2Cl_2 at low temperature, the hydrides **U*-*cis*** and **U*-*trans*** (4:1 ratio) can be observed by NMR spectroscopy. Data for **U*-*cis***: ^1H NMR (CD_2Cl_2, −40 °C; see above for atom labels and NOEs): δ = 8.50 (br, 1H, NH), 5.56 (pseudoquartet, 1H, ^3J(2,1) = 8.4, ^3J(2,4) = 6.6, ^3J(2,3) = 4.4 Hz, H^2), 5.27 (pseudoquintet, 1H, ^3J(1,Me) = 7 Hz, H^1), 3.85 (dd, 1H, ^2J(4,3) = 20.5 Hz, H^4), 2.93 (dd, 1H, H^3), 2.41 (d, 3H, MeCH), −21.32 (s, 1H, IrH).



Data for **U*-*trans***: ^1H NMR (CD_2Cl_2, −40 °C, see above for atom labels and NOEs): δ = 8.99 (s, 1H, NH), 5.78 (dq, 1H, ^3J(1,2) = 12.1, ^3J(1,Me) = 6 Hz, H^1), 5.67 (ddd, 1H, ^3J(2,3) = 9.5, ^3J(2,4) = 4 Hz, H^2), 4.35 (dd, 1H, ^2J(4,3) = 18 Hz, H^4), 2.69 (ddd, 1H, ^4J(3,NH) = 2.5 Hz, H^3), 1.06 (d, 3H, *Me*CH), −23.56 (s, 1H, IrH). To account for the unusual values of J(2,3) and J(2,4), the first being very high and bigger than the second, this complex must have a somewhat distorted conformation.

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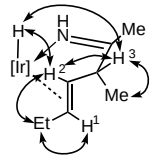
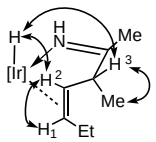
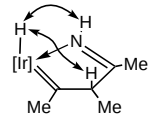


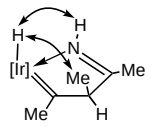
[Tp^{Me2}Ir[N(H)=C(Me)CH(Me)-*trans*-CH=CH(Et)](H)]BAr′$_4$ (10*-*trans*): This compound was produced in 50% yield starting from **4*** and following the procedure already described for compound **9*-*trans***. However, in this case the CH_2Cl_2 solution was heated at 80 °C overnight to ensure complete transformation of the isomer **10*-*cis***. ^{1}H NMR ($CDCl_3$, 25 °C; see above for atom labels and NOEs): $\delta = 8.58$ (br, 1H, NH), 5.92, 5.83, 5.71 (s, 1H each, CHpz), 5.43 (dd, 1H, $^3J(2,1) = 11.7$, $^3J(2,3) = 6.1$ Hz, H^2), 3.86 (m, 1H, $^3J(1,CH_2) = 6.7$ Hz, H^1), 3.26 (m, 1H, $^3J(3,Me) = 7.3$, $^4J(3,NH) = 1.8$ Hz, H^3), 2.43, 2.35, 2.30, 2.09, 2.06, 1.99 (s, 3H each, 6Mepz), 2.11 (d, 3H, ^4J(Me,NH) = 1.3 Hz, C(*Me*)=NH), 1.45 (d, 3H, CH*Me*), ≈1.0 (m, 2H, CH_2CH_3), 0.73 (t, 3H, CH_2CH_3, $^3J(H,H) = 7.6$ Hz), −17.25 (s, 1H, IrH); ^{13}C{^{1}H}NMR ($CDCl_3$, 25 °C): $\delta = 195.4$ (C=N), 151.2, 151.0, 149.5, 146.0, 145.7, 145.5 (Cqpz), 109.4, 108.2, 107.0 (CHpz), 73.9/70.1 (CHolef, $^1J(C,H) = 166$ and 156 Hz), 49.2 (CH^3, $^1J(C,H) = 126$ Hz), 24.3 (CH_2, $^1J(C,H) = 130$ Hz), 24.1 (*Me*C=N), 16.2, 15.1, 14.6, 14.1, 14.0, 12.5, 12.2, 12.1 (Mepz, *Me*CH, *Me*CH_2); IR (Nujol): $\tilde{\nu} = 3190$ (N-H), 2190 (Ir-H) cm^{-1}. If the reaction is carried out at −80 °C and then warmed to room temperature, a ca 1:6 mixture of **10*-*cis*** and **10*-*trans*** is obtained. Two other stereoisomers are also observed but they dissappear after a few hours at 25 °C (see Discussion).



Selected data for **10*-*cis***: ^{1}H NMR ($CDCl_3$, 25 °C; see above for atom labels and NOEss): $\delta = 8.40$ (br, 1H, NH), 5.89 (dd, 1H, $^3J(2,1) = 8.5$, $^3J(2,3) = 7$ Hz, H^2), 3.57 (m, 1H, H^1), 3.50 (m, 1H, H^3), 1.47 (d, 3H, ^3J(Me,3) = 7.3 Hz, *Me*CH^3), 1.10 (t, 3H, CH_2CH_3), −18.38 (s, 1H, IrH); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): $\delta = 196.8$ (C=N), 71.8 and 68.8 (CHolef, $^1J(C,H) = 168$ and 164 Hz), 47.7 (CH^3, $^1J(C,H) = 126$ Hz).

