Formation of 1,2,3-η³-butadienyl derivatives by photochemical C–H activation of Ir(I)-η⁴-1,3-diene complexes containing tris(pyrazolyl)borate ligands [1]

Olivier Boutry, Manuel L. Poveda *, Ernesto Carmona*

Departamento de Química Inorgánica-Instituto de Investigaciones Químicas, Universidad de Sevilla-Consejo Superior de Investigaciones Científicas, Apdo. 553, 41071 Seville, Spain

Abstract

Several Ir(I) complexes of composition [Tp′Ir(diene)], where Tp′ = hydrotris(1-pyrazolyl)borate, Tp or hydrotris(3,5-dimethyl-1-pyrazolyl)borate, Tp * and diene = conjugated diene, have been prepared by treating [Ir(μ-Cl)(coe)$_2$]$_2$ with the appropriate diene and then with KTp′. The series of related complexes [Tp * Ir(η⁴-2,3-RR′C$_4$H$_4$)] (R, R′ = H, 3; R = Me, R′ = H, 4; R, R′ = Me, 5) has been chosen for comparative studies on photochemical C–H bond activation reactions. These have been demonstrated to occur only at the C–R and C–R′ moieties. Both vinylic and allylic (CH$_3$) activations have been found for compound 4 (R = Me, R′ = H), while 3 seems to undergo exclusively central C–H vinylic addition to the metal centre with only low efficiency. The dimethyl substituted diene ligand of 5 is readily activated at one of the methyl groups, yielding the hydrido-allyl complex [Tp * Ir(H)(η³-CH$_2$C(C(Me)=CH$_2$)CH$_2$)] 11. The thermal activation of C$_6$H$_6$ by compound 5 to give the N$_2$-bridged binuclear species [Tp * Ir(H)(C$_6$H$_5$)]$_2$(μ-N$_2$) 12 is also reported.

Keywords: Ir complexes; C–H activation; Diene complexes

1. Introduction

Transition metal complexes of 1,3-dienes have played an important role in developing and understanding the chemistry of organic molecules bonded to metal fragments [1]. M-η⁴-diene derivatives are reactive intermediates in many catalytic processes and are also useful stoicheiometric reagents in organic synthesis [2]. They are known to undergo a variety of reactions that include coupling with olefin, acyl or other organic moieties as well as addition of both nucleophilic and electrophilic reagents [1–3].

Whilst photochemical transformations of, for example, metal carbonyls and 1,3-dienes may provide products resulting not only from carbonyl substitution but also from isomerizations due to H shifts, C–C bond formation and C–H cleavage reactions [4], well-defined examples of the direct addition of one of the diene C–H bonds to the transition metal atom are very scarce. This contrasts with the large number of complexes that arise

from the activation of the C–H bonds of simple alkenes. Butadienyl complexes are known, but metallation at, for instance, C$_2$ to provide compounds with structure of type **A** or **B** is usually achieved by deprotonation or desilylation of cationic η⁴-butadiene derivatives or by other indirect methods [5,6]. A recent preliminary communication has described what appears to be the first example of the activation of the terminal alkenic C–H bonds of coordinated 1,3-dienes [7], to give a complex structurally related to **C**.
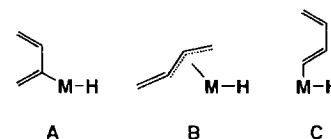
In the last few years we have shown that the complex [Tp * Ir(C$_2$H$_4$)$_2$] (Tp * = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) [8] is able to participate in a variety of C–H bond activations, including those of aromatic substrates [9] and cyclic ethers [10]. We now wish to report

* Corresponding authors.
[1] Dedicated to Professor M.L.H. Green, leading contemporary organometallic chemist, on the occasion of his sixtieth birthday.
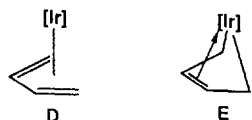
that the readily prepared [Tp* Ir(η⁴-1,3-diene)] can be photochemically activated to produce hydrido-1,2,3-η³-butadienyl species.
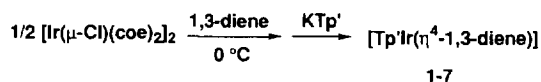
2. Results and discussion

2.1. Synthesis and spectroscopic characterization of [Tp'Ir(η⁴-1,3-diene)] complexes

The new complexes described in this work are best prepared following a synthetic route similar to that used for the synthesis of the bis(ethylene) derivatives [11–13], namely by treatment of the dimer [Ir(μ-Cl)(coe)₂]₂ (coe = cyclooctene) with the appropriate diene, followed by addition of the KTp' salt (Scheme 1). Work-up of the reaction mixtures affords the corresponding complexes 1–7 in good yields, in the form of white to pale yellow crystalline solids.

