

C–H Bond Activation of Benzene and Cyclic Ethers by TpIr^{III} Species

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Dedicated to Professor Helmut Werner on the occasion of his 65th birthday

Abstract: The bis(ethylene) complex $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2]$ (**1**) successively activates C–H bonds in two molecules of benzene to generate a mixture of the bis(phenyl) complexes $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_6\text{H}_5)_2\text{N}_2]$ (**4**) and $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_6\text{H}_5)_2(\mu\text{-N}_2)]$ (**5**). They contain a coordinated molecule of dinitrogen that acts as a terminal ligand in the former and as a bridge between the two metal centres in the latter. Compound **1** is also capable of activating regioselectively the two α -C–H bonds of the $-\text{OCH}_2-$ func-

tionality of THF to produce the Fischer carbene derivative $[\text{Tp}^{\text{Me}_2}\text{IrH}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)(=\overline{\text{C}}(\text{CH}_2)_3\text{O})]$ (**13**). Compounds **4** and **5** are unusual examples of stable $\text{Ir}^{\text{III}}\text{-N}_2$ compounds, whereas **13**, and other related complexes described in the paper, are distinctive

species that contain a hydride, an alkyl and a carbene functionality bound to the same metal centre. Trapping experiments with PMe_3 as the trapping reagent and isotopic labelling studies (^2H) provide useful mechanistic information on the reaction pathway that leads to **4** (and **5**). This is compared with the sequence of events that yield complex **13**. In each case the possibility of $\text{Tp}^{\text{Me}_2}\text{Ir}^{\text{V}}$ intermediates or transition states is considered.

Keywords: C–C coupling • C–H bond activation • carbenes • iridium • reaction mechanisms

Introduction

The selective activation of the C–H bonds of organic substrates by transition metal complexes and the subsequent conversion of the resulting products into functionalised organic compounds comprise an important and active area of research.^[1] Earlier studies on Ir systems that are capable of activating such bonds intermolecularly demonstrated the involvement of unsaturated Ir^{I} intermediates.^[1,2] This was found to be the case even when some Ir^{III} derivatives, such as $[\text{Cp}^*\text{IrH}(\eta^3\text{-C}_3\text{H}_5)]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$), were treated with C_6H_6 , the 16-electron species $[\text{Cp}^*\text{Ir}(\eta^2\text{-C}_3\text{H}_6)]$ was suggested as the active intermediate for the C–H bond rupture reaction.^[3] In

recent years, however, increasing evidence for related C–H activations involving Ir^{III} (and perhaps Ir^{IV} and Ir^{V}) centres has accumulated. For example, the intermediacy of $[\text{Cp}^*\text{IrMe}_2]$ has been proposed during the sequential activation of two molecules of C_6H_6 by the complexes $[\text{Cp}^*\text{IrMe}_2(\text{L})]$ ($\text{L} = \text{DMSO}$,^[4] PPh_3 ^[5]) to give the corresponding bis(phenyl) derivatives as the final products. This suggestion was in agreement with the inhibiting role played by the added ligand L. A more electrophilic compound $[\text{Cp}^*\text{IrMe}(\text{OTf})(\text{PMe}_3)]$ ($\text{OTf} = \text{OSO}_2\text{CF}_3$) and the cation $[\text{Cp}^*\text{IrMe}(\text{PMe}_3)]^+$ resulting from triflate abstraction are also able to activate the sp^3 C–H bonds of alkanes under mild conditions^[6] by means of Ir^{III} intermediates.

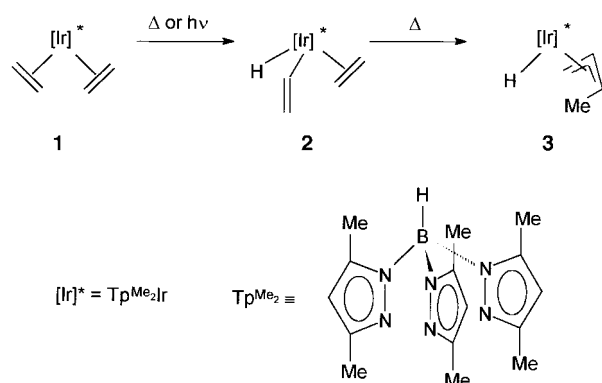
Owing to the existence of well-characterised inorganic and organometallic compounds of Ir^{V} , for example, $[\text{Cp}^*\text{IrMe}_4]$,^[7a] $[\text{IrH}_4(\text{SiR}_3)(\text{PPh}_3)_2]$ ^[7b] and $[\text{IrH}_4(\text{C}_6\text{H}_5\text{-2,6-(CH}_2\text{PrBu}_2)_2)]$,^[7c] it appears possible that these reactions, seemingly of the σ -bond metathesis type, could actually proceed through Ir^{V} intermediates formed by oxidative addition of a C–H bond to an Ir^{III} active species. Maitlis and co-workers have already advanced this hypothesis.^[4] Nevertheless, for the more electrophilic systems^[6] a concerted σ -bond metathesis of the kind postulated for complexes of the f and early d elements^[1] also seems to be a plausible reaction pathway. Other C–H activations such as those of substituted alkenes by the dication $[\text{Cp}^*\text{Ir}(\text{S})_3]^{2+}$ ($\text{S} = \text{solvent molecule}$) are best described as heterolytic C–H bond cleavages, the M–C bond being formed concomitantly with H^+ extrusion.^[8]

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Recent work from our laboratory has focused on the study of C–H activation reactions by Rh and Ir complexes of the hydrotris(pyrazolyl)borate ligands, Tp'.^[9] This paper centres upon the activation of the C–H bonds of C₆H₆ and of cyclic ethers (for example tetrahydrofuran) by the active intermediate [Tp^{Me2}Ir(CH=CH₂)(C₂H₅)] (Tp^{Me2} = tris(3,5-dimethylpyrazol-1-yl)hydroborato ligand). As already reported, this species forms from the Ir^{III} complex [Tp^{Me2}Ir(CH=CH₂)(C₂H₄)],^[9b] by the migratory insertion of C₂H₄ into the Ir–H bond. Part of this work has been communicated briefly.^[10]

Results

The activation of C₆H₆ by the Ir^{III} complex [Tp^{Me2}IrH(CH=CH₂)(C₂H₄)] (2): Previous work from our laboratory has shown that the Ir^I–ethylene complex [Tp^{Me2}Ir(C₂H₄)₂] (1) is transformed irreversibly into the thermodynamically more stable hydride–vinyl isomer 2 (Scheme 1) under thermal or photochemical conditions.^[9a,b]

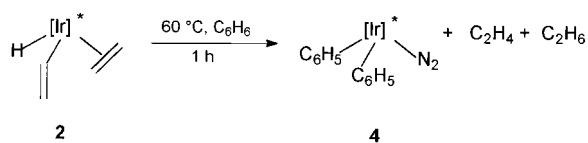


Scheme 1. Rearrangement of the bis(ethylene) complex **1**. Note: [Ir]^{*} = Tp^{Me2}Ir in all the schemes.

The thermal reaction (cyclohexane solvent) does not stop at the formation of **2**. As shown in Scheme 1, under the same conditions this compound undergoes further rearrangement to give the hydride–allyl complex **3** as a result of the coupling of the hydrocarbon-based ligands.

The use of C₆H₆ as the reaction solvent prevents the C–C coupling process that leads to **3**; the new complex **4** (and also the insoluble compound **5**, depending upon the reaction conditions, vide infra), is obtained instead. When **2** is employed as the starting material, conversion to **4** is fast (in less than 1 h) and no intermediates can be detected by ¹H NMR spectroscopy. From **1**, however, the overall reaction is slower and the presence of **2** as an active intermediate can be readily ascertained. The new derivative **4** exhibits a characteristic strong IR absorption at 2190 cm⁻¹ that can be assigned to $\tilde{\nu}(\text{N}\equiv\text{N})$ of a terminal N₂ ligand. NMR studies reveal the presence of phenyl groups, and all these data, coupled with the microanalytical results, suggest its formulation as [Tp^{Me2}Ir(C₆H₅)₂N₂] (**4**). Interestingly, rotation around the Ir–C₆H₅ bonds is slow on the NMR time scale,^[2d, 3, 11] as demonstrated by the observation of five distinct C–H aromatic resonances in the phenyl region of the ¹H and

¹³C{¹H} NMR spectra of **4**. As in other related derivatives,^[9c] this is a clear manifestation of the severe steric constraints imposed by the bulky Tp^{Me2} ligand. Scheme 2 shows the



Scheme 2. Activation of C₆H₆ by **1**.

generation of this bis(phenyl) derivative starting from **2**; the evolution of C₂H₄ and C₂H₆, but not of C₄ hydrocarbons, has been demonstrated by ¹³C NMR studies of the volatiles generated in the course of the reaction. Kinetic studies carried out on C₆D₁₂–C₆H₆ mixtures (Figure 1) reveal a linear

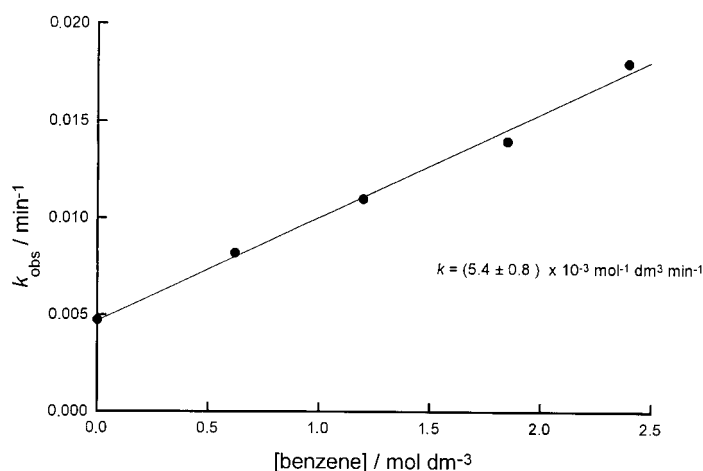
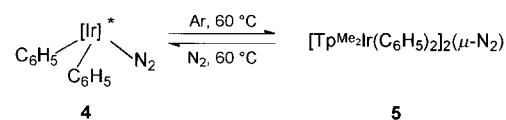


Figure 1. Variation of k_{obs} with [C₆H₆] for the thermal decomposition of **2**.

dependence of k_{obs} on the concentration of C₆H₆ ($k_{\text{obs}} = k_{\text{allyl}} + k[\text{C}_6\text{H}_6]$ with $k = (5.4 \pm 0.8) \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ min}^{-1}$; see Discussion Section). No saturation effects can be detected at concentrations of the aromatic hydrocarbon of up to 2.5 M.