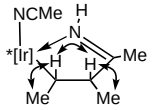


[Tp^{Me2}Ir(=C(Me)CH(Me)C(Me)=NH)(H)]BAr′$_4$ 11*-*syn*): A mixture of compound **8a*** (0.08 g, 0.136 mmol) and $[H(OEt_2)_2][B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]$ (0.14 g, 0.136 mmol) was dissolved in CH_2Cl_2 (10 mL) at −70 °C. A deep orange solution was immediately formed. After 10 min of stirring at this temperature, the cold bath was removed and the solvent was evaporated almost to dryness, under reduced pressure. The remaining solution was cooled again to −70 °C and petroleum ether (10 mL) added. Following vigorous stirring for a few minutes, an orange microcrystalline solid was separated by filtration. The solid was dissolved in a mixture of petroleum ether/dichloromethane (15 mL, 3:1) and cooled to −20 °C to provide orange crystals of the title compound (0.12 g, 60%). ^{1}H NMR ($CDCl_3$, 25 °C, see above for NOE's): $\delta = 9.89$ (br, 1H, NH), 5.92, 5.75 (s, 2H and 1H, CHpz), 2.53, 2.45, 2.42, 2.40, 2.28, 1.88 (s, 3H each, Mepz), 1.72 (d, $^3J(H,H) = 7.4$ Hz, CH*Me*), 1.64, 1.37 (s, 3H each, Me), 0.21 (qd, 1H, $^4J(H,NH) = 2$ Hz, C*H*Me), −15.68 (s, 1H, IrH); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): $\delta = 324.5$ (Ir=C), 192.3 (C=N), 151.7, 150.8, 148.6, 146.6, 146.1, 145.3 (Cqpz), 107.5, 107.4, 107.3 (CHpz), 82.2 (CH, $^1J(C,H) = 123$ Hz), 48.2 (Ir=C*Me*, $^1J(C,H) = 128$ Hz), 23.1 (CH*Me*), 15.8, 14.2, 13.0, 12.7, 12.1, 12.0, 11.1 (Me); IR (nujol): $\tilde{\nu} = 3320$ (N-H), 2152 (Ir-H) cm^{-1}; elemental analysis calcd (%) for: $C_{53}H_{46}B_2F_{24}N_7Ir \cdot \frac{1}{4}CH_2Cl_2$ (1471.25): C 43.4, H 3.2, N 6.7; found: C 43.5, H 3.2, N 6.4.

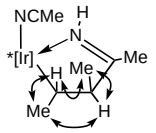


When a solid sample of compound **11*-*syn*** was dissolved in commercially available $CDCl_3$, a slow, somewhat erratic, and quantitative transformation into isomer **11*-*anti*** was observed. ^{1}H NMR ($CDCl_3$, 25 °C, see above for NOE's): $\delta = 9.60$ (br, 1H, NH), 5.93, 5.92, 5.75 (s, 1H each, CHpz), 2.67 (q, 1H, $^3J(H,H) = 7.5$ Hz, C*H*Me), 2.51, 2.45, 2.42, 2.40, 2.31, 1.87, 1.64 (Me), 1.52 (d, 3H, CH*Me*), 1.42 (s, 3H, Me), −15.28 (s, 1H, IrH).

[Tp^{Me2}Ir(CH(Me)CH(Me)C(Me)=NH)(HOMe)]BAr′$_4$ (12a*-*syn*): This compound was obtained by adding a drop of methanol to a $CDCl_3$ solution of **11*-*syn***. ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 9.46$ (br, 1H, NH), 5.86, 5.81, 5.56 (s, 1H each, CHpz), 4.39 (m, 1H, $^3J(H,H) = 10.2$, $^3J(H,Me) = 8.0$ Hz, IrC*H*Me), 1.36 (d, 3H, ^3J(Me,H) = 7.7 Hz, CH*Me*), 0.60 (d, 3H, IrCH*Me*). C*H*Me obscured by the methanol resonance. Starting with **11*-*anti***, **12a*-*anti*** was similarly obtained. ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 3.76$ (m, 1H, $^3J(H,Me) = 7.4$, $^3J(H,H) = 5$ Hz, IrC*H*Me), 2.87 (m, 1H, $^3J(H,Me) = 7.4$ Hz, C*H*Me), 1.32 (d, 3H, CH*Me*), 0.67 (d, 3H, IrCH*Me*).



[Tp^{Me2}Ir(CH(Me)CH(Me)C(Me)=NH)(NCMe)]BAr′$_4$ (12b*-*syn*): A solution of compound **8a*** (0.07 g, 0.12 mmol) in CH_2Cl_2 (10 mL) and NCMe (0.5 mL), cooled at −70 °C, was treated with $[H(OEt_2)_2][B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]$ (0.12 g, 0.12 mmol, in CH_2Cl_2, 5 mL). The resulting mixture was allowed to reach room temperature. After 15 min of stirring, the solvent was removed under vacuo, petroleum ether (10 mL) was added and the suspension obtained was cooled to −70 °C and vigorously stirred for 5 min, during which time a white powder was formed. The solid was separated by filtration and washed with petroleum ether (5 mL) at room temperature. The solid was dissolved in a mixture of petroleum ether/CH_2Cl_2 (10 mL, 3:1) and the reaction mixture cooled to −20 °C allowed the isolation of compound **12b*-*syn*** as a white microcrystalline solid (0.08 g, 45%). ^{1}H NMR ($CDCl_3$, 25 °C, see above for NOE's): $\delta = 8.63$ (br, 1H, NH), 5.87, 5.83, 5.69 (s, 1H each, CHpz), 4.22 (dq, 1H, $^3J(H,H) = 10$, $^3J(H,Me) = 8.1$ Hz, IrC*H*Me), 3.0 (m, 1H, $^3J(H,Me) = 7.7$, $^4J(H,NH) = 3$ Hz, C*H*Me), 2.45 (s, 3H, NC*Me*), 2.39, 2.35, 2.34, 2.33, 2.11, 1.93 (s, 3H each, Mepz), 2.17 (s, 3H, C(*Me*)=NH) 1.34 (d, 3H, CH*Me*), 0.68 (d, 3H, IrCH*Me*); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C): $\delta = 206.2$ (C=N), 150.9, 149,4, 149.1, 145.2, 144.5, 144.4 (Cqpz), 109.5, 108.8, 107.0 (CHpz), 58.7 (*C*HMe), 23.7, 22.8, 19.5, 14.3, 13.4, 13.1, 12.9, 12.6, 12.0, 11.9 (Me and IrCHMe), 3.1 (NC*Me*).



Addition of NCMe to a solution of complex **11*-*anti*** in $CDCl_3$ formed compound **12b*-*anti***. ^{1}H NMR for the species obtained with $NCCD_3$ ($CDCl_3$, 25 °C, see above for NOE's): $\delta = 8.75$ (br, 1H, NH), 5.88, 5.82, 5.70 (s, 1H each, 3CHpz), 3.61 (m, 1H, $^3J(H,Me) = 7.4$, $^3J(H,H) = 4.1$ Hz, IrC*H*Me), 2.81 (m, 1H, $^3J(H,Me) = 7.6$ Hz, C*H*Me), 2.38, 2.36, 2.34, 2.30, 2.15, 1.96 (s, 3H each, Mepz), 2.20 (d, 3H, ^4J (H,H) = 0.7 Hz, C*Me*=NH), 1.29 (d, 3H, CH*Me*), 0.78 (d, 3H, IrCH*Me*).

