# Formation of Hydrido–$\eta^3$-Allyl Complexes of $Ir^{III}$ by Sequential Olefinic C–H Bond Activation and C–C Coupling of Alkenyl and Olefin Ligands

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*In Memory of Professor Sir Geoffrey Wilkinson*

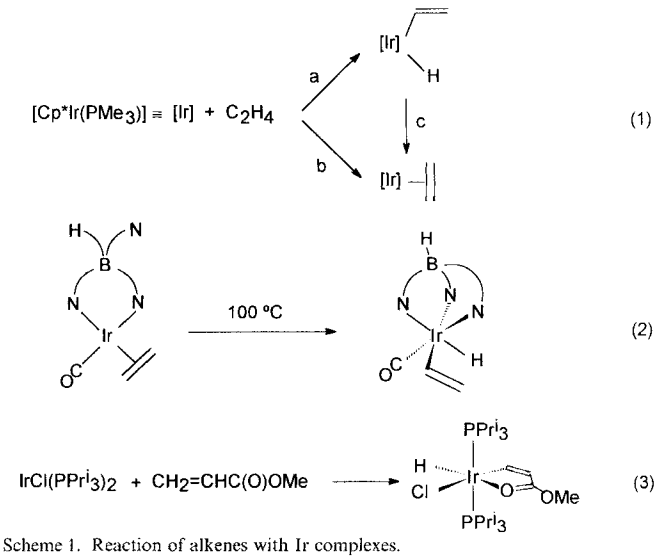
**Abstract:** The bis(ethene) complex [Tp*Ir-$(C_2H_4)_2$] (**1***) (Tp* = tris(3,5-dimethyl-1-pyrazol-1-yl)hydroborato) undergoes thermal rearrangement to the hydrido–allyl complex [Tp*IrH($\eta^3$-$C_3H_4$Me)] (**6***), through the intermediacy of the hydrido–vinyl complex [Tp*IrH($C_2H_3$)($C_2H_4$)] (**2***). The overall conversion of **1*** into **6*** corresponds formally to the dimerisation of ethene by an unprecedented pathway that involves sequential C–H bond activation of a coordinated olefin molecule and C–C bond formation by coupling of the resulting vinyl and ethene moieties. Similar transformations have been observed for monosubstituted olefins like propene and 1-butene, while the internal alkene *cis*-2-butene experiences allylic activation of an $sp^3$ C–H bond, which provides an alternative route to **6***. The extension of these investigations to the analogous complexes of the unsubstituted tris(pyrazolyl)hydroborato ligand Tp is also reported. Mechanistic studies on the formation of the C–C bond by coupling of the vinyl and the olefin ligands suggest the participation of a vinylidene complex (formed by α-H abstraction from the vinyl group), which then rearranges to an allene species. Evidence for the involvement of these and other key reaction intermediates is provided.

**Keywords**
alkene complexes · allyl complexes · C–H activation · C–C coupling · iridium

## Introduction

The transition metal mediated transformations of olefinic substrates are very important processes in the field of applied organometallic chemistry.[1] One of the basic reactions an alkene can undergo when exposed to a transition metal centre is the activation of its vinylic C–H bond to give a hydrido-vinyl species. Early work by Stoutland and Bergman[2] on the reaction of $C_2H_4$ with the iridium fragment {Cp*Ir($PMe_3$)} (Cp* = $C_5Me_5$; thermally generated from [Cp*IrH($C_6H_{11}$)($PMe_3$)]) showed that vinylic activation does not require the intermediacy of a π-olefin complex (Eq. (1), Scheme 1). Three different pathways (a, b and c) were disclosed in this study, the first two leading respectively to the hydrido–vinyl and the π-olefin products; the third pathway allows the high-temperature conversion of the former into the latter, which therefore is the thermodynamic isomer.

To our knowledge, the above is a general observation for mononuclear M–$C_2H_4$ complexes,[3] the only exception being




Scheme 1. Reaction of alkenes with Ir complexes.

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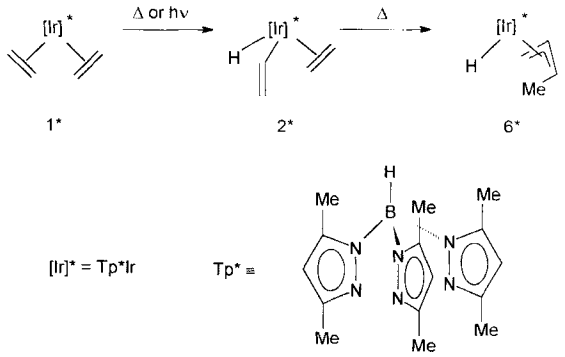
the complex $[Tp^{CF_3,Me}Ir(C_2H_4)(CO)]$, which converts irreversibly[4] at 100 °C into the hydrido vinyl $[Tp^{CF_3,Me}IrH(C_2H_3)(CO)]$ (Eq. (2), Scheme 1; $Tp^{CF_3,Me}$ = tris(3-trifluoromethyl-5-methylpyrazol-1-yl)hydroborato ligand). In agreement with previous studies by Werner and associates[5a] on the activation of $CH_2=CHCO_2Me$ (Eq. (3), Scheme 1), Graham[4] proposed that the stabilisation of the hydrido–vinyl element was achieved by coordination of the third pyrazolyl ring of the tris(pyrazolyl)borato ligand.[6] Later studies on other Ir complexes seemed to support this view.[5] Not unexpectedly, olefins bearing heteronuclear substituents are more prone to vinylic activation, particularly when the heteroatom can act as an auxiliary ligand.[5a, 7] The application of this strategy seems increasingly important in organic chemistry,[8] inasmuch as it can also be associated with the facile C–H activation of olefins, including ethene, in binuclear systems.[9]

We have briefly reported[10] that the bis(ethylene) complex $[Tp^*Ir(C_2H_4)_2]$ (**1***) ($Tp^*$ = $Tp^{Me_2}$ = tris(3,5-dimethylpyrazol-1-yl)hydroborato ligand) rearranges, both thermally and photochemically, into the isomeric hydrido–vinyl complex $[Tp^*IrH(C_2H_3)(C_2H_4)]$ (**2***) (Scheme 2), which in turns converts into the hydrido–crotyl $[Tp^*IrH(\eta^3\text{-}C_4H_7)]$ (**6***). We now document that, contrary to prior expectations based on Graham's report,[4] this occurs without change in the hapticity of the Tp* ligand. In addition, we fully address the thermal transformation of **1*** into **6*** in a process that formally corresponds to the dimerisation of ethene through a transition metal–ethene–vinyl intermediate. The catalytic dimerisation of olefins has been proposed to involve: 1) an M–H complex which undergoes initial $C_2H_4$ insertion in the so-called insertion–$\beta$-elimination process;[11] 2) the participation of a metallacyclopentane intermediate;[12] 3) photochemical vinylic activation on binuclear species[13] or functionalised olefins such as acrolein.[14] In the present case, the crucial step of the dimerisation reaction is the coupling of the vinyl and the ethene ligands to generate a four-carbon chain coordinated to the metal centre in an allylic fashion. At variance with a related, ruthenium-induced coupling reported previously,[15] this is proposed to proceed through a vinylidene species resulting from an $\alpha$-H elimination from the $Ir\text{–}CH=CH_2$ ligand.




Scheme 2. Rearrangement of bis(ethylene) complex **1*** ([Ir]* = Tp*Ir in all Schemes below).

**Editorial Board Member**:[*] *Ernesto Carmona was born in Sevilla, Spain, in 1948. He obtained his Ph.D. in 1974 under the guidance of Professor F. González at the University of Sevilla and then moved to England. For three years he worked at the Imperial College of Science and Technology (London) under the supervision of the late Professor Sir Geoffrey Wilkinson. It was during this time that he became interested in organometallic chemistry, carrying out research on manganese alkyls, transition metal hydrides, arenes and other related compounds. He then returned to the University of Sevilla, where he was appointed Assistant Professor in 1980. After brief stays at the Universities of Córdoba and Alabama (Tuscaloosa) he became full professor in Sevilla in 1983. In 1989/1990 he spent a one-year sabbatical leave with Professor M. L. H. Green at the University of Oxford. At present he is the Director of the newly created Centro de Investigaciones Científicas, Isla de la Cartuja. His research interests span organometallic and coordination chemistry, and his group has been actively involved in the activation of unsaturated molecules ($C_2H_4$, $CO_2$, etc.), insertion reactions, C–H bond activation and C–C bond-forming reactions. His current interests include the organometallic chemistry of the f elements, particularly directed toward the use of these compounds in alkene polymerisation reactions.*

[*] Members of the Editorial Board will be introduced to the readers with their first manuscript.

## Results and Discussion

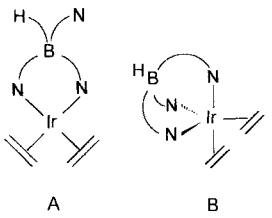
**Synthesis and structural characterisation of $[Tp^*Ir(C_2H_4)_2]$ (1*), $[Tp^*IrH(C_2H_3)(C_2H_4)]$ (2*) and $[Tp^*IrH(\eta^3\text{-}C_4H_7)]$ (6*)**: The bis(ethene) complex $[TpIr(C_2H_4)_2]$ (**1**), which contains the unsubstituted tris(pyrazolyl)hydroborato ligand Tp, was prepared several years ago independently by the groups of Oro[16] and Crabtree.[17] In an analogous low-temperature reaction of $[\{Ir(\mu\text{-}Cl)(coe)_2\}_2]$ (coe = cyclooctene, $C_8H_{14}$) with $C_2H_4$ and KTp*, the related species $[Tp^*Ir(C_2H_4)_2]$ (**1***) was obtained in approximately 70% yield, in the form of a white microcrystalline solid [Eq. (4)]. Compound **1*** exhibits relatively low

$$[\{Ir(\mu\text{-}Cl)(coe)_2\}_2] \xrightarrow[2)\ KTp^*]{1)\ C_2H_4,\ -20\,^\circ C,\ THF} \underset{\mathbf{1^*}}{[Tp^*Ir(C_2H_4)_2]} \qquad (4)$$

thermal stability, both in solution and as a pure solid, and has good solubility properties in $C_6H_6$, $Et_2O$, THF and $CH_2Cl_2$, but it is sparingly soluble in $C_6H_{12}$. Extensive decomposition is observed in $CHCl_3$ at 20 °C after 2–3 hours, while dissolution in $CH_3CN$ and DMSO requires heating at 60 °C and is accompanied by chemical transformation (see below). In the solid state, **1*** can be manipulated in air for short periods, but due to its long-term instability it must be stored under $N_2$ at temperatures of around 0 °C. Simultaneously to our work,[10a] complex **1*** was independently prepared by Venanzi and co-workers.[18]

Variable-temperature NMR studies show **1*** to be a highly fluxional molecule. The $^1$H NMR spectrum recorded at 20 °C ($C_6D_6$) shows two sharp singlets for the Me groups of the Tp* ligand at $\delta = 2.11$ and 2.39, indicating equilibration of the environments of the three pyrazolyl rings. In the $^{13}C\{^1H\}$ NMR spectrum ($C_6D_6$), the $C_2H_4$ carbon nuclei appear at $\delta = 26.2$ ($^1J(C,H) = 154$ Hz). This chemical shift is very close[17] to that reported for **1** ($\delta = 29.5$ in $CD_2Cl_2$) and this, and other similarities in the spectroscopic properties of the two compounds, may be taken as being indicative of identical solution structures. Dissolution of $C_2H_4$ does not alter the $^1$H and $^{13}C\{^1H\}$ NMR spectra of **1***; hence, no intermolecular exchange of ethylene seems to be taking place on the NMR timescale.

While the above and other data obtained for **1*** are in accord with the proposed formulation, distinction between the two possible limiting structures, namely, 4-coordinate, 16-electron square-planar ($\eta^2$-Tp* ligand) and five-coordinate, eighteen-electron trigonal-bipyramidal formulations (**A** and **B**, respectively) seems unattainable in the absence of further information. In contrast with the analogous complexes of the cyclopentadienyl-type ligands, $Rh^I$ and $Ir^I$ derivatives of the tris(pyrazolyl)hydroborato ligands can be found to exhibit either type of structure. Moreover, the two can coexist in rapid equilibrium or even experience more complex situations.[19] Since this question is of fundamental importance in connection with the C–H activation studies to be discussed below, it has been pursued further with the following results. Treatment of the starting complex $[\{Ir(\mu\text{-Cl})(coe)_2\}_2]$ with the bidentate ligand KBp* (Bp* = bis(3,5-dimethylpyrazol-1-yl)dihydroborate) under the conditions for the formation of $[Tp^*Ir(C_2H_4)_2]$ did not afford any isolable complex; extensive decomposition took place instead at room temperature. In the solid state, molecules of **1*** have a distorted trigonal-bipyramidal structure (**B**), as revealed by single-crystal X-ray studies to be discussed below. Finally in this regard, in the $^{13}C\{^1H\}$ CPMAS spectrum of a solid sample of **1***, the $^{13}$C nuclei of the Tp* ligand give rise to two sets of resonances with intensity ratio 2:1, while the ethene carbons resonate as broad signals at $\delta = 48$ and 5; the average of these two values is close to the singlet resonance in the $^{13}C\{^1H\}$ NMR solution spectrum. From all these data it is clear that complexes **1** and **1*** have the five-coordinate ground state structure **B**, both in solution and in the solid state.




