C–H Bond activation and C–C bond formation in the reaction of 2,5-dimethylthiophene with $\text{Tp}^{\text{Me}_2}\text{Ir}$ compounds†‡

Margarita Paneque,^{*a} Manuel L. Poveda,^a Ernesto Carmona^a and Verónica Salazar^b

^a Instituto de Investigaciones Químicas-Departamento de Química Inorgánica, Consejo Superior de Investigaciones Científicas-Universidad de Sevilla, Avda. Américo Vespucio 49, Isla de la Cartuja, 41092, Sevilla, Spain. E-mail: paneque@iiq.csic.es; Fax: 34 954 460565; Tel: 34 954 489557

^b Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Hidalgo, Carretera de Pachuca a Tulancingo Km 4.5, Pachuca, Hidalgo, México

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The bulky 2,5-dimethylthiophene (2,5-Me₂T) reacts at 60 °C with $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2$ to give a mixture of two $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{III})$ hydride products, **3** and **4**, that contain in addition a thienyl (**3**) or a thienyl-derived ligand (**4**). For the generation of **3** only sp^2 C–H activation is needed, but the formation of **4** requires also the activation of an sp^3 C–H bond and the formation of a new C–C bond (between vinyl and thienyl fragments). In the presence of 2,5-Me₂T, compound **4** reacts further to produce a complex thiophenic structure (**5**, characterized by X-ray methods) that derives formally from two molecules of 2,5-Me₂T and a vinyl fragment. Compounds **3–5** can be readily protonated by $[\text{H}(\text{OEt})_2][\text{BAr}'_4]$ ($\text{Ar}' = 3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$), with initial generation of carbene ligands (in the case of **3** and **5**) as a consequence of H^+ attack at the β -carbon of the Ir–thienyl unit. Free, substituted thiophenes, derived from the original 2,5-Me₂T, may be isolated in this way.

Introduction

The reactions of soluble transition metal compounds and common organic substrates that occurs with cleavage of C–H bonds and subsequent C–C bond formation find important applications in the synthesis of complex molecules.^{1,2} Sulfur-containing molecules such as thiophenes and the differently substituted thiophenes are the main sulfur-containing products in fossil materials. The study of their reactivity towards transition metal complexes has improved our knowledge of the mechanism of the hydrodesulfurization process (HDS)³ and provided valuable information on the elementary steps of this complex transformation. C–H, and in some cases C–S bond rupture have been demonstrated.^{4–9} In addition, important applications in various areas of chemistry¹⁰ have resulted from these investigations.

As a continuation of previous studies on the activation of thiophene and methyl-substituted thiophenes by $\text{Tp}^{\text{Me}_2}\text{Ir}$ and $\text{Tp}^{\text{Me}_2}\text{Rh}$ -complexes,¹¹ we now discuss the complex reaction that occurs between $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2$, **1**, and the sterically more demanding 2,5-dimethylthiophene (from now on represented by 2,5-Me₂T). While thiophene (in short T) and 2- and 3-methylthiophenes (2-MeT and 3-MeT, respectively) undergo vinylic C–H activation when reacted with $\text{Tp}^{\text{Me}_2}\text{Ir}$ compounds^{11a} (Scheme 1), the bulkier 2,5-Me₂T generates more elaborated reaction products that result from aliphatic and vinylic C–H activation, in some instances accompanied by C–C bond formation. A preliminary communication of this work has appeared.¹²

Results and discussion

Heating of a solution of **1** in hexane or cyclohexane converts it into its thermodynamically more stable hydride vinyl isomer,¹³

Scheme 1

$\text{Tp}^{\text{Me}_2}\text{Ir}(\text{H})(\text{CH}=\text{CH}_2)(\text{C}_2\text{H}_4)_2$, **2**. Since effecting the heating in aromatic hydrocarbon or ether solvents generates products of different nature resulting from C–H activation of the solvent, the activation of 2,5-Me₂T was investigated, using either **1** or **2** as the starting reagents. As shown in Scheme 2, a complex reaction

Scheme 2

† Electronic supplementary information (ESI) available: Experimental data for compounds **6b–d**, **7**, **8** and **15**. See <http://www.rsc.org/suppdata/dt/b4/b419414d/>

‡ This work is respectfully dedicated to the memory of Dr Juan C. Del Amo (1975–2004) who was a victim of the March-11 tragedy in Madrid.

ensues and it gives rise to two hydride compounds, **3** and **4** in a ca. 1 : 1 ratio as the main organometallic products (more than 80% of the crude mixture). Light hydrocarbons, mostly ethane, ethene and isomers of butene are also evolved (^1H as well as GC analysis of the volatiles).