Compounds **12c*** were obtained by the addition of water to $CDCl_3$ solutions of **11***. **12c*-*syn***: ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 8.92$ (br, 1H, NH), 5.86, 5.78, 5.60 (s, 1H each, CHpz), 4.53 (m, 1H, $^3J(H,H) = 9.1$ Hz, $^3J(H,Me) = 8.0$ Hz, IrC*H*Me), 3.34 (m, 1H, $^3J(H,Me) = 8.0$ Hz, C*H*Me), 1.40 (d, 3H, CH*Me*), *0.65* (d, 3H, IrCH*Me*). **12c*-*anti***: ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 9.11$ (br, 1H, NH), 5.87, 5.77, 5.62 (s, 1H each, CHpz), 3.92 (m, 1H, $^3J(H,Me) = 7.4$, $^3J(H,H) = 5.0$ Hz, IrC*H*Me), 2.93 (m, 1H, $^3J(H,Me) = 7.4$ Hz, C*H*Me), 1.50 (d, 3H, CH*Me*), 0.76 (d, 3H, IrCH*Me*).

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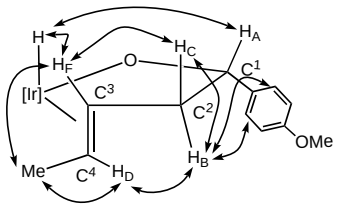
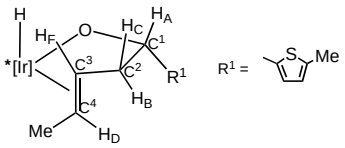
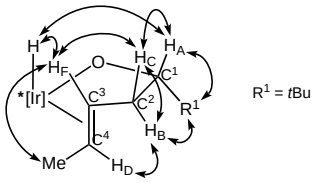


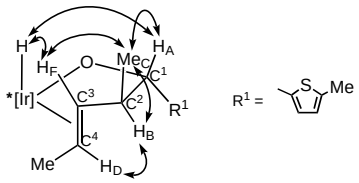
[Tp^{Me2}Ir(OCH(C$_6$H$_4$-*p*-OMe)CH$_2$-*trans*-CH=CHMe)(H)] (13a*): Freshly distilled anisaldehyde was added (0.09 mL, 0.73 mmol) to a suspension of [Tp^{Me2}Ir(C$_2$H$_4$)$_2$] (0.40 g, 0.73 mmol) in cyclohexane (0.6 mL). The solution was stirred al 60 °C for 6 h, after which time the solvent was evaporated under reduced pressure. Pentane (4 mL) was added and the suspension stirred vigorously for a few minutes. The pale brown solid formed was separated by filtration and dissolved in a mixture of Et$_2$O/petroleum ether (1:1, 7 mL). The solution obtained after filtration was slowly cooled to −20 °C to yield the titled compound as a brown microcrystalline solid, in 60 % yield (315 mg). ^{1}H NMR (CDCl$_3$, 25 °C; see above for atom labels and NOE's): δ = 7.29, 6.77 (d, 2H each, ^3J(H,H) = 8.6 Hz, 4CHar), 5.89, 5.71, 5.70 (s, 1H each, 3CHpz), 5.54 (dt, 1H, ^3J(F,D) = 11.4, ^3J(F,B) = ^3J(F,C) = 5.5 Hz, H$_F$), 4.84 (dd, 1H, ^3J(A,B) = 9.9 Hz, ^3J(A,C) = 4.4 Hz, H$_A$), 4.66 (dq, 1H, ^3J(D,Me) = 5.8 Hz, H$_D$), 3.74 (s, 3H, OMe), 2.8–2.0 (s, 3H each, 6Mepz), 2.54 (m, 1H, H$_C$), 1.71 (td, 1H, ^2J(B,C) = 10.7 Hz, H$_B$), 0.83 (d, 3H, *Me*CH$_D$), −18.63 (s, 1H, IrH); ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ = 158.2 (*C*OMe), 152.3, 151.6, 150.7, 144.3, 143.7, 143.1 (Cqpz), 140.9 (*C*$_q$CH$_A$), 127.2, 113.5 (CHar), 107.9, 106.9, 106.7 (CHpz), 95.2 (C^1, ^1J(C,H) = 140 Hz), 75.2 (C^3, ^1J(C,H) = 158 Hz), 69.2 (C^4, ^1J(C,H) = 155 Hz), 55.5 (OMe), 43.3 (C^2, ^1J(C,H) = 127 Hz), 17.5 (*Me*CH$_D$), 16.2, 14.5, 13.5, 13.2, 12.8, 12.8 (Mepz); IR (nujol): $\tilde{\nu}$ = 2181 cm^{-1} (Ir-H); elemental analysis calcd (%) for C$_{27}$H$_{38}$BN$_6$O$_2$Ir·½Et$_2$O (718): C 48.4, H 6.0, N 11.7; found: C 48.5, H 5.8, N 11.9.



[Tp^{Me2}Ir(OCH(C$_4$H$_2$(5-Me)S)CH$_2$-*trans*-CH=CHMe)(H)] (13b*): The compound [Tp^{Me2}Ir(C$_2$H$_4$)$_2$] (0.30 g, 0.55 mmol) was suspended in a mixture of freshly distilled 5-methylthiophene-2-aldehyde (0.06 mL, 0.55 mmol) and cyclohexane (1 mL). The solution was stirred for 6 h at 60 °C. After this period of time, the solvent was removed in vacuo, pentane (4 mL) was added and the mixture vigorously stirred for a few minutes. The brown solid formed was filtered and dissolved in a mixture (9 mL) of Et$_2$O/CH$_2$Cl$_2$/pentane (1:1:1). The solution was slowly cooled to −20 °C to yield compound **13b*** as a brown solid (220 mg, 60 %). ^{1}H NMR (C$_6$D$_6$, 25 °C; see above for atom labels): δ = 6.62, 6.46 (d, dq, 1H each, ^3J(H,H) = 3.4, ^4J(H,Meth) = 0.9 Hz, CHth and C*H*CMeth), 5.85, 5.70, 5.59 (s, 1H each, 3CHpz), 5.47 (dt, 1H, ^3J(F,D) = 10.2, ^3J(F,B) = ^3J(F,C) = 6.4 Hz, H$_F$), 4.96 (dd, 1H, ^3J(A,B) = 11.4, ^3J(A,C) = 6.2 Hz, H$_A$), 4.64 (dq, 1H, ^3J(D,Me) = 6.2 Hz, H$_D$), 2.67, 2.41, 2.39, 2.34, 2.24, 2.03 (s, 3H each, 6Mepz), 2.55 (m, 1H, H$_C$), 2.35 (s, 3H, Meth), 1.82 (m, 1H, H$_B$), 0.79 (d, 3H, *Me*CH$_D$), −18.61 (s, 1H, IrH); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 25 °C): δ = 152.3, 151.2, 150.4, 144.0, 143.3, 142.8 (Cqpz), 151.0, 136.8 (Cqth), 124.0, 121.2 (CHth), 107.8, 106.5, 106.4 (CHpz), 90.5 (C^1), 73.8 (C^3), 70.4 (C^4), 43.5 (C^2), 17.2 (*Me*CH$_D$), 15.9, 15.4, 14.1, 13.2, 12.9, 12.5, 12.5 (Mepz, Meth); IR (nujol): $\tilde{\nu}$ = 2166 cm^{-1} (Ir-H); elemental analysis calcd (%) for C$_{25}$H$_{36}$BN$_6$OSIr (671): C 44.7, H 5.3, N 12.5; found: C 44.0, H 5.4, N 12.1.