As already mentioned, a single-crystal X-ray analysis of **1*** demonstrates the tridentate coordination of the Tp* ligand. Figure 1 shows an ORTEP view of the molecules of this compound; crystal data and important bond lengths and angles are collected in Tables 1 and 2, respectively. The five-coordinate, eighteen-electron iridium centre has a distorted trigonal-bipyramidal environment, which is made up of the terdentate Tp* fragment and the two $\eta^2$-bound molecules of ethylene. The equatorial plane of this coordination polyhedron contains two of the N atoms of the tris(pyrazolyl)borato group (N12 and N22) as well as the carbon atoms of one of the ethylene ligands (C3 and C4). The three Ir–N distances are equal within the experimental limits of detection (2.16(1) Å, av.), and the three N-Ir-N bond angles of

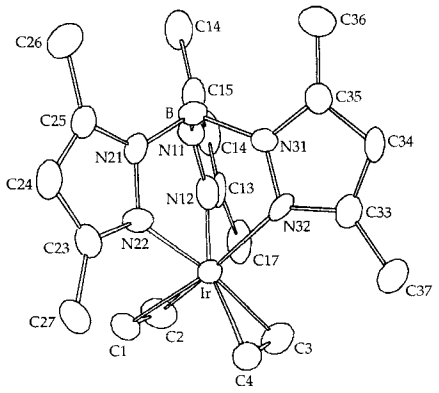



Figure 1. ORTEP drawing and atom labelling scheme of compound **1***.

Table 1. Crystal and refinement data for complex **1***.

| | |
|---|---|
| formula | $C_{19}H_{30}N_6BIr$ |
| molecular weight | 545.5 |
| crystal system | orthorhombic |
| space group | $P2_12_12_1$ |
| $a$, Å | 7.941(4) |
| $b$, Å | 13.402(6) |
| $c$, Å | 19.045(3) |
| $\alpha$, ° | 90 |
| $\beta$, ° | 90 |
| $\gamma$, ° | 90 |
| $Z$ | 4 |
| $V$, Å$^3$ | 2027(1) |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.79 |
| $F(000)$ | 1072 |
| $T$, K | 173 |
| diffractometer | Enraf-Nonius |
| radiation | graphite-monochromated $Mo_{K\alpha}$ ($\lambda = 0.71069$ Å) |
| $\mu(Mo_{K\alpha})$, cm$^{-1}$ | 65.8 |
| crystal dimensions, mm | 0.2 × 0.1 × 0.1 |
| $2\theta$ range, ° | 1–60 |
| scan technique | $\omega/2\theta$ |
| scan speed, ° cm$^{-1}$ | 1.50–16.48 |
| data collected | (0,0,0) to (11,18,26) |
| unique data | 3305 |
| observed reflections | 2521 |
| decay | ≤4% |
| standard reflections | 3/84 |
| weighting scheme | unit |
| $R = \sum\|\Delta^2F\|/\sum\|F_o\|$ | 4.0 |
| $Rw = (\sum w\|\Delta^2F\|/\sum w\|F_o\|^2)^{1/2}$ | 4.4 |
| maximum shift/error | 0.5213 |
| absorption correction range | 0.81–1.19 |

Table 2. Selected bond lengths (Å) and angles (°) for complex **1***.

| | | | |
|---|---|---|---|
| Ir–C1 | 2.16(1) | Ir–N22 | 2.17(1) |
| Ir–C2 | 2.15(2) | Ir–N32 | 2.15(1) |
| Ir–C3 | 2.08(2) | C1–C2 | 1.37(2) |
| Ir–C4 | 2.04(2) | C3–C4 | 1.47(2) |
| Ir–N12 | 2.17(1) | | |
| N12-Ir-N22 | 89.9(4) | N32-Ir-C1 | 161.3(5) |
| N12-Ir-N32 | 80.2(4) | N32-Ir-C2 | 160.4(5) |
| N22-Ir-N32 | 81.9(4) | | |

89.9(4), 80.2(4) and 81.9(4)° fall in the range usually observed for trihapto-bonded hydrotris(pyrazolyl)borato ligands.[16, 18]

The terdentate nature of the Tp* moiety of **1*** forces the two $C_2H_4$ molecules to occupy the remaining equatorial and axial positions of the distorted trigonal bipyramid. The axial N donor, N32, and the two carbons of the axial $C_2H_4$ define a plane which is almost perpendicular to the equatorial plane (dihedral angle 95.8(5)°). The $C_2H_4$ ligands are arranged in



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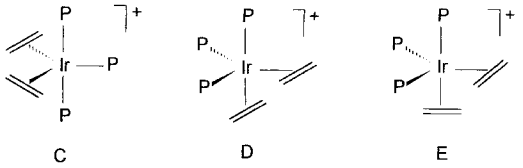
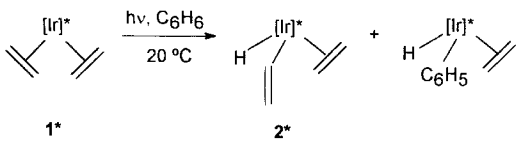
such a way that their axes are parallel to one another. A similar arrangement has been found in the somewhat related complex $[(\eta^5\text{-}C_5H_5)Rh(C_2H_4)_2]$, whose structure has been determined by gas-phase electron diffraction,[20] while in the cationic $Ir^I$ complex $[Ir(C_2H_4)_2(PMe_2Ph)_3]^+$, the two olefins are equatorial (structure **C**).[21] In the latter case, EHT calculations on the model compound $[Ir(C_2H_4)_2(PH_3)_3]^+$ reveal that conformations such as **D** and **E**, which have one $C_2H_4$ axial and the other equatorial, are higher in energy, owing to a combination of $\sigma$ and $\pi$ effects. In these studies **E** appears more stable than **D** although the energy difference between the two is small.[21]




The equatorial $C_2H_4$ molecule appears to be somewhat more strongly bonded to the $Ir^I$ centre than the axial ligand (av. Ir–C bond distances 2.06(2) and 2.15(2) Å, respectively). This is in accord with the above-mentioned calculations, which anticipate stronger electron retrodonation to the equatorial ethylene in structure **D**. In good agreement with this proposition, the C1–C2 bond length (1.37(2) Å) appears to be slightly shorter than that found for C3–C4 (1.47(2) Å). In fact, complex **1*** reacts quite readily at room temperature with phosphines to give complexes of composition $[Tp^*Ir(C_2H_4)(PR_3)]$ in which the ethylene ligand occupies the equatorial position.[22] For the two molecules of $C_2H_4$ of **1*** the C–C double bond lengths (1.37(2) and 1.47(2) Å) are longer than in free ethylene (1.339 Å),[23] but compare well with corresponding bond lengths in $[CpRh(C_2H_4)_2]$[20] and in $[Ir(C_2H_4)_2(PMe_2Ph)_3]BF_4\cdot 0.5H_2O$[21] (av. 1.457(7) and 1.421(22) Å, respectively). In the closely related phosphine adduct $[Tp^*Ir(C_2H_4)(PMe_2Ph)]$, in which the olefin is contained in the equatorial plane,[22] the Ir–C bonds and the C–C bond also have similar lengths (2.08(2) av. and 1.44(2) Å, respectively).

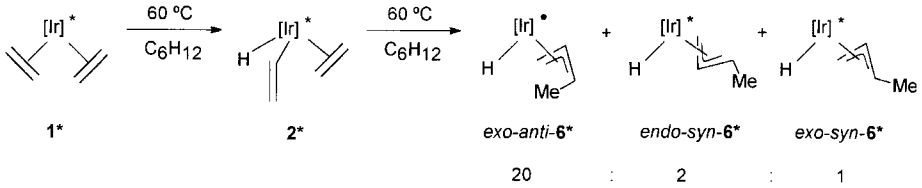
When a cyclohexane solution of **1*** (60 °C) was gently heated, a smooth transformation ensued (Scheme 2), which gave a mixture of the hydrido–vinyl complex **2*** and the hydrido–crotyl complex **6***. The same sequence of events was observed in the solid state, although higher temperatures (ca. 100 °C) were needed to achieve reasonable reaction rates. Full characterisation of **2*** was accomplished by $^1H$ and $^{13}C$ NMR studies of the reaction mixture at moderate conversions. Nevertheless, an alternative and more selective route to this complex was sought. The room-temperature photolysis of $C_6H_6$ solutions of **1*** (Scheme 3) gave




Scheme 3. Photolysis of **1***.

a mixture of **2*** and of the hydrido–phenyl complex $[Tp^*IrH(C_6H_5)(C_2H_4)]$. Pure **2*** was recovered from the mixture by chromatography, albeit with considerable loss of material. The use of other solvents ($Et_2O$, $CH_2Cl_2$) did not improve the yield of **2***. At the very late stages of this work we found that complex **2*** forms in almost quantitative yield when frozen, diluted cyclohexane suspensions of **1*** are irradiated at −60 °C. Characterisation of this white microcrystalline solid by NMR is straightforward (see Experimental Section) and needs no further comment. It is worth pointing out that the presence of several equivalents of $C_2H_4$ does not have a negative effect on the rate of the **1*** to **2*** rearrangement. This applies not only to the thermal ($C_6D_{12}$ solution, NMR monitoring), but also to the photochemical conversions. Therefore, the unsaturated species $\{Tp^*Ir(C_2H_4)\}$ is an unlikely intermediate for this C–H activation reaction.

The thermal conversion of **1*** into **2*** (Scheme 2) clearly indicates that the latter is the thermodynamically preferred isomer. However, this is only the first step in the thermal rearrangement of **1***. Heating cyclohexane solutions of this compound at 60 °C led to the gradual and irreversible formation of **6*** (Scheme 4).



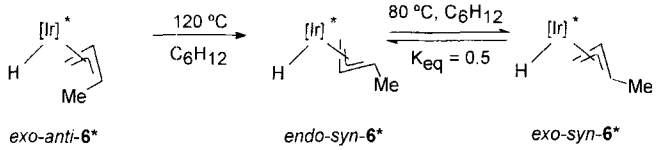

Scheme 4. Thermal rearrangements of **1*** and **2***.

Careful NMR monitoring of the course of reaction revealed the intermediary role played by the hydrido–vinyl complex **2***, which could be further demonstrated by the independent conversion of isolated, pure samples of **2*** into the same mixture of hydrido–crotyls, under identical reaction conditions. In addition, a kinetic role of complex **1*** in this C–C coupling reaction could be discounted by $PMe_3$ trapping experiments (see below). Complex **1*** is highly reactive towards this phosphine at room temperature, but none of the reaction products[22] were detected upon thermolysis of pure **2*** in the presence of this reagent. It is worth mentioning at this point that all the hydrido–allyls described in this paper display the NMR hydride signal at very high field (in the range $\delta = -25$ to $-30$). This allows them to be distinguished from the hydrido–vinyl precursors, which resonate at lower fields ($\delta \approx -15$ to $-20$). This situation contrasts with that found in the analogous Cp′–Ir systems, where the two kinds of compound exhibit very similar chemical shifts ($\delta \approx -15$ to $-20$).[2b, 3, 24]

NMR characterisation of the various isomers of **6*** (Scheme 4) follows previous reports in the literature for analogous complexes.[24, 25] The *anti* and *syn* distribution of the Me substituent can be readily ascertained from the values of the $J$(H,H) coupling constants within the allylic moiety and also from NOEDIFF measurements. The latter experiments, using the Ir–H signal as a probe, additionally allow the *exo* or *endo* configurations to be assigned.[26, 27]

The product ratio of Scheme 4 corresponds to the distribution of the crotyl complexes under kinetic control. Prolonged heating

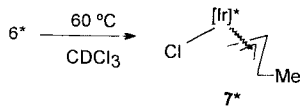
(3 days) of this mixture at higher temperatures ($C_6H_{12}$, ca. 120 °C) yielded exclusively the *endo–syn* and *exo–syn* crotyls in a 2:1 ratio (Scheme 5). The thermodynamic preference found for the *syn* isomer is in agreement with data for most π-allyl metal complexes.[28] The 2:1 ratio in which the *endo–syn* and *exo–syn* **6*** form under kinetic control, although coincident with the thermodynamic one, is not due to facile *exo–endo* interconversion, since these species only start exchanging at an appreciable rate at temperatures around 80 °C (Scheme 5). Evi-




Scheme 5. Distribution of the crotyl complexes **6*** formed under thermodynamic control.

dence for this comes from the following observation: heating compound **1*** in the solid state at 100 °C for 3–4 h yields the mixture of crotyls shown in Scheme 4. However, when solid **1*** was heated additionally at 150 °C for 3 days, an all-*syn endo*-**6***:*exo*-**6*** ratio of ca. 9:1 was produced, and this equilibrated in $C_6H_{12}$ solution upon heating at 80 °C.

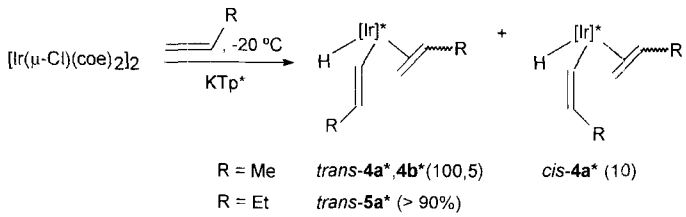
Compound **6*** is stable at room temperature in $CDCl_3$. Heating these solutions at 60 °C resulted in chlorination at the hydride site and concomitant formation of $CHDCl_2$. The chloro derivative [Tp*IrCl(*syn*-$\eta^3$-$C_4H_7$)] (**7***) was produced as an approximately 3:2 mixture of *endo* and *exo* isomers (Scheme 6).




Scheme 6. Reaction of **6*** with $CDCl_3$.

NMR monitoring of this transformation revealed that all the isomers of **6*** react at approximately the same rate in this transformation, which effects smoothly the normally difficult *anti–syn* conversion in these complexes.

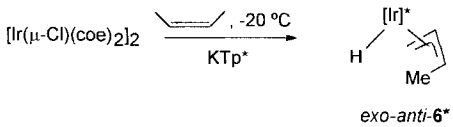
**Tp*Ir complexes derived from propene, 1-butene and 2-*cis*-butene:** Inspired by the results described in the previous section and with the additional purpose of gaining evidence relevant to the C–C coupling of olefins and vinyl ligands, we sought to extend this chemistry to the terminal olefins propene and 1-butene. The reactions of [{Ir(μ-Cl)(coe)$_2$}$_2$] with these olefins and KTp* (Scheme 7) yielded the olefinic C–H activation products as mix-




Scheme 7. Reaction of terminal olefins with [{Ir(μ-Cl)(coe)$_2$}$_2$] and KTp*.