Complex **3** has been obtained previously albeit by a different reaction pathway.^{11a} Its formation requires the activation of only one C–H bond, namely one of the sp^2 C–H bonds of 2,5-Me₂T. In contrast, that of **4** involves a more complex mechanistic pathway, as one sp^2 and one sp^3 C–H bonds must be broken and a new C–C bond must be formed. As can be seen in Scheme 2, complex **4** is a hydride and contains in addition one alkyl and one alkene termini that are part of an elaborated chelating hydrocarbonyl ligand. Formally, this ligand derives from the coupling of a molecule of 2,5-Me₂T and a vinyl fragment with loss of two hydrogen atoms. 1D and 2D NMR studies (see Experimental section) are in accord with the proposed formulation. Thus the Ir–H gives a singlet at δ –17.18 ppm in the ^1H NMR spectrum, whereas the diastereotopic Ir–CH₂ protons resonate as doublets at 3.40 and 2.66 ppm ($^2J_{\text{HH}} = 15.4$ Hz). These ^1H signals are associated with a $^{13}\text{C}\{^1\text{H}\}$ resonance at δ –11.4 ppm. As for the olefinic ligand, a characteristic vinyl pattern can be recognized at δ 6.04 (dd, $^3J_{\text{HH}} = 10.8$ and 8.1 Hz; $-\text{C}(\text{H})=\text{CH}_2$), and 3.85 and 2.66 (d and d, $^3J_{\text{HH}} = 8.1$ and 10.8 Hz, respectively, $-\text{C}(\text{H})=\text{CH}_2$). Only one of the stereoisomers that would result from the coordination of the two enantiotopic faces of the olefin is detected, the structure depicted in Scheme 2 being derived from the analysis of the NOESY spectrum (strong correlation peak between the $\text{H}_2\text{C}=\text{C}(\text{H})$ – and Ir–H signals). As found for somewhat related compounds the observed isomer appears to be the more favourable on steric grounds.¹⁴

The complexity of the reaction route leading to **4** makes it difficult gaining reliable mechanistic information. Nevertheless, in view of the structure of **4**, species **B** of Scheme 3 appears as a reasonable intermediate, for its conversion into **4** would require a simple sequence of two elementary steps, namely ethylene migratory insertion and β -H elimination. The insertion step is proposed to occur selectively into the Ir–C(sp^2) bond in view of the facility with which olefins and alkynes insert into electrophilic M–aryl bonds,¹⁵ including those of metallacyclic fragments that have aryl and alkyl termini.^{15d} The resulting six-membered metallacycle would rearrange readily into hydride **4**. Intermediate **B** itself derives from the activation of one sp^2 and one sp^3 C–H bonds of a molecule of 2,5-Me₂T. It seems plausible that 2,5-Me₂T traps the unsaturated $[\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_5)]$ intermediate,¹³ that would then transform into **B** with liberation of C_2H_6 (detected by ^1H NMR), as a consequence of the two C–H activations. Whether the vinylic (to give **D**) or the aliphatic C–H bond (to yield **E**) is cleaved first cannot actually be discerned although it seems reasonable that S-coordination may contribute

to comparatively faster generation of **E**. We have not attempted to investigate this problem any further.

Isolated samples of compound **3** do not rearrange further under the reaction conditions, whereas more prolonged heating of the **3** + **4** reaction mixture, or the use of higher reaction temperatures, causes gradual formation of a new species **5** at the expense of **4**. Accordingly, isolated samples of **4** transform quantitatively into **5** (eqn. (1)) when heated at 90 °C in neat 2,5-Me₂T.

The molecular complexity of **5** was determined by X-ray crystallography and reported when this work was communicated.¹² NMR studies are in agreement with the solid-state structure. Thus, ^1H NMR spectroscopy reveals the presence of a hydride ligand (δ –20.02 ppm) and of a single aromatic thiophenic proton (6.28 ppm). In addition, the thiophenic ligand is responsible for an AB quartet centered at 4.1 ppm, that can be attributed to the diastereotopic protons of the CH_2 unit that bridges the two thienyl rings. NOESY and ^1H – ^{13}C heteronuclear correlation experiments permit an assignment of the ^1H and $^{13}\text{C}\{^1\text{H}\}$ resonances that is also coherent with the solid-state structure (see Experimental section).