[Tp^{Me2}Ir(OCH(CMe$_3$)CH$_2$-*trans*-CH=CHMe)(H)] (13c*): Freshly distilled trimethylacetaldehyde was added (0.054 mL, 0.50 mmol) to a suspension of [Tp^{Me2}Ir(C$_2$H$_4$)$_2$] (0.21 g, 0.39 mmol) in cyclohexane (1 mL). The solution was stirred al 60 °C for 10 h, after which time the solvent was evaporated under reduced pressure. Pentane (5 mL) was added and afterwards evaporated under vacuo, and this procedure repeated three times in order to favor the elimination of the excess of the aldehyde. Pentane was added (30 mL) to the remaining solid and the mixture was vigorously stirred for a few minutes. The resulting solution was filtered, concentrated under reduced pressure, and purified by cromatography through silica gel (petroleum ether/Et$_2$O 7:3; R_f = 0.28). The filtrate was reduced to dryness and the residue extracted with Et$_2$O/pentane 1:5, concentrated and cooled to −20 °C. Compound **13c*** was isolated as a white microcristalline solid (120 mg, 50 %). ^{1}H NMR (C$_6$D$_6$, 25 °C; see above for atom labels and NOE's): δ = 5.90, 5.77, 5.61 (s, 1H each, 3CHpz), 5.41 (dt, 1H, ^3J(F,D) = 11.4, ^3J(F,B) = ^3J(F,C) = 5.2 Hz, H$_F$), 4.48 (dq, 1H, ^3J(D,Me) = 6.3 Hz, H$_D$), 3.57 (dd, 1H, ^3J(A,B) = 10.3, ^3J(A,C) = 6.3 Hz, H$_A$), 2.66, 2.45, 2.43, 2.37, 2.30, 2.08 (s, 3H each, 6Mepz), 2.25 (m, 1H, H$_C$), 1.55 (td, 1H, ^{2}J(B,C) = 11.1 Hz, H$_B$), 0.92 (s, 9H, CMe$_3$), 0.74 (d, 3H, MeCH$_D$), −18.75 (s, 1H, IrH); ^{13}C{^{1}H} NMR ([D$_6$]benzene, 25 °C): δ = 152.2, 151.3, 150.4, 143.7, 143.4, 143.2 (Cqpz), 107.8, 106.5, 106.2 (CHpz), 100.7 (C^1, ^1J(C,H) = 139 Hz), 74.6 (C^3, ^1J(C,H) = 158 Hz), 69.4 (C^4, ^1J(C,H) = 154 Hz), 36.1 (*C*Me$_3$), 34.9 (C^2, ^1J(C,H) = 126 Hz), 26.7 (C*Me*$_3$), 17.1 (*Me*CH$_D$), 15.9, 14.1, 13.6, 12.8, 12.5, 12.5 (Mepz); IR (nujol): $\tilde{\nu}$ = 2187 cm^{-1} (Ir-H); elemental analysis calcd (%) for C$_{24}$H$_{40}$BN$_6$OIr (631): C 45.6, H 6.3, N 13.3; found: C 45.6, H 6.3, N 13.5.



[Tp^{Me2}Ir(OCH(C$_4$H$_2$(5-Me)S)CH(Me)-*trans*-CH=CHEt)(H)] (14b*): The preparation of this derivative was performed as described for compound **13b***, starting from [Tp^{Me2}IrH(*trans*-CH=CHMe)(η^2-C$_3$H$_6$)] (0.30 g, 0.52 mmol) and freshly distilled 5-methylthiophene-2-aldehyde (0.056 mL, 0.52 mmol). Following chromatography (Et$_2$O/petroleum ether 4:6; R_f = 0.4) and evaporation of the solvent, the compound was dissolved in Et$_2$O/pentane 1:9 and cooled to −20 °C, yielding a pale brown solid (0.15 g, 50 %). ^{1}H NMR (CDCl$_3$, 25 °C; see above for atom labels and NOE's): δ = 6.62, 6.45 (d, dq, 1H each, ^3J(H,H) = 3.4, ^4J(H,Meth) = 2.1 Hz, CHth and C*H*CMeth,), 5.83, 5.69, 5.58 (s, 1H each, 3 CHpz), 5.07 (ddd, 1H, ^3J(F,D) = 11.2, ^3J(F,B) = 4.7, ^3J(F,H) = 1.4 Hz, H$_F$), 4.56 (m, 1H, H$_D$), 4.31 (d, 1H, ^3J(A,B) = 8.8 Hz, H$_F$), 2.70, 2.40, 2.37, 2.33, 2.23, 2.01 (s, 3H each, 6Mepz), 2.34 (s, 3H, Meth), 1.89 (m, 1H, H$_B$), 1.25 (d, 3H, ^3J(Me,B) = 6.7 Hz, Me$_C$), 1.05, 0.79 (m, 1H each, C*H*$_2$Me), 0.67 (t, 3H, ^3J(Me,H) = 7.4 Hz, CH$_2$*Me*), −18.44 (s, 1H, IrH); ^{13}C{^{1}H} NMR (CDCl$_3$, 25 °C): δ = 152.4, 151.1, 150.7, 143.9, 143.3, 142.7 (Cqpz), 150.5, 137.1 (Cqth), 123.8, 122.2 (CHth), 107.8, 106.5, 106.0 (CHpz), 97.1 (C^1, ^1J(C,H) = 141 Hz), 78.8 (C^3, ^1J(C,H) = 158 Hz), 73.8 (C^4, ^1J(C,H) = 154 Hz), 47.9 (C^2, ^1J(C,H) = 131 Hz), 25.3 (*C*H$_2$Me), 16.9 (Me$_C$), 15.9, 15.5, 14.9, 14.4, 13.3, 12.9, 12.6, 12.5 (Mepz, Meth, CH$_2$*Me*); IR (nujol): $\tilde{\nu}$ = 2166 cm^{-1} (Ir-H); elemental analysis calcd (%) for C$_{27}$H$_{40}$BN$_6$OSIr (699): C 46.3, H 5.7, N 12.0; found: C 46.9, H 5.7, N 12.1.

