Supporting Information

Alkenyl-functionalized NHC Iridium-based catalysts for hydrosilylation.

Alessandro Zanardi, Eduardo Peris, Jose A. Mata*

Departament Química Inorgànica i Orgànica, Universitat Jaume I, Av. Vicent Sos Baynat s/n, E-12071, Castelló, Spain.

Fax: 34 964728214. Tel: 34 964728243. E-mail: jmata@qio.uji.es

Summary: A family of alkene-functionalized N-heterocyclic carbene iridium complexes has been synthesized, providing a series of monocoordinated, bischeleate and pincer mixed alkenyl-NHC species. The coordination of the olefin is highly influenced by the nature of the substituents on the NHC ring, and on the length of the alkenyl branch. A fluxional process involving the coordination/decoordination of the olefin in the bis-allyl-NHC complexes has been studied, and the activation parameters have been determined by means of VT-NMR-spectroscopy. The monocoordinated complexes are highly active in the hydrosilylation of terminal alkynes, showing high selectivity on the Z-isomers, with no alpha isomers or dehydrogenative silylation processes observed.
1.- General Procedures.
2.- Catalytic studies.
3.- Crystallographic data.
   3.1 Experimental crystallographic data collection for compound 2a.
   3.2 Experimental crystallographic data collection for compound 2bPF6.
   3.3 Experimental crystallographic data collection for compound 3.
4.- NMR characterization of complex 1a.
5.- Variable-Temperature NMR Studies.
   5.1 Kinetic constant at the coalescence temperature for complex 1a.
   5.2 Line shape analysis data for complex 1a signal at 6.9 ppm.
   5.3 Line shape analysis data for complex 1a signal at 6.7 ppm.
6.- Ligand precursors
1.- General Procedures.
Syntheses and catalytic experiments were carried out under aerobic conditions and without solvent pretreatment. Reagents and solvents (reagent grade) commercially available were used as received unless otherwise stated. NMR spectra were recorded on Variant spectrometers operating at 300 or 500 MHz ($^1$H NMR) and 75 and 125 MHz ($^{13}$C NMR), respectively, and referenced to SiMe$_4$ ($\delta$ in ppm and $J$ in Hertz). NMR spectra were recorded at room temperature with CDCl$_3$ unless for the VT-NMR analyses. Assignments are based on $^1$H, $^{13}$C, APT and COSY experiments. A QTOF I (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal Z-spray-electrospray interface (Micromass, Manchester, UK) was used. The drying gas as well as nebulizing gas was nitrogen at a flow of 400L/h and 80 L/h respectively. The temperature of the source block was set to 120 °C and the desolvation temperature to 150°C. A capillary voltage of 3.5 KV was used in the positive scan mode and the cone voltage was set to 30V. Mass calibration was performed using a solution of sodium iodide in isopropanol:water (50:50) from m/z 150 to 1000 a.m.u. Sample solutions (aprox 1x10$^{-4}$ M) in dichloromethane:methanol (50:50) were infused via syringe pump directly connected to the interface at a flow of 10 μL/min. A 1 μg/mL solution of 3,5-diiodo-L-tyrosine was used as lock mass. Elemental analyses were carried out in a Euro EA 3000 Eurovector Analyser.

2.- Catalytic studies.
Hydrosilylation reactions were carried out in Schlenk tubes under aerobic conditions. In a typical experiment, alkyne (1 Eq.), dimethylphenylsilane (1 Eq.), catalyst (1 mol %), ferrocene (0.1 Eq.; Internal reference) and 10 ml of CHCl$_3$, were stirred at room temperature or 60 °C for 24 h. Conversion and isomer distribution was monitored by $^1$H NMR. Several aliquots of 0.5 mL were taken at the desired sampling time.
Table 1 Hydrosilylation of alkynes at room temperature (hydrosilane = HSiMe₂Ph).

| Entry | Catalyst<sup>a</sup> | Substrate     | Conv (%)<sup>b</sup> | α   | E  | Z  |
|-------|----------------------|---------------|-----------------------|-----|----|----|
| 1     | 1b                   | 1-Hexyne      | 21                    | --  | -- | 100|
| 2     | 1a                   | 1-Hexyne      | 68                    | --  | 7  | 93 |
| 3     | 1c                   | 1-Hexyne      | 25                    | --  | -- | 100|
| 4     | 3                    | 1-Hexyne      | 71                    | --  | 12 | 88 |
| 5     | 4                    | 1-Hexyne      | 46                    | --  | 9  | 91 |
| 6     | 5                    | 1-Hexyne      | 55                    | --  | 17 | 83 |
| 7     | 1b                   | Phenylacetylene | 57                   | --  | 34 | 66 |
| 8<sup>c</sup> | 1a             | Phenylacetylene | 92                   | --  | 28 | 72 |
| 9     | 1c                   | Phenylacetylene | 45                   | --  | 20 | 80 |
| 10    | 3                    | Phenylacetylene | 18                   | --  | 7  | 93 |
| 11    | 4                    | Phenylacetylene | 0                    |     |    |    |
| 12<sup>c</sup> | 5               | Phenylacetylene | 80                   | --  | 20 | 80 |

Aerobic conditions, Temp 25 ºC, Time 1 h, Solvent CHCl₃. <sup>a</sup>Catalyst loading (1 mol%); <sup>b</sup>Yields determined by ¹H NMR. <sup>c</sup>Catalyst active at least for three runs.
Table 2 Hydrosilylation of phenylacetylene at 60ºC (hydrosilane = HSiMe₂Ph).

| Entry | Catalyst<sup>a</sup> | Time (h) | Conv (%)<sup>b</sup> | α | E | Z |
|-------|----------------------|----------|----------------------|---|---|---|
| 1     | 1b                   | 1        | 70                   | -- | 10 | 90 |
| 2     | 1a                   | 1        | 100                  | -- | 23 | 77 |
| 3     | 1c                   | 1        | 67                   | -- | 12 | 88 |
| 4     | 3                    | 1        | 36                   | -- | 21 | 79 |
| 5     | 4                    | 1        | 55                   | -- | 26 | 74 |
| 6     | 5                    | 1        | 100                  | -- | 27 | 73 |
| 7     | 1b                   | 2        | 100                  | -- | 23 | 76 |
| 8     | 1a                   | 2        | 100                  | -- | 17 | 83 |
| 9     | 1c                   | 2        | 100                  | -- | 20 | 80 |
| 10    | 3                    | 2        | 100                  | -- | 20 | 80 |
| 11    | 4                    | 2        | 100                  | -- | 31 | 69 |
| 12    | 5                    | 2        | 100                  | -- | 35 | 65 |
| 13    | 1a<sup>c</sup>       | 2        | 85                   | -- | 30 | 70 |
| 14    | 1a<sup>d</sup>       | 2        | 45<sup>e</sup>       | -- | 35 | 65 |

Aerobic conditions, Temp 60 ºC, Solvent CHCl₃. <sup>a</sup>Catalyst loading (1 mol%) unless otherwise stated; <sup>b</sup>Yields determined by <sup>1</sup>H NMR. <sup>c</sup>Catalyst loading (0.1 mol%). <sup>d</sup>Catalyst loading (0.01 mol%). <sup>e</sup>Full conversion was achieved after 24h.
3.- Crystallographic data

A single crystal was mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Siemens Smart CCD diffractometer using graphite monochromated Mo-Kα radiation (λ=0.71073 Å) with a nominal crystal to detector distance of 4.0 cm. An hemisphere of data was collected based on three w-scans runs (starting ω=-28º) at values φ=0, 90 and 180 with the detector at 2θ=28º. At each of these runs, frames (606, 435 and 230 respectively) were collected at 0.3º intervals and 40 s per frame. The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS. (1) The raw intensity data were converted (including corrections for Lorentz and polarization effects) to structure amplitudes and their esd’s using the SAINT program (2).

(1) Sheldrick, G.M. SHELXTL, version 5.1, Bruker AXS, Inc., Madison, WI, 1997. 24.