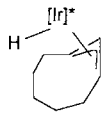
tures of the *cis*- and *trans*-alkenyl species in which the latter clearly predominated. An undetected bis(olefin) compound is a likely intermediate of these reactions. The *trans* and *cis* stereomers can be readily distinguished by means of the $^3J$(H,H) coupling constant between the vinylic protons (ca. 16 Hz, *trans*; 10 Hz, *cis*). For R = Me, two *trans* stereomers **4a*** and **4b*** were formed in a ca. 20:1 ratio. These might arise from the coordination of the propene ligand through either of its enantiofaces or, less likely, from restricted rotation around the Ir–propene bond. Since this aspect was of no relevance to the aims and conclusions of this work, it was not pursued any further. In a similar way, two *cis* stereomers were expected to form, but only one could be detected. Its $^1$H NMR data seems to be related to that of the major *trans* isomer, and it was therefore given an **a** label. Since the *cis* isomers are the less abundant, it appears that the concentration of the *cis*-**b** isomer is beyond the limits of detection by NMR. For the 1-butene system the *trans*-**5a*** stereomer predominates (>90%).

The direct observation of the olefinic C–H activation products in the reactions involving the terminal olefins RCH=CH$_2$ (R = Me, Et) suggests an important role of steric factors in this reaction. To confirm this hypothesis, an internal olefin, 2-*cis*-butene, was used. The reaction follows a different course (Scheme 8) and provides a product resulting from the activation of an sp$^3$ C–H bond, that is, it proceeds with allylic activation.[29]




Scheme 8. Reaction of an internal olefin with [{Ir(μ-Cl)(coe)$_2$}$_2$] and KTp*.

The *exo–anti* complex **6*** is the main product of the reaction (ca. 90%), although other unidentified species are also generated. Through this pathway of C–H activation observed for the bulkier *cis*-2-butene, the resulting Ir$^{III}$ complex attains a formally six-coordinate, eighteen-electron structure with the incorporation of only one organic fragment derived from one molecule of the original alkene. Contrary to our expectations, the reaction of [{Ir(μ-Cl)(coe)$_2$}$_2$] with KTp*, in the absence of added olefin, did not afford a complex with structure of type **F*** (i.e., the product of allylic activation). Instead, it furnished a complex mixture of at least five different compounds (with no major product), which was subsequently discarded.




When solutions of compounds **4*** and **5*** were heated, the expected coupling of the alkenyl and alkene moieties occurred. As a result, complexes **8*** and **9***, which contain six- and eight-carbon allylic chains, respectively, were formed (shown in Scheme 9 for the propene complexes **4***). As before, the kinetic distribution of isomers equilibrated slowly at 120 °C to a mixture of the all-*syn endo* and *exo* allyls (2:3).

Two of these isomeric compounds **8*** were further characterised by single-crystal X-ray studies: *exo*,Et*anti*-**8*** (for simplicity designated as **8a*** in the present structural discussion) and *endo*,all*syn*-**8*** (**8b***). Figures 2 and 3 show the corresponding



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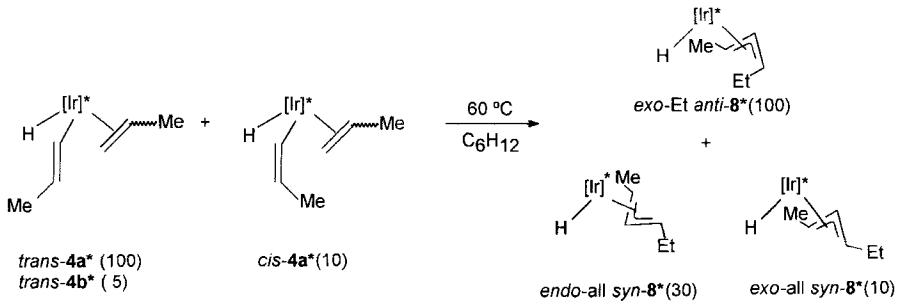



Scheme 9. Thermal rearrangements of **4***.

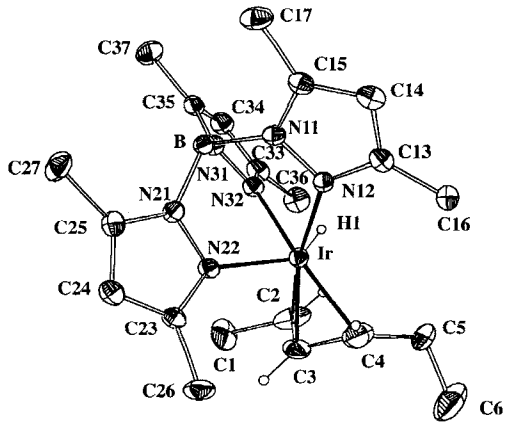



Figure 2. ORTEP drawing and atom labelling scheme of compound **8a***.

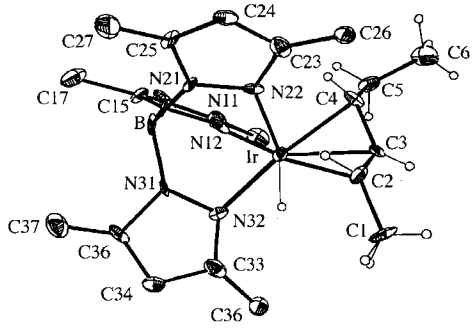



Figure 3. ORTEP drawing and atom labelling scheme of compound **8b***.

ORTEP perspective views; important crystal data and bond lengths and angles for the two compounds are summarised in Tables 3 and 4, respectively.

The coordination geometry of the Ir atom of each complex corresponds to a highly distorted octahedron, with the N atoms of the tripod ligand defining one of the faces, the remaining positions being occupied by the allyl ligand (formally two of them) and the hydride. There are significant differences in the three Ir–N separations in each complex, with one of the Ir–N bonds being appreciably longer than the others. Thus, the Ir–N22 bond length is approximately 2.25 Å in both compounds, while the other two Ir–N distances are of the order of 2.00–2.13 Å. Since N22 is *trans* to the hydride ligand, this lengthening can be clearly attributed to the high σ-*trans* influence characteristic of the hydride functionality. Similar Ir–N bond length differences have been observed in other hydride complexes of iridium containing tris(pyrazolyl)borato ligands.[16, 18] The Ir–H distances found in **8a*** and **8b*** (Table 4) fall within the range reported for these bonds.[16, 18, 25] Finally, regarding the coordination of the Tp* ligands, the N-Ir-N bond angles (in the range ca. 82.3(4)–92.3(8)°) are analogous to those encountered in **1*** and in other $\eta^3$-tris(pyrazolyl)borates.

Apart from the *exo* or *endo* configuration of the allyl ligands in **8a*** and **8b***, respectively, there appears to be significant differences in the coordination of this fragment in the two complexes. The Me substituent at C2 is *syn* in both compounds, but the Et group is *anti* in **8a*** and *syn* in **8b***. The Ir–C bond lengths seem to be longer in **8b*** than in **8a***, but these differences appear not to be important since the Ir–C bonds are equal within $\pm 3\sigma$. However, the coordination of the allyl moiety in **8b*** seems to be symmetrical, since the C2–C3 and C3–C4 bond lengths are identical (1.40(4) and 1.39(4) Å, respec-

Table 3. Crystal and refinement data for complexes **8a*** and **8b***.

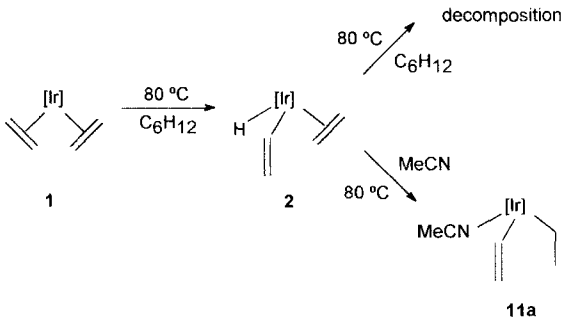
| | **8a*** | **8b*** |
|---|---|---|
| formula | $C_{21}H_{33}N_6BIr$ | $C_{21}H_{33}N_6BIr$ |
| molecular weight | 553.57 | 573.6 |
| crystal system | triclinic | monoclinic |
| space group | $P\bar{1}$ | $P2_1$ |
| $a$, Å | 8.690(1) | 7.873(2) |
| $b$, Å | 10.583(4) | 20.065(8) |
| $c$, Å | 13.390(4) | 7.955(3) |
| $\alpha$, ° | 74.27(4) | |
| $\beta$, ° | 80.38(2) | 113.54(3) |
| $\gamma$, ° | 87.56(2) | |
| $V$, Å$^3$ | 1168.6(6) | 1152.1(7) |
| $Z$ | 2 | 2 |
| $F(000)$ | 568 | 568 |
| $\rho_{calcd}$, g cm$^{-1}$ | 1.63 | 1.65 |
| $T$, K | 293 | 295 |
| $\mu$, cm$^{-1}$ | 57.08 | 57.9 |
| crystal dimensions, mm | 0.3 × 0.3 × 0.2 | 0.3 × 0.2 × 0.1 |
| diffractometer | Enraf-Nonius CAD4 | Enraf-Nonius CAD4 |
| radiation | graphite-monochromated $Mo_{K\alpha}$ ($\lambda$ = 0.71069 Å) | graphite-monochromated $Mo_{K\alpha}$ ($\lambda$ = 0.71069 Å) |
| scan technique | $\Omega/2\theta$ | $\Omega/2\theta$ |
| $\theta$, ° | $1 < \theta < 25$ | $1 < \theta < 30$ |
| data collected | (10, −12,0) to (10,12,15) | (−9,0,0) to (9,23,9) |
| unique data | 4119 | 3449 |
| unique data ($I$) $\geq 3\sigma(I)$ | 3300 | 2187 |
| $R$(int), % | 3.8 | 5.0 |
| standard reflns | 3/68 reflns | 3/138 reflns |
| $R_F$, % | 4.8 | 5.8 |
| $R_{wF}$, % | 5.5 | 7.1 |
| average shift/error | 0.009 | 0.10 |

Table 4. Selected bond lengths (Å) and angles (°) for compounds **8a*** and **8b***.

| | **8a*** | **8b*** | | **8a*** | **8b*** |
|---|---|---|---|---|---|
| Ir–C2 | 2.12(2) | 2.21(2) | C2-Ir-N12 | 160.1(6) | 171.3(9) |
| Ir–C3 | 2.05(2) | 2.24(2) | C3-Ir-N12 | 149.6(6) | 136.4(9) |
| Ir–C4 | 2.08(2) | 2.22(2) | C4-Ir-N32 | 160.1(6) | 169.9(9) |
| Ir–H | 1.8(1) | 1.7(2) | H-Ir-N22 | 157(5) | 165(16) |
| Ir–N12 | 2.11(1) | 2.00(3) | N12-Ir-N22 | 82.3(4) | 90.0(8) |
| Ir–N22 | 2.23(1) | 2.25(1) | N12-Ir-N32 | 83.7(4) | 86.4(9) |
| Ir–N32 | 2.13(1) | 2.05(2) | N22-Ir-N32 | 89.3(4) | 92.3(8) |
| C1–C2 | 1.59(3) | 1.49(5) | C1-C2-C3 | 103(2) | 124(3) |
| C2–C3 | 1.28(3) | 1.40(4) | C2-C3-C4 | 118(2) | 126(2) |
| C3–C4 | 1.54(3) | 1.39(4) | C3-C4-C5 | 120(2) | 120(2) |
| C4–C5 | 1.54(3) | 1.48(4) | C4-C5-C6 | 113(2) | 110(3) |
| C5–C6 | 1.47(3) | 1.50(5) | | | |

tively), but in **8a*** the C2–C3 bond (1.28(3) Å) is shorter than C3–C4 (1.54(3) Å). The latter has a length that corresponds essentially to a single C–C bond (compare, for example, the values for C1–C2, C4–C5 and C5–C6 collected in Table 4). It would therefore appear that there is a distortion toward a $\sigma-\pi^2$ coordination, with the pivotal σ-bond at the Et-substituted carbon. Similar distortions have been found in other allyl complexes of the transition metals including iridium.[25, 30] It is interesting to note that comparison of the spectral characteristics of **8a*** and **8b*** in solution indicates no important differences.

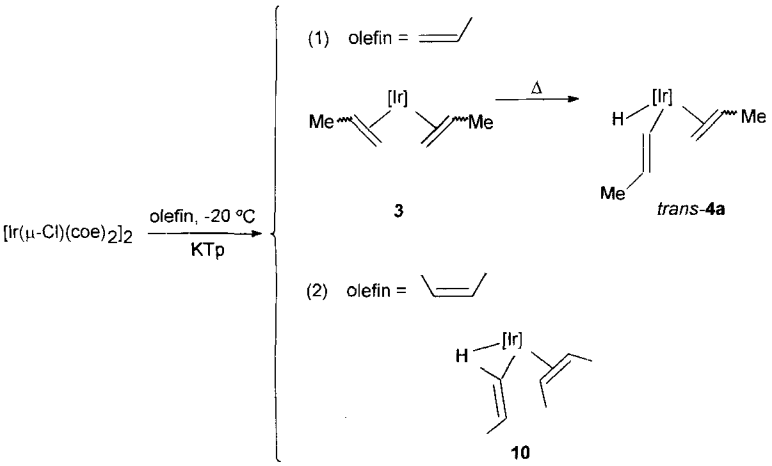
***Complexes of the unsubstituted Tp ligand:*** For the sake of completeness, we have extended the above studies to the analogous complexes of the unsubstituted Tp ligand. While Tanke and Crabtree[17] observed only decomposition of the bis(ethene) compound $[TpIr(C_2H_4)_2]$ (**1**) upon heating at 125 °C, we found that gentle heating of a cyclohexane solution of this species at 80 °C for 7 h produced an unidentified, insoluble solid, together with a solution of **1** and the known hydrido–vinyl complex **2** in a ca. 2:1 ratio, as determined by NMR in $CD_2Cl_2$ (Scheme 10).