[Tp^{Me2}Ir(O(H)CH(C$_4$H$_2$(5-Me)S)CH$_2$-*trans*-CH=CHMe)(H)]BAr'$_4$ (15b*): A mixture of complex **13b*** (0.04 g, 0.06 mmol) and [H(OEt$_2$)$_2$]-BAr'$_4$ (0.06 g, 0.06 mmol) was dissolved in 15 mL of cold (−70 °C) acetonitrile. After 10 min of stirring at this temperature the cold bath was removed, stirring was continued for 15 min at room temperature, and the solution was reduced to dryness. The residue was dissolved in a mixture of petroleum ether (10 mL) and CH$_2$Cl$_2$ (0.3 mL) and kept at −70 °C. Complex **15b*** was obtained as a brown microcrystalline solid (65 mg, 70 %). ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ = 6.94, 6.61 (2d, 1H each, ^3J(H,H) = 3.5 Hz, CHth), 6.02, 5.87, 5.70 (s, 1H each, CHpz), 5.95 (dt, 1H, ^3J(F,D) = 12.3, ^3J(F,B) = ^3J(F,C) = 6.0 Hz, H$_F$), 5.59 (brs, 1H, OH), 5.48 (dd, 1H, ^3J(A,B) = 12.1, ^3J(A,C) = 6.2 Hz, H$_A$), 5.04 (dq, 1H, ^3J(D,Me) = 6.2 Hz, H$_D$), 2.85, 2.35 (m, 1H each, CH$_C$H$_B$), 2.47, 2.39, 2.38, 2.35, 2.32, 2.09 (s, 3H each, Mepz), 2.40 (Meth), 0.85 (d, 3H, *Me*CH$_D$), −18.15 (s, 1H, IrH); ^{13}C{^{1}H}NMR (CD$_2$Cl$_2$, 25 °C): δ = 152.4, 152.2, 150.8, 147.2, 146.4, 146.3 (Cqpz), 144.1, 137.9 (Cqth), 129.1, 126.0 (CHth), 109.3, 108.3, 107.4 (CHpz),

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91.0 (C^1, ^1J(C,H) = 154 Hz), 79.8 (C^4, ^1J(C,H) = 155 Hz), 73.5 (C^3, ^1J(C,H) = 164 Hz), 38.3 (C^2, ^1J(C,H) = 130 Hz), 16.8, 16.0, 15.5, 14.4, 14.1, 12.9, 12.5, 12.4 (Mepz, C^4*Me*, Meth); IR (nujol): $\tilde{\nu}$ = 2195 cm^{-1} (Ir-H); elemental analysis calcd (%) for $C_{59}H_{52}B_2N_6F_{24}OSIr \cdot \frac{1}{2}CH_2Cl_2$ (1605): C 44.5, H 3.3, N 5.2; found: C 44.6, H 3.3, N 5.7.

[Tp^{Me2}Ir(O(H)CH(C$_4$H$_2$(5-Me)S)CH(Me)-*trans*-CH=CHEt)(H)]BAr′$_4$ (16b*): This complex was obtained from **14b***, in almost quantitative yield, following the procedure already described for complex **15b***. ^{1}H NMR ($CDCl_3$, 25 °C): δ = 6.87, 6,57 (d, 1H each, ^3J(H,H) = 2.2 Hz, CHth), 5.98, 5.81, 5.66 (s, 1H each, CHpz), 5.51 (dd, 1H, ^3J(F,D) = 11.9, ^3J(F,B) = 5.1 Hz, H_F), 4.86 (m, 2H, ^3J(D,CH_2) = 5.5, ^3J(A,B) = 11.0 Hz, H_D, H_A; the coupling constants were extracted from a spectrum recorded in C_6D_6, where H_D and H_A appear as clearly resolved dt and d, respectively), 2.45, 2.37, 2.36, 2.29, 2.03 (s, 1:1:1:2:1 ratio, Mepz), 2.38 (s, 3H, Meth), 2.26 (m, 1H, H_B), 1.33 (d, 3H, Me_C, ^3J(Me,B) = 6.7 Hz), 1.10, 0.83 (m, 1H each, ^2J(H,H) = 14.2, ^3J(H,Me) = 7.1 Hz, CH_2Me), 0.66 (t, 3H, CH_2*Me*), −18.16 (s, 1H, IrH). The OH proton was not located. ^{13}C{^{1}H}NMR ($CDCl_3$, 25 °C): δ = 152.1, 151.7, 150.6, 146.5, 145.9, 145.8 (Cqpz), 143.7, 138.0 (Cqth), 129.2, 125.8 (CHth), 109.3, 108.2, 107.5 (CHpz), 94.9 (C^1), 82.2 (C^4), 78.5 (C^3), 44.2 (C^2), 24.8 (CH_2Me), 16.0, 15.8, 14.4, 14.1, 12.8, 12.4, 12.4 (Mepz, CH_2*Me*, Meth); IR (nujol): $\tilde{\nu}$ = 2200 cm^{-1} (Ir-H); elemental analysis calcd (%) for $C_{61}H_{56}B_2N_6F_{24}OSIr$ (1590): C 46.0, H 3.5, N 5.3; found: C 45.4, H 3.6, N 5.6.

Crystal structure determinations of compounds 3a*, 9*-*trans* and 11*-*syn*: Detailed information about the crystal structure determination of compound **3a*** is given as Supporting Information. CCDC-179709 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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[1] a) D. Seebach, *Angew. Chem.* **1990**, *102*, 1363; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1320; b) B. M. Trost, *Angew. Chem.* **1995**, *107*, 285; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 259; c) *Transition Metals for Organic Synthesis*, *Vols. 1 and 2* (Eds.: M. Beller, C. Bolm), Wiley-VCH, Weinheim, **1998**; d) *The Chemistry of the Metal–Carbon Bond*, *Vol. 3* (Eds.: F. R. Hartley, S. Patai), and *Vol. 4* (Ed.: F. R. Hartley), Wiley, Chichester, **1985** and **1987**.