(2) a) SAINT version 5.0 Bruker Analytical X-ray Systems, Madison, WI, 1998. b) Sheldrick, G. M. SADABS Empirical absorption program, University of Göttingen, Göttingen, Germany, 1996.
3.1.- Experimental crystallographic data collection for compound 2a.

**Figure 1.** ORTEP diagram of complex 2a showing 50% probability ellipsoids. Hydrogen atoms and the counterion (BF₄⁻) have been omitted for clarity.

**Table 3.** Crystal data and structure refinement for 2a

| Property                              | Value                             |
|---------------------------------------|-----------------------------------|
| Identification code                   | str861m                           |
| Empirical formula                     | C17 H24 B F4 Ir N2                |
| Formula weight                        | 535.39                            |
| Temperature                           | 293(2) K                          |
| Wavelength                            | 0.71073 Å                         |
| Crystal system                        | Monoclinic                        |
| Space group                           | P2(1)/c                           |
| Unit cell dimensions                  | a = 8.1277(4) Å, b = 36.568(2) Å, c = 12.0502(6) Å |
| Volume                                | 3532.0(3) Å³                      |
| Z                                     | 8                                 |
| Density (calculated)                  | 2.014 Mg/m³                       |
Absorption coefficient 7.602 mm\(^{-1}\)

F(000) 2064

Crystal size 0.19 x 0.12 x 0.10 mm\(^3\)

Theta range for data collection 1.11 to 27.50°.

Index ranges -10<=h<=10, -47<=k<=44, -12<=l<=15

Reflections collected 24448

Independent reflections 8122 [R(int) = 0.0742]

Completeness to theta = 27.50° 99.9 %

Absorption correction Bruker SADABS

Refinement method Full-matrix least-squares on F\(^2\)

Data / restraints / parameters 8122 / 0 / 451

Goodness-of-fit on F\(^2\) 1.047

Final R indices [I>2sigma(I)] R1 = 0.0448, wR2 = 0.0778

R indices (all data) R1 = 0.0953, wR2 = 0.0942

Largest diff. peak and hole 1.281 and -1.175 e.Å\(^{-3}\)