Scheme 10. Thermal isomerisation of **1** and trapping of intermediate **2** with MeCN ([Ir] = TpIr).

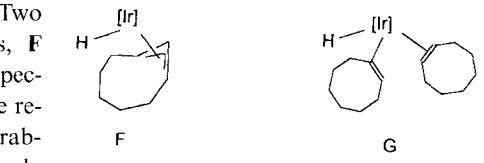
Further heating completely decomposed the mixture to the insoluble material. It is therefore evident that while the thermal isomerisation of **1** is possible the resulting complex **2** decomposes under the reaction conditions. In the presence of acetonitrile, the trapped ethyl species **11a** was formed in moderate yield (Scheme 10).

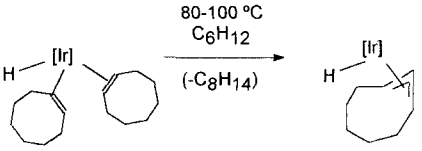
The use of the Tp ligand permited the detection of the bis(propene) complex **3** (reaction 1, Scheme 11) as a highly fluxional molecule, with structure probably similar to that found for compounds **1** and **1***. This complex rearranged readily in $C_6H_{12}$ solution to the hydrido–propenyls **4**, of which the *trans*-**4a** was the predominant isomer (>80%). Further conversion into the allyl coupling products occurred at 100 °C, but we did not attempt a full characterisation of the resulting complexes. Finally, *cis*-2-butene (reaction 2, Scheme 11) afforded directly the hydrido–butenyl complex **10**. Note that in this case the less bulky Tp ligand allows the coordination of two molecules of the olefin to the metal and hence the formation of a hydrido–vinyl–olefin complex as the product of olefinic C–H activation. No allyl species derived from the coupling of the organic moieties of this compound formed upon prolonged heating at 100 °C.




Scheme 11. Reaction of terminal (1) and internal (2) olefins with $[\{Ir(\mu\text{-}Cl)(coe)_2\}_2]$ and KTp.

Contradictory reports have led to some confusion regarding the room-temperature reaction of $[\{Ir(\mu\text{-}Cl)(coe)_2\}_2]$ with MTp (M = Na, K) in the absence of added olefin. Two different formulations, **F** and **G**, has been respectively advanced for the resulting product by Crabtree[17] and Oro;[16] only the latter proposal has been authenticated by X-ray methods. In our hands, the reaction always gave the cyclooctenyl complex of structure **G**. No evidence for the formation of the hydrido–allyl **F** could be obtained from this reaction, but contrary to Oro's results, we observed the thermal rearrangement of **G** to proceed as shown in Scheme 12, that is, with the allylic activation of a molecule of cyclooctene. The reaction rate of this transformation was not appreciably affected by the presence of a few equivalents of added coe.




Scheme 12. Thermal rearrangement of **G**.

**Vinylic C–H activation in olefin complexes of iridium with Tp and Tp* ligands:** As already mentioned, the conversion of **1*** into **2*** under thermal or photochemical conditions is not inhibited by free $C_2H_4$. Thus it seems that the vinylic activation is a direct intramolecular process. The higher thermodynamic stability of **2***, compared to **1***, contrasts with the situation found in the analogous cyclopentadienyl complexes where the opposite order of stability is found.[2, 3]

As discussed previously, the hapticity of the Tp′ ligand (Tp′ = Tp or Tp*) does not change during the conversion of our $[Tp'Ir(alkene)_2]$ compounds into the hydrido–alkenyl isomers, both the starting and the final products being eighteen electron species. Hence, at variance with Graham's observation[4]



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the driving force of this reaction cannot be ascribed to the coordination of a third pyrazolyl ring. Similarly, since the activated olefins do not contain donor atoms, the coordination of an auxiliary functionality responsible for the vinylic C–H activations observed by Werner and co-workers[5] cannot be invoked in our system.

It could be argued that the differences in the overall electron-donor properties of the Tp′ and Cp′ ligands might be responsible for the higher stability of $Ir(C_2H_3)H$ relative to $Ir-C_2H_4$, but these differences are very small.[31] While steric factors could additionally be invoked (the cone angle values[6a, 32] are Tp*, 224; Tp, 184; Cp*, 142; Cp, 110°), we favour the explanation that the higher stability of $Tp'Ir(C_2H_3)H$ compared to $Tp'Ir-C_2H_4$ results from the combination of two factors, which combine to overcome the otherwise unfavourable energetics of the $Ir-C_2H_4$ to $Ir(C_2H_3)H$ conversion. These are 1) the harder nature of the Tp ligands (compared to the softer cyclopentadienyls), which obviously prefer to bind the harder $Ir^{III}$ centres; and 2) their well-known propensity to enforce six-coordination at the metal,[33] a situation that is highly favourable for $Ir^{III}$.

Comparative studies of the vinylic C–H activation reaction for a variety of $[Tp'Ir(alkene)_2]$ complexes show some interesting trends:

1) Derivatives of the bulkier Tp* ligand are more reactive than those of the unsubstituted Tp analogue.
2) An important influence of the alkyl substituent within the olefin is apparent: in the series of complexes $[TpIr(alkene)_2]$, the less reactive $C_2H_4$ derivative requires heating to 80 °C for the reaction to occur, the propene complex undergoes this transformation at room temperature, and the *cis*-2-butene species is too unstable to be isolated under ambient conditions.
3) The olefin substituent directs the site of activation very efficiently. As summarised above the *trans* C–H bond has the highest preference (Figure 4, position 1), while the C–H unit *gem* to the R group (position 3) is readily activated if it is the only site available, as in *cis* disubstituted olefins (e.g. cyclooctene).

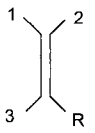
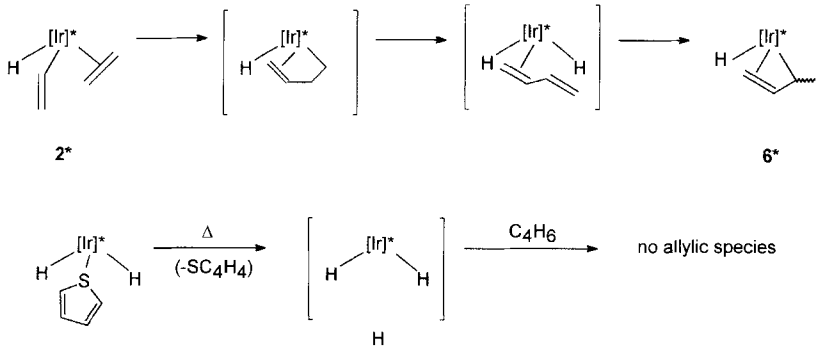


Figure 4.

The observations outlined above suggest that steric effects play an important role in the C–H activation reactions. They also seem responsible for the allylic C–H activation of *cis*-2-butene observed in the Tp* system. It is important to recall that the TpIr fragment induces vinylic activation of this olefin. Hence, a simple way for the sterically hindered Tp*–Ir–*cis*-2-butene system to attain a formally six-coordinate, eighteen-electron structure, while at the same time incorporating only one molecule of the bulky olefin, is the formation of the hydrido–allyl complex **6*** (Scheme 8).

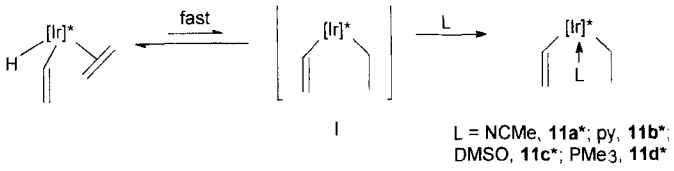
**$Ir^{III}$-mediated coupling of vinyl and olefin ligands:** While the allyl complexes **6***, **8*** and **9*** can be obtained in one-pot reactions starting from $[\{Ir(\mu\text{-}Cl)(coe)_2\}_2]$, KTp* and the appropriate olefin, the results discussed in the previous section reveal the participation of the corresponding $Ir^{III}$–vinyl–olefin derivatives as key reaction intermediates. Although our report of the overall transformation of **1*** into **6*** constitutes the first example for the formation of an allyl complex from an $M(C_2H_4)_2$ complex,[10] and could be regarded as a new pathway for olefin dimerisation, the coupling of vinyl and $C_2H_4$ moieties is not without precedent in the literature. For example, Lehmkuhl and co-workers observed the formation of allylic species in the coordination sphere of Ru centres,[15] while Knox and co-workers disclosed the rearrangement of a $Ru_2-C_2H_3$ complex to a hydrido–butadiene species in the presence of $C_2H_4$.[34] To account for these transformations, the insertion of $C_2H_4$ into the $M-CH=CH_2$ bond to give a bifunctional four-carbon chain was proposed as the first step, in close resemblance to the common insertion–$\beta$-elimination process for the dimerisation of ethene.[11] For our system, such a mechanism could be represented as shown in Scheme 13 (top). In this context, we note that:

1) In accord with studies by Brookhart and co-workers,[35] mechanistic evidence accumulated during the progress of this work shows that olefin insertion into the Ir–H bond (vide infra) is much more facile than into the Ir–C bond of the $Ir-CH=CH_2$ linkage.
2) If such a mechanism were applicable for the reaction we describe, one would expect that generation of an unsaturated $\{Tp^*IrH_2\}$ fragment **H** in the presence of butadiene should give the hydrido–crotyl complex **6*** (Scheme 13; bottom). The above fragment is generated readily, during the thermal activation of the thiophene complex $[Tp^*IrH_2(SC_4H_4)]$,[36b] but it does not give the expected allyl under the reaction conditions at which the latter complex forms.



Scheme 13. Mechanism for the dimerisation of ethene based on ref. [15] (top) and evidence discounting this mechanism (bottom).

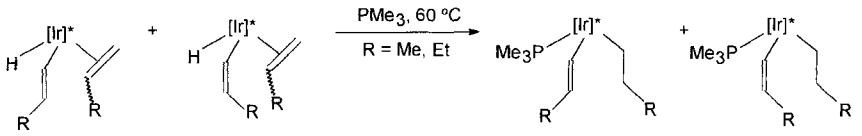
As mentioned already, ethene insertion into the Ir–H bond of **2*** is a facile process, and the resulting Ir–vinyl–ethyl intermediate **I** is readily trapped when solutions of **2*** are heated at moderate temperatures (60 °C) in the presence of various Lewis bases (Scheme 14). Acetonitrile was found to be the best trapping-agent for this reaction, whereas carbon monoxide did not react at all (2 atm, 60 °C); only **6*** was obtained in the presence of the latter. It should be mentioned, however, that this last observation does not imply the intrinsic instability of $Tp^*Ir^{III}$ carbonyl species. We have found that, once formed, this type of species is highly reluctant to undergo carbon monoxide extrusion.[36a, 37a] THF and other cyclic ethers are also able to trap



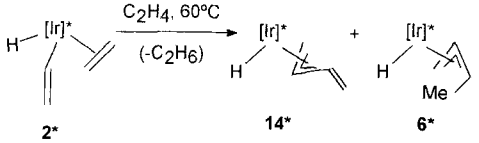

Scheme 14. Trapping of intermediate **I** with various Lewis bases.

intermediate **I**, but in this case the system evolves to form hydrido–carbene derivatives of $Ir^{III}$.[37b] Kinetic studies for the disapearance of **2***, carried out in $CD_2Cl_2$/[$D_6$]DMSO mixtures at 52 °C, are in accord with a rate-law of the type $k_{obs} = k_1 + k_2$[DMSO] in the range of concentrations studied (0.46–1.83 mol dm$^{-3}$), with $k_1 = 4.25 \times 10^{-5}$ s$^{-1}$ and $k_2 = 1.41 \times 10^{-4}$ mol$^{-1}$ dm$^3$ s$^{-1}$ (the first term corresponds to the formation of the allylic species).

The two following experimental observations are also of importance in connection with the mechanism of the C–C coupling reaction: 1) Related insertions of the olefin ligand into the Ir–H bond of complexes **4*** and **5*** (derived respectively from propene and 1-butene) were observed when the kinetic mixtures of the alkenyls were heated at 60 °C in the presence of $PMe_3$ (Scheme 15). 2) The thermal reaction of **2*** with a few equivalents of $C_2H_4$ in $C_6D_{12}$ (Scheme 16) yielded the allyls **6*** and

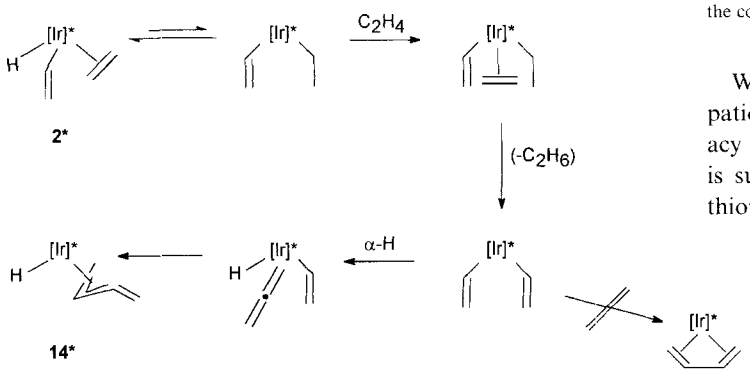



Scheme 15. Transformations of **4*** and **5*** in the presence of $PMe_3$.




Scheme 16. Transformation of **2*** in the presence of $C_2H_4$.