While it is not easy to rationalize the formation of the chelating thiophenic ligand in **5**, which results from the formal coupling of two thienyl moieties and a vinyl fragment, it seems reasonable that the first reaction step for the conversion represented in eqn. (1) is the migratory insertion of the olefin ligand into the Ir–H bond. In accord with this assumption, the interaction of **4** with different Lewis bases (eqn. (2)) yields adducts **6** that contain a metallacyclohexene moiety. The two iridium-bound methylene groups of **6** originate characteristic low-frequency $^{13}\text{C}\{^1\text{H}\}$ NMR signals that in the case of the PMe_3 adduct **6b**, appear at δ –16.1 and –16.2 ppm. Both have accidentally the same coupling with the ^{31}P nucleus (8 Hz).

Scheme 3

On these grounds, it seems plausible that an adduct of type **6**, containing a coordinated molecule of 2,5-Me₂T, is the first product of the reaction of **4** and the substituted thiophene. The same holds for the analogous reaction between **4** and thiophene, but interestingly in this case **4** converts into the known^{11a} bis(thienyl) compound represented in eqn. (3), with liberation of 2,5-dimethyl-3-ethylthiophene. The latter results may be explained assuming the step-wise, vinylic activation of two molecules of thiophene by **4**, but due to its complex nature the generation of **5** according to eqn. (1) can only be approached in a very broad and general manner, assuming that it is the consequence of two C–H activation and one C–C bond-forming steps. Not unexpectedly in view of its chelate and sterically encumbered nature, compound **5** is inert toward displacement of the neutral sulfur donor atom by Lewis bases (no reaction with an excess of PMe_3 , 120 °C, 3 days). Notwithstanding, as discussed in the following paragraphs, the reaction with protic acids allows detachment of the organic thiophenic entity.

We have considered it of interest to study the reactions of compounds **3–5** with acids, since different reaction outcomes may be anticipated for the protonation of their Ir–C(alkyl) or Ir–C(thienyl) bonds. For comparative purposes, related thienyl derivatives have also been investigated and in all cases the strong protic acid $[\text{H}(\text{OEt}_2)_2][\text{BAR}'_4]$, has been employed ($\text{Ar}' = 3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$).¹⁶

One of the simplest reactions investigated is the protonation of the hydride thienyl **3**, which occurs according to eqn. (4), and gives the cationic hydride **7**. Compound **7** contains two coordinated molecules of 2,5-Me₂T. The related complex $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{H})(2\text{-SC}_4\text{H}_3)(\text{NCMe})$,^{11a} obtained by NCMe displacement of the coordinated molecule of thiophene in $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{H})(2\text{-SC}_4\text{H}_3)(\text{SC}_4\text{H}_4)$,^{11a} produces the analogous adduct **8** (eqn. (4)).

Although the formation of **7** and **8** could be viewed as the result of the direct protonation of the Ir–C(thienyl) bond of the corresponding precursors, the well-known tendency of late transition metal alkenyls to undergo protonation at the β -carbon to yield cationic alkylidene species^{14a,17,18} suggests that a less simple reaction pathway could be operative. To confirm this possibility the thienyl complex $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{H})(2\text{-SC}_4\text{H}_3)(\text{PMe}_3)$ ^{11a} was protonated at -70°C (Scheme 4). A cationic Fischer-type carbene complex, **9**, is formed as a mixture of two rotamers (*ca.* 5 : 1 ratio). At room temperature it evolves over a period of several hours, to give the cationic hydride **10**, but the rearrangement is sufficiently slow to allow full solution characterization by NMR methods at 0°C . Apart from other NMR data collected in the Experimental section the carbene carbon is responsible for the $^{13}\text{C}\{^1\text{H}\}$ resonance located at δ 259.7 ppm (major rotamer, $^2J_{\text{CP}} = 9$ Hz) whereas the Ir–H functionality resonates at -18.47 ppm in the ^1H NMR spectrum.