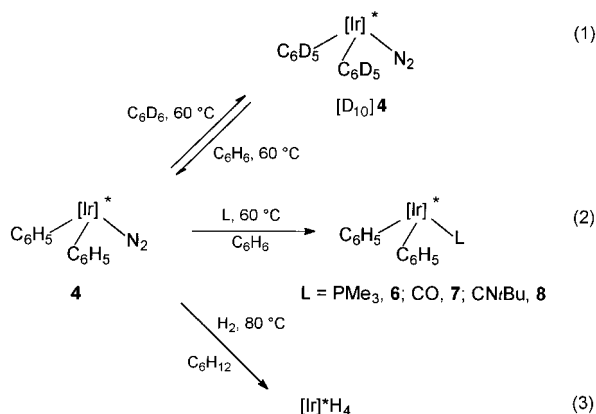
As briefly mentioned above, a very insoluble second complex **5** may also result from this reaction in amounts depending upon the conditions, in particular the concentration of the starting product **1** or **2**. Its IR spectrum shows no band attributable to $\tilde{\nu}(\text{N}\equiv\text{N})$, but a Raman absorption at 2130 cm⁻¹ indicates the existence of a symmetrical Ir–N≡N–Ir entity. This and other data favour the formulation in Scheme 3, a conclusion further supported by the X-ray studies



Scheme 3. Equilibrium between mononuclear and binuclear Ir^{III}–dinitrogen complexes.

described below. Compounds **4** and **5** interconvert under appropriate conditions (Scheme 3), but there is a substantial kinetic barrier for the two transformations.

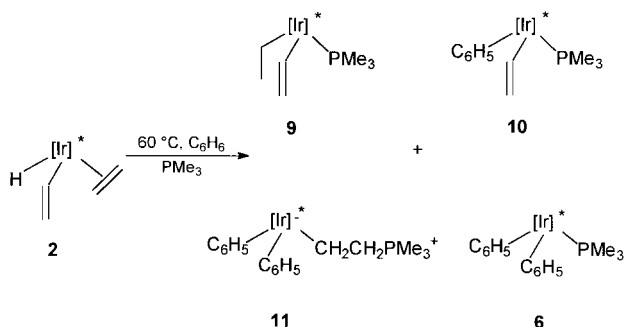
Reactivity studies on these complexes are best effected with the monomer species **4** because of its higher solubility. This compound is a rather reactive molecule even though it has a high thermal stability and remains unaltered after being heated in C₆H₆ at 60 °C under N₂. However, that phenyl exchange involving free benzene does take place under these conditions is demonstrated unambiguously by the deuteration experiments depicted in Equation (1), Scheme 4. Substitution



Scheme 4. Some chemical reactions of **4**.

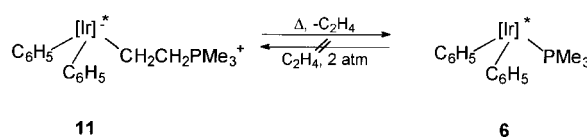
of the coordinated N₂ ligand by other donor molecules such as PMe₃, CO and CN*t*Bu is also feasible under the conditions described above and generates the corresponding adducts **6**–**8** [Eq. (2), Scheme 4]. These new compounds have NMR properties very similar to those of **4**, including restricted rotation around the Ir–C₆H₅ bond. In addition they exhibit IR absorptions characteristic of the coordinated Lewis base; for example the $\tilde{\nu}(\text{CO})$ and $\tilde{\nu}(\text{CN})$ values of **7** and **8**, are 2026 and 2163 cm⁻¹, respectively. As Scheme 4 [Eq. (3)] also shows, compound **4** reacts with H₂ at 80 °C to produce the known tetrahydride [Tp^{Me2}IrH₄].^[12] An interesting transformation that occurs when **4** is heated in THF will be discussed in the following section.

In an attempt to trap possible intermediates of the C₆H₆ activation reaction, complex **2** was heated in C₆H₆, under N₂, in the presence of PMe₃. This experiment cannot be carried out with **1** because of the facility with which the substitution reaction that gives [Tp^{Me2}Ir(C₂H₄)(PMe₃)] takes place, even at room temperature.^[9f] NMR spectroscopy reveals the formation of the complexes shown in Scheme 5; **9** is the only one of these that is formed in the absence of C₆H₆ (with C₆H₁₂ or neat



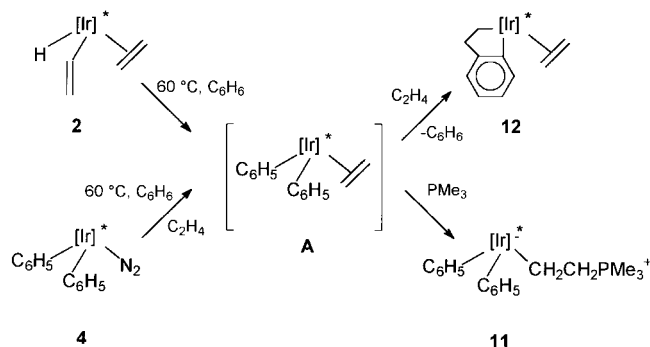
Scheme 5. PMe₃-trapping experiments carried out with **2**.

PMe₃ as the solvent).^[9b] However, the formation of this species becomes important only when the concentration of PMe₃ is very high (C₆H₆:PMe₃ = 1:1, v/v), whereas **11** and **6** are strongly favoured at low concentrations of PMe₃. Complexes **6**, **9** and **10** are very soluble in C₆H₆. However, **11** is only sparingly soluble in most common solvents although it has been completely characterised by NMR spectroscopy in [D₆]DMSO. Particularly relevant in this respect are the ²J(H,P) value of 14 Hz for the PMe₃ group and the ¹J(C,P) coupling constant of 35 Hz for the methylene carbon bound to phosphorus, which clearly suggest the existence of a zwitterionic [Ir–CH₂CH₂⁺PMe₃]⁻ functionality.^[13] It looks likely that complex **11** results from the nucleophilic attack of PMe₃ on the ethylene ligand of the unobserved species [Tp^{Me2}Ir(C₆H₅)₂(C₂H₄)] (**A**) and also that its insolubility allows its isolation. When **11** is heated at 60 °C in CH₂Cl₂ it is converted irreversibly into complex **6** (Scheme 6).



Scheme 6. Thermal transformation of the zwitterion **11**.

The successful trapping of the ethylene derivative **A** in the form of the zwitterionic compound **11** by the action of PMe₃ led us to attempt its isolation or detection. However, heating **1** or **2** in C₆H₆ under Ar gives only a very complex mixture of products, mostly unidentified, and if an ethylene atmosphere is used the metallated species **12** can be observed in 70% yield along with other unidentified species (Scheme 7). As expected, complex **12** is also obtained when the dinitrogen species **4**

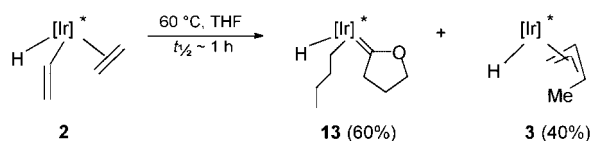


Scheme 7. Involvement of **A** in a series of reactions.

is heated with C₂H₄ in C₆H₆ solution. It is clear that the postulated ethylene adduct is generated under these conditions. This is further supported by the preferential production of **6** and **11** in the presence of small amounts of PMe₃. It can be concluded that **A** is kinetically very labile with respect to both the extrusion and the insertion pathways. This prevents its isolation and even its detection as a free complex.

Regioselective, double C_α–H activation of cyclic ethers by TpIr^{III} complexes: When compound **1** or **2** is heated at 60 °C in THF, the purported vinyl–ethyl intermediate^[9b]

$[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{CH}=\text{CH}_2)(\text{C}_2\text{H}_5)]$ can progress along two competitive reaction pathways. One is responsible for the formation of the hydride–allyl species **3**; the other involves the activation of tetrahydrofuran and leads to the new product **13** (Scheme 8), which is readily isolable from the reaction



Scheme 8. Activation of THF by **2**.

mixture by fractional crystallisation. The characterisation of this compound required extensive one- and two-dimensional NMR investigations, the proposed structure being subsequently confirmed by X-ray studies (vide infra). A hydride signal at -17.90 and a distinctively low-field $^{13}\text{C}\{^1\text{H}\}$ resonance at $\delta = 258.8$ ^[14] are clear indications of the presence of the Ir–H and Ir=C < functionalities, respectively. The hydride–vinyl complex **2** is again the active species, but the results of the reactions depicted in Schemes 2 and 8 indicate that THF is much less efficient than C_6H_6 in trapping the reactive $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{CH}=\text{CH}_2)(\text{C}_2\text{H}_5)]$ intermediate.

It is evident that compound **13** results from a regioselective double C–H activation at one of the α -carbon atoms of THF. Formally, one of the H atoms becomes incorporated into the alkyl chain derived from the coupling of the two original C_2 ligands, whereas the other remains bound to the metal centre. Monitoring of the reaction by ^1H NMR spectroscopy reveals no detectable intermediates, and also that, as expected,^[9b] the allyl species **3** is stable in THF under the reaction conditions. At variance with the PMe_3 trapping experiments already described for the C_6H_6 activation, only the PMe_3 adduct $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{CH}=\text{CH}_2)(\text{C}_2\text{H}_5)(\text{PMe}_3)]$ (**9**)^[9b] is formed when **2** is heated in THF in the presence of an excess of PMe_3 .

Diethyl ether appears not to be activated by this system, but other cyclic ethers, when used as neat solvents, do participate in the sequence of chemical events summarised in Scheme 8 (Table 1). After the statistical corrections, it is clear that the

methyl group of 2-MeTHF favours the C–H activation (probably by enhancing the coordination capability of the ether functionality; vide infra), since the resulting carbene, obtained as a 1:1 mixture of stereoisomers, amounts to approximately 55% of the reaction products. A second ether functionality in the ring has only a very modest effect on the reactivity of the OCH_2 group (see the entry for diolane in Table 1), and six-membered cyclic ethers are less prone than their C_4O counterparts to undergo this transformation. This may be attributable to steric hindrance associated with the coordination to the Ir centre and it could be responsible for the lack of observable activation of tetrahydropyran. In accord with the expectations, 2,5-Me₂THF and 2,2,5,5-Me₄THF give only the allyl product **3** when used as the reaction solvents.