Analytical and NMR spectroscopic data are in accord with the proposed formulation, ¹H and ¹³C resonances of the diene moiety being particularly useful for structural characterization purposes. The diene ligand is bonded to the Ir centre in the expected η⁴-s-cis conformation, as shown schematically in D.

Fig. 1. Experimental and simulated spectra of complex 3. See Section 3 for assignments.

It is interesting to note that the terminal carbon atoms of the diene ligands resonate invariably at fairly high fields, e.g. 3.9 ppm in 3. This may suggest an important contribution of resonance form E to the electronic ground-state structure of this molecule. A similar proposal, which is in agreement with the results of photoelectron spectroscopy studies carried out on similar complexes [14], has been advanced for the somewhat related cyclopentadiene complex [CpIr(η⁴-C₅H₆)] [15]. We note, however, that the ¹J(CH) values remain nor-

mal for coordinated olefins (in the range 150–170 Hz) and on this basis we prefer to describe compounds 1–7 as Ir(I) species (as opposed to the Ir(III) formulation implied by resonance structure E), with important back-donation from the electron-rich Ir(I) centre to the coordinated diene. Not unexpectedly, the ¹H NMR spectra of some of the diene complexes 1–7 exhibit second-order effects within the diene entities. Full sets of coupling constants for these compounds have been obtained by computer simulation (see Section 3), a representative case is illustrated in Fig. 1.

A final question regarding the characterization of compounds 1–7 concerns the hapticity of the tris(pyrazolyl)borate ligand, a problem often difficult to unveil in Rh(I) and Ir(I) compounds of this type [16]. These complexes are often fluxional and the solid-state structure may be different from that found in solution. The Tp' derivatives 1–7 display variable fluxionality, the faster rates of exchange correspond to the more sterically congested ligand distributions around the iridium centre. Thus, while a 2:1 arrangement is found, at room temperature, for the pyrazolyl rings of [TpIr(CH₂=CHCH=CH₂)] 1, the more sterically encumbered [Tp* Ir(CH₂=C(Me)C(Me)=CH₂] 5 exhibits chemically equivalent pyrazolyl rings under the same conditions. Similar to the situation found for other [Tp'Ir(olefin)₂] complexes [16,17], the fluxional behaviour of our compounds may be interpreted as associated with five-coordinate, 18-electron ground-state solution structures with the respective square-planar, 16-

Tp' ligand	Tp	Tp	Tp*	Tp*	Tp*	Tp*	Tp*
Diene		Me Me		Me	Me Me		
Compound	1	2	3	4	5	6	7

Scheme 1.

electron formulations being readily accessible. As the steric pressure of the ligands increases the equilibration between the two types of structure becomes easier.

2.2. C–H photochemical activation of [Tp* Ir(η⁴-1,3-diene)] complexes

Work carried out in our laboratory [17,18] has shown that the activation of one of the C–H bonds of a coordinated C_2H_4 ligand in [Tp* Ir(C₂H₄)₂] proceeds either thermally or photochemically, with formation of the isomeric hydrido-vinyl complex [Tp* Ir(H)(C₂H₃)(C₂H₄)], as shown in Eq. (1). Similarly, photochemical activation of the unsubstituted Tp derivative [TpIr(C₂H₄)₂] affords the corresponding hydrido-vinyl [12].

$$[Tp^*Ir(C_2H_4)_2] \xrightarrow{\Delta\ or\ hv} [Tp^*Ir(H)(C_2H_3)(C_2H_4)] \quad (1)$$
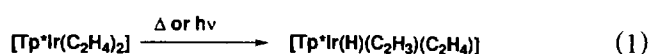
During the course of our studies on iridium complexes of the tris(pyrazolyl)borate ligands [9,10,17], we have found that the Tp* derivatives display distinctively higher reactivity towards C–H activation reactions than the Tp analogues. Consequently we have chosen the related complexes [Tp* Ir(η⁴-1,3-diene)] in which the 1,3-diene is C_4H_6, 3; 2-Me-C_4H_5, 4; or 2,3-Me₂-C_4H_4, 5 to carry out photochemical studies aimed at C–H activation within the diene ligand.