[2] a) J. P. Colman, S. L. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, **1987**; b) A. Yamamoto, *Organotransition Metal Chemistry*, Wiley, New York, **1986**; c) R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, 3rd ed., Wiley, New York, **2001**.

[3] a) K. H. Dötz, *Angew. Chem.* **1984**, *96*, 573; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 587; b) K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreissl, U. Schubert, K. Weiss in *Transition Metal Carbene Complexes*, Verlag Chemie, Weinheim, **1983**; c) F. Zaragoza Dörwald, *Metal Carbenes in Organic Synthesis*, Wiley-VCH, Weinheim, **1999**; d) A. de Meijere, H. Schirmer, M. Duetsch, *Angew. Chem.* **2000**, *112*, 4124; *Angew. Chem. Int. Ed.* **2000**, *39*, 3964.

[4] a) H. Enders, *Comprehensive Coordination Chemistry*, *Vol. 2* (Eds.: G. Wilkinson, R. D. Guillard, J. A. McCleverty), Pergamon Press, Oxford, **1987**, Chapter 13.7; b) R. A. Michelin, M. Mozzon, R. Bertani, *Coord. Chem. Rev.* **1996**, *147*, 299; c) C. Bianchini, A. Meli, M. Peruzzini, A. Vacca, F. Vizza, *Organometallics* **1991**, *10*, 645; d) G. Erker, D. Kowalski, R. Noe, C. Krüger, M. Nolte, *Tetrahedron Lett.* **1994**, *35*, 6665; e) G. Erker, R. Pfaff, *Organometallics* **1993**, *12*, 1921; f) S. G. Feng, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1994**, *116*, 8613; g) S. G. Feng, P. S. White, J. L. Templeton, *Organometallics* **1994**, *13*, 1214; h) M. A. Dewey, J. A. Gladysz, *Organometallics* **1990**, *9*, 1351; i) Y. Yamamoto, Y. Kubota, Y. Honda, H. Fukui, N. Asao, H. Nemoto, *J. Am. Chem. Soc.* **1994**, *116*, 3161; j) S. E. Denmark, N. Nakajima, O. J.-C. Nicaise, *J. Am. Chem. Soc.* **1994**, *116*, 8797; k) G. C. Martin, J. M. Boncella, E. J. Wucherer, *Organometallics* **1991**, *10*, 2804.

[5] a) P. Legzdins, S. A. Lumb, V. G. Young, Jr., *Organometallics* **1998**, *17*, 854; b) D. M. Tellers, J. C. M. Ritter, R. G. Bergman, *Inorg. Chem.* **1999**, *38*, 4810; c) C. S. Chin, D. Chong, B. Lee, H. Jeong, G. Won, Y. Do, Y. J. Park, *Organometallics* **2000**, *19*, 638; d) C. S. Chin, D. Chong, S. Lee, Y. J. Park, *Organometallics* **2000**, *19*, 4043.

[6] a) J. M. Fernández, K. Emerson, R. H. Larsen, J. A. Gladysz, *J. Am. Chem. Soc.* **1986**, *108*, 8268; b) C. M. Garner, N. Q. Méndez, J. J. Kowalczyk, J. M. Fernández, K. Emerson, R. D. Larsen, J. A. Gladysz, *J. Am. Chem. Soc.* **1990**, *112*, 5146; c) D. D. Dalton, J. M. Fernández, K. Emerson, R. D. Larsen, A. M. Arif, J. A. Gladysz, *J. Am. Chem. Soc.* **1990**, *112*, 9198; d) B. Heisr, A. Kühn, H. Werner, *Chem. Ber.* **1985**, *118*, 1531; e) H. Werner, B. Heiser, U. Schubert, K. Ackermann, *Chem. Ber.* **1985**, *118*, 1517; f) H. Werner, *Angew. Chem.* **1990**, *102*, 1109; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1077.

[7] P. J. Daff, A. Monge, P. Palma, M. L. Poveda, C. Ruiz, P. Valerga, E. Carmona, *Organometallics* **1997**, *16*, 2263; b) E. Gutiérrez-Puebla, A. Monge, M. Paneque, M. L. Poveda, V. Salazar, E. Carmona, *J. Am. Chem. Soc.* **1999**, *121*, 248; c) M. H. Chisholm, J. C. Huffman, E. A. Lucas, A. Sousa, W. E. Streib, *J. Am. Chem. Soc.* **1992**, *114*, 2710; d) J. L. Caldarelli, L. E. Wagner, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1994**, *116*, 2878.

[8] See for example: a) G. S. Bodner, D. E. Smith, W. G. Hatton, P. C. Heah, S. Georgiou, A. L. Rheingold, S. J. Geib, J. P. Hutchinson, J. A. Gladysz, *J. Am. Chem. Soc.* **1987**, *109*, 7688; b) S. G. Feng, P. S. White, J. L. Templeton, *J. Am. Chem. Soc.* **1992**, *114*, 2951; c) H. Zhen, C. Wang, Y. Hu, T. C. Flood, *Organometallics* **1998**, *17*, 5397.

[9] a) P. M. Maitlis, H. C. Long, R. Quyoum, M. L. Turner, Z. Wang, *Chem. Commun.* **1996**, 1 and references therein; b) R. Beckhaus, *J. Chem. Soc. Dalton Trans.* **1997**, 1991.

[10] a) E. Gutiérrez-Puebla, A. Monge, M. C. Nicasio, P. J. Pérez, M. L. Poveda, E. Carmona, *Chem. Eur. J.* **1998**, *4*, 11; b) Y. Alvarado, O. Boutry, E. Gutiérrez-Puebla, A. Monge, M. C. Nicasio, M. L. Poveda, P. J. Pérez, C. Ruiz, C. Bianchini, E. Carmona, *Chem. Eur. J.* **1997**, *3*, 860; c) M. Paneque, M. L. Poveda, V. Salazar, S. Taboada, E. Carmona, E. Gutiérrez-Puebla, A. Monge, C. Ruiz, *Organometallics* **1999**, *18*, 139; d) C. Slugovc, I. Padilla-Martínez, S. Sirol, E. Carmona, *Coord. Chem. Rev.* **2001**, *213*, 129.