**Table 4.** Bond lengths [Å] and angles [°] for 2a.

| Bond       | Length  | Bond       | Length  | Bond       | Length  |
|------------|---------|------------|---------|------------|---------|
| Ir(1)-C(1) | 1.934(9) | C(2)-C(3)  | 1.374(13) |
| Ir(1)-C(5) | 2.214(8) | C(4)-C(5)  | 1.531(12) |
| Ir(1)-C(6) | 2.225(9) | C(5)-C(6)  | 1.404(12) |
| Ir(1)-C(15)| 2.230(8) | C(7)-C(8)  | 1.511(13) |
| Ir(1)-C(9) | 2.261(9) | C(8)-C(9)  | 1.373(13) |
| Ir(1)-C(14)| 2.266(8) | C(10)-C(11)| 1.368(12) |
| Ir(1)-C(11)| 2.270(9) | C(10)-C(17)| 1.519(13) |
| Ir(1)-C(10)| 2.289(8) | C(11)-C(12)| 1.481(12) |
| Ir(1)-C(8) | 2.308(8) | C(12)-C(13)| 1.567(13) |
| C(1)-N(2)  | 1.318(10)| C(13)-C(14)| 1.505(12) |
| C(1)-N(1)  | 1.358(11)| C(14)-C(15)| 1.386(11)|
| F(1)-B(1)  | 1.380(12)| C(15)-C(16)| 1.496(12)|
| B(1)-F(2)  | 1.350(12)| C(16)-C(17)| 1.545(13)|
| B(1)-F(3)  | 1.374(12)| Ir(31)-C(31)| 1.936(9)|
| B(1)-F(4)  | 1.381(13)| Ir(31)-C(36)| 2.179(9)|
| N(1)-C(2)  | 1.385(11)| Ir(31)-C(35)| 2.185(9)|
| N(1)-C(4)  | 1.470(10)| Ir(31)-C(44)| 2.239(8)|
| N(2)-C(3)  | 1.383(11)| Ir(31)-C(45)| 2.274(8)|
| N(2)-C(7)  | 1.481(11)| Ir(31)-C(39)| 2.279(9)|
| Bond                  | Distance     | Bond                  | Distance     | Bond                  | Distance     |
|----------------------|--------------|----------------------|--------------|----------------------|--------------|
| Ir(31)-C(40)         | 2.284(9)     | C(6)-Ir(1)-C(14)     | 160.0(3)     |
| Ir(31)-C(41)         | 2.294(8)     | C(15)-Ir(1)-C(14)    | 35.9(3)      |
| Ir(31)-C(38)         | 2.309(10)    | C(9)-Ir(1)-C(14)     | 114.7(4)     |
| N(31)-C(31)          | 1.341(11)    | C(1)-Ir(1)-C(11)     | 164.6(4)     |
| N(31)-C(32)          | 1.392(11)    | C(5)-Ir(1)-C(11)     | 118.2(3)     |
| N(31)-C(34)          | 1.444(11)    | C(6)-Ir(1)-C(11)     | 104.7(3)     |
| C(31)-N(32)          | 1.333(11)    | C(15)-Ir(1)-C(11)    | 92.5(3)      |
| F(31)-B(31)          | 1.376(12)    | C(9)-Ir(1)-C(11)     | 85.6(4)      |
| B(31)-F(34)          | 1.330(14)    | C(14)-Ir(1)-C(11)    | 78.2(3)      |
| B(31)-F(33)          | 1.360(12)    | C(1)-Ir(1)-C(10)     | 160.0(3)     |
| B(31)-F(32)          | 1.370(13)    | C(5)-Ir(1)-C(10)     | 85.9(3)      |
| N(32)-C(33)          | 1.378(11)    | C(6)-Ir(1)-C(10)     | 86.6(4)      |
| N(32)-C(37)          | 1.458(11)    | C(15)-Ir(1)-C(10)    | 78.3(3)      |
| C(32)-C(33)          | 1.345(13)    | C(9)-Ir(1)-C(10)     | 113.9(4)     |
| C(34)-C(35)          | 1.544(14)    | C(14)-Ir(1)-C(10)    | 85.0(3)      |
| C(35)-C(36)          | 1.389(14)    | C(11)-Ir(1)-C(10)    | 34.9(3)      |
| C(37)-C(38)          | 1.523(14)    | C(1)-Ir(1)-C(8)      | 73.9(4)      |
| C(38)-C(39)          | 1.352(15)    | C(5)-Ir(1)-C(8)      | 142.5(3)     |
| C(40)-C(41)          | 1.384(13)    | C(6)-Ir(1)-C(8)      | 117.2(4)     |
| C(40)-C(47)          | 1.508(14)    | C(15)-Ir(1)-C(8)     | 114.9(4)     |
| C(41)-C(42)          | 1.506(13)    | C(9)-Ir(1)-C(8)      | 35.0(3)      |
| C(42)-C(43)          | 1.520(13)    | C(14)-Ir(1)-C(8)     | 82.3(3)      |
| C(43)-C(44)          | 1.503(12)    | C(11)-Ir(1)-C(8)     | 91.1(4)      |
| C(44)-C(45)          | 1.391(13)    | C(10)-Ir(1)-C(8)     | 126.0(3)     |
| C(45)-C(46)          | 1.510(12)    | N(2)-C(1)-N(1)       | 106.7(8)     |
| C(46)-C(47)          | 1.507(14)    | N(2)-C(1)-Ir(1)      | 128.9(7)     |
| C(1)-Ir(1)-C(5)      | 76.8(3)      | N(1)-C(1)-Ir(1)      | 123.9(7)     |
| C(1)-Ir(1)-C(6)      | 85.4(4)      | F(2)-B(1)-F(3)       | 110.8(9)     |
| C(5)-Ir(1)-C(6)      | 36.9(3)      | F(2)-B(1)-F(1)       | 111.7(9)     |
| C(1)-Ir(1)-C(15)     | 91.2(4)      | F(3)-B(1)-F(1)       | 109.0(9)     |
| C(5)-Ir(1)-C(15)     | 88.3(3)      | F(2)-B(1)-F(4)       | 110.0(9)     |
| C(6)-Ir(1)-C(15)     | 124.3(4)     | F(3)-B(1)-F(4)       | 108.4(9)     |
| C(1)-Ir(1)-C(9)      | 83.7(4)      | F(1)-B(1)-F(4)       | 106.8(9)     |
| C(5)-Ir(1)-C(9)      | 119.3(4)     | C(1)-N(1)-C(2)       | 110.3(7)     |
| C(6)-Ir(1)-C(9)      | 85.3(4)      | C(1)-N(1)-C(4)       | 116.3(7)     |
| C(15)-Ir(1)-C(9)     | 149.5(4)     | C(2)-N(1)-C(4)       | 133.3(8)     |
| C(1)-Ir(1)-C(14)     | 96.4(3)      | C(1)-N(2)-C(3)       | 110.6(7)     |
| C(5)-Ir(1)-C(14)     | 124.1(3)     | C(1)-N(2)-C(7)       | 114.1(7)     |
C(3)-N(2)-C(7) 135.3(8)  C(44)-Ir(31)-C(45) 35.9(3)
C(3)-C(2)-N(1) 105.4(8)  C(31)-Ir(31)-C(39) 82.8(4)
C(2)-C(3)-N(2) 107.0(8)  C(36)-Ir(31)-C(39) 86.6(5)
N(1)-C(4)-C(5) 107.7(7)  C(35)-Ir(31)-C(39) 120.9(4)
C(6)-C(5)-C(4) 121.1(8)  C(44)-Ir(31)-C(39) 145.7(4)
C(6)-C(5)-Ir(1) 72.0(5)  C(45)-Ir(31)-C(39) 110.8(4)
C(4)-C(5)-Ir(1) 110.6(6)  C(31)-Ir(31)-C(40) 164.8(4)
C(5)-C(6)-Ir(1) 71.2(5)  C(36)-Ir(31)-C(40) 103.7(4)
N(2)-C(7)-C(8) 109.2(7)  C(35)-Ir(31)-C(40) 117.6(4)
C(9)-C(8)-C(7) 122.2(9)  C(44)-Ir(31)-C(40) 92.7(4)
C(9)-C(8)-Ir(1) 70.7(6)  C(45)-Ir(31)-C(40) 78.7(3)
C(7)-C(8)-Ir(1) 109.1(6)  C(39)-Ir(31)-C(40) 84.5(4)
C(8)-C(9)-Ir(1) 74.4(5)  C(31)-Ir(31)-C(41) 159.9(4)
C(11)-C(10)-C(17) 124.8(9)  C(36)-Ir(31)-C(41) 87.9(4)
C(11)-C(10)-Ir(1) 71.8(5)  C(35)-Ir(31)-C(41) 86.1(4)
C(17)-C(10)-Ir(1) 111.7(6)  C(44)-Ir(31)-C(41) 77.3(3)
C(10)-C(11)-C(12) 126.0(9)  C(45)-Ir(31)-C(41) 84.5(3)
C(10)-C(11)-Ir(1) 73.3(5)  C(39)-Ir(31)-C(41) 115.0(4)
C(12)-C(11)-Ir(1) 110.8(6)  C(40)-Ir(31)-C(41) 35.2(3)
C(11)-C(12)-C(13) 113.0(7)  C(31)-Ir(31)-C(38) 73.0(4)
C(14)-C(13)-C(12) 114.6(7)  C(36)-Ir(31)-C(38) 117.2(5)
C(15)-C(14)-C(13) 124.2(8)  C(35)-Ir(31)-C(38) 142.3(4)
C(15)-C(14)-Ir(1) 70.6(5)  C(44)-Ir(31)-C(38) 112.1(4)
C(13)-C(14)-Ir(1) 112.9(6)  C(45)-Ir(31)-C(38) 79.6(4)
C(14)-C(15)-C(16) 125.8(9)  C(39)-Ir(31)-C(38) 34.3(4)
C(14)-C(15)-Ir(1) 73.5(5)  C(40)-Ir(31)-C(38) 91.9(4)
C(16)-C(15)-Ir(1) 111.7(6)  C(41)-Ir(31)-C(38) 126.9(4)
C(15)-C(16)-C(17) 112.8(8)  C(31)-N(31)-C(32) 109.1(8)
C(10)-C(17)-C(16) 114.9(8)  C(31)-N(31)-C(34) 115.8(8)
C(31)-Ir(31)-C(36) 83.7(4)  C(32)-N(31)-C(34) 135.0(8)
C(31)-Ir(31)-C(35) 76.3(4)  N(32)-C(31)-N(31) 106.9(8)
C(36)-Ir(31)-C(35) 37.1(4)  N(32)-C(31)-Ir(31) 127.9(7)
C(31)-Ir(31)-C(44) 93.2(4)  N(31)-C(31)-Ir(31) 124.5(7)
C(36)-Ir(31)-C(44) 127.0(4)  F(34)-B(31)-F(33) 111.5(10)
C(35)-Ir(31)-C(44) 90.7(4)  F(34)-B(31)-F(32) 113.8(11)
C(31)-Ir(31)-C(45) 98.2(4)  F(33)-B(31)-F(32) 110.4(10)
C(36)-Ir(31)-C(45) 162.6(4)  F(34)-B(31)-F(31) 107.1(10)
C(35)-Ir(31)-C(45) 126.5(4)  F(33)-B(31)-F(31) 108.9(10)
| Bond                        | Angle (°) | Bond                        | Angle (°) |
|-----------------------------|-----------|-----------------------------|-----------|
| F(32)-B(31)-F(31)          | 104.7(10) | C(41)-C(40)-C(47)          | 123.2(9)  |
| C(31)-N(32)-C(33)          | 110.4(8)  | C(41)-C(40)-Ir(31)         | 72.8(5)   |
| C(31)-N(32)-C(37)          | 116.4(7)  | C(47)-C(40)-Ir(31)         | 107.9(6)  |
| C(33)-N(32)-C(37)          | 133.2(8)  | C(40)-C(41)-C(42)          | 126.3(9)  |
| C(33)-C(32)-N(31)          | 107.1(8)  | C(40)-C(41)-Ir(31)         | 72.0(5)   |
| C(32)-C(33)-N(32)          | 106.6(8)  | C(42)-C(41)-Ir(31)         | 112.4(6)  |
| N(31)-C(34)-C(35)          | 107.4(8)  | C(41)-C(42)-C(43)          | 114.8(8)  |
| C(36)-C(35)-C(34)          | 119.1(10) | C(44)-C(43)-C(42)          | 112.7(8)  |
| C(36)-C(35)-Ir(31)         | 71.2(6)   | C(45)-C(44)-C(43)          | 126.6(9)  |
| C(34)-C(35)-Ir(31)         | 110.6(6)  | C(45)-C(44)-Ir(31)         | 73.4(5)   |
| C(35)-C(36)-Ir(31)         | 71.7(6)   | C(43)-C(44)-Ir(31)         | 111.3(6)  |
| N(32)-C(37)-C(38)          | 106.0(8)  | C(44)-C(45)-C(46)          | 123.8(9)  |
| C(39)-C(38)-C(37)          | 123.0(10) | C(44)-C(45)-Ir(31)         | 70.7(5)   |
| C(39)-C(38)-Ir(31)         | 71.6(6)   | C(46)-C(45)-Ir(31)         | 112.1(6)  |
| C(37)-C(38)-Ir(31)         | 110.9(6)  | C(47)-C(46)-C(45)          | 114.8(7)  |
| C(38)-C(39)-Ir(31)         | 74.1(6)   | C(46)-C(47)-C(40)          | 115.6(8)  |
3.2.- Experimental crystallographic data collection for compound 2bPF₆.

![ORTEP diagram of complex 2bPF₆ showing 50% probability ellipsoids. Hydrogen atoms and the counterion (PF₆⁻) have been omitted for clarity.]

**Figure 2.** ORTEP diagram of complex 2bPF₆ showing 50% probability ellipsoids. Hydrogen atoms and the counterion (PF₆⁻) have been omitted for clarity.