With the asymmetry of these complexes and the nonsymmetrical nature of the majority of the carbene ligands studied, restricted rotation around the Ir=C bond could give rise to more than one rotamer. However, only one species is observed in each case, in accord with the existence of just one rotamer in solution or, alternatively, with fast rotation around the Ir=C bond in the temperature range studied (down to -70°C). For complex **15**, which contains a symmetrical =C(OCH₂)₂ cyclic carbene ligand, the two methylene carbon nuclei are equivalent and moreover the OCH₂CH₂O protons appear as an AB multiplet. While we realize that **15** is a rather singular species within the series investigated (the presence of two heteroatoms bound to the carbene carbon shifts the corresponding ^{13}C resonance to $\delta = 206$, that is, 50 ppm to lower field than the other members of the series), the data obtained suggest that the rotation around the Ir=C bond must be fast on the NMR time scale. A similar situation has been found for related Ir=C < moieties^[14] whereas for $[\text{Os}(\text{NH}_3)_4(\text{H}_2)(=\text{COCH}_2\text{CH}_2\text{CH}_2)]^{2+}$ the barrier to rotation appears to be of the order of 24 kcal mol^{-1} .^[15]

To try to understand the mechanism of the activation of THF we thermolysed **1** in $[\text{D}_8]\text{THF}$; we found lower yields of the C–D activation product, due to a significant isotope effect ($[\text{H}]\mathbf{13}:[\text{D}_n]\mathbf{13} \approx 2.2:1$). The deuteriospecies $[\text{D}_n]\mathbf{13}$ can nevertheless be isolated from the reaction mixture, and NMR studies indicate almost complete deuteration at the metal and incorporation of 2–3 deuterium atoms at the α and β carbon atoms of the hydrocarbon chain ($n \approx 9-10$). The complexity of the NMR spectra of **13** and $[\text{D}_n]\mathbf{13}$ prevents a more detailed analysis of this transformation.

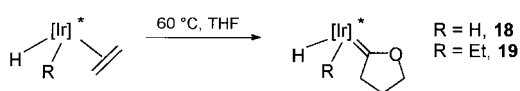
We have found that other $\text{Tp}^{\text{Me}_2}\text{Ir}$ complexes that are able to generate a $\{\text{Tp}^{\text{Me}_2}\text{Ir}(\text{R})(\text{R}')\}$ fragment ($\text{R}, \text{R}' = \text{H}, \text{alkyl}, \text{aryl}$), and have in addition a vacant or readily accessible coordination site, are able to activate THF. For example, the complexes $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{H})(\text{R})(\text{C}_2\text{H}_4)]$ ^[9f] give rise, cleanly, to the carbene species **18** and **19** (Scheme 9) when they are heated in THF. In this case the C–H bond activation becomes the only accessible reaction route. Once more, the addition of PMe_3 inhibits this process by formation of the known $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_5)(\text{R})(\text{PMe}_3)]$ adducts ($\text{R} = \text{H}, \text{C}_2\text{H}_5$)^[9f]. Similarly the bis(phenyl) derivative

Table 1. Thermal decomposition of complex **1** in cyclic ethers.^[a]

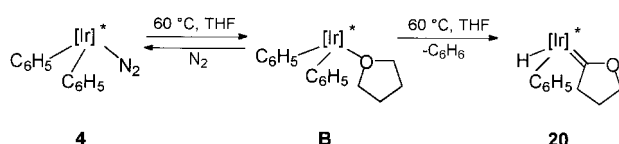
Solvent					
	3 (40%)	3 (45%)	3 (20%)	3	3 (60%)
	+	+	+	[c]	+
	(60%)	(55%)	(50%)	(30%)	(40%)

[a] All reactions performed at 60°C to completion (ca. 8 h); percentage yields are in parentheses and refers to the crude materials (^1H NMR); $[\text{Ir}]^* \equiv \text{Tp}^{\text{Me}_2}\text{Ir}(\text{nBu})$.

[b] Mixture of the two possible diastereoisomers (1:1) ratio. [c] No carbene formed in more than trace amounts.

Scheme 9. Activation of THF by $[\text{Tp}^{\text{Me}_2}\text{IrH}(\text{R})(\text{C}_2\text{H}_4)]$ complexes.

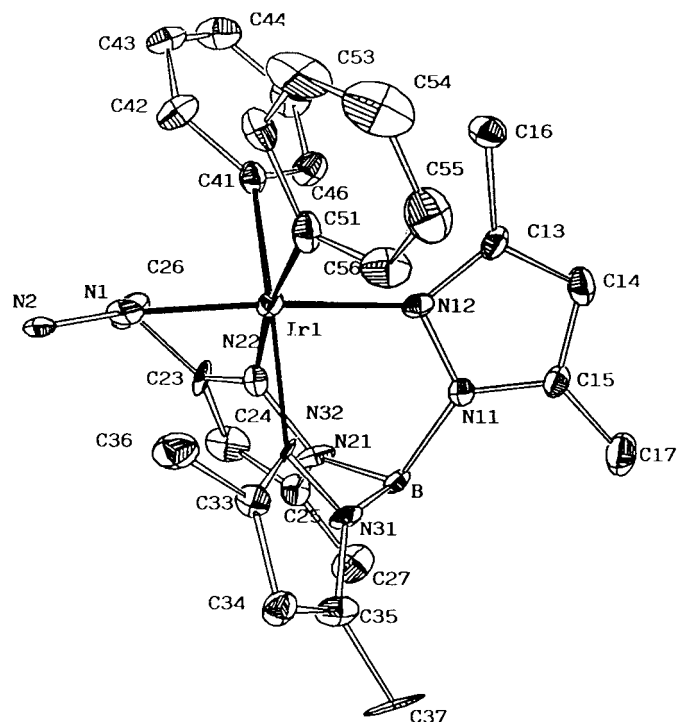
4 undergoes a related reaction to produce the carbene **20** (Scheme 10). When complex $[\text{D}_0]\mathbf{4}$ is heated in $[\text{D}_8]\text{THF}$, the deuteride complex $[\text{D}_7]\mathbf{20}$ and $\text{C}_6\text{H}_5\text{D}$ are formed. This clearly rules out the intermediacy of an Ir^I–benzyne complex in this transformation.

Scheme 10. Detection of a THF adduct in the reaction of **4** with tetrahydrofuran.

Pertinent to the comments above on the initial step of the THF activation is the detection (by ¹H NMR monitoring) of an intermediate species that can be formulated as the THF adduct **B**. It is noteworthy that because of a kinetic isotope effect of approximately 3:1 (no attempt has been made to quantify this more precisely), $[\text{D}_8]\mathbf{B}$, clearly formed by treatment of **4** with $[\text{D}_8]\text{THF}$, has a long enough lifetime to allow its relative concentration to become about 60% within this product mixture. Hence NMR characterisation is feasible and proves the presence of two phenyl groups, whose rotation around the Ir–C₆H₅ bonds is less restricted than for other analogous compounds (four somewhat broad resonances associated with the *ortho* and *meta* protons can be detected at room temperature). The ²H NMR spectrum of $[\text{D}_8]\mathbf{B}$ shows two 1:1 resonances with chemical shifts very close to those of free $[\text{D}_8]\text{THF}$. All these data, and the facility with which this compound reverts smoothly to **4** when heated under N₂, support the proposed formulation.

Crystal and molecular structures of complexes 5 and 13: A survey of the literature reveals that the two C–H activations under study possess some unusual features and produce uncommon compounds with unexpected structures. Since structural characterisation of some of these complexes by X-ray techniques seemed essential, we directed our efforts to isolating them in the form of single crystals. Most surprisingly, only a few Ir–N₂ complexes have been reported yet,^[16] and at the time of our original report none had been structurally authenticated by X-ray crystallography. During the preparation of this paper a second example has appeared in the literature.^[16c] As for the carbene derivatives, the observed nonradical-mediated, double C–H activation under such mild conditions was also unprecedented at the time of our original report^[10a] (see below). Moreover compound **13**, and other members of the same family reported here, contain a metal fragment bound to a hydride, an alkyl and a carbene functionality, a situation we believe to have been previously unknown.

The dinitrogen-bridged binuclear compound **5** crystallises in the space group *C2/c* and consists of molecules that have the geometry shown in Figure 2. A summary of selected

Figure 2. ORTEP drawing and atom-labelling scheme for **5**. For clarity only one of the two Ir fragments bound to N₂ is shown.

bonding parameters is contained in Table 2. As can be seen in Figure 2, a partial ORTEP representation of only one of the two Ir fragments in addition to the bridging N₂ ligand, the coordination geometry is close to a distorted octahedron. The three coordinated N atoms of the Tp^{Me}₂ group define the vertices of one of the triangular faces, the opposite face being

Table 2. Selected bond lengths [Å] and angles [°] for complex **5**.