[11] a) S. Trofimenko, *Scorpionates—The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, **1999**; b) S. Trofimenko, *Chem. Rev.* **1993**, *93*, 943; c) N. Kitajima, W. B. Tolman, *Prog. Inorg. Chem.* **1995**, *43*, 418; d) G. Parkin, *Adv. Inorg. Chem.* **1995**, *42*, 291; e) the abbreviations used in this paper for the tris(pyrazolyl)borates are those proposed by Trofimenko in ref. [11b]. Tp′ stands for any ligand of this type. Tp = hydrotris(pyrazolyl)borate; Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borate. For simplicity, in this article bold alphabetic characters (from **A** to **Z** or numerals), refer to species that contain the unsubstituted Tp ligand, whereas addition of an asterisk to the above symbols implies reference to the Tp^{Me2} analogues. An apostrophe (′) is employed in a general way to refer to either the Tp or the Tp^{Me2} derivatives.

[12] For preliminary communications of this work see: a) Y. Alvarado, P. J. Daff, P. J. Pérez, M. L. Poveda, R. Sánchez- Delgado, E. Carmona, *Organometallics* **1996**, *15*, 2192; b) F. M. Alías, M. L. Poveda, M. Sellin, E. Carmona, *Organometallics* **1998**, *17*, 4124.

[13] An interesting process is the preparation of pyridines by cocycloaddition of two alkynes and a nitrile. For some examples see: a) H. Bönnemann, *Angew. Chem.* **1985**, *97*, 264; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 248; b) J. A. Varela, L. Castedo, C. Saá, *J. Org. Chem.* **1997**, *62*, 4189; c) J. A. Varela, L. Castedo, C. Saá, *J. Am. Chem. Soc.* **1998**, *120*, 12147; d) T. Takahashi, F.-Y. Tsai, M. Kotora, *J. Am. Chem. Soc.* **2000**, *122*, 4994; e) Y. Yamamoto, R. Ogawa, K. Itoh, *J. Am. Chem. Soc.* **2001**, *123*, 6189.

[14] *Lewis Acids in Organic Synthesis*, *Vol. 2* (Ed.: H. Yamamoto), Wiley-VCH, Weinheim, **1999**.

[15] a) *Applied Homogeneous Catalysis with Organometallic Compounds, Vols. 1 and 2* (Eds.: B. Cornils, W. A. Herrmann), VCH, Weinheim, **1996**; b) I. Paterson, *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming, C. H. Heathcock), Pergamon Press, Oxford, **1999**, Chapter 1.9; c) D. L. Boger, *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, I. Fleming, C. H. Heathcock), Pergamon Press, Oxford, **1999**, Chapter 4.3.

[16] a) J. R. Bleeke, M. F. Ortwerth, A. M. Rohde, *Organometallics* **1995**, *14*, 2813; b) J. R. Bleeke, M. F. Ortwerth, M. Y. Chiang, *Organometallics* **1992**, *11*, 2740; c) P. Deshong, D. R. Sidler, P. J. Rybczynski, G. A. Slough, A. Rheingold, *J. Am. Chem. Soc.* **1988**, *110*, 2575; d) J. Chen, L. M. Daniels, R. J. Angelici, *J. Am. Chem. Soc.* **1990**, *112*, 199.

[17] a) H. Werner, T. Daniel, T. Braun, O. Nürnberg, *J. Organomet. Chem.* **1994**, *480*, 145; b) G. C. Martin, J. M. Boncella, E. J. Wucherer, *Organometallics* **1991**, *10*, 2804; c) A. C. Filippou, C. Völkl, P. Kiprof, *J. Organomet. Chem.* **1991**, *415*, 375; d) A. S. Guram, R. F. Jordan, *J. Org. Chem.* **1993**, *58*, 5595; e) for a highly distorted structure see: M. D. Curtis, J. Real, W. Hirpo, W. H. Butler, *Organometallics* **1990**, *9*, 66.

[18] a) M. D. Curtis, K. B. Shiu, W. M. Butler, *J. Am. Chem. Soc.* **1986**, *108*, 1550; b) M. D. Curtis, K. B. Shiu, W. M. Butler, J. C. Huffman, *J. Am. Chem. Soc.* **1986**, *108*, 3335; see also: D. L. Reger, M. F. Huff, A. L. Rheingold, B. S. Haggerty, *J. Am. Chem. Soc.* **1992**, *114*, 579.

[19] M. J. Fernández, M. J. Rodríguez, L. A. Oro, F. J. Lahoz, *J. Chem. Soc. Dalton Trans.* **1989**, 2073.

[20] R. S. Tanke, R. H. Crabtree, *Inorg. Chem.* **1989**, *28*, 3444.

[21] a) J. Schwartz, D. W. Hart, B. McGiffert, *J. Am. Chem. Soc.* **1974**, *96*, 5613; b) M. D. Fryzuk, L. Huang, N. T. McManus, P. Paglia, S. T. Rettig, G. S. White, *Organometallics* **1992**, *11*, 2979; c) J. Wolf, H. Werner, *Organometallics* **1987**, *6*, 1164; d) S. R. Allen, P. K. Baker, S. G. Barnes, M. Bottrill, M. Green, A. G. Orpen, I. D. Williams, A. J. Welch, *J. Chem. Soc. Dalton Trans.* **1983**, 927; e) J. S. Merola, *Organometallics* **1989**, *8*, 2975.

[22] a) F. M. Alías, M. L. Poveda, M. Sellin, E. Carmona, *J. Am. Chem. Soc.* **1998**, *120*, 5816; b) J. R. Bleeke, M. F. Ortwerth, M. Y. Chiang, *Organometallics* **1993**, *12*, 985; c) M. A. Esteruelas, F. J. Lahoz, E. Oñate, L. A. Oro, C. Valero, B. Zeier, *J. Am. Chem. Soc.* **1995**, *117*, 7935; d) M. I. Bruce, *Chem. Rev.* **1991**, *91*, 197; e) S. Jung, K. Ilg, J. Wolf, H. Werner, *Organometallics* **2001**, *20*, 2121.

[23] M. Brookhart, B. Grant, A. F. Volpe, Jr., *Organometallics* **1992**, *11*, 3920.

[24] The nomenclature *cis* and *trans* refers to the relationship between the hydrogens in the coordinated olefin termini.

[25] The nomenclature *syn* and *anti* refers to the relationship between the hydride and the incoming proton.

[26] In our preliminary communication (ref. [12a]) this isomerization was attributed to adventitious water.

[27] E. Gutiérrez-Puebla, M. A. Monge, C. Ruiz-Valero, personal communication.

[28] R. G. Bergman, *Polyhedron* **1995**, *14*, 3227.