**Table 5.** Crystal data and structure refinement for 2bPF₆.

| Property                              | Value                                  |
|---------------------------------------|----------------------------------------|
| Identification code                   | str862mm                               |
| Empirical formula                     | C₁₇H₂₂Cl₂F₆IrN₂P                       |
| Formula weight                        | 662.44                                 |
| Temperature                           | 293(2) K                               |
| Wavelength                            | 0.71073 Å                              |
| Crystal system                        | Monoclinic                             |
| Space group                           | P2(1)/c                                |
| Unit cell dimensions a = 15.2900(11) Å| α = 90°                                 |
| b = 10.7009(8) Å                      | β = 96.789(2)°                         |
| c = 12.7347(10) Å                     | γ = 90°                                 |
| Volume                                | 2069.0(3) Å                            |
| Z                                      | 4                                      |
| Density (calculated)                  | 2.127 Mg/m³                            |
| Absorption coefficient                | 6.848 mm⁻¹                             |
| F(000)                                | 1272                                   |
| Crystal size                          | 0.12 x 0.11 x 0.08 mm³                 |
| Theta range for data collection       | 1.34 to 25.00°                         |
| Index ranges                          | -18≤h≤13, -12≤k≤12, -14≤l≤15           |
| Reflections collected                 | 8374                                   |
| Independent reflections               | 3109 [R(int) = 0.0518]                 |
| Completeness to theta = 25.00°        | 85.4 %                                 |
Refinement method
Data / restraints / parameters
Goodness-of-fit on F^2
Final R indices [I>2sigma(I)]
R indices (all data)
Largest diff. peak and hole

Table 6. Bond lengths [Å] and angles [°] for 2b

| Bond                        | Length [Å]     | Bond                        | Length [Å] | Angle [°]     |
|-----------------------------|----------------|-----------------------------|------------|---------------|
| Ir(1)-C(1)                  | 1.944(12)      | C(10)-C(11)                 | 1.31(3)    |
| Ir(1)-C(15)                 | 2.186(14)      | C(10)-C(17)                 | 1.53(3)    |
| Ir(1)-C(9)                  | 2.203(12)      | C(11)-C(12)                 | 1.49(2)    |
| Ir(1)-C(5)                  | 2.221(14)      | C(12)-C(13)                 | 1.50(3)    |
| Ir(1)-C(8)                  | 2.247(12)      | C(13)-C(14)                 | 1.51(2)    |
| Ir(1)-C(6)                  | 2.248(18)      | C(14)-C(15)                 | 1.29(2)    |
| Ir(1)-C(11)                 | 2.253(13)      | C(15)-C(16)                 | 1.58(3)    |
| Ir(1)-C(14)                 | 2.257(13)      | C(16)-C(17)                 | 1.44(3)    |
| Ir(1)-C(10)                 | 2.266(19)      | C(1)-Ir(1)-C(15)            | 91.9(5)    |
| P(1)-F(5)                   | 1.472(19)      | C(1)-Ir(1)-C(9)             | 85.3(5)    |
| P(1)-F(3)                   | 1.522(14)      | C(15)-Ir(1)-C(9)            | 124.7(6)   |
| P(1)-F(1)                   | 1.537(18)      | C(1)-Ir(1)-C(5)             | 76.2(5)    |
| P(1)-F(2)                   | 1.540(16)      | C(15)-Ir(1)-C(5)            | 115.6(5)   |
| P(1)-F(6)                   | 1.559(13)      | C(9)-Ir(1)-C(5)             | 117.1(6)   |
| Cl(1)-C(2)                  | 1.685(17)      | C(1)-Ir(1)-C(8)             | 75.4(5)    |
| N(1)-C(1)                   | 1.320(18)      | C(15)-Ir(1)-C(8)            | 89.2(6)    |
| N(1)-C(2)                   | 1.407(19)      | C(9)-Ir(1)-C(8)             | 36.8(6)    |
| N(1)-C(4)                   | 1.454(18)      | C(5)-Ir(1)-C(8)             | 142.6(5)   |
| C(1)-N(2)                   | 1.336(16)      | C(1)-Ir(1)-C(6)             | 83.7(6)    |
| C(2)-C(3)                   | 1.694(13)      | C(15)-Ir(1)-C(6)            | 151.4(6)   |
| N(2)-C(3)                   | 1.408(19)      | C(9)-Ir(1)-C(6)             | 83.3(6)    |
| N(2)-C(7)                   | 1.44(2)        | C(5)-Ir(1)-C(6)             | 35.9(5)    |
| C(2)-C(3)                   | 1.35(2)        | C(8)-Ir(1)-C(6)             | 116.7(6)   |
| C(4)-C(5)                   | 1.567(19)      | C(1)-Ir(1)-C(11)            | 166.0(5)   |
| C(5)-C(6)                   | 1.38(2)        | C(15)-Ir(1)-C(11)           | 91.2(5)    |
| C(7)-C(8)                   | 1.52(2)        | C(9)-Ir(1)-C(11)            | 104.1(6)   |
| C(8)-C(9)                   | 1.41(2)        | C(5)-Ir(1)-C(11)            | 90.2(5)    |
Table of bond angles (°) in the molecule:

| Bond          | Angle  |
|---------------|--------|
| C(6)-Ir(1)-C(11) | 87.1(6) |
| C(1)-Ir(1)-C(14) | 97.4(6) |
| C(15)-Ir(1)-C(14) | 33.8(6) |
| C(9)-Ir(1)-C(14) | 158.0(7) |
| C(5)-Ir(1)-C(14) | 84.6(6) |
| C(8)-Ir(1)-C(14) | 122.8(6) |
| C(6)-Ir(1)-C(14) | 118.7(7) |
| C(11)-Ir(1)-C(14) | 77.9(6) |
| C(1)-Ir(1)-C(10) | 160.0(7) |
| C(15)-Ir(1)-C(10) | 79.5(7) |
| C(9)-Ir(1)-C(10) | 84.9(6) |
| C(5)-Ir(1)-C(10) | 123.8(6) |
| C(8)-Ir(1)-C(10) | 86.4(6) |
| C(6)-Ir(1)-C(10) | 112.4(8) |
| C(11)-Ir(1)-C(10) | 33.8(6) |
| C(14)-Ir(1)-C(10) | 85.5(6) |
| F(5)-P(1)-F(3) | 88.4(17) |
| F(5)-P(1)-F(1) | 102(2) |
| F(3)-P(1)-F(1) | 87.4(10) |
| F(5)-P(1)-F(2) | 174(2) |
| F(3)-P(1)-F(2) | 90.5(13) |
| F(1)-P(1)-F(2) | 84.3(17) |
| F(5)-P(1)-F(6) | 94.0(16) |
| F(3)-P(1)-F(6) | 177.4(14) |
| F(1)-P(1)-F(6) | 93.3(10) |
| F(2)-P(1)-F(6) | 87.1(13) |
| F(5)-P(1)-F(4) | 82.3(17) |
| F(3)-P(1)-F(4) | 94.7(10) |
| F(1)-P(1)-F(4) | 175.7(14) |
| F(2)-P(1)-F(4) | 91.8(16) |
| F(6)-P(1)-F(4) | 84.5(9) |
| C(1)-N(1)-C(2) | 109.8(12) |
| C(1)-N(1)-C(4) | 117.7(12) |
| C(2)-N(1)-C(4) | 132.5(14) |
| N(1)-C(1)-N(2) | 108.4(12) |
| N(1)-C(1)-Ir(1) | 124.5(9) |
3.3.- Experimental crystallographic data collection for compound 3.