Scheme 4

Taking these results into account it seems probable that the protonations represented in eqn. (4) may proceed by a similar

route to yield cationic hydride carbenes that rearrange by means of a 1,2-H shift from iridium to the carbene carbon, followed by β -H elimination. Somewhat similar results have been reported for the rhenium complex $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(2\text{-SC}_4\text{H}_3)(\text{NO})(\text{PPh}_3)$,¹⁹ but in other instances different mechanistic pathways have been suggested.²⁰

The Ir–C(alkyl) bond of compound **4** undergoes direct protonolysis to provide the cationic olefin derivative **11** (eqn. (5)). If a Lewis base is not deliberately added, the sixth coordination position of the metal is occupied by a molecule of adventitious water. This is actually a relatively common observation in our work with these iridium systems that exhibits moderate stability towards air even in solution. Despite the cationic nature of **11**, displacement of the olefin terminus of the thiophenic ligand is not facile because the addition of a Lewis base induces also the migration of the hydride ligand onto the olefin and formation of an alkyl complex, as represented in eqn. (6) for the reaction with NCMe.

Finally, the protonation of the heterometallacyclic compound **5** has been investigated, with the results summarized in Scheme 5. As expected, the reaction gives initially an alkylidene complex **13** ($\text{Ir}=\text{CR}_2$ at δ 252 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum) that contains a hydride ligand in a position adjacent to the carbene. Hence, **13** rearranges into **14** by means of migratory insertion and β -H elimination. Effecting the protonation in NCMe allows isolation of adduct **15**, that contains a coordinated molecule of the nitrile, and the heating of either **14** or **15** in NCMe at 80°C (Scheme 6) permits liberation of the dithiophenic neutral ligand.

Scheme 5

In summary, at variance with the activation of T, 2-MeT and 3-MeT by $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2$,^{11a} the sterically more demanding 2,5-Me₂T reacts with $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2$ in a more complex manner to afford unexpected derivatives that result from aliphatic and vinylic C–H activation as well as from C–C bond formation. The observed generation of coupled thiophenes may be of interest regarding the observation of complex thiophenic molecules in the course of the HDS process.³ Moreover, as Scheme 4 shows, transition metal catalysis under acidic conditions could give rise to very reactive metal–thiophenic carbenes.

Scheme 6

Experimental

All manipulations were performed under dry, oxygen-free dinitrogen, following conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. The compounds $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2$, ^{13}C $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{H})(\text{CH}=\text{CH}_2)(\text{C}_2\text{H}_4)$, ^{13}C $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{H})(2\text{-C}_4\text{H}_3\text{S})(\text{L})$ ($\text{L} = \text{SC}_4\text{H}_4$, NCMe and PMe_3)^{11a} and the acid $[\text{H}(\text{OEt})_2][\text{BAR}'_4]$ ($\text{Ar}' = 3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$)¹⁶ were prepared by the published procedures. Microanalyses were by the Micro-analytical Services of the Instituto de Investigaciones Químicas (Sevilla). Infrared spectra were recorded on Perkin Elmer model 883 and FT-16PC and Bruker Vector 22 spectrometers; NMR spectra on Bruker AMX-300, AMX-500, DPX-300, DRX-400 and DRX-500 spectrometers. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ resonances of the solvent were used as internal standard, but the chemical shifts are reported with respect to TMS. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were referenced to 80% H_3PO_4 . Most of the NMR assignments are based on ^1H - ^1H decoupling experiments, and homo- and heteronuclear two-dimensional spectra. No NMR data are reported for the BAR'_4 anion since they are of very little structural value (essentially coincident in all compounds and with those of NaBAR'_4). All compounds display an IR absorption between 2525 and 2520 cm^{-1} , corresponding to $\nu(\text{BH})$, in accord with the proposed tridentate, κ^3 -coordination.