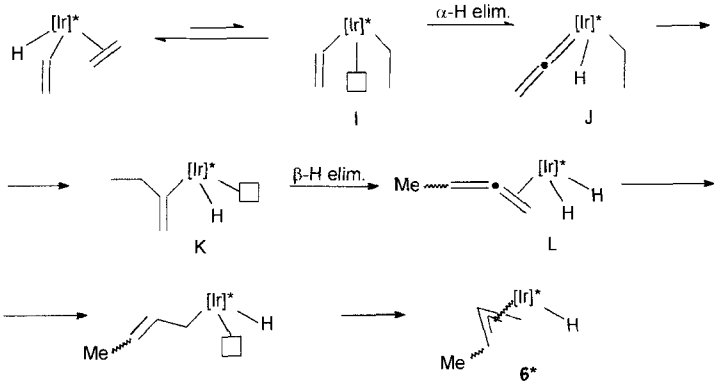
**14***, along with $C_2H_6$ (detected by NMR). By analogy with the reactions of **2*** with Lewis bases described above, we propose that ethene traps the unsaturated Ir–ethyl–vinyl intermediate of Scheme 17. Unlike the NCMe and other Lewis base adducts of type **11***, the ethene adduct is unstable and eliminates $C_2H_6$,




Scheme 17. Mechanism for the formation of **14*** (Scheme 16).

probable by sigma-bond methatesis[38] to yield a bis(vinyl) species in a process similar to that proposed for the activation of $C_6H_6$[37a] by compound **2***. While no evidence for [Tp*Ir($\eta^4$-$C_4H_6$)][36c] can be found in this reaction, the formation of the known[36c] allyl species **14*** points to the intermediacy of a vinylidene species[39] formed by α-H abstraction from one of the vinyl ligands.[40] The coupling of vinyl and vinylidene ligands proposed in the last step finds precedent in recent literature reports.[41]

On the basis of the mechanistic evidence gained during the course of this study and presented in detail in the previous sections, the general mechanism shown in Scheme 18 can be proposed for the C–C coupling of vinyl and olefin ligands in the coordination sphere of the Tp*$Ir^{III}$ centres. All the proposed intermediates are $Ir^{III}$ species. The involvement of any $Ir^{I}$ intermediate, like [Tp*Ir($\eta^2$-butene)], can be safely discounted, owing to the lack of trapped products in the presence of CO, this reagent being extremely reactive towards [Tp*Ir(olefin)$_2$] complexes.[22] Thus, the reaction is triggered by the formal insertion of the olefin into the Ir–H bond to give an unsaturated (or agostic)[42a] alkyl–vinyl intermediate **I**. This could then undergo an α-H abstraction from the α-vinyl carbon with concomitant formation of the vinylidene species **J**. The insertion of the carbene ligand into the Ir–alkyl bond would be responsible for the C–C bond-forming reaction,[41a, 43] which generates vinyl intermediate **K** possessing H atoms at the β carbon (α-vinyl substituent). Following β-H elimination,[42b, c, 43] rotation of the allene and insertion of the coordinated C=C bond into the Ir–H bond would finally afford the allyl products.




Scheme 18. General mechanism for the C–C coupling of vinyl and olefin ligands in the coordination sphere of the Tp*$Ir^{III}$ centres.

We have already furnished evidence in support of the participation of intermediates **I** and **J** in this reaction. The intermediacy of a species of type **L** (i.e., a bis(hydrido)allene derivative) is supported by the formation of the $\eta^3$-allyl **15*** when the thiophene complex [Tp*$IrH_2$($SC_4H_4$)] (vide supra) is heated at 60 °C in the presence of allene (Scheme 19). Finally, an intermediate of type **K** could be responsible for the formation of the iridapyrrole [Tp*Ir(C(Et)=C(H)-C(Ph)NH)(H)] (Scheme 20) formed when the bis(ethene) compound **1*** is heated with PhCN in the presence of $H_2O$ as the reaction catalyst.[36a, 44] The for-



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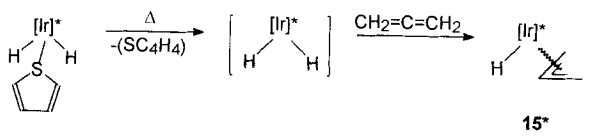
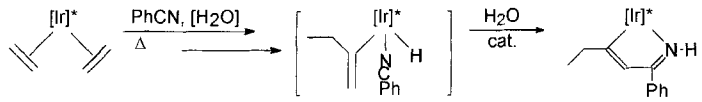


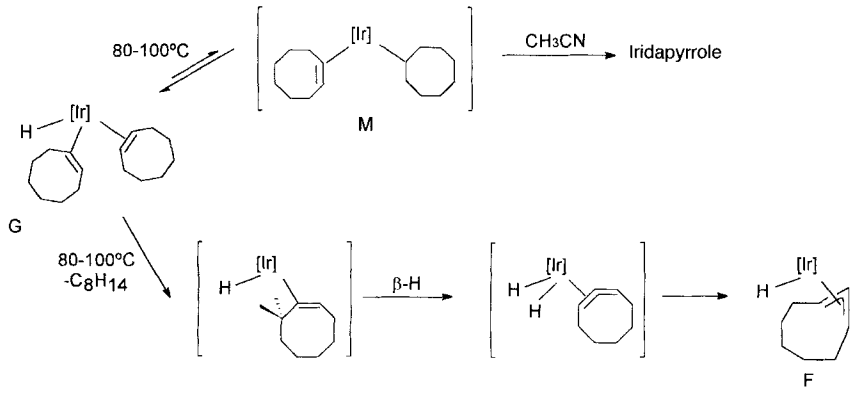

Scheme 19. Evidence for the intermediacy of **L** (Scheme 18).




Scheme 20. Evidence for the intermediacy of **K** (Scheme 18).

mation of this and related iridapyrroles has been demonstrated to be a general reaction for vinyl complexes of the type described in this paper.

One additional aspect of this work which should be addressed concerns the allylic activation of internal olefins. The cyclooctenyl complex **G** can experience the transformations shown in Scheme 21. In the presence of acetonitrile, the alkyl–




Scheme 21. Possible mechanism for the allylic activation of cyclooctene.

vinyl intermediate **M** forms by migration of the hydride ligand onto the coordinated olefin. This vinyl complex cannot undergo α-H elimination and subsequent coupling with the coordinated cyclooctyl fragment, but it can experience vinyl-to-nitrile coupling yielding an iridapyrrole complex.[44] In the absence of nitrile, irreversible dissociation of cyclooctene yields an unsaturated hydrido–vinyl species, which gives an allene compound by β-H elimination. If this hypothesis is correct, the observed allylic activation of cyclooctene would involve, in the first step, the activation of a vinyl hydrogen. A similar explanation may be offered for the formation of the hydrido–crotyl compound **6*** from *cis*-2-butene, although in this case direct allylic activation appears in principle more feasible.

Two points that are worth emphasising before closing concern the very important roles played by the vinyl and tris(pyrazolyl) ligands in the reactions described in this work. With respect to the former, it should be additionally noted that vinyl intermediates are being increasingly implicated in a number of interesting transformations.[45] As for the latter, the different behaviour exhibited by the Tp′ complexes we have reported in this and in previous contributions,[10a, 36b, 37, 44] in comparison with other related systems containing Cp′ or tripod ligands,[24, 46] stems from the ability of the tris(pyrazolyl)borato units to stabilise the $Ir^{III}$ products and to prevent the formation of $Ir^{I}$ intermediates. For example, the ethyl–vinyl intermediate $[Tp^*Ir(C_2H_5)(C_2H_3)]$ does not collapse to an $Ir^{I}$–olefin compound, in contrast to the somewhat similar Cp*[24] and triphos[46] derivatives. Also, the $Ir^{III}$ bis(vinyl) intermediate of Scheme 17 does not experience the expected reductive elimination to the corresponding $Ir^{I}$–butadiene complex, a process typically found in reactions of late transition-metal $M(CH=CH_2)_2$ fragments.[47]

## Experimental Section

All preparations and manipulations were carried out under oxygen-free nitrogen or argon 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 $[\{IrCl(coe)_2\}_2]$,[48] $[TpIr(C_2H_4)_2]$,[16, 17] $[TpIrH(C_8H_{13})(\eta^2\text{-}C_8H_{14})]$,[16] and $[Tp^*IrH_2(thiophene)]$[36b] and the ligands $KHB(pz)_3$,[49] KTp, and $KHB(3,5\text{-}Me_2\text{-}pz)_3$[49] (KTp*) were prepared according to literature procedures. Microanalysis were by Pascher Microanalytical Laboratory, Remagen (Germany) and the Microanalytical Service of the University of Sevilla. Infrared spectra were recorded on Perkin Elmer model 683 and 883 spectrometers, NMR spectra on Varian XL-200 and Bruker AMX-300 and AMX-500 spectrometers. The $^1H$ and $^{13}C\{^1H\}$ resonance of the solvent were used as the internal standard, but chemical shifts are reported with respect to TMS. $^{31}P$ NMR shifts are referenced to external 85% $H_3PO_4$. Most of the NMR assignements are based on extensive $^1H$–$^1H$ decoupling experiments, NOEDIFF measurements and homo- and heteronuclear two-dimensional spectra.

**$[Tp^*Ir(C_2H_4)_2]$ (1*)**: Complex $[\{IrCl(C_8H_{14})_2\}_2]$ (1 g, 1.11 mmol) was suspended in 80 mL of THF at −20 °C. Ethylene was bubbled through the mixture for 10 min to give a colourless solution to which KTp* (0.75 g, 2.22 mmol) was added. The reaction mixture became reddish and gradually darkened during the following 4 h of stirring at room temperature. Volatiles were stripped off under vacuum, and the residue extracted with 50 mL of a 1:1 mixture of $Et_2O$ and $CH_2Cl_2$. The resulting suspension was centrifuged to eliminate the potassium chloride and the solution was partially evaporated until cloudy. Cooling at −20 °C afforded pale yellow crystals of **1*** in 70% yield. $^1H$ NMR (200 MHz, $C_6D_6$, 25 °C): $\delta = 5.51$ (s, 3H, 3C–$H_{pyr}$), 2.40 (s, 8H, $2C_2H_4$), 2.39 (s, 9H, 3Me), 2.11 (s, 9H, 3Me); $^{13}C\{^1H\}$ NMR (50 MHz, $C_6D_6$, 25 °C): $\delta = 151.5$, 143.4 (1:1 ratio, *C*-Me), 107.6 (C–$H_{pyr}$), 26.2 ($C_2H_4$, $^1J(C,H) = 154$ Hz), 14.7, 12.5 (1:1 ratio, C–*Me*); $C_{19}H_{30}BN_6Ir$ (545.52): calcd C 41.7, H 5.5, N 15.4; found C 41.1, H 5.8, N 15.0.

**$[TpIr(CH_2{=}CHMe)_2]$ (3)**: The bis(propene) complex **3** was prepared following the same procedure, but employing propene and KTp. However, owing to its thermal instability (it converts into the hydrido–propenyl isomer), it was isolated as a crude solid and stored at −20 °C. Yield: 80%. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 8$–6 (d, d, t, 3H each, C–$H_{pyr}$), 3.5–1.8 (broad humps, C–$H_{olef}$), 0.65 (brs, Me); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 138.5$, 134.9, 105.1 (C–$H_{pyr}$), 29.2, 26.1, 25.4 (*C*HMe, $CH_2$ and CH*Me*).

**$[Tp^*IrH(CH{=}CH_2)(CH_2{=}CH_2)]$ (2*)**:
*Procedure A*: The bis(ethylene) complex **1*** (0.2 g, 0.37 mmol) was dissolved in benzene (50 mL), and the solution photolysed with a UV lamp (Hg, 500 W) for 2 h. Volatiles were removed under vacuum and the crude solid obtained was investigated by NMR. A 2.5:1 mixture of complex **2*** and a phenyl derivative (see text) was identified. Analytical samples of **2*** could be obtained upon chromatographic separation on silica gel and petroleum ether as the eluent. The minor product remained in the column and was not separated for characterisation purposes.

*Procedure B*: complex **1*** (0.2 g, 0.37 mmol) was suspended in cyclohexane (30 mL) and the suspension was frozen and cooled at −40 °C. The matrix was photolysed at that temperature for several hours (4–6) and then allowed to reach the room temperature. The resulting solution was taken to dryness and the residue was investigated by NMR. The hydrido complex **2*** was the unique product in solution. Attemps to scale up the experiment resulted in a considerable decrease in the conversion yield.

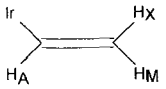


Figure 5.

$^1$H NMR (200 MHz, $C_6D_6$, 25 °C; see Figure 5 for atom labels): $\delta$ = 7.38, 5.63, 4.94 (3H, Ir–CH=$CH_2$, AMX spin system, $^3J$(A,M) = 10, $^3J$(A,X) = 18, $^3J$(M,X) = 3 Hz), 5.73, 5.56, 5.40 (s, 1H, 1H, 1H, C–$H_{pyr}$), 3.90, 3.10 (2 m, AA'XX' spin system, $C_2H_4$), 2.50, 2.36, 2.21, 2.12, 2.06, 1.80 (6Me), −16.90 (Ir–H). $^{13}$C{$^1$H} NMR (50 MHz, $C_6D_6$, 25 °C): $\delta$ = 126.4 (*C*H=$CH_2$, $^1J$(C,H) = 142 Hz), 118.8 (CH=*C*$H_2$, $^1J$(C,H) = 151 Hz), 108.0, 107.0, 106.7 (C–$H_{pyr}$), 43.9 ($C_2H_4$, $^1J$(C,H) = 161 Hz), 16.4, 15.2, 15.2, 14.0, 12.4, 12.4 (C-*Me*); IR (Nujol): $\tilde{\nu}$ = 2200 cm$^{-1}$ (Ir–H). $C_{19}H_{30}BN_6Ir$ (545.52): calcd C 41.7, H 5.5, N 15.4; found C 41.8, H. 5.7, N 15.4.