[29] a) Ref. [6f]; b) M. C. Fermin, J. W. Bruno, *J. Am. Chem. Soc.* **1993**, *115*, 7511; c) P. A. Chetcuti, J. A. Walker, C. B. Knobler, M. F. Hawthorne, *Organometallics* **1988**, *7*, 641; d) P. P. M. de Lange, M. van Wijnkoop, H.-W. Frühauuf, K. Vrieze, K. Goubitz, *Organometallics* **1993**, *12*, 428.

[30] The concentrations of D_2O used in these studies are low enough to make any correction unnecessary. In our case the concentration–activity relationship of water is linear over all the $[D_2O]$ range studied. See: a) G. Bell, A. E. M. Jansen, P. J. Halling, *Enzyme Microb. Technol.* **1997**, *20*, 471; b) C. Bergquist, B. M. Bridgewater, C. J. Harlan, J. R. Norton, R. A. Friesner, G. Parkin, *J. Am. Chem. Soc.* **2001**, *123*, 10581; c) J. R. Reimers, L. E. Hall, *J. Am. Chem. Soc.* **1999**, *121*, 3730.

[31] a) T. H. Lowry, K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, Harper & Row, New York, **1987**, Chapter 2; b) Y. Lee, *Chem. Soc. Rev.* **1995**, 223.

[32] E. A. Carter, W. A. Goddard III, *Organometallics* **1988**, *7*, 675.

[33] a) J. E. Muir, A. Haynes, M. J. Winter, *Chem. Commun.* **1996**, 1765; b) P. Bergamini, E. Costa, C. Gauter, A. G. Orpen, P. G. Pringle, *J. Chem. Soc. Dalton Trans.* **1996**, 861; c) P. Bergamini, E. Costa, A. G. Orpen, P. G. Pringle, M. B. Smith, *Organometallics* **1995**, *14*, 3178; d) R. A. Michelin, R. Bertani, M. Mozzon, G. Bombieri, F. Benetollo, M. de F. G. Guedes da Silva, A. J. L. Pombeiro, *Organometallics* **1993**, *12*, 2372; e) J. C. Green, C. N. Jardine, *J. Chem. Soc. Dalton Trans.* **2001**, 274; f) N. J. Cooper, M. L. H. Green, *J. Chem. Soc. Dalton Trans.* **1979**, 1121; g) J. C. Hayes, N. J. Cooper, *J. Am. Chem. Soc.* **1982**, *104*, 5570.

[34] a) D. L. Thorn, T. H. Tulip, *J. Am. Chem. Soc.* **1981**, *103*, 5984; b) D. L. Thorn, *Organometallics* **1982**, *1*, 879; c) D. L. Thorn, T. H. Tulip, *Organometalics* **1982**, *1*, 1580; d) T. W. Bell, D. M. Haddleton, A. McCamley, M. G. Partridge, R. N. Perutz, H. Willner, *J. Am. Chem. Soc.* **1990**, *112*, 9212; e) M. B. France, J. Feldman, R. H. Grubbs, *J. Chem. Soc. Chem. Commun.* **1994**, 1307; f) J. R. Bleeke, R. Behm, *J. Am. Chem. Soc.* **1997**, *119*, 8503; g) J. S. Yeston, R. G. Bergman, *Organometallics* **2000**, *19*, 2947.

[35] a) J. Yang, J. Yin, K. A. Abboud, W. M. Jones, *Organometallics* **1994**, *13*, 971; b) D. J. Crowther, Z. Zhang, G. J. Palenik, W. M. Jones, *Organometallics* **1992**, *11*, 622; c) D. J. Crowther, S. Tivakornpannarai, W. M. Jones, *Organometallics* **1990**, *9*, 739; d) N. J. Conti, D. J. Crowther, S. Tivakornpannarai, W. M. Jones, *Organometallics* **1990**, *9*, 175; e) Y. Stenstrom, A. E. Koziol, G. J. Palenik, W. M. Jones, *Organometallics* **1987**, *6*, 2079.

[36] H. Werner, W. Stüer, M. Laubender, C. Lehmann, R. Herbst-Irmer, *Organometallics* **1997**, *16*, 2236.

[37] D. A. Ortmann, B. Weberndörfer, J. Schöneboom, H. Werner, *Organometallics* **1999**, *18*, 952.

[38] T. Braun, O. Gevert, H. Werner, *J. Am. Chem. Soc.* **1995**, *117*, 7291.

[39] H. F. Lueke, B. A. Arndtsen, P. Burger, R. G. Bergman, *J. Am. Chem. Soc.* **1996**, *118*, 2517.

[40] a) R. R. Schrock, S. W. Seidel, N. C. Mösch-Zanetti, K.-Y. Shih, M. B. O'Donoghue, W. M. Davis, W. M. Reiff, *J. Am. Chem. Soc.* **1997**, *119*, 11876; b) R. R. Schrock, S. W. Seidel, N. C. Mösch-Zanetti, D. A. Dobbs, K.-Y. Shih, W. M. Davis, *Organometallics* **1997**, *16*, 5195.

[41] H. Fischer, H. Jungklaus, *J. Organomet. Chem.* **1997**, *572*, 105.

[42] a) M. Oki, *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*, VCH, Weiheim, **1985**; b) J. E. Anderson, *J. Chem. Soc. Chem. Commun.* **1996**, 93; c) M. L. H. Green, A. Sella, L.-L. Wong, *Organometallics* **1992**, *11*, 2650.

[43] The change of the face of the coordinated olefin can occur by a dissociation-association mechanism or by a different pathway, see: a) T. Penag, J. A. Gladysz, *J. Am. Chem. Soc.* **1992**, *114*, 4174; b) C. P. Casey, T. L. Underiner, P. C. Vosejpka, G. A. Slough, J. A. Cavney, R. K. Hayashi, *Organometallics* **1997**, *16*, 2189.

[44] For leading studies on comparative migration rates in early transition metal systems see: G. Parkin, E. Bunel, B. J. Burger, M. S. Trimmer, A. Van Asselt, J. E. Bercaw, *J. Mol. Catal.* **1987**, *41*, 21.

[45] a) M. Brookhart, D. M. Lincoln, *J. Am. Chem. Soc.* **1988**, *110*, 8719; b) M. Brookhart, E. Hauptman, D. M. Lincoln, *J. Am. Chem. Soc.* **1992**, *114*, 10394; c) Y. Han, L. Deng, T. Ziegler, *J. Am. Chem. Soc.* **1997**, *119*, 5939.

[46] F. Martínez, Ph. D. Thesis, University of Seville (Spain), **1997**.

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