The butadiene derivative 3 is very resistant to photochemical activation, but upon prolonged photolysis at room temperature (50 h) ca. 40% conversion to a hydrido-allyl isomer 8 and to other unidentified species is observed.

$$\text{(2)}$$

[Ir]* = Tp*Ir
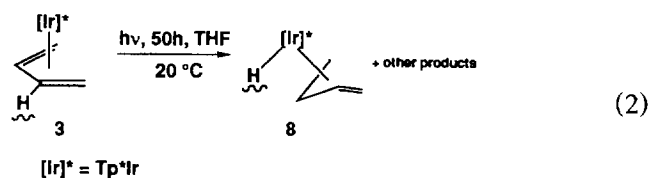
Following chromatographic separation (silica gel) complex 8 can be isolated in ca. 20% yield. This species should be more adequately described as a 1,2,3-η³-butadienyl derivative, a rather unexplored type of organometallic compound whose characteristics have been reviewed recently [6]. ¹H, ¹³C and ¹H–¹³C HETCOR sudies are in accord with the proposed structure. The endo conformation assigned to the allylic moiety is based on NOEDIFF measurements (throughout this paper we use the exo–endo and syn–anti conventional nomenclature as has been applied to Cp′–Ir complexes; for details see, for example, Ref. [19]). The formation of complex 8 clearly indicates that the reaction proceeds with activation of one of the two internal C–H bonds.

The resulting butenyl species attains a six-coordinate, 18-electron structure by additional coordination of the pendant alkenic moiety.

The presence of a Me substituent in one of the internal carbons of the coordinated diene offers an alternative photochemical pathway. As represented in Eq. (3), under similar reaction conditions the 2-methyl-butadiene compound 4 provides a mixture of two complexes, 9 and 10, in a 1:4 ratio.

$$\text{(3)}$$
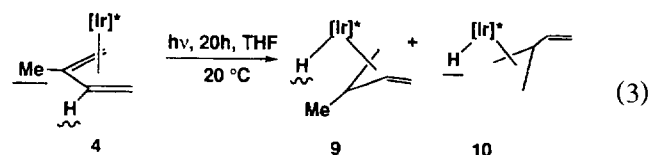
An overall conversion of ca. 85% is achieved after 20 h of irradiation at room temperature. The less abundant of the two isomers, 9, is structurally related to 8, i.e. is a 1,2,3-η³-butadienyl complex that exhibits spectroscopic features very similar to those found for this last species. The major isomer is also a hydrido-allyl, but contains a vinyl group as the substituent of the central allylic carbon. Hence it derives from the activation of one of the C–H bonds of the methyl group of the original diene ligand. The coordinated allylic unit has identical CH_2 termini, the presence of a plane of symmetry in the molecules of 10 being further reflected in the observation of two sets of resonances with intensity ratio 2:1 for the Tp* ligand. It is worth mentioning that the experimentally found 1:4 ratio of 9 to 10 is close to that statistically expected, therefore indicating a low selectivity for the photoactivation reaction.

In accord with the expectations raised by these results, photolysis of the 2,3-dimethylbutadiene compound 5 yields the allylic species 11 (above 80% isolated yield).

$$\text{(4)}$$
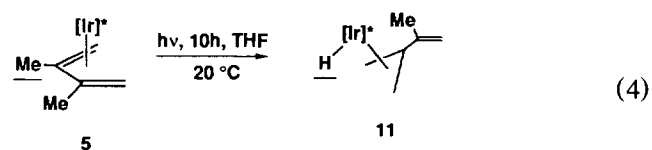
The similarity between the structures of compounds 10 and 11 can be inferred by inspection of their corresponding NMR data. Fig. 2 shows a portion of the ¹H–¹³C HETCOR spectrum that allows full assignement of, among others, the Me groups of this molecule.

In recent times we have studied the activation of the C–H bonds of different olefins coordinated to Tp′Ir fragments [17]. The bis(ethylene) derivative [Tp* Ir(C₂H₄)₂] affords the hydrido-vinyl species [Tp* Ir(H)(C₂H₃)(C₂H₄)], both photochemically and thermally (60 °C), but for propene activation of the CH_2 moiety is more facile as concluded from the formation
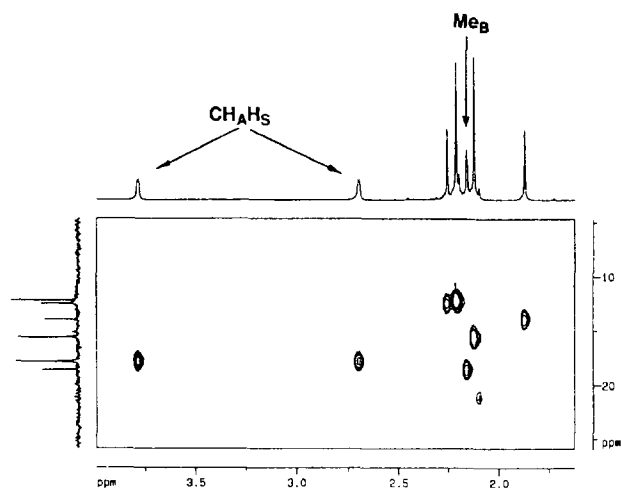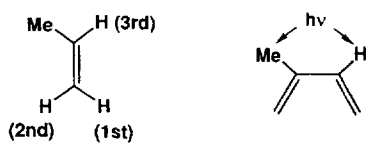
Fig. 2. Partial ^1H–^{13}C HETCOR spectrum of complex 11. See Section 3 for assignments.

of the compound [Tp* Ir(H)(CH=CHMe)(C$_3$H$_6$)] when [Ir(μ-Cl)(coe)$_2$]$_2$ is reacted with C$_3$H$_6$ and KTp* at 0°C [17].