**[TpIrH(CH=CHMe)($CH_2$=CHMe)] (4)**: A THF solution of complex **3** was heated at 60 °C for 6 h. The solvent was removed under vacuum and the residue investigated by NMR, revealing quantitative formation of the hydrido–propenyl complex **4**. *trans*-Propenyl major isomer: $^1$H NMR (200 MHz, $C_6D_6$, 25 °C; see Figure 6 for atom labels): $\delta$ = 8.0–6.5 (9 m, 1H each,

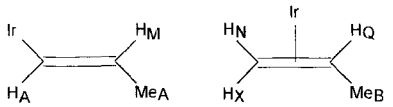


Figure 6.

C–$H_{pyr}$), 6.48 (dq, 1H, $H_A$, $^3J$(A,M) = 15.4, $^4J$(H,$Me_A$) = 1.4 Hz), 5.13 (dq, 1H, $H_M$, $^3J$(H,$Me_A$) = 6.1 Hz), 3.6–3.3 (m, ABC spin system, 3H, $H_N$, $H_X$, $H_Q$), 2.10 (dd, 3H, $Me_A$), 1.12 (d, 3H, $Me_B$, $^3J$(Me,$H_Q$) = 5.8 Hz), −16.0 (s, 1H, Ir–H); $^{13}$C{$^1$H} NMR (50 MHz, $C_6D_6$, 25 °C): $\delta$ = 145–105 (9C–$H_{pyr}$), 128.7 (Ir–CH=*C*HMe, $^1J$(C,H) = 150 Hz), 118.2 (Ir–*C*H=CHMe, $^1J$(C,H) = 132 Hz), 57.0 ($CH_2$=*C*HMe, $^1J$(C,H) = 158 Hz), 49.0 (*C*$H_2$=CHMe, $^1J$(C,H) = 160 Hz), 23.4, 17.2 (Me); IR (Nujol): $\tilde{\nu}$ = 2180 cm$^{-1}$ (Ir–H).

**Synthesis of hydrido derivatives [Tp'IrH($CR^1$=$CHR^2$)($CHR^1$=$CHR^2$)]** (Tp' = Tp*, $R^1$ = H, $R^2$ = Me, **4***; Tp' = Tp*, $R^1$ = H, $R^2$ = Et, **5***; Tp' = Tp, $R^1$ = Me, $R^2$ = Me, **10**): [{IrCl($C_8H_{14}$)$_2$}$_2$] (0.2 g, 0.22 mmol) was suspended in 30 mL of THF at −20 °C, and propene was passed through the mixture for 3–5 min. KTp* (0.15 g, 0.44 mmol) was added to the resulting orange solution. The reaction mixture was allowed to reach the room temperature, and after 5 h of stirring a violet solution was obtained. The solvent was evaporated under vacuum and the residue was extracted with 25 mL of acetone. After centrifugation and partial evaporation of the solvent, the solution was cooled to −78 °C to give colourless crystals of **4*** in 75% yield.

The 1-butene derivative **5*** was obtained in the same way and crystallised from a petroleum ether solution. Yield: 70%. The *cis*-2-butene analogue **10** was also prepared by the same procedure.

**[Tp*IrH(CH=CHMe)($CH_2$=CHMe)] (4*)**: *trans*-propenyl major isomer: $^1$H NMR (500 MHz, $C_6D_6$, 25 °C): $\delta$ = 6.54 (dq, 1H, $H_A$, $^3J$(A,M) = 15.8, $^4J$(H,$Me_A$) = 1.4 Hz), 5.75, 5.52, 5.44 (s, 1H, 1H, 1H, C–$H_{pyr}$), 4.94 (dq, 1H, $H_M$, $^3J$(H,$Me_A$) = 6.1 Hz), 4.04 (d, 1H, $H_X$, $^3J$(X,Q) = 11.6 Hz), 3.94 (ddq, 1H, $H_Q$, $^3J$(Q,N) = 8.1, $^3J$(H,$Me_B$) = 5.7 Hz), 3.67 (d, 1H, $H_N$), 2.44, 2.44, 2.24, 2.13, 2.04, 2.03 (s, 3H each, 6Me), 2.01 (dd, 3H, $Me_A$), 1.09 (d, 3H, $Me_B$), −17.21 (s, 1H, Ir–H); $^{13}$C{$^1$H} NMR (50 MHz, $C_6D_6$, 25 °C): $\delta$ = 155–140 (6*C*–Me), 125.4 (Ir–CH=*C*HMe, $^1J$(C,H) = 150 Hz), 115.6 (Ir–CH=CHMe, $^1J$(C,H) = 135 Hz), 108.4, 106.9, 106.4 (C–$H_{pyr}$), 53.7 ($CH_2$=*C*HMe, $^1J$(C,H) = 160 Hz), 49.3 (*C*$H_2$=CHMe, $^1J$(C,H) = 162 Hz), 25–10 (8Me); IR (Nujol): $\tilde{\nu}$ = 2175 cm$^{-1}$ (Ir–H).

Minor *trans*-propenyl isomer: $^1$H NMR (500 MHz, $C_6D_6$, 25 °C): $\delta$ = 8.14 (d, 1H, $H_A$, $J$(A,M) = 15.5 Hz), 5.03 (dq, 1H, $H_M$, $^3J$(H,$Me_A$) = 6.2 Hz), 4.40 (m, 1H, $H_Q$), 3.61 (d, 1H, $H_X$, $^3J$(X,Q) = 12.5 Hz), 3.31 (d, 1H, $H_N$, $^3J$(N,Q) = 8.5 Hz), −24.23 (s, 1H, Ir–H).

*cis*-Propenyl isomer: $^1$H NMR (500 MHz, $C_6D_6$, 25 °C): $\delta$ = 6.36 (d, 1H, $H_A$, $^3J$(A,M) = 10 Hz), 4.21 (d, 1H, $H_X$, $^3J$(X,Q) = 11.6 Hz), 3.80 (m, 1H, $H_Q$), 3.46 (d, 1H, $H_N$, $^3J$(N,Q) = 8.5 Hz), −17.14 (s, 1H, Ir–H). The $H_M$ resonance could not be located. $C_{21}H_{34}BN_6Ir$ (573.56): calcd C 44.0, H 6.0, N 14.6; found C 44.0, H. 6.2, N 14.6.

**[Tp*IrH(CH=CHEt)($CH_2$=CHEt)] (5*)**: *trans*-Butenyl major isomer: $^1$H NMR (500 MHz, $C_6D_6$, 25 °C; see Figure 7 for atom labels): $\delta$ = 6.55 (dt,

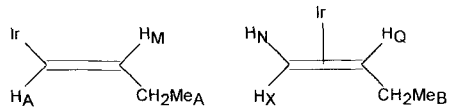


Figure 7.

1H, $H_A$, $^3J$(A,M) = 16.0, $^4J$(H,$CH_2$) = 1.3 Hz), 5.77, 5.54, 5.44 (s, 1H, 1H, 1H, C–$H_{pyr}$), 4.98 (dt, 1H, $H_M$, $^3J$(H,$CH_2$ = 6.3 Hz), 4.03 (d, 1H, $H_X$, $^3J$(X,Q) = 11.4 Hz), 3.95 (m, 1H, $H_Q$), 3.63 (d, 1H, $H_N$, $^3J$(N,Q) = 8.1 Hz), 2.47, 2.47, 2.24, 2.13, 2.04, 2.04 (s, 3H each, 6Me), 2.33 (m, 2H, $CH_2Me_A$), 1.39 (m, 2H, $CH_2Me_B$), 1.04 (t, 3H, $CH_2$*Me*$_A$, $^3J$(H,H) = 7.5 Hz), 0.94 (m, 3H, $CH_2Me_B$), −17.17 (s, 1H, Ir–H); $^{13}$C{$^1$H} NMR (125 MHz, $C_6D_6$, 25 °C): $\delta$ = 151.4, 150.5, 150.0, 143.4, 142.9, 142.6 (*C*–Me), 133.6 (Ir–CH=*C*HEt, $^1J$(C,H) = 146 Hz), 113.4 (Ir–*C*H=CHEt, $^1J$(C–H) = 133 Hz), 108.4, 106.9, 106.4 (C–$H_{pyr}$), 60.7 ($CH_2$=*C*HEt, $^1J$(C,H) = 152 Hz), 47.9 (*C*$H_2$=CHEt, $^1J$(C,H) = 160 Hz), 32.5 ($CH_2Me_A$), 30.5 (*C*$H_2$Me$_B$), 26.2, 17.2, 16.0, 15.9, 14.8, 14.7, 12.4, 12.3 (6C–*Me* and $Me_A$, $Me_B$). Data for the minor isomers (< 10%) not reported.

**[TpIrH(*cis*-CMe=CHMe)(*cis*-CHMe=CHMe)] (10)**: $^1$H NMR (500 MHz, $CDCl_3$, 25 °C): $\delta$ = 5.58 (qq, 1H, Ir–CMe=C*H*Me, $^3J$(H,Me) = 6.0, $^4J$(H,Me) = 1.3 Hz), 4.72, 4.13 (dq, 1H, 1H, C*H*Me=C*H*Me, $^3J$(H,H) = 8.0, $^3J$(H,Me) = 5.7 Hz), −18.13 (s, 1H, Ir–H).

**Synthesis of the hydrido–allyl complexes 6*, 8* and 9***: The bis(ethylene) **1*** (0.25 g, 0.46 mmol) was suspended in cyclohexane (10 mL), and the mixture was heated at 60 °C with stirring. Monitoring of the reaction by $^1$H NMR spectroscopy showed the initial formation of **2*** and **6***, but after heating at this temperature for about 24 h **6*** was the only detectable species. The resulting solution was taken to dryness and the residue was dissolved in petroleum ether (10 mL). Upon partial evaporation and cooling at −20 °C, off-white crystals of **6*** were collected in 80% yield.

The related complexes **8*** and **9*** were prepared in a similar fashion, but using the hydrido–vinyl compounds **4*** and **5*** as the starting materials. Compound **9*** displays similar NMR data to those detailed for **8*** (see below).

**Solid-state thermolysis of 1***: The bis(ethylene) complex **1*** was cleanly converted into the hydrido–allyl **6*** upon heating solid samples at 100 °C (oil bath) for 4 h under a nitrogen atmosphere. The resulting white solid was investigated by $^1$H NMR (500 MHz, $CDCl_3$) and shown to contain a mixture of the hydrido–allyl isomers shown in Scheme 4 (average of two runs). When the heating was carried out at 150 °C for 3 d the isomer ratio *endo*-**6***:*exo*-**6*** changed to ca. 9:1.

***exo,anti*-[Tp*IrH($\eta^3$-$CH_2$CHCHMe)] (6*)**: $^1$H NMR (200 MHz, $C_6D_6$, 25 °C; see Figure 8 for atom labels): $\delta$ = 5.66, 5.62, 5.42 (s, 1H, 1H, 1H, C $H_{pyr}$), 5.06 (dt, 1H, $H_C$, $^3J$($H_C$,$H_A$) = 10.2, $^3J$($H_C$,$H_S^1$) ≈ $^3J$($H_C$,$H_S^2$) = 6.9 Hz), 4.32 (quint, 1H, $H_S^2$, $^3J$(H,$Me_A$) = 6.5 Hz), 3.29 (d, 1H, $H_S^1$), 2.74 (d, 1H, $H_A$), 2.36, 2.29, 2.17, 2.14, 2.12, 2.07 (s, 3H each, 6Me), 1.53 (d, 3H, $Me_A$), −29.02 (s, 1H, Ir–H); $^{13}$C{$^1$H} NMR (50 MHz, $C_6D_6$, 25 °C): $\delta$ = 129.3, 117.9, 109.1, 143.2, 142.5, 142.3 (*C*–Me), 108.7, 105.8, 105.7 (C–$H_{pyr}$), 78.7 (C–$H_C$, $^1J$(C,H) = 160 Hz), 28.7 (*C*HMe, $^1J$(C,H) = 150 Hz), 20.2, 16.9, 16.4, 14.7, 12.7, 12.4, 12.1 (7Me), 16.2 ($CH_2$, $^1J$(C,H) = 156 Hz); IR (Nujol): $\tilde{\nu}$ = 2220 cm$^{-1}$ (Ir–H); $C_{19}H_{30}BN_6Ir$ (573.56): calcd C 41.8, H 5.5, N 15.4; found C 41.8, H. 5.7, N 15.4.

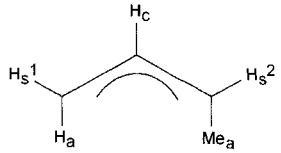


Figure 8.

***endo,syn*-[Tp*IrH($\eta^3$-$CH_2$CHCHMe)] (6*)**: $^1$H NMR (500 MHz, $CDCl_3$, 25 °C; see Figure 9 for atom labels): $\delta$ = 5.80, 5.77, 5.64 (s, 1H, 1H, 1H, C–$H_{pyr}$), 4.83 (td, 1H, $H_C$, $^3J$($H_C$,$H_A^1$) ≈ $^3J$($H_C$,$H_A^2$) = 9.8, $^3J$($H_C$,$H_S$) =



0947-6539/97/0306-0870 $ 17.50+.50/0 Chem. Eur. J. 1997, 3, No. 6

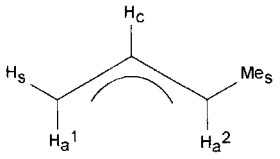



Figure 9.