Ir1–N12	1.99 (2)	Ir2–N12'	2.14 (2)
Ir1–N22	2.16 (2)	Ir2–N22'	2.01 (2)
Ir1–N32	2.20 (2)	Ir2–N32'	2.14 (2)
Ir1–N1	1.93 (2)	Ir2–N1'	1.94 (2)
Ir1–C41	2.06 (2)	Ir2–C41'	2.03 (2)
Ir1–C51	2.05 (2)	Ir2–C51'	2.09 (3)
N1–N1'	1.13 (3)		
C41–Ir1–C51	95 (1)	C41'–Ir2–C51'	94.0 (9)
N1–Ir1–C51	95.6 (8)	N1'–Ir2–C51'	90.4 (9)
N1–Ir1–C41	91.0 (8)	N1'–Ir2–C41'	95.5 (8)
N32–Ir1–C51	87.9 (8)	N32'–Ir2–C51'	176.3 (8)
N32–Ir1–C41	176.9 (8)	N32'–Ir2–C41'	89.6 (8)
N32–Ir1–N1	88.1 (7)	N32'–Ir2–N1'	89.2 (8)
N22–Ir1–C51	171.9 (9)	N22'–Ir2–C51'	93.5 (9)
N22–Ir1–C41	89.1 (8)	N22'–Ir2–C41'	84.9 (8)
N22–Ir1–N32	88.0 (7)	N22'–Ir2–N1'	176.0 (7)
N12–Ir1–C51	86.3 (8)	N22'–Ir2–N32'	86.8 (7)
N12–Ir1–C41	92.2 (8)	N12'–Ir2–C51'	89.9 (8)
N12–Ir1–N1	176.1 (7)	N12'–Ir2–C41'	173.6 (8)
N12–Ir1–N32	88.6 (7)	N12'–Ir2–N1'	90.2 (7)
N12–Ir1–N22	86.7 (7)	N12'–Ir2–N32'	87.4 (7)
Ir1–N1–N1'	174.2 (2)	N12'–Ir2–N22'	89.2 (7)
		Ir2–N1'–N1	174 (2)

determined by the two coordinated phenyl carbons and an N atom of the bridging N₂ unit. As expected, the strongest Ir–N(pyrazolyl) interaction is that corresponding to the pyrazolyl ring *trans* to the most weakly bound N₂ ligand (1.99 compared with 2.18 Å, on average). The two Ir–C bond lengths (at 2.05 Å) are identical within experimental error and compare well with the values found in other Ir^{III}–C₆H₅ complexes already reported in the literature.^[2c,d] From a structural point of view, the most interesting interaction is that of the bimetallic Ir–N≡N–Ir central unit, which is characteristically linear (Ir–N–N' = 174(2)°) and indicative of a relatively strong Ir–N₂–Ir bonding interaction (compare, for example, the Ir1–N1 separation of 1.93(2) Å with the Ir–N(pyrazolyl) shortest distance of 1.99(2) Å, which are essentially identical within experimental error). Within the N₂ ligand, the N–N bond length is very similar to that of the free ligand (1.13(3) compared with 1.10 Å) and close to those reported for other M–N₂–M linkages.^[16] Considering that the Ir atom has a formal oxidation state of +III, the strength of the Ir–N bonds in this complex (and by extension in the mononuclear species **4**) appears remarkable.

Figure 3 shows an ORTEP perspective view of the molecules of the Fischer carbene complex **13**; structural parameters and other X-ray data for this compound are collected in Tables 3 and 4. The tendency of the Tp' ligands to impose six-coordinated, approximately octahedral geometry, as already encountered for **5**, is manifested by the distorted octahedral environment of the Ir centre of **13** with almost rectangular N–Ir–N angles (approximately 86° on average). As expected, the Ir–N bond

Table 3. Crystal and refinement data for complexes **5** and **13**.

	5	13
formula	C ₅₄ H ₆₄ B ₂ N ₁₄ Ir ₂	C ₂₃ H ₃₈ BN ₆ IrO
<i>M_r</i>	1339.3	617.6
crystal system	monoclinic	triclinic
space group	<i>C2/c</i>	<i>P1</i>
<i>a</i> [Å]	54.89 (2)	10.435 (8)
<i>b</i> [Å]	10.920 (5)	10.809 (4)
<i>c</i> [Å]	19.791 (7)	13.888 (2)
α [°]		81.54 (2)
β [°]	91.90 (3)	68.43 (4)
γ [°]		63.02 (3)
<i>Z</i>	8	2
<i>V</i> [Å ³]	11856 (1)	1298.8 (6)
ρ calcd [g cm ⁻³]	1.50	1.58
<i>F</i> (000)	5296	616
<i>T</i> [K]	295	293
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation	graphite-monochromated (MoK α) (λ = 0.71069 Å)	graphite-monochromated (MoK α) (λ = 0.71069 Å)
μ [cm ⁻¹]	45.1	65.8
crystal dimensions [mm]	0.4 × 0.07 × 0.07	0.13 × 0.13 × 0.5
θ range [°]	1 < θ < 25	1 < θ < 27
scan technique	$\Omega/2\theta$	$\theta/2\theta$
data collected	(–65,0,0) to (65,13,23)	(–13, –13,0) to (13,13,17)
unique data	10386	5642
unique data [<i>I</i> ≥ 2 σ (<i>I</i>)]	5123	2521
<i>R</i> (int) [%]	3.5	0.01
standard reflections	3/58	3/216
weighting scheme	unit	$w = 1/(a + bF_0)^2$
<i>R_f</i> [%]	6.3	2.6
<i>wR_f</i> [%]	8.2	2.9
average shift/error	0.004	0.001

trans to the hydride ligand (Ir–N32) is the longest (2.170(5) Å), although it is not very different from the other two, which are identical within experimental error (approximately 2.150 Å). The separation of the Ir centre from the carbene carbon, 1.881(5) Å, is consistent with partial double bond character for this interaction and it is in the range found for other neutral Fischer carbene complexes of Ir^{III} (1.87 Å in [IrCl₃(=CCL₂)(PPh₃)₂] for example^[17]). It is, however, significantly shorter than in some cationic compounds of Ir^{III} that contain the same 2-oxacyclopentylidene ligand.^[14, 18]

Discussion

Work described in the Results section and in a previous paper^[9b] clearly demonstrates that the chemical pathway followed by compound **1** during its participation in different C–H or C–C bond activation or formation reactions consists of its isomerisation to the hydride–vinyl Ir^{III} isomer **2**, followed by migration of the hydride ligand onto the remaining molecule of ethylene to generate a highly reactive intermediate species (Scheme 11). This could be stabilised by a β -C–H agostic interaction^[19] or, less probably, by η^2 coordination of the vinyl

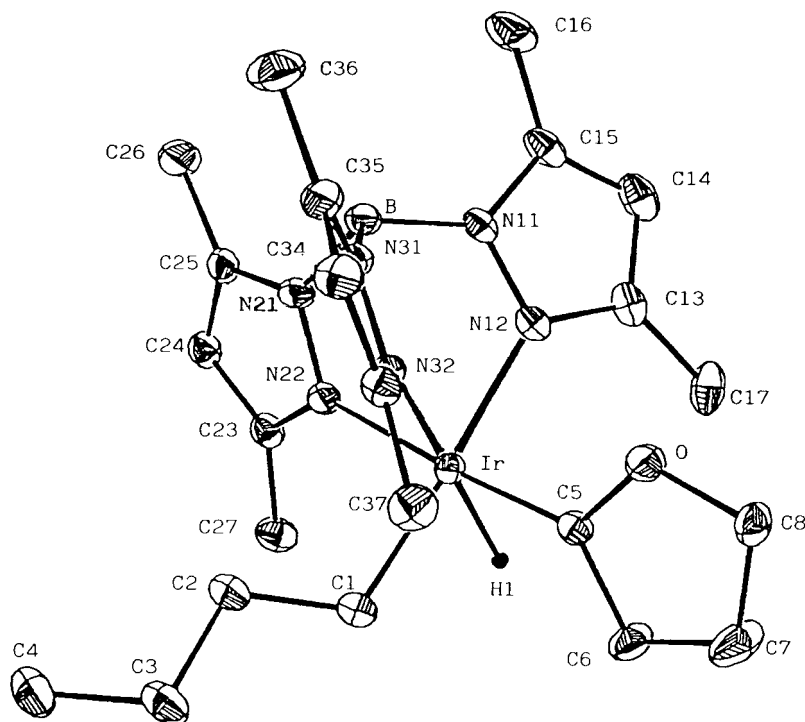
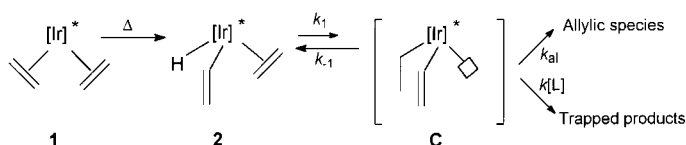
Figure 3. Molecular structure of the Fischer carbene **13**.

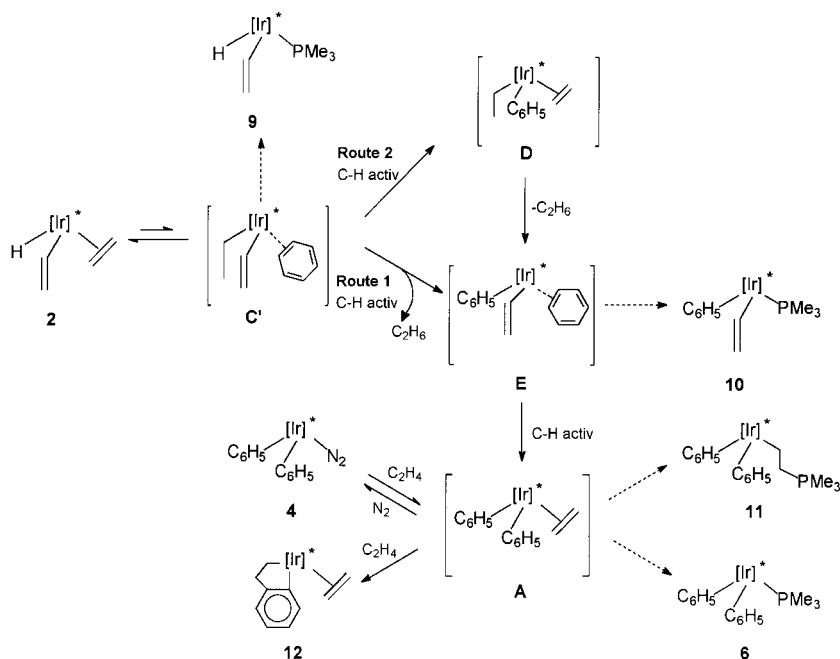
Table 4. Selected bond lengths [\AA] and angles [$^\circ$] for complex **13**.

Ir–C1	2.106 (5)	Ir–H1	1.8 (1)
Ir–C5	1.881 (5)	C5–C6	1.498 (7)
Ir–N12	2.150 (4)	C5–O	1.325 (8)
Ir–N22	2.148 (4)		
Ir–N32	2.171 (6)		
C1–Ir–N12	175.5 (2)	H1–Ir–C1	79(1)
C1–Ir–C5	92.0 (2)	Ir–C5–O	120.8 (4)
C5–Ir–N22	175.4 (2)	Ir–C5–C6	131.4 (5)
H1–Ir–N32	170.1 (1)	C6–C5–O	107.8 (5)
H1–Ir–C5	79 (1)		

Scheme 11. Proposed mechanism for the evolution of **2**.

ligand.^[20] In the absence of a suitable substrate, **C** is converted into hydride–allyl products in a C–C bond-forming rearrangement^[9b] whereas Lewis bases [pyridine, $\text{N}=\text{CR}$, DMSO; PMe_3 starting with **2**] lock the ethyl–vinyl structure and yield $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{CH}=\text{CH}_2)(\text{C}_2\text{H}_5)(\text{L})]$ adducts that display a different kind of reactivity.