Compounds 3 and 4

The bis(ethylene) compound $\text{Tp}^{\text{Me}_2}\text{Ir}(\text{C}_2\text{H}_4)_2$ (0.10 g, 0.173 mmol) was dissolved in a mixture (1 mL, 1 : 2) of freshly distilled 2,5-dimethylthiophene and cyclohexane. The solution was stirred for 8 h at 60°C , and the solvent evaporated under vacuum. NMR monitoring of the crude product reveals a *ca.* 1 : 1 mixture of 3 and 4. The excess of 2,5-Me₂T was eliminated by successive addition of pentane and subsequent evaporation (8 mL, 3 $\times$). Addition of Et_2O (3 mL) and pentane (1 mL), filtration and cooling overnight to -20°C provided 4 as a pale brown solid (0.035 g, 30% yield). The resulting mother-liquors were evaporated to dryness *in vacuo* and a mixture (4 mL) of Et_2O -pentane (1 : 1) was added, and the solution cooled to -20°C , to yield 3 as a brown solid (0.035 g, 28% yield). Identical results are obtained when the Ir(III) compound 2 is employed as the starting material. Compound 3 can be prepared alternatively as described in ref. 9a, where the spectroscopic and analytical data are also reported. For 4: IR (Nujol): $\nu(\text{IrH})$ 2176 cm^{-1} . ^1H NMR (C_6D_6 , 25°C): δ 6.55 (s, 1 H CH_{th}), 6.04 (dd, 1 H, $^3J_{\text{AC}} = 10.8$, $^3J_{\text{AB}} = 8.1$ Hz, H_A), 5.66, 5.46, 5.44 (s, 1 H each, 3 CH_{pz}), 3.85 (d, 1 H, H_C), 2.90 (d, 1 H, H_B), 3.40, 2.66 (d, 1 H each, $^2J_{\text{HH}} = 15.4$ Hz, IrCH_2), 2.44, 2.21, 2.18, 2.13, 2.04, 1.68 (s, 3 H each, 6 Me_{pz}), 2.23 (s, 3 H, Me_{th}), -17.18 (s, 1 H, IrH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25°C): δ 154.4, 151.5, 150.4, 149.0, 145.3, 143.0 (C_{qpz}), 143.1, 142.5, 141.2 (C_{qth}), 121.1 (CH_{th}), 107.7, 106.8, 106.6 (CH_{pz}), 67.4 (CH_A , $^1J_{\text{CH}} = 163$ Hz), 50.7 (CH_BH_C , $^1J_{\text{CH}} = 159$ Hz), 16.5

(Me_{th}), 13.7, 13.3, 13.0, 12.3, 12.1, 12.1 (Me_{pz}), -11.4 (IrCH_2 , $^1J_{\text{CH}} = 131$ Hz). Anal. Calc. for $\text{C}_{23}\text{H}_{32}\text{BN}_6\text{SIr}$: C, 44.0; H, 5.1; N, 13.3. Found: C, 44.7; H, 5.2; N, 12.8%.

Compound 5

Compound 4 (0.08 g, 0.12 mmol) was dissolved in freshly distilled 2,5-Me₂T (2 mL) and the solution stirred 24 h at 85°C . After this period of time, the solvent was evaporated under reduced pressure, pentane added (5 mL) and the mixture stirred vigorously for a few minutes. The solid obtained was separated by filtration and dissolved in a mixture (8 mL) of Et_2O -pentane (6 : 2). The solution was cooled to -20°C to yield compound 5 as a pale green microcrystalline solid (90% yield). This material can be recrystallized by the slow diffusion of MeOH (1 mL) into a solution in CH_2Cl_2 (4 mL), at room temperature. In this way, monocrystals appropriate for X-ray diffraction were obtained (0.06 g, 70%). IR (Nujol): $\nu(\text{IrH})$ 2110 cm^{-1} . ^1H NMR (C_6D_6 , 25°C): δ 6.28 (s, 1 H CH_{th}), 5.66, 5.46 (s, 2 : 1, 3 CH_{pz}), 4.12, 4.04 (d, 1 H each, $^2J_{\text{AB}} = 14.6$ Hz, CH_AH_B , respectively), 2.47, 2.28, 2.23, 2.14, 2.01, 1.38 (s, 3 H each, 6 Me_{pz}), 2.43, 1.50, 1.26 (s, 3 H each, Me_{th}), 2.33 (m, 2 H, CH_2Me), 0.91 (t, 3 H, $^3J_{\text{HH}} = 7.6$ Hz, CH_2Me), -20.02 (s, 1 H, IrH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25°C): δ 151.6, 151.3, 143.2, 142.7, 142.6 (2 : 1 : 1 : 1 : 1, C_{qpz}), 145.3 (C^6), 143.2 (C^{10}), 141.0 (C^4), 138.2 (C^3), 131.0 (C^{11}), 128.0 (C^8), 123.8 (C^9), 117.1 (C^7), 105.8, 105.7, 105.6 (CH_{pz}), 29.0 (C^5), 22.1 (C^2), 15.4, 13.1, 12.5, 12.3, 12.2 (1 : 1 : 1 : 2 : 1, Me_{pz}), 15.2, 14.4, 13.3 (Me_{th}), 13.3 (C^1). Anal. Calc. for $\text{C}_{29}\text{H}_{39}\text{BN}_6\text{S}_2\text{Ir}$: C, 47.1; H, 5.2; N, 11.3. Found: C, 46.7; H, 5.5; N, 11.4%.