![Figure 3. ORTEP diagram of complex 3 showing 35% probability ellipsoids. Hydrogen atoms have been omitted for clarity.](image-url)
Table 7. Crystal data and structure refinement for 3.

| Parameter                              | Value                                      |
|----------------------------------------|--------------------------------------------|
| Identification code                    | str871m                                    |
| Empirical formula                      | C21 H32 Cl Ir N2                            |
| Formula weight                         | 540.14                                     |
| Temperature                            | 293(2) K                                   |
| Wavelength                             | 0.71073 Å                                  |
| Crystal system                         | Triclinic                                  |
| Space group                            | P-1                                        |
| Unit cell dimensions                   | a = 12.0233(11) Å, b = 13.9740(14) Å, c = 14.7666(15) Å |
|                                        | α = 64.168(2)°, β = 85.560(3)°, γ = 89.213(2)° |
| Volume                                 | 2225.8(4) Å³                               |
| Z                                      | 4                                          |
| Density (calculated)                   | 1.612 Mg/m³                                |
| Absorption coefficient                 | 6.124 mm⁻¹                                 |
| F(000)                                 | 1064                                       |
| Crystal size                           | 0.13 x 0.11 x 0.09 mm³                     |
| Theta range for data collection        | 1.62 to 25.0°                              |
| Index ranges                           | -13≤h≤14, -14≤k≤16, -11≤l≤17               |
| Reflections collected                  | 12840                                      |
| Independent reflections                | 7842 [R(int) = 0.0421]                     |
| Completeness to theta = 25.00°         | 100.0 %                                    |
| Absorption correction                  | Bruker SADABS                               |
| Refinement method                      | Full-matrix least-squares on F²            |
| Data / restraints / parameters         | 7842 / 32 / 448                            |
| Goodness-of-fit on F²                  | 1.005                                       |
| Final R indices [I>2sigma(I)]          | R1 = 0.0468, wR2 = 0.1019                  |
| R indices (all data)                   | R1 = 0.0898, wR2 = 0.1205                  |
| Largest diff. peak and hole            | 1.104 and -0.768 e.Å⁻³                    |
Table 8. Bond lengths [Å] and angles [°] for 3.

| Bond                  | Length [Å]   | Bond                  | Length [Å]   |
|-----------------------|--------------|-----------------------|--------------|
| Ir(1)-C(1)            | 2.030(10)    | N(31)-C(31)           | 1.379(12)    |
| Ir(1)-C(15)           | 2.108(10)    | N(31)-C(34)           | 1.447(13)    |
| Ir(1)-C(14)           | 2.110(11)    | C(31)-N(32)           | 1.353(11)    |
| Ir(1)-C(18)           | 2.171(10)    | N(32)-C(33)           | 1.387(12)    |
| Ir(1)-C(19)           | 2.190(12)    | N(32)-C(39)           | 1.454(11)    |
| Ir(1)-Cl(1)           | 2.358(3)     | C(32)-C(33)           | 1.323(14)    |
| N(1)-C(2)             | 1.366(12)    | C(44)-C(45)           | 1.436(15)    |
| N(1)-C(11)            | 1.376(12)    | C(44)-C(51)           | 1.485(15)    |
| N(1)-C(4)             | 1.478(12)    | C(45)-C(46)           | 1.513(15)    |
| C(1)-N(2)             | 1.329(12)    | C(46)-C(47)           | 1.528(16)    |
| N(2)-C(3)             | 1.377(13)    | C(47)-C(48)           | 1.506(15)    |
| N(2)-C(9)             | 1.430(12)    | C(48)-C(49)           | 1.389(14)    |
| C(2)-C(3)             | 1.327(14)    | C(49)-C(50)           | 1.529(16)    |
| C(4)-C(5)             | 1.504(12)    | C(50)-C(51)           | 1.575(17)    |
| C(5)-C(6)             | 1.537(12)    | C(34)-C(35)           | 1.496(12)    |
| Cl(31)-Ir(31)         | 2.360(3)     | C(35)-C(36)           | 1.580(15)    |
| C(6)-C(7)             | 1.420(19)    | C(36)-C(37)           | 1.386(19)    |
| C(7)-C(8)             | 1.009(18)    | C(37)-C(38)           | 1.016(18)    |
| C(9)-C(10)            | 1.489(15)    | C(39)-C(40)           | 1.489(11)    |
| C(10)-C(11)           | 1.53(2)      | C(40)-C(41)           | 1.640(18)    |
| C(11)-C(12)           | 1.521(10)    | C(41)-C(42)           | 1.43(2)      |
| C(12)-C(13)           | 0.97(3)      | C(42)-C(43)           | 1.04(2)      |
| C(14)-C(15)           | 1.399(15)    | C(1)-Ir(1)-C(15)      | 93.4(4)      |
| C(14)-C(21)           | 1.525(18)    | C(1)-Ir(1)-C(14)      | 93.6(4)      |
| C(15)-C(16)           | 1.529(15)    | C(15)-Ir(1)-C(14)     | 38.7(4)      |
| C(16)-C(17)           | 1.423(15)    | C(1)-Ir(1)-C(18)      | 162.1(4)     |
| C(17)-C(18)           | 1.486(16)    | C(15)-Ir(1)-C(18)     | 81.4(4)      |
| C(18)-C(19)           | 1.392(16)    | C(14)-Ir(1)-C(18)     | 92.9(5)      |
| C(19)-C(20)           | 1.541(19)    | C(1)-Ir(1)-C(19)      | 160.6(5)     |
| C(20)-C(21)           | 1.449(19)    | C(15)-Ir(1)-C(19)     | 94.6(5)      |
| Ir(31)-C(31)          | 2.020(10)    | C(14)-Ir(1)-C(19)     | 81.8(5)      |
| Ir(31)-C(45)          | 2.103(10)    | C(18)-Ir(1)-C(19)     | 37.2(4)      |
| Ir(31)-C(44)          | 2.137(11)    | C(1)-Ir(1)-Cl(1)      | 87.0(3)      |
| Ir(31)-C(49)          | 2.180(10)    | C(15)-Ir(1)-Cl(1)     | 160.4(3)     |
| Ir(31)-C(48)          | 2.180(9)     | C(14)-Ir(1)-Cl(1)     | 160.8(4)     |
| N(31)-C(32)           | 1.365(12)    | C(18)-Ir(1)-Cl(1)     | 92.2(3)      |
| Bond                         | Angle (°)  | Bond                         | Angle (°)  |
|------------------------------|------------|------------------------------|------------|
| C(19)-Ir(1)-Cl(1)           | 91.3(4)    | C(31)-Ir(31)-C(45)          | 92.3(4)    |
| C(2)-N(1)-C(1)              | 109.8(9)   | C(31)-Ir(31)-C(44)          | 95.1(4)    |
| C(2)-N(1)-C(4)              | 125.7(9)   | C(45)-Ir(31)-C(44)          | 39.6(4)    |
| C(1)-N(1)-C(4)              | 124.2(8)   | C(31)-Ir(31)-C(49)          | 157.6(4)   |
| N(2)-C(1)-N(1)              | 104.4(9)   | C(45)-Ir(31)-C(49)          | 99.0(5)    |
| N(1)-C(1)-Ir(1)             | 127.9(8)   | C(44)-Ir(31)-C(49)          | 81.8(5)    |
| N(1)-C(1)-Ir(1)             | 127.6(7)   | C(31)-Ir(31)-C(48)          | 165.2(4)   |
| C(1)-N(2)-C(3)              | 111.4(9)   | C(45)-Ir(31)-C(48)          | 81.8(4)    |
| C(1)-N(2)-C(9)              | 125.5(10)  | C(44)-Ir(31)-C(48)          | 88.9(4)    |
| C(3)-N(2)-C(9)              | 122.9(9)   | C(49)-Ir(31)-C(48)          | 37.2(4)    |
| C(3)-C(2)-N(1)              | 107.7(10)  | C(31)-Ir(31)-Cl(31)         | 88.0(3)    |
| C(2)-C(3)-N(2)              | 106.7(10)  | C(45)-Ir(31)-Cl(31)         | 155.6(4)   |
| N(1)-C(4)-C(5)              | 111.6(9)   | C(44)-Ir(31)-Cl(31)         | 164.6(3)   |
| C(4)-C(5)-C(6)              | 113.6(10)  | C(49)-Ir(31)-Cl(31)         | 89.6(3)    |
| C(7)-C(6)-C(5)              | 113.9(14)  | C(48)-Ir(31)-Cl(31)         | 91.9(3)    |
| C(8)-C(7)-C(6)              | 144(3)     | C(32)-N(31)-C(31)           | 110.5(9)   |
| N(2)-C(9)-C(10)             | 115.3(9)   | C(32)-N(31)-C(34)           | 126.8(9)   |
| C(9)-C(10)-C(11)            | 113.0(12)  | C(31)-N(31)-C(34)           | 122.6(9)   |
| C(12)-C(11)-C(10)           | 112.7(18)  | N(32)-C(31)-N(31)           | 103.8(9)   |
| C(13)-C(12)-C(11)           | 134(5)     | N(32)-C(31)-Ir(31)          | 127.5(8)   |
| C(15)-C(14)-C(21)           | 124.3(14)  | N(31)-C(31)-Ir(31)          | 128.6(7)   |
| C(15)-C(14)-Ir(1)           | 70.6(6)    | C(31)-N(32)-C(33)           | 110.8(9)   |
| C(21)-C(14)-Ir(1)           | 112.3(8)   | C(31)-N(32)-C(39)           | 124.6(9)   |
| C(14)-C(15)-C(16)           | 122.9(12)  | C(33)-N(32)-C(39)           | 124.4(9)   |
| C(14)-C(15)-Ir(1)           | 70.7(6)    | C(33)-C(32)-N(31)           | 107.9(10)  |
| C(16)-C(15)-Ir(1)           | 110.6(8)   | C(32)-C(33)-N(32)           | 107.1(10)  |
| C(17)-C(16)-C(15)           | 118.2(11)  | C(45)-C(44)-C(51)           | 123.9(10)  |
| C(16)-C(17)-C(18)           | 115.7(11)  | C(45)-C(44)-Ir(31)          | 68.9(6)    |
| C(19)-C(18)-C(17)           | 124.3(13)  | C(51)-C(44)-Ir(31)          | 114.3(8)   |
| C(19)-C(18)-Ir(1)           | 72.1(7)    | C(44)-C(45)-C(46)           | 123.0(11)  |
| C(17)-C(18)-Ir(1)           | 111.9(8)   | C(44)-C(45)-Ir(31)          | 71.5(6)    |
| C(18)-C(19)-C(20)           | 125.4(14)  | C(46)-C(45)-Ir(31)          | 109.8(8)   |
| C(18)-C(19)-Ir(1)           | 70.7(6)    | C(45)-C(46)-C(47)           | 115.0(9)   |
| C(20)-C(19)-Ir(1)           | 110.1(9)   | C(48)-C(47)-C(46)           | 110.9(9)   |
| C(21)-C(20)-C(19)           | 114.9(12)  | C(49)-C(48)-C(47)           | 125.8(11)  |
| C(20)-C(21)-C(14)           | 117.8(12)  | C(49)-C(48)-Ir(31)          | 71.4(6)    |
| Bond                        | Angle (°) |
|-----------------------------|-----------|
| C(47)-C(48)-Ir(31)         | 112.8(8)  |
| C(48)-C(49)-C(50)          | 124.2(12) |
| C(48)-C(49)-Ir(31)         | 71.4(6)   |
| C(50)-C(49)-Ir(31)         | 108.6(8)  |
| C(49)-C(50)-C(51)          | 111.7(10) |
| C(44)-C(51)-C(50)          | 112.4(10) |
| N(31)-C(34)-C(35)          | 111.1(9)  |
| C(34)-C(35)-C(36)          | 109.6(11) |
| C(37)-C(36)-C(35)          | 113.5(16) |
| C(38)-C(37)-C(36)          | 128(2)    |
| N(32)-C(39)-C(40)          | 112.4(8)  |
| C(39)-C(40)-C(41)          | 108.9(11) |
| C(42)-C(41)-C(40)          | 103.4(18) |
| C(43)-C(42)-C(41)          | 121(3)    |
4.- NMR characterization of complex 1a.