C–H activation of the methyl substituent of the olefin or of the olefinic hydrogen *gem* to this methyl group are also feasible as deduced from the results of the studies carried out with other substituted olefins and Tp' ligands [17]. It is worth pointing out that the activation of the coordinated 1,3-dienes investigated in this work never takes place at the terminal methylene unit. Instead, olefinic or allylic C–H activation occurs, leading to formally six-coordinate, 18-electron species.

2.3. Thermal C–H activation of C_6H_6 by complex 5

We have explored the ability of some of the Ir(I)–diene complexes to induce intermolecular C–H bond activation reactions. While a detailed study of the thermal behaviour of complexes 1–7 in different hydrocarbon media is not yet available, the results obtained indicate that they are able to participate in this kind of process. Thus, when a solution of compound 5 in benzene is heated at 120°C under an atmosphere of N$_2$, a white, microcrystalline complex 12 can be collected after crystallization from Et$_2$O. Molecular weight determinations (see Section 3) indicate a dimeric formulation, whereas ^1H NMR spectroscopy shows the presence of a hydride ligand (δ −18.18) in addition to signals due to the Tp* ligand and to a phenyl fragment.

The latter, as normally found in Tp*–Ir complexes, does not undergo rotation around the Ir–C bond on the NMR timescale and consequently gives rise to five well-resolved resonances between 6.33 and 7.56 ppm [9,20]. An IR absorption at 2150 cm^{-1} can be assigned to ν(Ir–H), but no other bands appear in this region. The above data, together with the appearance of a Raman signal at 2160 cm^{-1}, support the formulation of 12 as a binuclear, dinitrogen-bridged complex.

$$ (5) $$
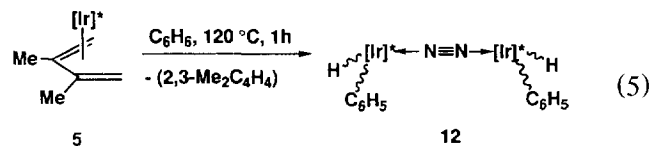
Only one stereoisomer appears to form in this reaction. Dinitrogen complexes of Ir(III) are very rare [21], the first examples of thermally stable species of this type have been reported recently by our own group [9].

In summary, a simple, straightforward and high-yield route to [Tp'Ir(η^4-1,3-diene)] complexes has been developed, and this may open the way to potential applications of these derivatives in organic synthesis [1–3]. The 1,3-butadiene species [Tp* Ir(η^4-C$_4$H$_6$)] is very reluctant to undergo photochemically induced C–H activations, but the presence of one methyl substituent in the internal carbons allows not only olefinic C–H bond addition to the metal centre but also C–H activation within the methyl group. In both cases the resulting organic fragment bonds to the Ir(III) centre in an allylic fashion, thereby allowing the adoption of a six-coordinate, 18-electron structure which can be anticipated as the most favourable one for Ir(III) complexes, particularly for those containing Tp' ligands which themselves are known to enforce six-coordination [22].

3. Experimental section

Microanalyses were by the Analytical Service of the University of Sevilla. The spectroscopic instruments used were Perkin–Elmer models 577 and 684 for IR spectra and Varian XL-200, Bruker AMX 300 and AMX 500 for NMR. ^1H and ^{13}C NMR spectra were referenced using the proton and carbon resonances of the deuterated solvent, but chemical shifts are reported with respect to SiMe$_4$. Most of the NMR assignments are based upon extensive ^1H–^1H decoupling, NOED-IFF, COSY, proton-coupled ^{13}C spectra and HETCOR experiments. All preparations were carried out under oxygen free nitrogen, following conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether employed had a boiling point in the range 40–60°C. The complex [IrCl(coe)$_2$]$_2$ and KTp' were synthesized by published procedures [23,24]. NMR spectral simulations were carried out with LAO-

COON and DAVINS programs [25]. We thank Professor A. Vacca (University of Firenze, Italy) for a copy of these programs.