Compound 6a

Compound 4 (0.10 g, 0.16 mmol) was dissolved in acetonitrile (15 mL) and the mixture heated at 90°C for 3 h, after which time a pale brown solution was formed. The solvent was eliminated under reduced pressure and the residue washed with pentane and dried *in vacuo*, to yield the title compound in almost quantitative yield. IR (Nujol): $\nu(\text{NC})$ 2280 cm^{-1} . ^1H NMR (C_6D_6 , 25°C): δ 6.66 (s, 1 H, CH_{th}), 5.76, 5.66, 5.44 (s, 1 H each, 3 CH_{pz}), 4.19, 3.99 (d, 1 H each, $^2J_{\text{AB}} = 15.8$ Hz, IrCH_2C_q), 3.12, 3.02, 2.88, 2.77 (m, 1 H each, IrCH_2CH_2), 2.55, 2.41, 2.40, 2.35, 2.21, 2.19, 2.10 (s, 3 H each, 6 Me_{pz} and NCMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 25°C): δ 151.1, 148.9, 148.4, 142.6, 142.2, 142.1 (C_{qpz}), 141.5, 139.9, 132.2 (C_{qth}), 128.4 (CH_{th}), 113.0 (NCMe), 108.4, 106.8, 106.6 (CH_{pz}), 29.3 (IrCH_2CH_2), 15.1, 14.5, 13.6, 13.4, 12.7, 12.2, 12.1 (Me_{pz} and Me_{th}), 1.2 (NCMe), -10.9 , -14.3 (IrCH_2). Anal. Calc. for $\text{C}_{23}\text{H}_{35}\text{BN}_7\text{SIr}$: C, 44.8; H, 5.2; N, 14.6. Found: C, 44.6; H, 5.2; N, 14.2%.

Compound 9

A mixture of complex $\text{Tp}^{\text{Me}_2}\text{IrH}(2\text{-C}_4\text{H}_3\text{S})(\text{PMe}_3)$ (0.01 g, 0.015 mmol) and the acid $[\text{H}(\text{OEt})_2][\text{B}(\text{3,5-(F}_3\text{C)}_2\text{C}_6\text{H}_3)_4]$ (0.016 g, 0.015 mmol) was dissolved in CH_2Cl_2 (10 mL) cooled to -70°C , a yellow color being observed. After 10 min, the solution was slowly warmed to room temperature, and after 10 min stirring the solvent was evaporated under reduced pressure,

petroleum ether (bp = 40–60 °C) was added (15 mL) and the mixture stirred vigorously for a few minutes, inducing the precipitation of compound **9** as a yellow powder, in almost quantitative yield. If the solution of this compound is maintained at room temperature for 15 h, it transforms quantitatively into compound **10**. CDCl₃ solutions of compound **9** contain a thermodynamic mixture of two rotamers in a 5 : 1 ratio. The NMR data included below correspond to the major isomer. IR (Nujol): $\nu(\text{IrH})$ 2188 cm⁻¹. ¹H NMR (CDCl₃, 0 °C): δ 7.33, 7.06 (d, 1 H each, ³J_{HH} = 5.5 Hz, SCHCH), 5.86, 5.85, 5.58 (s, 1 H each, 3 CH_{pz}), 3.30, 3.19 (AB spin system, 2 H, ²J_{AB} = 23.5 Hz, CH₂), 2.43, 2.36, 2.30, 2.23, 1.64, 1.42 (s, 3 H each, 6 Me_{pz}), 1.55 (d, 9 H, ²J_{HP} = 10.3 Hz, PMe₃), -18.47 (d, 1 H, ²J_{HP} = 19.0 Hz, IrH). ¹³C{¹H} NMR (CDCl₃, 0 °C): δ 259.7 (Ir=C, ²J_{CP} = 9 Hz), 155.0, 152.7 (SCHCH), 152.7, 150.3, 150.0, 147.3, 146.0, 145.0 (C_{qpz}), 108.2, 108.0, 106.6 (CH_{pz}), 57.5 (CH₂, ¹J_{CH} = 143 Hz), 18.7 (d, ¹J_{CP} = 41 Hz, PMe₃), 17.0, 16.4, 14.4, 12.7, 12.7, 12.6 (Me_{pz}). ³¹P{¹H} NMR (CDCl₃, 0 °C): δ -47.4. Anal. Calc. for C₅₄H₄₈B₂N₆F₂₄PSIr: C, 42.8; H, 3.1; N, 5.5. Found: C, 42.9; H, 2.9; N, 5.7%.