6.9 Hz), 3.33 (dq, 1H, $H_A^2$, $^3J(H,Me_S)$ = 5.9 Hz), 3.21 (dd, 1H, $H_S$, $^2J(H_S,H_A^1)$ = 2.3 Hz), 2.40, 2.39, 2.35, 2.10, 2.05, 1.97 (s, 3H each, 6Me), 1.48 (d, 3H, $Me_S$), −28.55 (s, 1H, Ir–H). $H_A^1$ is immersed in the Me region (COSY); $^{13}C\{^1H\}$ NMR (125 MHz, $CD_3COCD_3$, 25 °C): δ = 151.0, 150.9, 150.6, 143.1, 142.7, 142.5 (*C*–Me), 109.0, 106.0, 105.7 (C–$H_{pyr}$), 82.1 (C–$H_C$, $^1J(C,H)$ = 158 Hz), 37.5 (*C*HMe, $^1J(C,H)$ = 154 Hz), 23.6, 16.1, 15.9, 14.4, 13.0, 12.9, 12.7 (7 Me), 18.7 ($CH_2$, $^1J(C,H)$ = 153 Hz).

***exo,syn*-[Tp*IrH($\eta^3$-$CH_2CHCHMe$)] (6*)**: $^1H$ NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.84, 5.77, 5.60 (s, 1H, 1H, 1H, C–$H_{pyr}$), 4.74 (td, 1H, $H_C$, $^3J(H_C,H_A^1) \approx {}^3J(H_C,H_A^2)$ = 9.6, $^3J(H_C,H_S)$ = 6.9 Hz), 3.12 (dq, 1H, $H_A^2$, $^3J(H,Me_S)$ = 5.9 Hz), 3.01 (dd, 1H, $H_S$, $^2J(H_S,H_A^1)$ = 1.0 Hz), 2.36, 2.33, 2.31, 2.30, 2.28, 2.18 (s, 3H each, 6Me), 1.30 (d, 3H, $Me_S$), −29.78 (s, 1H, Ir–H), $H_A^1$ is immersed in the Me region (COSY); $^{13}C\{^1H\}$ NMR (125 MHz, $CD_3COCD_3$, 25 °C): δ = 151.4, 151.4, 150.7, 143.2, 142.7, 142.5 (*C*–Me), 109.0, 106.3, 105.7 (C–$H_{pyr}$), 83.6 (C–$H_C$, $^1J(C,H)$ = 160 Hz), 32.8 (*C*HMe, $^1J(C,H)$ = 160 Hz), 20.7, 16.7, 16.3, 15.7, 13.2, 12.6, 10.8 (Me and $CH_2$).

***exo*,Et *anti*-[Tp*IrH($\eta^3$-CHMeCHCHEt)] (8*)**: $^1H$ NMR (500 MHz, $C_6D_6$, 25 °C; see Figure 10 for atom labels): δ = 5.74, 5.55, 5.48 (s, 1H, 1H, 1H, C–$H_{pyr}$), 4.86 (dd, 1H, $H_C$, $^3J(H_C,H_A)$ = 9.1, $^3J(H_C,H_S)$ = 7.4 Hz), 4.27 (ddd, 1H, $H_S$, $^3J(H_S,CH_2)$ = 10.7, 2.7 Hz), 3.43 (dq, 1H, $H_A$, $^3J(H,Me_S)$ = 5.8 Hz), 2.36, 2.34, 2.15, 2.12, 2.07 (s, 3H, 3H, 6H, 3H, 3H, 6Me), 2.21 (m, 1H, C*H*HMe), 1.32 (d, 3H, $Me_S$), 1.25 (t, 3H, $CH_2$*Me*), 1.03 (m, 1H, CH*H*Me), −29.19 (s, 1H, Ir–H); $^{13}C\{^1H\}$ NMR (125 MHz, $C_6D_6$, 25 °C): δ = 151.4, 151.2, 150.3 (*C*–Me), 143.4, 142.5 (1:2 ratio, *C*–Me), 108.6, 106.1, 105.4 (C–$H_{pyr}$), 82.4 (C–$H_C$, $^1J(C,H)$ = 160 Hz), 32.7 (C–$H_S$, $^1J(C,H)$ = 150 Hz), 31.4 (C–$H_A$, $^1J(C,H)$ = 155 Hz), 30.1 (*C*$H_2$Me), 20.2 ($CH_2$*Me*), 19.8 ($Me_S$), 16.7, 15.3, 15.3, 12.6, 12.4, 12.1 (6Me); IR(KBr): $\tilde{\nu}$ = 2210 $cm^{-1}$ (Ir–H).

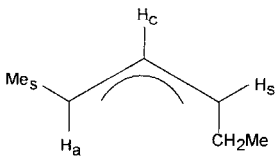



Figure 10.

***endo*,all *syn*-[Tp*IrH($\eta^3$-CHMeCHCHEt)] (8*)**: $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C; see Figure 11 for atom labels): δ = 5.80, 5.76, 5.67 (s, 1H, 1H, 1H, C–$H_{pyr}$), 4.52 (t, 1H, $H_C$, $^3J(H_C,H_A^1) \approx {}^3J(H_C,H_A^2)$ = 9.6 Hz), 3.16 (dq, 1H, $H_A^1$, $^3J(H,Me_S)$ = 6.1 Hz), 3.11 (td, 1H, $H_A^2$, $^3J(H,CH_2)$ = 9.6, 3.5 Hz), 2.5–2.0 (Me), 1.43 (d, 3H, $Me_S$), 1.13 (t, 3H, $CH_2$*Me*), −29.11 (s, 1H, Ir–H). C*H*$_2$Et protons not located. $^{13}C\{^1H\}$ NMR (75 MHz, $C_6D_6$, 25 °C): δ = 85.3 (C–$H_C$, $^1J(C,H)$ = 154 Hz), 42.2, 34.5 (C–$H_A$, $^1J(C,H)$ = 147 and 151 Hz), 31.9 (*C*$H_2$Me), 24–12 (Me).

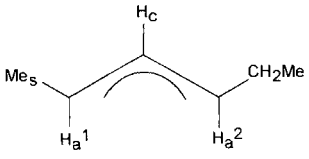



Figure 11.

***exo*,all *syn*-[Tp*IrH($\eta^3$-CHMeCHCHEt)] (8*)**: $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.79, 5.78, 5.65 (s, 1H, 1H, 1H, C–$H_{pyr}$), 4.72 (t, 1H, $H_C$, $^3J(H_C,H_A^1) \approx {}^3J(H_C,H_A^2)$ = 9.4 Hz), 2.89 (dq, 1H, $H_A^1$, $^3J(H,Me_S)$ = 6.1 Hz), 2.82 (td, $H_A^2$ $^3J(H,CH_2)$ = 9.1, 3.5 Hz), 2.5–2.0 (Me), 1.32 (d, 3H, $Me_S$), 1.15 (t, 3H, $CH_2$*Me*), −30.61 (s, 1H, Ir–H). C*H*$_2$Et protons not located.

***exo*,Pr *anti*-[Tp*IrH($\eta^3$-CHEtCHCHPr)] (9*)**: Selected $^1H$ NMR data (500 MHz, $CDCl_3$, 25 °C; see Figure 12 for atom labels): δ = 4.90 (dd, 1H, $H_C$, $^3J(H_C,H_A)$ = 10 Hz, $^3J(H_C,H_S)$ = 7 Hz), 4.28 (ddd, 1H, $H_S$, $^3J(H_S,CH_2)$ = 10,5, 2,6 Hz), 3.46 (dt, 1H, $H_A$, $^3J(H,CH_2)$ = 9 Hz), −29.10 (s, 1H, Ir–H).

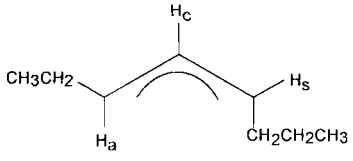



Figure 12.

***endo*,all *syn*-[Tp*IrH($\eta^3$-CHEtCHCHPr)] (9*)**: Selected $^1H$ NMR data (500 MHz, $CDCl_3$, 25 °C; see Figure 13 for atom labels): δ = 4.63 (t, 1H, $H_C$, $^3J(H_C,H_A^1)$ = $^3J(H_C,H_A^2)$ = 10 Hz), 3.30 (m, 2H, $H_A^1$, $H_A^2$), −28.60 (s, 1H, Ir–H).

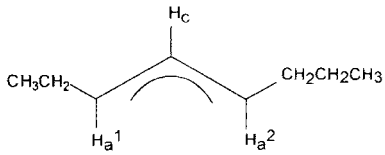



Figure 13.

**Reaction of [Tp*IrH$_2$($SC_4H_4$)] with allene:** The thiophene complex [Tp*IrH$_2$($SC_4H_4$)][36b] was dissolved in cyclohexane and heated at 60 °C for 8 h under 1 atm of allene $CH_2$=C=$CH_2$. The volatiles were removed under vacuum and the residue investigated by $^1H$ NMR. The hydrido–allyl [Tp*IrH($\eta^3$-$CH_2CHCH_2$)] (**15***) was detected in >90% yield.

*endo*-**15***: $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): δ = 5.76, 5.63 (s, 2H, 1H, C–$H_{pyr}$), 5.09 (tt, 1H, $H_C$, $^3J(H_C,H_A)$ = 10.1, $^3J(H_C,H_S)$ = 6.6 Hz), 3.38 (dd, 2H, 2$H_S$, $^2J(H_S,H_A)$ = 2.0 Hz), 2.55 (dd, 2H, 2$H_A$), 2.5–2.0 (Me), −27.98 (s, 1H, Ir–H). In $C_6D_6$ this last resonance appears at −27.55.

*exo*-**15***: $^1H$ NMR (500 MHz, $C_6D_6$, 25 °C): δ = 4.93 (tt, 1H, $H_C$, $^3J(H_C,H_A)$ = 10.1, $^3J(H_C,H_S)$ = 6.5 Hz), 3.31 (d, 2H, 2$H_S$), 2.57 (d, 2H, 2$H_A$), −28.76 (s, 1H, Ir–H).

**Synthesis of [Tp*IrCl($\eta^3$-$CH_2CHCHMe$)] (7*)**: Complex **6*** (0.1 g, 0.19 mmol) was dissolved in $CDCl_3$ (2 mL), and the solution heated at 60 °C for 6–8 h. The reaction was readily monitored by $^1H$ NMR.

*syn*-**7***: major isomer: $^1H$ NMR (500 MHz, $CDCl_3$, 25 °C): δ = 5.84, 5.80, 5.46 (s, 1H, 1H, 1H, C–$H_{pyr}$), 4.97 (td, 1H, $H_C$, $^3J(H_C,H_A^1) \approx {}^3J(H_C,H_A^2)$ = 11.4, $^3J(H_C,H_S)$ = 7.5 Hz), 4.83 (dq, 1H, $H_A^2$, $^3J(H,Me_S)$ = 5.7 Hz), 4.48 (dd, 1H, $H_S$, $^2J(H_S,H_A^1)$ = 2.9 Hz), 3.79 (dd, 1H, $H_A^1$), 2.5–1.9 (6Me), 1.58 (d, 3H, $Me_S$).

*Minor isomer*: $^1H$ NMR (500 MHz, $CDCl_3$, 25 °C): δ = 6.09 (td, 1H, $H_C$, $^3J(H_C,H_A^1) \approx {}^3J(H_C,H_A^2)$ = 10.5, $^3J(H_C,H_S)$ = 7.5 Hz), 5.88, 5.75, 5.44 (s, 1H, 1H, 1H, C–$H_{pyr}$), 4.44 (dd, 1H, $H_S$, $^2J(H_S,H_A^1)$ = 1.9 Hz), 4.33 (dq, 1H, $H_A^2$, $^3J(H,Me_S)$ = 5.7 Hz), 3.33 (dd, 1H, $H_A^1$), 2.6–2.2 (6Me), 1.35 (d, 3H, $Me_S$).

**Preparation of Ir$^{III}$ adducts [Tp′Ir(CH=$CH_2$)($CH_2CH_3$)L] and [Tp*Ir-(CH=CHMe)($CH_2CH_2CH_3$)($PMe_3$)] (12*)**:

**11a** (Tp′ = Tp, L = NCMe): A solution of complex **1** (0.06 g, 0.13 mmol) in acetonitrile (10 mL) was heated at 80 °C for 18 h. Partial removal of the solvent in vacuo and cooling at −20 °C furnished a crude solid from which, after several recrystallisation steps, complex **11a** was obtained as a white microcrystalline solid in 50% yield. $^1H$ NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.01 (dd, 1H, $H_A$, $^3J(A,X)$ = 18.0, $^3J(A,M)$ = 10.5 Hz), 7.7–6.0 (m, 9H, C–$H_{pyr}$), 5.70 (dd, 1H, $H_M$, $^3J(M,X)$ = 3.6 Hz), 4.85 (dd, 1H, $H_X$), 2.42 (s, 3H, NCMe), 1.60 (m, 2H, $CH_2CH_3$), 0.95 (t, 3H, $CH_2CH_3$, $^3J(H,H)$ = 7.3 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 139.3, 139.1, 134.6, 134.4, 134.1, 105.2, 105.1 (1:2:1:1:1:2:1 ratio, C–$H_{pyr}$), 138.4 (Ir–CH=$CH_2$), 115.9 (Ir–CH=$CH_2$), 111.4 (*N*CMe), 16.6 (Ir–$CH_2CH_3$), 4.0 (NC*Me*), −10.7 (Ir–$CH_2CH_3$); $C_{15}H_{21}BN_7Ir$ (514.04): calcd C 35.9, H 4.2, N 19.5; found C 35.9, H 4.3, N 19.8.