**Figure 4**: Proton NMR of complex 1a at 25 ºC

**Figure 5**: Proton NMR of complex 1a at -15 ºC
Figure 6: TOCSY 1D NMR of complex 1a at -10 °C

Figure 7: $^{13}$C NMR of complex 1a at 25 °C
Figure 8: Cosy NMR experiment of complex 1a at -5 ºC
5.- Variable-Temperature NMR Studies.

The room temperature $^1$H NMR of complex 1a showed a different environment for the two azole-ring protons at 6.89 and 6.67 ppm. This observation and the low frequency alkene resonances are consistent with one olefin coordination. The upper and lower side of the iridium complex is different making all the residences magnetically inequivalent. The natural line width of the signals at room temperature is broad (e.g. 6.89 ppm, $w_{1/2} = 9.43$ Hz; solvent CDCl$_3$ $w_{1/2} = 0.98$ Hz) indicating that a fluxional process is involved.$^{1-3}$ Complex 1a dynamics agree with a coordination/decoordination from the olefin, Scheme 3. Metal-carbene rotation is not feasible as observed previously in rhodium analogous complexes.$^{4, 5}$ Studies by Enders show that hindered rotation is found for NHC-rhodium(I) complexes with bulky cyclooctadiene or norbornadiene ligands.$^{6, 7}$

![Scheme 1](image)

Scheme 1. Dynamic process for complex 1a.

Compound 1a shows a sharp AB pattern for the azole-ring protons at -15 °C. At this temperature, completed NMR assignment has been made by HETCOR and COSY experiments. As the temperature is increased, the peaks broaden and coalesce into a singlet at 50 °C. The rate constant ($k = 253$ s$^{-1}$) and the free energy ($\Delta G^\ddagger = 15.4$ Kcal/mol) at 50 °C shows that the fluxional process is fast and feasible. A set of variable-temperature $^1$H spectra for 1a was measured, and these are shown in Figure 9. At -15 °C, all of the signals are relatively sharp and reveal two nonequivalent azole-ring protons at 6.89 and 6.67 ppm, in the ratio 1:1. A line shape analysis$^8$ from the data of figure 4 (-15 °C to 40 °C in CDCl$_3$) affords the rate constants and thermodynamic parameters, which are summarized in Figure 10. The olefin coordination/decoordination fluxional process is governed by enthalpy with negligible variation of entropy as expected for an intramolecular exchange. The thermodynamic
parameters are in good agreement with experimental and theoretical data for olefin coordination.\textsuperscript{9-11}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{Variable temperature analysis for compound 1a from -15 °C to 40 °C. Solvent CDCl$_3$, 5 mM, 500 MHz.}
\end{figure}

A similar variable temperature study of complex 1a has been done using $^{13}$C NMR (75 MHz). The two different signals from the carbons attach directly to the azol ring appear at 52.6 and 52.2 ppm. As the temperature is increased, the peaks broaden and coalesce into a singlet at 35 °C. The rate constant is $k = 62.9$ s$^{-1}$ and the free energy $\Delta G^\circ = 15.5$ Kcal/mol. The results agree well with the ones obtained previously using $^1$H NMR.
Figure 10. Complex 1a line shape Analysis. Selected signal at 6.89 ppm, H_{imid}. Linear regression from Eq. \ln(k/T) = -(\Delta H^\neq/T)(1/T) + \Delta S^\neq/R + 23.76. Results: \Delta H^\neq = 20.9 Kcal/mol; \Delta S^\neq = 17.4 Kcal/mol.