Compound 10

As mentioned above, compound **9** slowly evolves in solution to compound **10** at room temperature. The transformation is complete after 15 h at 25 °C. ¹H NMR (CDCl₃, 25 °C): δ 7.23, 7.09 (d, 2 H each, ³J_{HH} = 2.2 Hz, 4 CH_{th}), 5.96, 5.79, 5.52 (s, 1 H each, 3 CH_{pz}), 2.44, 2.33, 2.32, 2.18, 2.10, 1.20 (s, 3 H each, 6 Me_{pz}), 1.51 (d, 9 H, ²J_{HP} = 10.3 Hz, PMe₃), -21.02 (d, 1 H, ²J_{HP} = 18.4 Hz, IrH).

Compound 11

A mixture of compound **4** (0.01 g, 0.02 mmol) and the acid [H(OEt₂)₂][(3,5-(F₃C)₂C₆H₃)₄B] (0.016 g, 0.015 mmol) were dissolved in CH₂Cl₂ (10 mL) at -50 °C, with the formation of a brown solution. After 10 min the mixture is slowly warmed to room temperature and stirred for 1 h. The solvent was evaporated under vacuo, petroleum ether (bp = 40–60 °C) (15 mL) was added, and the suspension cooled to -70 °C and stirred to provide a brown powder, which was filtered and washed with petroleum ether (5 mL) and dried *in vacuo*. Compound **11** is isolated in high yields (0.027 g, 90%). IR (Nujol): $\nu(\text{IrH})$ 2200 cm⁻¹. ¹H NMR (CDCl₃, 25 °C): δ 6.94 (dd, 1 H, ³J_{AC} = 13.3, ³J_{AB} = 8.9 Hz, H_A), 6.61 (s, 1 H, H_D), 6.02, 5.88, 5.67 (s, 1 H each, 3 CH_{pz}), 4.77 (dd, 1 H, ²J_{CB} = 0.7 Hz, H_C), 3.73 (dd, 1 H, H_B), 2.76, 2.36 (s, 3 H each, Me_A, Me_B), 2.45, 2.38, 2.35, 2.32, 2.17, 2.05 (s, 3 H each, 6 Me_{pz}), -18.64 (s, 1 H, IrH). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 151.5, 151.2, 151.1, 146.3, 146.0, 145.8 (C_{qpz}), 142.1 (CMe_A), 139.7 (CMe_B), 128.6 (CCH_A), 123.2 (CH_{th}), 108.8, 108.7, 107.6 (CH_{pz}), 72.9 (CH_A, ¹J_{CH} = 165 Hz), 49.5 (CH_BH_C, ¹J_{CH} = 163 Hz), 14.9, 14.3, 14.2, 13.8, 13.7, 13.5, 13.5, 12.9 (Me_{pz}, Me_A and Me_B). Anal. Calc. for C₅₃H₄₇B₂N₆OF₂₄SiIr: C, 42.8; H, 3.2; N, 5.6. Found: C, 43.3; H, 3.0; N, 5.7%.

Compound 12

Compound **11** (0.05 g, 0.03 mmol) was dissolved in acetonitrile (10 mL) and the resulting solution was stirred for 20 h at 80 °C. The solvent was then evaporated under reduced pressure and pentane (10 mL) was added. After cooling down to -70 °C and stirring vigorously for a few minutes, the solid formed was separated by filtration and washed with petroleum ether

(bp = 40–60 °C) (5 mL) and dried *in vacuo*. Compound **12** was isolated as a brown microcrystalline solid (0.04 g, 75%). ¹H NMR (CDCl₃, 25 °C): δ 6.56 (s, 1 H, CH_{th}), 5.86, 5.84 (s, 1 : 2, 3 CH_{pz}), 2.73, 2.03 (m, 2 H each, CH₂CH₂Ir), 2.52 (s, 6 H, 2 NCMe), 2.39, 2.36, 2.18, 2.15 (s, 2 : 2 : 1 : 1, 6 Me_{pz}), 2.38, 2.36 (s, 3 H each, 2 Me_{th}). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 150.8, 149.6, 145.1, 144.6 (2 : 1 : 2 : 1, C_{qpz}), 150.5, 138.8, 135.5 (C_{th}), 126.1 (CH_{th}), 118.1 (NCMe), 108.8, 107.2 (2 : 1, CH_{pz}), 28.3 (IrCH₂CH₂, ¹J_{CH} = 126 Hz), 15.1, 13.8, 12.7, 11.9 (1 : 2 : 1 : 2, Me_{pz}), 12.9, 12.8 (Me_{th}), 3.2 (NCMe, ¹J_{CH} = 139 Hz), -5.2 (IrCH₂, ¹J_{CH} = 127 Hz). Anal. Calc. for C₅₉H₅₁B₂N₈F₂₄SiIr: C, 45; H, 3.2; N, 7.1. Found: C, 44.8; H, 3.1; N, 7.2%.