Interestingly, and in contrast to soft substrates such as PMe_3 or CO ,^[9f] C_6H_6 is unable to displace ethylene directly from **1**, but, as illustrated in this and other reports,^[9c] **C** is able to induce the activation of the C–H bonds of aromatic molecules and of cyclic ethers through different reaction pathways that probably require prior coordination of the organic molecule to the Ir^{III} centre. In the case of C_6H_6 , the bis(phenyl) compound **4** is formed. From the nature of the liberated hydrocarbons, the dependence of k_{obs} on the concentration of benzene and the results of the trapping experiments carried out with PMe_3 , the sequence of events presented in Scheme 12 can be proposed for this transformation. Adducts

Scheme 12. Proposed mechanisms for the C–H bond activation of C_6H_6 by **2**.

containing weakly bound benzene^[21] are proposed as active intermediates and, whereas we have no direct evidence for their formation, the direct or indirect characterisation of related adducts that contain C_2H_4 in place of C_6H_6 , for example $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_4)]$ (vide infra), $[\text{Tp}^{\text{Me}_2}\text{IrH}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)]$ ^[9f] or $[\text{Tp}^{\text{Me}_2}\text{IrH}(\text{CH}=\text{CH}_2)(\text{C}_2\text{H}_4)]$ (**2**), can be taken to favour this hypothesis. Two alternative reaction pathways, routes 1 and 2, involving H transfer from the activated molecule of C_6H_6 to the Ir-bound carbon atom of the ethyl and to the vinyl hydrocarbon fragments, respectively, may be considered for the first C–H activation step. Proceeding along the first pathway (route 1, Scheme 12) the activated H_5C_6 –H atom could bind to the ethyl α -C, liberating C_2H_6 and forming intermediate **E**. The detection of the PMe_3 adduct **10** in the course of the trapping experiments previously described may be considered in support of this proposal. Alternatively (or additionally), **C'** could be converted into the ethyl–phenyl species **D** (route 2) by H transfer to the α -carbon of the vinyl group. Then **D** could undergo C_2H_6 elimination to give **E**, by means of a vinylic C–H activation similar to that occurring in other related species such as the postulated $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{CH}=\text{CH}_2)(\text{Et})(\text{C}_2\text{H}_4)]$ formed upon reaction of **2** with C_2H_4 .^[9b] This second mechanistic pathway is also in accord with the results of the THF activation reaction (see below). As discussed below, the generation in the latter process of an *n*-butyl chain is best rationalised by means of the migratory insertion of C_2H_4 into the Ir– C_2H_5 bond of an intermediate that results from H transfer to the vinyl α -C during the first C–H activation step of THF. If route 2 is the reaction pathway we have to conclude that the $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{R})(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)]$ intermediates evolve differently depending upon the nature of R (for $\text{R} = \text{C}_6\text{H}_5$ or $\text{CH}=\text{CH}_2$, by vinylic activation; and for $\text{R} = \text{C}_4\text{H}_7\text{O}$, by insertion).

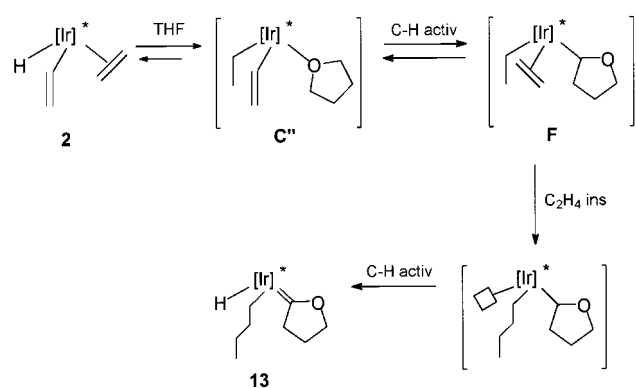
Intermediate **A** has not been isolated or detected by spectroscopic methods; nevertheless the formation of complexes **4**, **6**, **11** and **12** under the conditions of Scheme 12 argues in favour of the intermediary role assigned to this species. Its conversion into the N_2 complex **4** can be considered unusual for the following reasons. Firstly, whereas on electronic grounds and on the basis of the observed chemical behaviour the $\text{Tp}^{\text{Me}_2}\text{Ir}^{\text{III}}\text{–C}_2\text{H}_4$ bond is not expected to be particularly strong, several neutral complexes prepared in our laboratory are more stable towards extrusion of the olefin,^[22] and do not form ylides with PMe_3 , a reaction more typical of cationic ethylene derivatives.^[23] Secondly, replacement of the C_2H_4 ligand by N_2 (from the inert atmosphere) gives the Ir– N_2 compounds **4** and **5**, which have remarkable thermal stability: they survive prolonged heating at 60°C , under an atmosphere of N_2 . In marked contrast, the few known $\text{Ir}^{\text{III}}\text{–N}_2$ complexes exhibit poor thermal stability.^[16, 24]

It is conceivable that the instability of intermediate **A** towards loss of ethylene is

mostly steric in origin, a consequence of the steric congestion introduced by the two phenyl groups in the already sterically demanding $\{\text{Tp}^{\text{Me}_2}\text{Ir}\}$ fragment. Similar arguments may be used to explain the unexpected thermodynamic and kinetic stability of **4** and **5**. Electronic effects, albeit weak, operate in the right direction. A $\tilde{\nu}(\text{N}_2)$ absorption for **4** appears at 2190 cm^{-1} ; although this is in the high-energy limit for $\tilde{\nu}(\text{N}\equiv\text{N})$ in $\text{M}-\text{N}_2$ complexes (approximately $2210-1900\text{ cm}^{-1}$),^[16, 24] it is indicative of some $\text{Ir}-\text{N}_2$ back-donation. The small cone angle of the linear N_2 ligand also allows it to satisfy the coordination unsaturation of the $\{\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_6\text{H}_5)_2\}$ fragment without adding extra steric pressure. This, and the unavailability for these compounds of common low-energy decomposition pathways such as α - and β -H eliminations, could account for their enhanced kinetic stability. The formation of a $[\text{Tp}^{\text{Me}_2}\text{Ir}(\eta^2\text{-benzyne})]$ complex appears to be unfavourable and this decomposition route can be ruled out on the grounds that the reaction of $[\text{D}_0]\mathbf{4}$ with $[\text{D}_8]\text{THF}$ gives $[\text{D}_7]\mathbf{20}$ plus $\text{C}_6\text{H}_5\text{D}$.^[25]

The purported $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{CH}=\text{CH}_2)(\text{C}_2\text{H}_5)_2]$ intermediate **C** is also able to activate the sp^3 C–H bonds of cyclic ethers. This activation is regiospecific and involves two C–H bonds adjacent to the ether functionality. However, in this case the reaction yields, along with the C–H activation complex **13**, the hydride–allyl isomer **3** derived from the C–C coupling of the vinyl and the ethyl groups. Clearly, THF is much less efficient than C_6H_6 in the trapping of **C**. Tetrahydropyran is even less effective in this regard, to the point that no carbene product is generated in this reaction, only the hydride–allyl **3**. The enormous difference in the reactivity of **C** compared with C_6H_6 and cyclic ethers is additionally demonstrated by the formation of the phenyl–carbene complex **20** when **2** is heated in an approximately 400:1 THF– C_6H_6 mixture.

Scheme 13 summarises a plausible mechanistic pathway for this reaction. Coordination of the ether to the Ir^{III} centre



Scheme 13. Proposed mechanism for the formation of Fischer carbene complexes.

before C–H activation (intermediate **C''**) is supported by the detection of the THF adduct **B** of Scheme 10. Thereafter H transfer to the vinyl group would give intermediate **F**, which has the C_2H_4 and C_2H_5 ligands needed to construct the $n\text{-C}_4\text{H}_9$ chain by migratory insertion chemistry. In the final step, the vacant coordination site of the Ir centre is taken up by a hydride ligand resulting from an α -H elimination within the 2-

oxacyclopentyl–iridium linkage. The deuteration studies disclosed in the Results section indicate that both the coordination of THF and the first C–H activation step are reversible. Clearly, the second activation is driven by the high thermodynamic stability of Fischer carbene complexes of this kind.^[26, 27] In this transformation H transfer from THF to the $\text{Ir}-\text{C}_2\text{H}_5$ moiety of **C''** does not seem to occur; otherwise the n -butyl chain could not be formed. Nevertheless, it is unlikely that this is a very high-energy process, since the Ir^{III} derivatives $[\text{Tp}^{\text{Me}_2}\text{IrH}(\text{R})(\text{C}_2\text{H}_4)]$ ($\text{R}=\text{H}, \text{C}_2\text{H}_5$) give rise to the related complexes **18** and **19** (Scheme 9) in reactions that require a similar transfer to an $\text{Ir}-\text{C}_2\text{H}_5$ bond.

The activation of cyclic ethers presented in this paper constitutes a new, unprecedented route to cyclic Fischer carbene complexes. Before we made our original report^[10a] we were only aware of a photochemically induced radical process that produces an $\{\text{M}(\text{=}\overline{\text{C}}\text{C}(\text{CH}_2)_3\text{O})\}$ fragment.^[28] Subsequently, a series of $[\text{Os}(\text{H}_2)(\text{carbene})]$ complexes has been obtained directly from cyclic ethers,^[15] and other reports concerning similar activation of ethers, including Et_2O , have appeared in the literature.^[29, 30] Also, the formation of $\{\text{M}=\text{C}<\}$ fragments in reactions that give rise to double C–H bond activations has received attention recently.^[31] An important transformation that effects the removal of the two H atoms of $-\text{OCH}_2-$ groups is their oxidation, whether stoichiometric^[32] or catalytic,^[33] to the corresponding cyclic lactone.