3.1. Preparation of [TpIr(C₄H₆)] 1 and [Tp* Ir(C₄H₆)] 3

Through a cold (− 15 °C) solution of [IrCl(coe)₂]₂ (0.2 g, 0.22 mmol) in THF (25 cm³), butadiene was bubbled for 5 min. A colourless solution resulted, which was then treated with 0.155 g KTp* (0.46 mmol) dissolved in 20 cm³ THF. After stirring at room temperature for 5 h the volatiles were removed in vacuo and the residue extracted with 40 cm³ Et_2O–CH_2Cl_2 (5:1). Centrifugation and cooling at − 20 °C afforded complex 3 as a white crystalline powder in 80% yield.
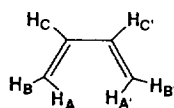

¹H NMR (200 MHz, CDCl₃, 25 °C): δ 5.86, 5.64 (s, 1H, 2H, C–H pyr), 5.47 (m, 2H, 2H_C), 2.56 (m, 2H, 2H_B), 2.39, 2.31, 2.25, 2.17 (s, 3H, 6H, 3H, 6H, 6Me), − 0.14 (m, 2H, 2H_A). Spectral simulation yields the following coupling constants: J(A,B) = 3.9, J(A,C) = 6.2, J(B,C) = 5.7, J(B,C′) = 0.5, J(C,C′) = 3.7, J(A,C′) = 0.9 Hz. ¹³C{¹H} NMR (50 MHz, CDCl₃, 25 °C): δ 153.3, 151.1 (1:2 ratio, C–Me), 142.9, 142.6 (1:2 ratio, C–Me), 107.5, 106.6 (2:1 ratio, C–H pyr), 68.4 (C–H_C, ¹J(C,H) = 170 Hz), 14.4, 14.0, 12.8, 12.5 (1:2:2:1 ratio, C–Me), 3.9 (CH_A H_B, ¹J(C,H) = 154, 150 Hz). Anal. Found: C, 42.0; H, 5.1; N, 15.4. C₁₉H₂₈BN₆Ir Calc.: C, 42.0; H, 5.2; N, 15.5%.

Complex 1 was obtained following a similar procedure but using only Et_2O to extract the compound. Slow evaporation of the solvent gave colourless needles in 70% yield. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ 8.0–6.0 (m, 9H, 1:2 pattern, C–H pyr), 4.93 (m, 2H, 2H_C), 2.08 (m, 2H, 2H_B), 0.16 (dd, 2H, 2H_A, ³J(A,C) = 5.4, ²J(A,B) = 3.9 Hz). ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ 145–105 (2:1 pattern, C–H pyr), 73.7 (C–H_C, ¹J(C,H) = 166 Hz), 8.8 (CH_A H_B, ¹J(C,H) = 154, 150 Hz). Anal. Found: C, 34.2; H, 3.7; N, 18.3. C₁₃H₁₆BN₆Ir Calc.: C, 34.0; H, 3.5; N, 18.3%.

3.2. Preparation of [Tp* Ir(2-MeC₄H₅)] 4

0.1 g [IrCl(coe)₂]₂ (0.11 mmol) was suspended in 20 cm³ THF and the flask cooled at − 20 °C. Then 0.5 cm³ 2-methylbutadiene was added and the resulting mixture stirred for 10 min. The now pale yellow solution was treated with 0.077 g KTp* (0.23 mmol) in THF

(20 cm³) and stirred for 4 h at room temperature. The solvent was evaporated in vacuo and the residue extracted with 20 cm³ Et_2O. Centrifugation and cooling at − 20 °C furnished a white crystalline powder in 80% yield.
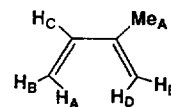
¹H NMR (200 MHz, CDCl₃, 25 °C): δ 5.81, 5.67, 5.65 (s, 1H, 1H, 1H, C–H pyr), 5.35 (t, 1H, H_C, ³J(C,A) ≈ ³J(C,B) = 6.2 Hz), 2.91 (d, 1H, H_E, ²J(E,D) = 4.3 Hz), 2.42, 2.37, 2.33, 2.30, 2.26, 2.21 (s, 3H each, 6Me), 2.25 (s, 3H, Me_A), 0.06 (d, 1H, H_D), − 0.19 (dd, 1H, H_A, ²J(A,B) = 3.5 Hz). The H_B resonance is immersed in the Me region. ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C): δ 153.3, 151.2, 151.2, 143.1, 142.7, 142.6 (C–Me), 108.0, 107.3, 106.7 (C–H pyr), 83.7 (C–Me_A), 72.6 (C–H_C), 21.7 (Me_A), 15.4, 14.7, 14.3, 13.1, 12.7, 12.6 (6C–Me), 5.4, 2.8 (CH₂). Anal. Found: C, 43.3; H, 5.4; N, 14.5. C₂₀H₃₀BN₆Ir Calc.: C, 43.1; H, 5.4; N, 15.1%.