Compound 13

A mixture of compound **5** (0.015 g, 0.02 mmol) and the acid [H(OEt₂)₂][(3,5-(F₃C)₂C₆H₃)₄B] (0.020 g, 0.02 mmol) was dissolved in CDCl₃ (0.5 mL) in a NMR tube. A ¹H NMR spectrum was registered immediately at 25 °C, and afterwards the sample was cooled to 0 °C to register the ¹³C{¹H} NMR, to reveal the formation of the title compound. ¹H NMR (CDCl₃, 25 °C): δ 6.80 (s, 1 H, CH_{th}), 6.02, 5.97, 5.82 (s, 1 H each, 3 CH_{pz}), 4.40, 4.00 (d, 1 H each, ²J_{HH} = 15.8 Hz, C_qCH₂C_q), 3.38 (br q, 1 H, ³J_{HMe} = 7.6 Hz, CHMe), 2.6–1.0 (s, 6 Me_{pz} and 2 Me_{th}), 1.16 (t, 3 H, ³J_{HH} = 6.5 Hz, CH₂Me), 0.74 (d, 3 H, CHMe), -17.69 (s, 1 H, IrH). The methylene protons CH₂Me were not located. ¹³C{¹H} NMR (CDCl₃, 0 °C): δ 252.3 (Ir=C). Due to the complexity of the spectrum and the low ratio signal/noise, the remaining resonances were not assigned.

Compound 14

A mixture of compound **5** (0.008 g, 0.010 mmol) and the acid [H(OEt₂)₂][(3,5-(F₃C)₂C₆H₃)₄B] (0.011 g, 0.010 mmol) was dissolved in CH₂Cl₂ (5 mL) at -70 °C. After 10 min stirring, the cold bath was removed and the sample allowed to warm to room temperature. After 20 min stirring under these conditions, the solvent was evaporated to dryness, pentane added (10 mL) and the mixture cooled again to -70 °C and stirred. Compound **14** was obtained as a brown solid in almost quantitative yield. IR (Nujol): $\nu(\text{OH})$ 3419 cm⁻¹, $\nu(\text{IrH})$ 2171 cm⁻¹. ¹H NMR (CDCl₃, 25 °C): δ 6.75, 6.70 (s, 1 H each, 2 CH_{th}), 5.89, 5.81, 5.61 (s, 1 H each, 3 CH_{pz}), 4.23, 3.97 (d, 1 H each, ²J_{HH} = 13 Hz, CH₂), 3.37 (s, 2 H, OH₂), 2.57, 2.42 (m, 1 H each, CH₂Me), 2.40, 2.39, 2.36, 2.34, 2.22, 2.22, 2.17, 1.87, 1.42 (s, 3 H each, 6 Me_{pz} and 3 Me_{th}), 1.15 (t, 3 H, ³J_{HH} = 7.5 Hz, CH₂Me), -20.40 (s, 1 H, IrH). ¹³C{¹H} NMR (CDCl₃, 25 °C): δ 153.4, 151.7, 150.3, 146.2, 145.7, 145.4 (C_{qpz}), 145.5, 142.3, 139.1, 137.6, 135.0, 134.0 (C_{th}), 132.3, 127.8 (CH_{th}), 107.9, 107.0, 106.8 (CH_{pz}), 25.9 (CH₂Me), 22.9 (CH₂), 14.9, 14.8, 13.9, 13.7, 13.3, 13.1, 12.7, 12.6, 12.4, 12.0 (Me_{pz}, Me_{th} and CH₂Me). Anal. Calc. for C₆₁H₅₃B₂N₆F₂₄SiIr: C, 45.7; H, 3.4; N, 5.2. Found: C, 46.3; H, 3.4; N, 5.2%.

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