There are two further important issues. The first concerns the $\text{Tp}^{\text{Me}_2}\text{Ir}^{\text{III}}$ formulation proposed for all active intermediates, which is in marked contrast to the participation of $\text{Cp}^*\text{Ir}^{\text{I}}$ species in the related C–H bond activations induced by iridium complexes of the cyclopentadienyl ligands. For example, whereas $[\text{Cp}^*\text{Ir}(\eta^2\text{-butene})]$ seems to be a relevant intermediate in the activation of C_6H_6 by $[\text{Cp}^*\text{IrH}(\eta^3\text{-C}_4\text{H}_7)]$,^[3] a low-energy route to an analogous $[\text{Tp}^{\text{Me}_2}\text{Ir}(\eta^2\text{-butene})]$ species, starting from the ethyl–vinyl intermediate **C**, does not seem feasible. As discussed at length previously,^[9b] this may be a consequence of the high propensity of the Tp' ligands to impose pseudooctahedral six-coordination of the metal centre, as first suggested by Curtis and co-workers.^[34] This is not a general situation, however, and the high stability of the Ir^{III} oxidation state is an additional important factor. Our own experience in the analogous Rh system^[9e] and the results of Graham,^[35] Jones,^[36] Bergman^[37] and co-workers for other related reactions, favour $\text{Tp}'/\text{Rh}^{\text{I}}$ intermediates. This fact has been addressed theoretically^[38] and may reflect the differences in the stability of the oxidation state for these two elements.

The second issue of concern relates to the detailed mechanism of the C–H bond activation, that is, whether it occurs through Ir^{V} intermediates formed by C–H oxidative addition or by σ -bond metathesis without a change in the oxidation state of the metal. In a previous section we have shown that there is evidence in support of the coordination of the ether to the metal before the H atom is transferred. For C_6H_6 , the evidence is (at best) indirect, but nonetheless the suggestion of η^2 -coordination is not unreasonable. This, however, does not answer the above question.^[39] The arguments of Maitlis^[4] in favour of C–H oxidative addition to $[\text{Cp}^*\text{IrMe}_2]$, however well-founded they may be, are not

directly applicable to our case because of the differences in the nature and behaviour of the Cp' and the Tp' ligands. For [Cp*IrMe(PMe₃)]⁺, recent theoretical studies also support this view.^[40] Tp'Ir^V is accessible, as demonstrated by the preparation in our laboratory of several stable Tp^{Me2}Ir^V compounds,^[41] most notably [Tp^{Me2}IrH₄].^[12] Moreover, {Tp^{Me2}Ir(R)(R')} fragments exhibit considerable electrophilicity at the metal, as demonstrated, for instance, by the reactivity of [Tp^{Me2}Ir(C₆H₅)₂(C₂H₄)], or the fact that CH₃CN is a very efficient reagent for trapping [Tp^{Me2}Ir(R)(R')] units, whilst PMe₃ is less effective and the strong π-acceptor carbon monoxide has a very low kinetic propensity for coordination.^[9b] Thus, oxidative addition to Ir^{III} is possible and may play a dominant role under conditions of not very severe steric hindrance, for example, when several of the remaining coordination positions are occupied by hydride ligands.^[41] In systems with very bulky environments (for example when R and R' are hydrocarbon groups), direct transfer from the coordinated substrate to R or R' (σ-bond metathesis) would seem a more reasonable mechanistic pathway. It is evident that further work is needed on these and related systems in order to clarify this important question.

Experimental Section

All preparations and manipulations were carried out under oxygen-free nitrogen or argon following conventional Schlenk techniques. Solvents were dried rigorously and degassed before use. Light petroleum, b.p. 40–60 °C, was used. The complexes [Tp^{Me2}Ir(C₂H₄)₂]^[2b] and [Tp^{Me2}IrH(R)(C₂H₄)] (R = H, Et)^[2f] were prepared according to literature procedures. Microanalysis were by Pascher Microanalytical Laboratory, Remagen (Germany) and the Microanalytical Service of the University of Sevilla (Spain). Infrared spectra were recorded on Perkin-Elmer 683 and 883 spectrometers, NMR spectra on Varian XL-200 and Bruker AMX-300 and AMX-500 spectrometers. The ¹H and ¹³C resonances of the solvent were used as internal standards, but chemical shifts are reported with respect to TMS. ³¹P NMR shifts were referenced to external 85% H₃PO₄. Most of the NMR assignments are based on extensive ¹H–¹H decoupling experiments, NOE-DIFF measurements and homo- and heteronuclear two-dimensional spectra (pyr = pyrazolyl).

Synthesis of the complexes 4 and 5: A solution of compound **1** (0.35 g, 0.55 mmol) in C₆H₆ (5 mL) was heated under N₂ at 60 °C for 3 h. The yellowish suspension was pumped off to dryness and the residue was treated with petroleum ether (15 mL). Upon concentration and cooling of the resulting solution to –20 °C, pale yellow crystals of **4** (0.1 g) were obtained. The remaining solid was extracted with a Et₂O–CH₂Cl₂ mixture (1:1, v/v; 20 mL). Filtration followed by concentration and cooling produced **5** (0.3 g) as pale yellow needles.

[Tp^{Me2}Ir(C₆H₅)₂(N₂)] (4): ¹H NMR (500 MHz, C₆D₆, 20 °C): δ = 8.32, 7.31, 7.03, 6.79, 6.57 (dt, td, tt, dt, dt, ³J(H,H) = 7.6, ⁴J(H,H) = 1.6 Hz, 2H each; *o*-, *m*-, *p*-, *m'*-, *o'*-H of the phenyl rings), 5.51, 5.46 (s, 2H, 1H; CH_{pyr}), 2.14, 2.09, 1.56, 1.14 (s, 6H, 3H, 6H, 3H; 6Me); ¹³C{¹H} NMR (125 MHz, C₆D₆, 20 °C): δ = 152.7, 151.1, 143.5, 143.2 (1:2:1:2; C_q (pyr)), 130.2 (C_q of the phenyl rings), 139.3, 135.2, 126.7, 126.6, 122.7 (CH of the phenyl rings), 108.4, 107.3 (1:2; CH_{pyr}), 15.8, 12.7, 12.5, 12.0 (1:2:1:2 ratio; 6Me); IR (Nujol): $\tilde{\nu}$ = 2190 cm⁻¹ (N≡N); C₂₇H₃₂BN₈Ir (671.6): calcd C 48.3, H 4.8, N 16.7; found C 47.5, H 4.9, N 15.9.

[Tp^{Me2}Ir(C₆H₅)₂(μ-N₂)] (5): ¹H NMR (500 MHz, C₆D₆, 20 °C): The spectrum of this very insoluble material consists in the aromatic region (9.2–6.2) of a complex pattern of multiplets that are in accord with the presence of two sets of slowly rotating phenyl rings; that is, there is no effective symmetry element interchanging the two halves of the molecules; Raman: $\tilde{\nu}$ = 2130 cm⁻¹ (N≡N); C₃₄H₄₆B₂N₁₄Ir₂ (1316.5): calcd C 49.2, H 4.9, N 14.9; found C 49.4, H 5.0, N 14.6.

Synthesis of the complexes 6, 7 and 8: Neat PMe₃ (0.02 mL, 0.2 mmol) was added to a solution of **4** (0.1 g, 0.16 mmol) in C₆H₆ (10 mL). The reaction mixture was heated at 60 °C for 3 h. The volatiles were removed under vacuum and the residue was dissolved in petroleum ether (10 mL). After partial evaporation, the solution was cooled at –20 °C affording **6** as pale brown crystals (70% yield). Compound **7** was prepared, in a similar way, in a Fisher–Porter bottle pressurised with CO (2 atm) and was obtained in 80% yield as pale brown crystals. By the same procedure, complex **8** was synthesised as yellow crystals in 77% yield.

[Tp^{Me2}Ir(C₆H₅)₂(PMe₃)] (6): ¹H NMR (200 MHz, C₆D₆, 20 °C): δ = 7.97, 6.89, 6.67, 6.41, 6.29 (dt, td, tt, dt, dt, ³J(H,H) = 7.4, ⁴J(H,H) = 1.6 Hz, 2H each; *o*-, *m*-, *p*-, *m'*-, *o'*-H of the phenyl rings), 5.84, 5.65 (s, 2H, 1H; CH_{pyr}), 2.51, 2.43, 1.49, 0.57 (s, 6H, 3H, 6H, 3H; 6Me), 1.45 (d, 9H, ²J(P,H) = 9.5 Hz; PMe₃); ¹³C{¹H} NMR (50 MHz, CD₃COCD₃, 20 °C): δ = 151.5, 151.3, 144.8, 143.5 (1:2:2:1; C_q (pyr)), 131.8 (d, ²J(P,C) = 8 Hz; C_q of the phenyl rings), 143.0, 141.1, 125.5, 125.3, 121.3 (s, d, s, s, s, ¹J(P,C) = 5 Hz; CH of the phenyl ring), 108.8, 108.4 (d, s, 2:1, ⁴J(P,C) = 4 Hz; CH_{pyr}), 17.3 (d, ¹J(P,C) = 37 Hz; PMe₃), 16.8, 14.8, 13.2, 13.1 (2:1:2:1; 6Me); ³¹P{¹H} NMR (80 MHz, C₆D₆, 20 °C): δ = –52.2; C₃₀H₄₁BN₆IrP (720.3): calcd C 50.0, H 5.7, N 11.7; found C 51.1, H 6.3, N 10.8.

[Tp^{Me2}Ir(C₆H₅)₂(CO)] (7): ¹H NMR (200 MHz, C₆D₆, 20 °C): δ = 8.46, 7.24, 7.00, 6.77, 6.68 (dt, td, tt, dt, dt, ³J(H,H) = 7.5, ⁴J(H,H) = 1.6 Hz, 2H each; CH of the phenyl rings), 5.52, 5.47 (s, 1H, 2H; CH_{pyr}), 2.11, 2.10, 1.66, 1.17 (s, 6H, 3H, 6H, 3H; 6Me); ¹³C{¹H} NMR (50 MHz, C₆D₆, 20 °C): δ = 169.7 (CO), 152.6, 151.3, 143.4 (1:2:3; C_q (pyr)), 129.2 (C_q of the phenyl rings), 138.8, 138.1, 127.1, 123.0 (1:1:2:1; CH of the phenyl rings), 108.3, 107.2 (1:2; CH_{pyr}), 15.3, 13.7, 12.3, 12.1 (1:2:1:2; 6Me); IR (Nujol): $\tilde{\nu}$ = 2026 cm⁻¹ (CO); C₂₈H₃₂BN₆IrO (672.2): calcd C 50.0, H 4.8, N 12.5; found C 50.0, H 5.2, N 12.1.