3.3. Preparation of [TpIr(2,3-Me₂C₄H₄)] 2 and [Tp* Ir(2,3-Me₂C₄H₄)] 5

These complexes were obtained following a similar procedure to that used for the synthesis of 4. Starting with 0.500 g [IrCl(coe)₂]₂ (0.56 mmol), 1 cm³ dimethylbutadiene and the corresponding amount of KTp or KTp*, they were obtained in 70–80% yield as pale yellow crystalline powders after crystallization from Et_2O–petroleum ether mixtures.
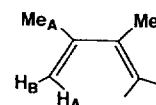

2. ¹H NMR (500 MHz, C₆D₆, 25 °C): δ 7.8–5.8 (m, 9H, 1:2 pattern, C–H pyr), 2.12 (d, 2H, 2H_B, ²J(B,A) = 3.4 Hz), 1.94 (s, 6H, 2Me_A), 0.51 (d, 2H, 2H_A). ¹³C{¹H} NMR (50 MHz, C₆D₆, 25 °C): δ 145–105 (2:1 pattern, C–H pyr), 83.3 (C–Me_A), 18.5 (Me_A), 14.9 (CH₂, ¹J(C,H) = 151 Hz). Anal. Found: C, 36.9; H, 4.3; N, 17.2. C₁₅H₂₀BN₆Ir Calc.: C, 37.0; H, 4.1; N, 17.2%.

5. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 5.54 (s, 3H, C–H pyr), 2.87 (d, 2H, 2H_B, ²J(B,A) = 4.0 Hz), 2.20 (s, 6H, 2Me_A), 2.19, 2.09 (s, 9H, 9H, 6Me), 0.51 (d, 2H, 2H_A). ¹³C{¹H} NMR (75 MHz, C₆D₆, 25 °C): δ

151 (br, C–Me), 142.1 (C–Me), 107.7 (C–H pyr), 86.8 (C–Me$_A$), 21.2 (Me$_A$), 15.2, 12.6 (br, s, C–Me), 5.3 (CH$_2$). Anal. Found: C, 44.9; H, 5.7; N, 14.8. C$_{21}$H$_{32}$BN$_6$Ir Calc.: C, 44.1; H, 5.6; N, 14.7%.

3.4. Preparation of [Tp*Ir(C$_5$H$_6$)] 6 and [Tp*Ir(C$_6$H$_{10}$)] 7

To a suspension of [IrCl(coe)$_2$]$_2$ (0.1 g, 0.11 mmol) in THF (10 cm^3) was added 2 cm^3 of recently distilled cyclopentadiene at room temperature. After 20 min of stirring the resulting yellow mixture was reacted with KTp* (0.077 g in 10 cm^3 THF) and stirred for an additional 3 h. Evaporation of the solvent to dryness, extraction with a 2:1 Et$_2$O–CH$_2$Cl$_2$ mixture (30 cm^3) and cooling at −20 °C furnished complex 6 in 40% yield in the form of a white microcrystalline solid.
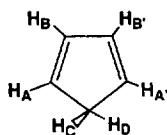
^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ 5.68 (s, 3H, C–H pyr), 5.59 (m, 2H, 2H$_B$), 2.98 (m, 2H, 2H$_A$), 2.94 (dt, 1H, H$_C$, ^2J(C,D) = 9.8, ^3J(C,A) = 1.9 Hz), 2.84 (d, 1H, H$_D$), 2.28 (s, 9H, 3Me), 2.17 (br s, 9H, 3Me). Computer simulation yields the following additional coupling constants: J(A,A′) = 1.9, J(A,B) = 2.4, J(B,B′) = 2.6 Hz. ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$, 25 °C): δ 151.5, 142.8 (C–Me), 107.1 (C–H pyr), 67.0 (C–H$_B$, ^1J(C,H) = 176 Hz), 44.5 (CH$_C$H$_D$, ^1J(C,H) = 136, 130 Hz), 15.3, 12.6 (C–Me), 5.3 (C–H$_A$, ^1J(C,H) = 166 Hz). Anal. Found: C, 43.0; H, 5.1; N, 14.1. C$_{20}$H$_{28}$BN$_6$Ir Calc.: C, 43.2; H, 5.1; N, 15.1%.

Starting with 0.1 g [IrCl(coe)$_2$]$_2$, 0.5 cm^3 1,3-cyclohexadiene and 0.077 g KTp*, and after 6 h of reaction at room temperature, complex 7 was obtained as a white solid in 75% yield following crystallization at −20 °C (40 cm^3 Et$_2$O–CH$_2$Cl$_2$, 3:1 ratio).
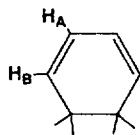

^{1}H NMR (200 MHz, CDCl$_3$, 25 °C): δ 5.8, 5.6 (br, 1H, 2H, C–H pyr), 5.24 (m, 2H, 2H$_A$), 3.39 (m, 2H, 2H$_B$), 2.31, 2.21 (s, br, 9H each, 6Me), 1.46, 0.41 (m, 2H each, 2CH$_2$). ^{13}C{^{1}H} NMR (50 MHz, CDCl$_3$, 25 °C): δ