5.1.- Kinetic constant at the coalescence temperature for complex 1a.

| Coalescence T (K) | Equation                        | \Delta v (Hz) | k (s^{-1}) |
|-------------------|---------------------------------|---------------|------------|
| 323.15            | \begin{align*} k &= \pi \Delta v / 1.414 \\
|                   | k &= 2.22[(\Delta v)^2 + 6*(Jab)^2]^{0.5} \end{align*} | 113.95        | 253.13     |

Jab(Hz) = 1.999
5.2.- Line shape analysis data for complex 1a signal at 6.9ppm.

| Temp (K) | w (Hz) | wo (Hz) | w - wo (Hz) | k = n (w - wo) (s⁻¹) | k/T | 1/T | ln(k/T) |
|----------|-------|---------|------------|----------------------|-----|-----|---------|
| 258,15   | 3,47  |         |            |                      |     |     |         |
| 263,15   | 3,76  | 3,47    | 0,29       | 0,91106185           | 0,00346214 | 0,00380011 | -5,6658687 |
| 268,15   | 3,48  | 3,47    | 0,01       | 0,03141593           | 0,00011716 | 0,00372926 | 9,05198684  |
| 273,15   | 4,13  | 3,47    | 0,66       | 2,07345112           | 0,00759089 | 0,00366099 | 4,88080667  |
| 278,15   | 3,89  | 3,47    | 0,42       | 1,31946889           | 0,00474373 | 0,00359518 | 5,35093124  |
| 283,15   | 4,47  | 3,47    | 1          | 3,1415926            | 0,01109515 | 0,0035317  | 4,50124692  |
| 288,15   | 5,15  | 3,47    | 1,68       | 5,27787557           | 0,01831642 | 0,00347041 | 3,99995752  |
| 293,15   | 6,27  | 3,47    | 2,8        | 8,79645928           | 0,03000668 | 0,00341122 | 3,50633514  |
| 298,15   | 9,43  | 3,47    | 5,96       | 18,7238919           | 0,06280024 | 0,00335402 | 2,76779637  |
| 303,15   | 14,09 | 3,47    | 10,62      | 33,3637134           | 0,11005678 | 0,0032987  | 2,20675885  |
| 308,15   | 20,75 | 3,47    | 17,28      | 54,2867201           | 0,17616979 | 0,00324517 | 1,73630705  |
| 313,15   | 42,03 | 3,47    | 38,56      | 121,139811           | 0,38684276 | 0,00319336 | 0,94973697  |
| 318,15   | 126,32| 3,47    | 122,85     | 385,944651           | 1,21309021 | 0,00314317 | 0,193171    |

Eyring Equation: \( \ln(k/T) = -(\Delta H/R)(1/T) + \Delta S/R + 23.76 \)
\( \Delta H = 20.9 \) Kcal/mol
\( \Delta S = 17.42 \) cal/mol/K

\[ y = -10525x + 32,526 \]
\[ R^2 = 0.9955 \]
The Arrhenius Activation Energy $E_a$: $\ln k = \ln k_0 - \frac{E_a}{RT}$

$E_a = 21.50\text{ Kcal/mol}$.
5.3.- Line shape analysis data for complex 1a signal at 6.7 ppm.

| Temp (K) | w (Hz) | wo (Hz) | w - wo (Hz) | K (s⁻¹) | k/T      | 1/T    | ln(k/T) |
|----------|--------|---------|-------------|---------|----------|--------|---------|
| 258,15   | 3.55   | 3.55    | 0.24        | 0.75398222 | 0.00286522 | 0.00380011 | -5.8551107 |
| 263,15   | 3.79   | 3.55    | -0.02       | 0.002863185 | -0.00023432 | 0.00372926 | #¡NUM!   |
| 268,15   | 3.53   | 3.55    | 0.53        | 1.66504408 | 0.00609571 | 0.00366099 | -5.1001695 |
| 273,15   | 3.82   | 3.55    | 0.27        | 0.84823   | 0.00304954 | 0.00359518 | -5.7927639 |
| 278,15   | 4.41   | 3.55    | 0.86        | 2.70176964 | 0.00954183 | 0.0035317 | -4.6520698 |
| 283,15   | 5.16   | 3.55    | 1.61        | 5.05796409 | 0.01755323 | 0.00347041 | -4.04251713 |
| 288,15   | 6.25   | 3.55    | 2.7         | 8.48230002 | 0.02893502 | 0.00341122 | -3.54270278 |
| 293,15   | 7.55   | 3.55    | 5.75        | 18.0641575 | 0.06058748 | 0.00335402 | -2.80366699 |
| 303,15   | 10.24  | 3.55    | 12.44       | 32.1699082 | 0.10611878 | 0.0032987 | -2.2431962 |
| 308,15   | 16.76  | 3.55    | 19.15       | 52.653092 | 0.17088638 | 0.00325417 | -1.76686171 |
| 313,15   | 41.5   | 3.55    | 40.95       | 130.376093 | 0.41633752 | 0.00319336 | -0.87625901 |
| 318,15   | 129.3  | 3.55    | 123.85      | 406.207423 | 1.27678115 | 0.00314317 | 0.24434218 |

Eyring Equation: \( \ln(k/T) = -(\Delta H/R)(1/T) + \Delta S/R + 23.76 \)

\( \Delta H = 22.7 \text{ Kcal/mol} \)

\( \Delta S = 23.24 \text{ cal/mol/K} \)
The Arrhenius Activation Energy $E_a$: \( \ln k = \ln k_0 - \frac{E_a}{RT} \)
$E_a = 23.27 \text{ Kcal/mol.}$

6.- Ligand precursors

1-(4-pentenyl)-imidazole. A mixture of imidazole (1.4 g, 20.6 mmol), KOH (1.4 g, 25.7 mmol), TBABr (200mg, 0.62 mmol) and a four drops of water were stirred for 1 h at room temperature. After, pentenyl bromide (2.8 ml, 24.7 mmol) was added and the suspension was stirred at room temperature for 24 h. The mixture was quenched with water (20 ml), extracted with CH$_2$Cl$_2$ (3 x 50 ml) and dry over Na$_2$SO$_4$. The volatiles were removed under reduced pressure and the crude was purified through a flash silica-gel chromatography with acetone/CH$_2$Cl$_2$ (1:1). Yield: 2.34 g, 83%, orange oil. $^1$H NMR (500 MHz, CDCl$_3$): \( \delta \) 7.43 (s, 1H, NCH$_2$N), 7.03 (s, 1H, NCH$_2$N), 6.87 (s, 1H, NCHCHN), 5.79 (m, 1H, -CH=CH$_2$), 5.05 (m, 2H, -CH=CH$_2$), 3.94 (m, 2H, NCH$_2$N), 2.07 (m, 2H, -CH$_2$), 1.90 (m, 2H, -CH$_2$N).

1, 3-Bis(4-pentenyl)-imidazolium Bromide. 4-pentenyl bromide (1ml, 8.76 mmol) and N-pentenylimidazole (1g, 7.3 mmol) were reacted without solvent for 4h at 80 °C. The solid was washed with Et$_2$O (3 x 50 mL) and dry under vacuum. Yield: 1.8 g, 86%. $^1$H NMR (500 MHz, CDCl$_3$): \( \delta \) 10.59 (s, 1H, NCHN), 7.42 (s, 2H, NCHCHN),
5.76 (m, 2H, -CH=CH2), 5.03 (m, 4H, -CH=CH2), 4.38 (t, $^3J_{HH} =$ 7.2 Hz, 4H, NCH2-), 2.15 (m, 4H, -CH2-), 2.08 (m, 4H, -CH2-). $^{13}$C NMR (75.4 MHz, CDCl3): $\delta$ 136.5 (NCN), 136.1 (-CH=CH2), 122.6 (NCHCHN), 116.2 (-CH=CH2), 49.2 (NCH2-), 30.0 (-CH2-), 29.2 (-CH2-).

1, 3-Bis(2-propenyl)-imidazolium Bromide. This ligand precursor prepared according to literature methodologies. To a suspension of allyl amine (7.5 mL, 0.1 mol) and hydrochloric acid (8.5 mL, 0.05 mol aqueous solution 6M) in toluene (20 mL) at 0 °C, was added dropwise formaldehyde (3.8 mL, 0.05 mol) during 10 min while the solution temperature was kept below 3 °C. Glyoxal (5.73 mL, 0.05 mol) was then added dropwise and the temperature kept below 25 °C overnight. Azeotropic distillation (Dean-Stark) and solvent removal afforded a pale yellow oil. Anion exchange afforded the pure product. Yield (6.9 g, 80%). $^1$H NMR (300 MHz, CDCl3): $\delta$ 10.7 (s, 1H, NCHN), 7.53 (s, 2H, CH=CH) 5.99 – 5.94 (m, 2H, -CH=CH2), 5.43 – 5.40 (m, 4H, -CH=C=H2), 4.93 (s, 4H, N-CH2-). $^{13}$C NMR (75.4 MHz, CDCl3): $\delta$ 137.4 (NCN), 130.4 (CH=CH), 122.6 (-CH=CH2), 122.3 (-CH=CH2), 52.3 (NCH2-).