[Tp^{Me2}Ir(C₆H₅)₂(CNtBu)] (8): ¹H NMR (200 MHz, C₆D₆, 20 °C): δ = 8.43, 7.35, 7.07, 6.85 (d, t, m, m, 2H, 2H, 2H, 4H; CH of the phenyl rings), 5.66, 5.63 (s, 2H, 1H; CH_{pyr}), 2.20, 1.73, 1.32, 1.00 (s, 6H, 6H, 3H, 3H; 6Me), 1.00 (s, 9H; CMe₃); ¹³C{¹H} NMR (75 MHz, C₆D₆, 20 °C): δ = 151.9, 150.8, 142.9, 142.7 (C_q (pyr)), 132.9 (C_q of the phenyl rings), 140.2, 137.7, 126.4, 126.0, 121.6 (CH of the phenyl rings), 107.9, 106.8 (1:2; CH_{pyr}), 56.4 (CMe₃), 30.0 (CMe₃), 15.6, 13.8, 12.5, 12.3 (1:2:1:2; 6Me). The IrCNtBu was not located; IR (Nujol): $\tilde{\nu}$ = 2163 cm⁻¹ (CN); C₃₂H₄₁BN₇Ir (727.3): calcd C 52.8, H 5.7, N 13.5; found C 53.0, H 5.9, N 13.9.

Synthesis of [Tp^{Me2}Ir(C₆H₅)₂(CH₂CH₂PMe₃)] (11): Neat PMe₃ (0.1 mL, 0.1 mmol) was added to a solution of **1** (0.1 g, 0.18 mmol) in C₆H₆ (2 mL). The reaction mixture was heated at 60 °C for 3 h to give a yellow solution and a white solid. The volatiles were removed under vacuum and the residue was investigated by ¹H NMR. The zwitterionic species **11** was detected in 80% yield. This complex was purified by recrystallisation from Et₂/CH₂Cl₂ mixtures (1:1). ¹H NMR (300 MHz, [D₆]DMSO, 20 °C): δ = 7.62, 6.77, 6.43, 6.25 (d, t, t, m, ³J(H,H) = 7.3 Hz, 2H, 2H, 2H, 4H; CH of the phenyl rings), 5.74, 5.66 (s, 1H, 2H; CH_{pyr}), 2.39, 2.38, 1.20, 0.68 (s, 3H, 6H, 6H, 3H; 6Me), 1.91, 1.13 (m, 2H, 2H; CH₂P, IrCH₂), 1.57 (d, ²J(H,P) = 14 Hz, 9H; PMe₃); ¹³C{¹H} NMR (75 MHz, [D₆]DMSO, 20 °C): δ = 149.0, 148.1, 145.3, 141.4 (2:1:1:2; C_q (pyr)), 140.4 (C_q of the phenyl rings), 142.1, 135.6, 124.1, 123.2, 117.2 (C–H of the phenyl rings), 106.4, 106.0 (2:1; CH_{pyr}), 26.0 (d, ¹J(C,P) = 35 Hz; CH₂P), 15.1, 12.7, 12.6, 12.4 (1:2:1:2; 6Me), 7.0 (d, ¹J(C,P) = 53 Hz; PMe₃), –17.0 (d, ²J(C,P) = 10 Hz; IrCH₂); ³¹P{¹H} NMR (120 MHz, [D₆]DMSO, 20 °C): δ = 20.1; C₃₂H₄₅BN₆IrP (748.3): calcd C 51.3, H 6.1, N 11.2; found C 51.0, H 5.7, N 11.1.

Reaction of [Tp^{Me2}Ir(C₆H₅)₂N₂] with C₂H₄: The dinitrogen complex **4** was dissolved in C₆H₆ and heated at 60 °C under C₂H₄ (1 atm) for 3 h. The resulting solution was taken to dryness and the residue analysed by ¹H NMR. The metallocyclic compound [Tp^{Me2}Ir(CH₂CH₂-*o*-C₆H₄)(C₂H₄)] (**12**) was observed in 70% yield along with other unidentified species. ¹H NMR (300 MHz, C₆D₆, 20 °C): δ = 7.28, 7.19, 7.05, 6.84 (d, d, t, t, ³J(H,H) = 7.6 Hz, 1H each; CH of the phenyl ring), 5.67, 5.58, 5.28 (s, 1H each; CH_{pyr}), 3.94, 3.57 (m, AA'XX' spin system, C₂H₄), 3.52, 3.24, 2.90 (dd, t, t, dd, 1:1:1:1, ³J(H,H) = 17.0, ³J(H,H) = 10.3, ³J(H,H) = 9.4, ³J(H,H) = 8.5 Hz; Ir–CH₂CH₂), 2.22, 2.16, 2.13, 2.09, 1.97, 1.52 (s, 3H each; 6Me); ¹³C{¹H} NMR (75 MHz, C₆D₆, 20 °C): δ = 159.1 (C_q of the phenyl ring), 151.6, 150.1, 149.2, 142.5 (1:1:1:1:2; C_q (pyr)), 137.4 (C_q of the phenyl ring), 135.0, 123.6, 122.8, 121.6 (1:1:1:1; CH of the phenyl ring), 109.1, 108.5, 108.4 (1:1:1; CH_{pyr}), 59.2 (¹J(C,H) = 162 Hz; C₂H₄), 40.8 (Ir–CH₂CH₂), 14.7, 14.5, 12.8, 12.7, 12.4 (1:1:1:1:2; 6Me), –4.4 (Ir–CH₂CH₂).

Synthesis of the complexes 13 and 14: A solution of **1** (0.15 g, 0.27 mmol) in THF (10 mL) was heated at 60 °C for 8 h. After removal of the volatiles ¹H NMR of the residue showed the presence of two compounds in a 1:1 ratio, identified as the hydride–allyl species **3** and the carbene **13**. They were isolated as white and yellow microcrystalline powders, respectively, by fractional crystallisation from petroleum ether solution. With 2-MeTHF the two diastereoisomers **14** were obtained by the same procedure (55 % by ¹H NMR) and crystallised from petroleum ether.

[Tp^{Me}IrH(CH₂CH₂CH₂CH₃)=C(CH₂)₂O] (13): ¹H NMR (500 MHz, C₆D₆, 20 °C): δ = 5.80, 5.67, 5.61 (s, 1 H each; CH_{pyr}), 3.8 (m, 2 H; OCH₂), 3.4, 1.97 (m, 1 H each; Ir–CH₂Pr), 2.70, 2.25, 2.18, 2.15, 2.14, 1.80 (s, 3 H each; 6 Me), 2.13 (m, 2 H; Ir=CCH₂), 1.77 (m, 2 H; (CH₂)₂CH₂CH₃), 1.47, 1.35 (m, 1 H each; CH₂CH₂Et), 1.32 (m, 2 H; CH₂CH₂CH₂O), 1.15 (t, ³J(H,H) = 7.5 Hz, 3 H; (CH₂)₃CH₃), –17.90 (s, 1 H; IrH); ¹³C{¹H} NMR (125 MHz, C₆D₆, 20 °C): δ = 258.8 (Ir=C), 152.1, 148.9, 148.0, 143.6, 142.8, 142.5 (6 C_q (pyr)), 106.0, 105.8, 104.8 (CH_{pyr}), 78.2 (¹J(C,H) = 150 Hz; CH₂O), 56.6 (¹J(C,H) = 129 Hz; Ir=CCH₂), 36.2 (CH₂CH₂Et), 28.0 ((CH₂)₂CH₂CH₃), 22.8 (¹J(C,H) = 132 Hz; CH₂CH₂CH₂O), 15.0 ((CH₂)₃CH₃), 14.6, 14.4, 13.3, 12.4, 12.2 (1:1:1:2:1; 6 Me), –12.2 (¹J(C,H) = 120 Hz; IrCH₂); IR (Nujol): $\tilde{\nu}$ = 2128 cm⁻¹ (IrH); C₂₃H₃₈BN₆IrO (617.6); calcd C 44.7, H 6.1, N 13.6; found C 43.7, H 6.3, N 13.0.

[Tp^{Me}IrH(CH₂CH₂CH₂CH₃)=C(CH₂)₂CH(Me)O] (14): As mentioned above, this compound was obtained as a 1:1 mixture of diastereoisomers. ¹H NMR (200 MHz, C₆D₆, 20 °C): δ = –18.12, –17.98 (IrH); ¹³C{¹H} NMR (50 MHz, C₆D₆, 20 °C): δ = 260.0 (Ir=C), 87.9, 87.5 (OCHMe), 57.5, 56.8 (Ir=CCH₂), –12.0, 12.4 (IrCH₂).

Synthesis of the complexes 15, 16 and 17: A solution of **1** (0.15 g, 0.28 mmol) in 1,3-dioxane (5 mL) was heated at 60 °C for 8 h. The residue obtained after the evaporation of the solvent was studied by ¹H NMR spectroscopy, which confirmed the presence of the hydride–allyl species **3** and the two carbene isomers **15** and **16** in a 1:2.5:1.5 ratio. Complexes **15** and **16** could not be isolated separately by fractional crystallisation, but both were characterised spectroscopically as a mixture. Complex **17** was obtained similarly from dioxane.

[Tp^{Me}IrH(CH₂CH₂CH₂CH₃)=C(O)(CH₂)₂O] (15): ¹H NMR (500 MHz, C₆D₆, 20 °C): δ = 5.77, 5.64, 5.55 (s, 1 H each; CH_{pyr}), 3.23 (s, 4 H; OCH₂CH₂O), 3.08, 1.86 (m, 1 H each; IrCH₂Pr), 2.67, 2.23, 2.15, 2.13, 2.02, 1.76 (s, 3 H each; 6 Me), 1.55 (m, 2 H; (CH₂)₂CH₂CH₃), 1.3 (m, 2 H; CH₂CH₂Et), 0.98 (t, ³J(H,H) = 7.3 Hz, 3 H; (CH₂)₃CH₃), –17.66 (s, 1 H; IrH); ¹³C{¹H} NMR (125 MHz, C₆D₆, 20 °C): δ = 206.4 (Ir=C), 151.9, 148.9, 147.9, 143.6, 142.7, 142.4 (C_q (pyr)), 106.2, 106.0, 105.0 (C–H_{pyr}), 67.2 (OCH₂), 36.5 (CH₂CH₂Et), 27.7 ((CH₂)₂CH₂CH₃), 15.0 ((CH₂)₃CH₃), 14.7, 14.6, 13.3, 12.4, 12.1 (1:1:1:2:1; 6 Me), –12.2 (IrCH₂); IR (Nujol): $\tilde{\nu}$ = 2140 cm⁻¹ (IrH); C₂₂H₃₆BN₆IrO₂ (619.6); calcd C 42.9, H 5.8, N 14.3; found C 43.9, H 5.6, N 13.7. These microanalytical data are for the **15/16** mixture.