151.4, 142.7 (s, br, C–Me), 108.2, 106.2 (s, br, C–H pyr), 68.0 (C–H$_A$, ^1J(C,H) = 168 Hz), 25.2 (CH$_2$, ^1J(C,H) = 128 Hz), 22.0 (C–H$_B$, ^1J(C,H) = 152 Hz), 14.2, 12.8 (br, s, C–Me). Anal. Found: C, 44.7; H, 5.3; N, 14.3. C$_{21}$H$_{30}$BN$_6$Ir Calc.: C, 44.3; H, 5.3; N, 14.8%.

3.5. Photochemical activation of complex 3

1 g [Tp*Ir(C$_4$H$_6$)] in 100 cm^3 THF was irradiated with UV light for 2 days. Overheating of the reaction flask was avoided by using a closed water refrigeration circuit. The resulting brown mixture was evaporated to dryness and extracted with 20 cm^3 petroleum ether. Chromatography on silica allows the separation of complex 8 which, after crystallization from petroleum ether, was obtained as a white crystalline powder in 20% yield.
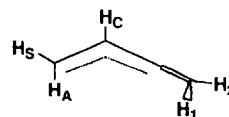

^{1}H NMR (500 MHz, C$_6$D$_6$, 25 °C): δ 5.63, 5.62, 5.47 (s, 1H, 1H, 1H, C–H pyr), 5.52 (d, 1H, H$_1$, ^2J(H,H) = 2.2 Hz), 4.78 (d, 1H, H$_2$), 4.77 (dd, 1H, H$_C$, ^3J(C,A) = 10.7, ^3J(C,S) = 7.4 Hz), 3.40 (d, 1H, H$_S$), 2.98 (d, 1H, H$_A$), 2.4–1.9 (6Me), −24.45 (s, 1H, Ir–H). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 25 °C): δ 151.1, 150.7, 150.6, 150.5 (C–Me and C–CH$_1$H$_2$), 142.9, 142.8 (1:2 ratio, C–Me), 109.0, 107.5, 107.4 (C–H pyr), 98.8 (CH$_1$H$_2$, ^1J(C,H) = 160 Hz), 59.2 (C–H$_C$, ^1J(C,H) = 167 Hz), 27.7 (CH$_S$H$_A$, ^1J(C,H) = 154 Hz), 15.4, 15.3, 14.0, 12.3, 12.2, 12.1 (6Me). IR (KBr): ν(Ir–H) 2235, 2175 cm^{-1}. Anal. Found: C, 42.5; H, 5.3; N, 15.4. C$_{19}$H$_{28}$BN$_6$Ir Calc.: C, 42.0; H, 5.2; N, 15.5%.

3.6. Photochemical activation of complex 4

0.3 g [Tp*Ir(2-MeC$_4$H$_5$)] was dissolved in 100 cm^3 THF and irradiated with UV light for 20 h. After removal of the volatiles, NMR analysis of the crude mixture indicated 70% conversion and the presence of complexes 9 and 10 in a ca. 1:4 ratio. This residue was chromatographed on SiO$_2$ to afford, in separate fractions, complexes 9 (less than 20 mg) and 10 (60 mg) as white microcrystalline powders.
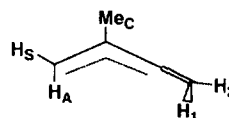
9. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 5.67, 5.65, 5.48 (s, 1H, 1H, 1H, C–H pyr), 5.41 (s, 1H, H_1), 4.73 (s, 1H, H_2), 3.42 (s, 1H, H_S), 3.21 (s, 1H, H_A), 2.69 (d, 3H, Me_C, J(Me,H–Ir) = 1.8 Hz), 2.40, 2.21, 2.20, 2.15, 2.07, 1.96 (s, 3H each, 6Me), −24.77 (br q, 1H, Ir–H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): δ 152.5, 150.9, 150.1, 150.1 (C–Me and C–CH_1H_2), 142.8, 142.6 (1:2 ratio, C–Me), 107.5, 105.4 (1:2 ratio, C–H pyr), 97.7 (CH_1H_2, ^{1}J(C,H) = 160 Hz), 80.7 (C–Me_C), 29.8 (CH_SH_A, ^{1}J(C,H) = 155 Hz), 26.2 (C–Me_C), 15.6, 15.5, 13.8, 12.4, 12.3, 12.1 (6Me). IR (KBr): ν(Ir–H) 2240, 2190 cm^{-1}. Anal. Found: C, 43.4; H, 5.3; N, 14.9. $C_{20}H_{30}BN_6Ir$ Calc.: C, 43.1; H, 5.4; N, 15.1%.
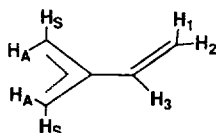
10. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 6.67 (dd, 1H, H_3, ^{3}J(H_3,H_1) = 17.3, ^{3}J(H_3,H_2) = 10.6 Hz), 5.63 (s, 2H, 2C–H pyr), 5.49 (d, 1H, H_1), 5.43 (s, 1H, C–H pyr), 4.85 (d, 1H, H_2), 3.68 (s, 2H, $2H_S$), 2.70 (s, 2H, $2H_A$), 2.25, 2.19, 2.11, 1.82 (s, 1:2:2:1 ratio, 6Me), −27.65 (s, 1H, Ir–H). ^{13}C{^{1}H} NMR (50 MHz, C_6D_6, 25 °C): δ 145.2 (C–H_3, ^{1}J(C,H) = 164 Hz), 112.2 (CH_1H_2, ^{1}J(C,H) = 158 Hz), 93.1 (C–CH_AH_S), 20.0 (CH_AH_S, ^{1}J(C,H) = 188 Hz). IR (KBr): ν(Ir–H) 2205 cm^{-1}. Anal. Found: C, 43.6; H, 5.7; N, 14.9. $C_{20}H_{30}BN_6Ir$ Calc.: C, 43.1; H, 5.4; N, 15.1%.