**11a*** (Tp′ = Tp*, L = NCMe): In a glass ampoule, complex **1*** (0.06 g, 0.11 mmol) was heated in acetonitrile (10 mL) at 60 °C for 18 h. The resulting solution was concentrated in vacuo and cooled to −20 °C. Complex **11a*** was obtained in 90% yield as a white microcrystalline solid. $^1H$ NMR (500 MHz, $CDCl_3$, 25 °C): δ = 8.24 (dd, 1H, $H_A$, $^3J(A,X)$ = 17.8, $^3J(A,M)$ = 10.3 Hz), 5.75, 5.68, 5,64 (s, 1H, 1H, 1H, C–$H_{pyr}$), 5.55 (dd, 1H, $H_M$, $^3J(M,X)$ = 3.6 Hz), 4.73 (dd, 1H, $H_X$), 2.47 (s, 3H, NCMe), 2.36, 2.33, 2.32, 2.31, 2.22, 2.19 (s, 3H each, 6Me), 2.12, 1.90 (m, 1H, 1H, $CH_2CH_3$), 0.43 (t, 3H, $CH_2CH_3$, $^3J(H,H)$ = 7.6 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): δ = 151.6, 149.7, 142.7, 142.6, 142.4 (2:1:1:1:1 ratio, *C*–Me), 138.3 (Ir–*C*H=$CH_2$), 114.3 (Ir–CH=*C*$H_2$), 111.6 (*N*CMe), 107.1, 106.3, 106.1 (C–$H_{pyr}$), 15.4 (Ir–$CH_2CH_3$), 13.6, 13.2, 12.9, 12.5, 12.3, (1:1:1:1:2 ratio, C–*Me*), 3.9 (NC*Me*), −11.9 (Ir–*C*$H_2CH_3$); $C_{21}H_{33}BN_7Ir$ (574.04): calcd C 43.0, H 5.6, N 16.7; found C 43.2, H 5.7, N 17.0.

**[$D_3$]-11a*** (Tp′ = Tp*, L = NCC$D_3$): $^1H$ NMR (500 MHz, $CD_3CN$, 25 °C): δ = 8.05 (dd, 1H, $H_A$, $^3J(A,X)$ = 17.8, $^3J(A,M)$ = 10.3 Hz), 5.82, 5.74 (s, 1H, 2H, C–$H_{pyr}$), 5.47 (dd, 1H, $H_M$, $^3J(M,X)$ = 3.6 Hz), 4.72 (dd, 1H, $H_X$), 2.37,

2.36, 2.34, 2.34, 2.19, 2.18 (s, 3H each, 6Me), 2.92, 2.15 (m, 1H, 1H, $CH_2CH_3$), 0.41 (t, 3H, $CH_2CH_3$, $^3J$(H,H) = 7.6 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $CD_3CN$, 25 °C): $\delta$ = 152.7, 151.4, 151.3, 144.4, 144.1 (1:1:1:2:1 ratio, C–Me), 137.6 (Ir–$CH$=$CH_2$), 115.7 (Ir–CH=$CH_2$), 108.3, 107.4, 107.1 (C–$H_{pyr}$), 16.2 (Ir–$CH_2CH_3$), 13.9, 13.7, 13.3, 13.2, 12.6, 12.5 (C–*Me*), –12.0 (Ir–$CH_2CH_3$).

**11b*** (Tp′ = Tp*, L = pyridine): Complex **11b*** was prepared similarly by heating **1*** at 60 °C in neat pyridine for 18 h. $^1H$ NMR (500 MHz, $C_6D_6$, 25 °C): $\delta$ = 8.63 (d, 1H, C–$H_{py}$, $^3J$(H,H) = 5.7 Hz), 8.49 (dd, 1H, $H_A$, $^3J$(A,X) = 18.0, $^3J$(A,M) = 10.7 Hz), 7.90 (d, 1H, C–$H_{py}$, $^3J$(H,H) = 5.5 Hz), 6.64 (t, 1H, C–$H_{pyr}$, $^3J$(H,H) = 7.6 Hz), 6.37 (t, 1H, C–$H_{pyr}$), 6.02 (dd, 1H, $H_M$, $^2J$(M,X) = 3.3 Hz), 5.79 (t, 1H, C–$H_{py}$), 5.73, 5.72, 5.68 (s, 1H, 1H, 1H, C–$H_{pyr}$), 5.13 (dd, 1H, $H_X$), 2.79 (dq, 1H, $CH_AH_BCH_3$, $^2J$(A,B) = 11.1, $^3J$(H,H) = 7.5 Hz), 2.69, 2.27, 2.26, 2.18, 1.51, 1.50 (s, 3H each, 6Me), 2.08 (dq, 1H, $CH_AH_BCH_3$), 0.99 (t, 3H, $CH_2CH_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $C_6D_6$, 23 °C): $\delta$ = 140.1 (Ir–$CH$=$CH_2$), 118.6 (Ir–CH=$CH_2$), –6.9 (Ir–$CH_2CH_3$).

**[$D_6$]-11c*** (Tp′ = Tp*, L = [$D_6$]DMSO): In an NMR tube, complex **1*** was suspended in 0.5 mL of [$D_6$]DMSO. The resulting mixture was heated at 60 °C in a water bath until complete disolution of the starting material. NMR monitoring at this point showed total conversion to complex **11c***. $^1H$ NMR (500 MHz, [$D_6$]DMSO, 25 °C): $\delta$ = 7.87 (dd, 1H, $H_A$, $^3J$(A,X) = 17.8, $^3J$(A,M) = 10.3 Hz), 5.91, 5.86, 5.80 (s, 1H, 1H, 1H, C–$H_{pyr}$), 5.56 (dd, 1H, $H_M$, $^3J$(M,X) = 3.2 Hz), 4.59 (dd, 1H, $H_X$), 2.46, 2.38, 2.34, 2.28, 2.17, 2.16 (s, 3H each, 6Me), 0.39 (t, 3H, $CH_2CH_3$, $^3J$(H,H) = 7.3 Hz). The $CH_2CH_3$ protons could not be located; $^{13}C\{^1H\}$ NMR (125 MHz, [$D_6$]DMSO, 25 °C): $\delta$ = 151.1, 150.4, 149.3, 143.6, 143.5, 142.9 (*C*–Me), 133.4 (Ir–$CH$=$CH_2$), 119.8 (Ir–CH=$CH_2$), 108.2, 107.8, 107.8 (C–$H_{pyr}$), 15.6, 15.2, 14.7, 13.9, 12.6, 12.6, 12.5 ($CH_2CH_3$ and 6C–*Me*), –10.6 (Ir–$CH_2CH_3$).

**11d*** (Tp′ = Tp*, L = $PMe_3$): Complex **1*** (0.08 mg, 0.15 mmol) was suspended in neat $PMe_3$ (1 mL) and heated for 10 h at 60 °C. The solution was taken to dryness and the residue was extracted with petroleum ether (10 mL). Upon partial evaporation and cooling at –20 °C white crystals of **11d*** were collected in 75% yield. $^1H$ NMR (200 MHz, $C_6D_6$, 25 °C): $\delta$ = 8.60 (ddd, 1H, $H_A$, $^3J$(A,X) = 17.6, $^3J$(A,M) = 10.3, $^3J$($H_A$,P) = 1.2 Hz), 6.20 (dd, 1H, $H_M$, $^2J$(M,X) = 3.6 Hz), 5.73, 5.65, 5.57 (s, 1H, 1H, 1H, C–$H_{pyr}$), 5.07 (dd, 1H, $H_X$), 2.57, 2.29, 2.27, 2.22, 2.19, 2.04 (s, 3H each, 6Me), 2.45 (m, 2H, Ir–$CH_2$), 1.13 (d, 9H, $PMe_3$, $^2J$(H,P) = 9.4 Hz), 0.80 (t, 3H, Ir–$CH_2CH_3$ $^3J$(H,H) = 7.6 Hz); $^{13}C\{^1H\}$ NMR (50 MHz, $C_6D_6$, 25 °C): $\delta$ = 150.6, 150.2, 149.7 (d, s, s, 1:1:1 ratio, *C*–Me, $^3J$(C,P) = 4 Hz), 143.6, 143.1, 142.5 (C–*Me*), 136.3 (d, Ir–$CH$=$CH_2$, $^2J$(C,P) = 11 Hz) 118.1 (d, Ir–CH=$CH_2$, $^3J$(C,P) = 4 Hz), 107.5, 107.4, 107.3 (C–$H_{pyr}$), 16.2, 16.1, 15.2, 14.6, 12.9, 12.7 (1:1:1:1:2:1 ratio, Ir–$CH_2CH_3$ and 6C–*Me*), 15.2 (d, $PMe_3$, $^1J$(C,P) = 38 Hz), –15.1 (d, Ir–$CH_2CH_3$, $^2J$(C,P) = 6 Hz); $^{31}P\{^1H\}$ NMR (80 MHz, $C_6D_6$, 25 °C): $\delta$ = –48.5.

**[Tp*Ir(CH=CHMe)($CH_2CH_2CH_3$)($PMe_3$)] (12*)**: Similarly and by using complex **4*** as starting material complex **12*** was isolated as a white crystalline solid in 70% yield. Major *trans*-propenyl isomer: $^1H$ NMR (500 MHz, $C_6D_6$, 25 °C): $\delta$ = 7.67 (d, 1H, $H_A$, $^3J$(A,M) = 15.8 Hz), 5.73, 5.65, 5.58 (s, 1H, 1H, 1H, C–$H_{pyr}$), 5.02 (dq, 1H, $H_M$, $^3J$(H,$Me_A$) = 6.1 Hz), 2.47, 2.26, 2.25, 2.23, 2.21, 2.07 (s, 3H each, 6Me), 2.32 (m, 2H, IrC$H_2$Et), 2.15 (d, 3H, $Me_A$), 1.21 (m, 5H, IrCH$_2$*Et*), 1.13 (d, 9H, $PMe_3$, $^2J$(H,P) = 9.2 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $C_6D_6$, 25 °C): $\delta$ = 150.4, 149.9, 149.7, 143.3, 143.0, 142.0 (*C*–Me), 125.2 (d, Ir–CH=*C*HMe, $^3J$(C,P) = 4 Hz), 124.2 (d, Ir–*C*H=CHMe, $^2J$(C,P) = 10 Hz), 107.4, 107.3, 107.2 (d, s, s, 1:1:1 ratio, $CH_{pyr}$, $^4J$(C,P) = 4 Hz), 24.6 (Ir–$CH_2CH_2CH_3$), 23.2 ($Me_A$), 17.7 (Ir–$CH_2CH_2CH_3$), 16–12 (6C–*Me*), 15.4 (d, $PMe_3$, $^1J$(C,P) = 37 Hz), –3.9 (d, Ir–$CH_2$Et, $^2J$(C,P) = 6 Hz); $^{31}P\{^1H\}$ NMR (120 MHz, $C_6D_6$, 25 °C): $\delta$ = –50.2. Minor *cis*-propenyl isomer: $^1H$ NMR (500 MHz, $C_6D_6$, 25 °C): $\delta$ = 7.62 (d, 1H, $H_A$, $J$(A,M) = 10 Hz), 6.15 (dq, 1H, $H_M$, $^3J$(H,$Me_A$) = 5 Hz); $^{13}C\{^1H\}$ NMR (125 MHz, $C_6D_6$, 25 °C): $\delta$ = 126.3 (Ir–CH=*C*HMe), 120.4 (d, Ir–*C*H=CHMe, $^2J$(C,P) = 10 Hz), –5.9 (d, Ir–$CH_2$Et, $^2J$(C,P) = 7 Hz); $^{31}P\{^1H\}$ NMR (120 MHz, $C_6D_6$, 25 °C): $\delta$ = –51.2; $C_{24}H_{41}BN_6PIr$ (647.62): calcd C 44.5, H 6.4, N 13.0; found C 44.6, H. 6.7, N 12.4.

**Synthesis of [TpIrH($\eta^3$-$C_8H_{13}$)] (F)**: Complex **G**[16] (0.04 g, 0.08 mmol) was dissolved in cyclohexane (10 mL) and the solution was heated at 80 °C for 24 h. The solvent was evaporated under vacuum and the residue, a microcrystalline white solid, was investigated by $^1H$ NMR. Only complex **F** was detected in solution, attesting to the quantitative conversion of **G** into **F**. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ = 8.1–6.0 (m, 9H, 2:1 ratio, C–$H_{pyr}$), 4.44 (t, 1H, $H_C$, $^3J$($H_C$,$H_S$) = 7.5 Hz), 4.00 (q, 2H, 2$H_S$, $^3J$(H,$CH_2$) = 8.0 Hz), 2.7–1.3 (m, 10H, 5 $CH_2$), –26.01 (s, 1H, Ir–H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 25 °C): $\delta$ = 145.8, 137.9, 135.1, 133.7, 105.8, 104.7 (2:1:1:2:2:1 ratio, C–$H_{pyr}$), 88.2 (C–$H_C$), 38.0, 37.6, 29.1, 26.6 ($CH_2$ and C–$H_S$).

**Crystal structure determinations of 1*, 8a* and 8b***: A light yellow crystal of prismatic shape of complex **1*** was coated with epoxy resin and mounted in a kappa diffractometer equipped with an Enraf-Nonius FR558SH low-temperature device. The cell dimensions were refined by least-squares fitting the $\theta$ values of the 25 reflections with a $2\theta$ range of 13–27°. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ir were taken from the International Tables for X-ray Crystallography.[50] The structure was solved by Patterson and Fourier methods. An empirical absorption correction[51] was applied at the end of the isotropic refinements. A final refinement was undertaken with unit weights and anisotropic thermal motion for the non-hydrogen atoms. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions. No trend in $\Delta F$ vs. $F_o$ or $\sin\theta/\lambda$ was observed. Final difference showed no significantly electron density. Most of the calculations were carried out with the X-Ray 80 system.[52]

For complexes **8a*** and **8b***, colourless prismatic crystals were coated with epoxy resin and mounted in a kappa diffractometer. The cell dimensions were refined by least-squares fitting the $\theta$ values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion correction for Ir were taken from the reference given above. The structures were solved by Patterson and Fourier methods. Empirical absorption corrections were applied at the end of the isotropic refinement.[51] Final refinement were undertaken with fixed isotropic factors and coordinates for all *H* atoms, except H1 whose coordinates were located in $\Delta F$ and refined. Final difference synthesis showed no significantly electron density.

Most of the calculations were carried out with the X-Ray 80 system.[52] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100295. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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