[Tp^{Me}IrH(CH₂CH₂CH₂CH₃)=C(CH₂O)(CH₂)₂O] (16): ¹H NMR (500 MHz, C₆D₆, 20 °C): δ = 5.82, 5.64, 5.62 (s, 1 H each; CH_{pyr}), 4.75 (almost collapsed AB system, 2 H; OCH₂O), 3.63, 3.51 (AB quartet, ²J(H,H) = 17 Hz, 2 H; Ir=CCH₂), 2.86, 2.07 (m, 1 H each; IrCH₂Pr), 2.67, 2.26, 2.20, 2.18, 2.16, 1.96 (s, 3 H each; 6 Me), 1.69 (2 H; (CH₂)₂CH₂CH₃), 1.62, 1.60 (m, 2 H; CH₂CH₂Et), 1.10 (t ³J(H,H) = 7.3 Hz, 3 H; (CH₂)₃CH₃), –18.59 (s, 1 H; IrH); ¹³C{¹H} NMR (125 MHz, C₆D₆, 20 °C): δ = 151.1, 148.8, 147.9, 143.0, 142.4, 142.0 (6 C_q (pyr)), 106.0, 105.8, 104.7 (CH_{pyr}), 103.1 (OCH₂O), 92.2 (Ir=CCH₂), 35.5 (CH₂CH₂Et), 28.1 ((CH₂)₂CH₂CH₃), 15.1 ((CH₂)₃CH₃), 14.4, 14.2, 13.5, 12.3, 12.2 (1:1:1:2:1; 6 Me), –12.4 (IrCH₂); IR (Nujol): $\tilde{\nu}$ = 2130 cm⁻¹ (IrH).

[Tp^{Me}IrH(CH₂CH₂CH₂CH₃)=C(CH₂O)(CH₂)₂O] (17): ¹H NMR (300 MHz, C₆D₆, 20 °C): δ = 5.83, 5.66, 5.60 (s, 1 H each, CH_{pyr}), 3.78, 3.70 (AB quartet, ²J(H,H) = 20 Hz, 2 H; Ir=CCH₂), 3.39, 3.31 (m; OCH₂), 3.31, 1.18 (m, 1 H each; IrCH₂Pr), 3.18 (m, 2 H; OCH₂), 2.67, 2.23, 2.14, 2.13, 1.89 (s; 6 Me), 1.56 (m, 2 H; (CH₂)₂CH₂CH₃), 1.12, 0.97 (m, 2 H; CH₂CH₂Et), 0.96 (t, ³J(H,H) = 7.3 Hz, 3 H; (CH₂)₃CH₃), –18.9 (s, 1 H; IrH); ¹³C{¹H} NMR (75 MHz, C₆D₆, 20 °C): δ = 255.8 (Ir=C), 151.9, 148.7, 147.9, 143.5, 142.6, 142.3 (6 C_q (pyr)), 86.4 (Ir=CCH₂), 69.2 (CH₂O), 62.2 (CH₂O), 35.6 (CH₂CH₂Et), 27.7 ((CH₂)₂CH₂CH₃), 15.2 ((CH₂)₃CH₃), 14.4, 14.3, 13.3, 12.4, 12.2 (1:1:1:2:1; 6 Me), –11.7 (IrCH₂); IR (Nujol): $\tilde{\nu}$ = 2120 cm⁻¹ (IrH); C₂₃H₃₈BN₆IrO₂ (633); calcd C 43.5, H 6.0, N 13.3; found C 43.8, H 6.2, N 13.1.

Synthesis of complexes 18 and 19: A solution of the compound [Tp^{Me}IrH₂(C₂H₄)] (0.04 g, 0.08 mmol) in THF (10 mL) was heated at 60 °C for 12 h. The solution was pumped off and the residue was dissolved in C₆D₆ and analysed by ¹H NMR spectroscopy, which showed that **18** was the only product. The ethyl derivative **19** was prepared similarly, but with [Tp^{Me}IrH(C₂H₅)(C₂H₄)] as the starting material. It was obtained as a yellow microcrystalline solid from petroleum ether solutions.

[Tp^{Me}IrH₂(C(CH₂)₂O)] (18): ¹H NMR (500 MHz, C₆D₆, 20 °C): δ = 5.73, 5.58 (s, 2 H, 1 H; CH_{pyr}), 3.61 (t, 2 H; OCH₂), 2.32 (t, 2 H; Ir=CCH₂), 2.67, 2.27, 2.18, 1.95 (s, 3 H, 6 H, 3 H, 6 H; 6 Me), 1.11 (q, ³J(H,H) = 7.5 Hz, 2 H; CH₂CH₂CH₃), –16.94 (s, 2 H; IrH); ¹³C{¹H} NMR (125 MHz, C₆D₆, 20 °C): δ = 258.0 (Ir=C), 151.7, 148.5, 143.0, 142.5 (1:2:1:2, 6 C_q (pyr)), 105.1, 104.8 (1:2, CH_{pyr}), 77.9 (OCH₂), 62.8 (Ir=CCH₂), 23.1 (CH₂CH₂CH₃), 17.2, 15.2, 12.2 (1:2:3, 6 Me).

[Tp^{Me}IrH(CH₂CH₃)=C(CH₂)₂O] (19): ¹H NMR (300 MHz, C₆D₆, 20 °C): δ = 5.80, 5.67, 5.61 (s, 1 H each; CH_{pyr}), 3.67 (m, 2 H; OCH₂), 3.35 (dq, ²J(H,H) = 12.2 Hz, 1 H; IrCH_AH_BCH₃), 2.75, 2.27, 2.19, 2.18, 2.02, 1.80 (s, 3 H each; 6 Me), 2.0 (m, 1 H; IrCH_AH_BCH₃), 2.0 (m, 2 H; Ir=CCH₂), 1.15 (m, 2 H; CH₂CH₂CH₂), 1.14 (t, ³J(H,H) = 7.8 Hz, 3 H; IrCH₂CH₃), –17.92 (s, 1 H; IrH); ¹³C{¹H} NMR (75 MHz, C₆D₆, 20 °C): δ = 258.5 (Ir=C), 151.8, 148.6, 147.7, 143.3, 142.5, 142.2 (6 C_q (pyr)), 106.0, 105.8, 104.8 (CH_{pyr}), 78.3 (¹J(C,H) = 154 Hz; OCH₂), 56.5 (¹J(C,H) = 128 Hz; Ir=CCH₂), 22.8 (CH₂CH₂CH₂), 18.0 (IrCH₂CH₃), 15.0, 14.6, 13.3, 12.4, 12.2 (1:1:1:2:1; 6 Me), –20.9 (IrCH₂); IR (Nujol): $\tilde{\nu}$ = 2127 cm⁻¹ (IrH); C₂₁H₃₄BN₆IrO (589); calcd C 42.9, H 5.8, N 14.3; found C 43.9, H 5.6, N 13.7.

Synthesis of [Tp^{Me}IrH(C₆H₅)=C(CH₂)₂O] (20): A solution of **4** (0.12 g, 0.18 mmol) in THF (10 mL) was heated at 60 °C for 3 h. The solvent was removed under vacuum and the residue was extracted with petroleum ether (15 mL). Filtration, concentration and cooling of the resulting solution at –20 °C afforded complex **20** as a microcrystalline solid (52 % yield). ¹H NMR (500 MHz, C₆D₆, 20 °C): δ = 8.70, 7.37, 7.08, 6.92, 6.85 (br d, br t, t, br t, br d, 1 H each; C₆H₅), 5.83, 5.65, 5.51 (s, 1 H each; CH_{pyr}), 3.71, 3.56 (m, 1 H, 1 H; OCH₂), 2.32, 2.22, 2.15, 1.92, 1.86, 1.59 (s, 3 H each; 6 Me), 2.30, 2.09 (m, 1 H, 1 H; Ir=CCH₂), 1.03 (m, 2 H; CH₂CH₂CH₂), –17.31 (s, 1 H; IrH); ¹³C{¹H} NMR (125 MHz, C₆D₆, 20 °C): δ = 262.7 (Ir=C), 152.8, 148.7, 148.6, 143.1, 142.9, 142.7 (6 C_q (pyr)), 137.2 (C_q of the phenyl ring), 145.8, 139.9, 125.9, 120.9 (1:1:1:2; CH of the phenyl ring), 106.3, 106.1, 105.9 (CH_{pyr}), 79.3 (OCH₂), 55.6 (Ir=CCH₂), 22.1 (CH₂CH₂CH₂), 15.0, 14.8, 14.4, 12.7, 11.8, 11.7 (6 Me); IR (Nujol): $\tilde{\nu}$ = 2132 cm⁻¹ (IrH); C₂₅H₃₄BN₆IrO (638.3); calcd C 47.0, H 5.4, N 13.2; found C 46.9, H 5.3, N 13.0.

Crystal structure determinations of 5 and 13

Compound 5: A yellow prism-shaped crystal of complex **5** was coated with epoxy resin and mounted on a kappa diffractometer. The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections. The intensities were corrected for Lorentz and polarisation effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ir were taken from ref. [42]. The structure was solved by Patterson and Fourier methods. An empirical absorption correction^[43] was applied at the end of the isotropic refinement. A final mixed refinement was undertaken with fixed isotropic factors and coordinates for H atoms. Most of the calculations were carried out with the X-Ray 80 system.^[44]

Compound 13: A pale green crystal was mounted on the diffractometer and the cell dimensions were refined by least-squares fitting of the setting angles of 25 reflections. Three reflections monitored periodically during data collection revealed no crystal decomposition. The intensities were corrected for Lorentz and polarisation effects. Scattering factors for neutral atoms and an anomalous dispersion correction for the Ir atom were taken from ref. [42]. The structure was solved by Patterson and Fourier methods. An empirical absorption correction^[43] was applied at the end of the isotropic refinement. The H1 atom was located in a final difference Fourier synthesis at the highest peak of the map. In order to prevent bias on ΔF versus F_0 or $(\sin \theta)/\lambda$, the last steps of the refinement were carried out with weights $w = 1/(a + bF_0)^2$. A final refinement was performed with fixed isotropic temperature factors and calculated positions for H atoms (except for H1, the coordinates of which were refined). X-Ray 80 was used for most of the calculations.^[44] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications, refcode YEBLIA for complex **5** and refcode PALTUR for complex **13**. Copies of the data can be obtained free of charge on application to CCDC,

12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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