3.7. Photochemical activation of complex 5

Starting with 0.3 g [Tp* Ir(2,3-Me$_2$C$_4$H$_4$)], irradiation for 8 h in THF (100 cm^3) gave complex **11** in 80% yield after crystallization from petroleum ether–Et$_2$O (10 cm^3, 5:1 ratio, −20 °C).
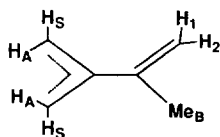
^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 5.65 (br s, 1H, H_1), 5.63, 5.44 (s, 2H, 1H, C–H pyr), 5.06 (br s, 1H, H_2), 3.80 (d, 2H, $2H_S$, ^{2}J(H_S,H_A) = 1.7 Hz), 2.71 (d, 2H, $2H_A$), 2.26, 2.21, 2.14, 1.88 (s, 1:2:2:1 ratio, 6Me), 2.17 (s, 3H, Me_B), −27.65 (s, 1H, Ir–H). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6, 25 °C): 150.6, 150.4, 148.0,

142.4 (C–Me and C–Me_B), 113.9 (CH_1H_2, ^{1}J(C,H) = 156 Hz), 108.4, 105.5 (1:2 ratio, C–H pyr), 96.4 (C–CH_AH_S), 18.6 (Me_B), 17.9 (CH_AH_S, ^{1}J(C,H) = 155 Hz), 15.6, 14.0, 12.6, 12.3 (2:1:1:2 ratio, 6Me). IR (KBr): ν(Ir–H) 2220 cm^{-1}. Anal. Found: C, 44.6; H, 5.6; N, 14.2. $C_{21}H_{32}BN_6Ir$ Calc.: C, 44.1; H, 5.6; N, 14.7%.

3.8. Synthesis of [Tp* Ir(H)(C$_6$H$_5$)]$_2$(μ-N$_2$) 12

Complex **5** (0.150 g) was dissolved in 5 cm^3 C_6H_6 and heated at 120 °C (thick-wall ampoule) for 1 h. The brown solution was evaporated to dryness and the resulting residue extracted with 70 cm^3 Et$_2$O. Cooling at −20 °C provided a white precipitate of **12**. ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ 6.33, 6.71, 6.87, 6.92, 7.56 (d, t, t, t, d, 1H each, C_6H_5), 5.46, 5.66, 5.80 (s, 1H each, C–H pyr), 2.45, 2.35, 2.34, 1.96, 1.53, 1.14 (s, 3H each, 6Me), −18.18 (s, 1H, Ir–H). ^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$, 25 °C): δ 151.9, 150.5, 150.2, 143.7, 143.1, 142.6 (C–Me), 142.1, 137.9, 126.4, 126.2, 121.5 (C–H_{phen}), 130.8 (Ir–C), 106.3, 105.4 (2:1 ratio, C–H pyr), 15.6, 13.0, 12.9, 12.3, 12.0 (1:1:1:2:1 ratio, C–Me). IR (CHCl$_3$): ν(Ir–H) 2150 cm^{-1}. Raman: 2160 cm^{-1} (N≡N). M (Signer's method [26], CHCl$_3$) Found: 1180. $C_{42}H_{56}B_2N_{14}Ir_2$ Calc.: 1163. Anal. Found: C, 43.2; H, 4.8; N, 16.4. $C_{42}H_{56}B_2N_{14}Ir_2$ Calc.: C, 43.4; H, 4.4; N, 16.9%.

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