4, 5-dichloro-1-(2-propenyl)-imidazole. Allyl bromide (690 μL, 8 mmol) and KOH (616 mg, 11 mmol) were added to a solution of 4,5-dichloroimidazole (1g, 7.3 mmol) in MeOH (15 ml). The mixture was stirred, under reflux, at 68 °C for 24 hours. After filtration, the volatiles were removed under reduced pressure. The mixture was quenched with water (20 ml), extracted with CH2Cl2 (3 x 50 ml) and dry over Na2SO4. A colourless oil of 4, 5-dichloro-1-(2-propenyl)-imidazole was obtained. Yield (1.07 g, 71 %). $^1$H NMR (500 MHz, CDCl3): $\delta$ 7.36 (s, 1H, NCHN), 5.94 (m, 1H, NCH2CH=CH2), 5.33 d, $J_{HH} =$ 10.2 HZ, NCH2CH=CHH_{cis}, 5.17 (d, 1H, NCH2CH=CHH_{trans}, $J_{HH} =$ 15 Hz), 4.51 (d, 2H, NCH2CH=CH2, $J_{HH} =$ 5.7 Hz)

4, 5-dichloro-1,3-Bis(2-propenyl)-imidazolium Bromide. Allyl bromide (1.38 mL, 16 mmol) and 4, 5-dichloro-1-(2-propenyl)-imidazole (2.4 g, 14 mmol) were reacted without solvent for 12h at 70 °C. The solid was washed with Et2O (3 x 50 mL) and dry under vacuum. Yield: 3.5 g, 85%. $^1$H NMR (300 MHz, CDCl3): $\delta$ 8.82 (s, 1H, NCHN), 6.02 – 5.97 (m, 2H, -CH=CH2), 5.54 – 5.47 (m, 4H, -CH=CH2), 4.82 (d, 4H,
3J_H-H = 6.3 Hz, N-CH_2-.^{13}C NMR (75.4 MHz, CDCl_3): \( \delta \) 136.8 (N-C), 128.1 (C-Cl), 124.1 (-CH=CH_2), 123.9 (-CH=CH_2), 51.8 (NCH_2-).

4, 5-dimethyl-1,3-Bis(2-propenyl)-imidazolium Hexafluorophosphate. This ligand precursor was prepared following the methodology described for compound 1, 3-Bis(2-propenyl)-imidazolium Chloride. To a suspension of Allyl amine (7.5 mL, 0.1 mol) and hydrochloric acid (8.5 mL, 0.05 mol aqueous solution 6M) in toluene (20 mL) at 0 ºC was added dropwise formaldehyde (3.8 mL, 0.05 mol) during 10 min while the solution temperature was kept below 3 ºC. 2,3-Butanedione (4.5 mL, 0.05 mol) was then added dropwise and the temperature kept below 25 ºC overnight. Azeotropic distillation (Dean-Stark) and solvent removal afforded a colourless impure oil. The anion exchange (by PF_6- ) afforded the pure product. Yield (7.9 g, 75%). ^1H NMR (300 MHz, CDCl_3): \( \delta \) 8.5 (s, 1H, NCH=N), 5.99 – 5.90 (m, 2H, -CH=CH_2), 5.42 (d, 2H, 3J_H-H = 10.5 Hz, -CH=CH_2), 5.27 (d, 2H, 3J_H-H = 17.1 Hz, -CH=CH_2), 4.68 (d, 4H, 2J_H-H = 6.0 Hz, N-CH_2), 2.17 (s, 6H, C-CH_3).

3-methyl, 1-(2-propenyl)-imidazolin-2-ylidene [(1, 2, 5, 6-\( \eta \))-1-5-cyclooctadiene] chloro iridium (5). Silver oxide (70 mg, 0.3 mmol) was added to a solution of 3-methyl-1-propenylimidazolium bromide^{13} (122 mg, 0.6 mmol) in CH_2Cl_2. The solution was stirred at room temperature for 1h and then [IrCl(COD)]_2 (200 mg, 0.3 mmol) was added. The mixture was stirred at room temperature for 2h and then filtered through Celite. After evaporation of the solvent, the excess of silver oxide was precipitated in a mixture of CH_2Cl_2/hexanes. The filtrate was cold at -20ºC and compound 5 precipitated as a white solid. Yield: 180 mg (65%). ^1H NMR (500 MHz, CDCl_3): \( \delta \) 6.83 (s, 1H, NCHCHN), 6.64 (s, 1H, NCHCHN), 4.67 (m, 1H, COD), 4.18 – 4.12 (m, 3H, NCHHCH=CH_2, NCHHCH=CH_2 COD), 3.92 (s, 3H, -CH_3), 3.65 (d, 3J_H-H = 11.5 Hz, NCHHCH=CH_2), 3.54 (m, 1H, COD), 3.44 (m, 1H, COD), 2.93 (m, 1H, COD), 2.70 (m, 2H, COD), 2.49 (m, 1H, COD), 2.35 – 2.25 (m, 3H, COD and NCH_2CH=CHH), 1.93 (m, 1H, COD), 1.90 (d, 1H, 3J_Htrans = 9.3 Hz, NCH_2CH=CHH), 1.61 – 1.59 (m, 1H, COD). ^13C NMR (75 MHz, CDCl_3): \( \delta \) 160.88 (C-Ir), 123.16 (CH imidazole), 117.35 (CH imidazole), 98.50 (CH cod), 97.62 (CH cod), 60.39 (NCH_2CH=CH_2), 55.10 (CH cod), 52.59 (NCH_2CH=CH_2), 46.92 (CH cod), 40.40 (NCH_2CH=CH_2), 37.26 (NCH_3), 35.51 (CH_2 cod), 32.93 (CH_2 cod), 29.53
CH₂ cod), 28.02 (CH₂ cod). Electrospray Ms. Cone 25V. m/z (fragment): [M-Cl]^− = 423.

References:

1. C. J. Bourgeois, H. Huang, R. B. Larichev, L. N. Zakharov, A. L. Rheingold and R. P. Hughes, Organometallics, 2007, 26, 264-271.
2. S. Burling, S. Douglas, M. F. Mahon, D. Nama, P. S. Pregosin and M. K. Whittlesey, Organometallics, 2006, 25, 2642-2648.
3. J. W. Faller and P. P. Fontaine, J. Organomet. Chem., 2006, 691, 5798-5803.
4. M. J. Doyle and M. F. Lappert, J. Chem. Soc.-Chem. Commun., 1974, 679-680.
5. A. R. Chianese, X. W. Li, M. C. Janzen, J. W. Faller and R. H. Crabtree, Organometallics, 2003, 22, 1663-1667.
6. D. Enders, H. Gielen, J. Runsink, K. Breuer, S. Brode and K. Boehn, Eur. J. Inorg. Chem., 1998, 913-919.
7. D. Enders and H. Gielen, J. Organomet. Chem., 2001, 617, 70-80.
8. J. Sandstrom, Dynamic NMR Spectroscopy, Academic Press, London, 1982.
9. F. A. Jalon, B. R. Manzano, F. Gomez-de la Torre, A. M. Lopez-Agenjo, A. M. Rodriguez, W. Weissensteiner, T. Sturm, J. Mahia and M. Maestro, J. Chem. Soc.-Dalton Trans., 2001, 2417-2424.
10. C. P. Casey, M. A. Fagan and S. L. Hallenbeck, Organometallics, 1998, 17, 287-289.
11. M. V. Galakhov, G. Heinz and P. Royo, Chem. Commun., 1998, 17-18.
12. A. J. Arduengo, U. S., Patent 6 177575, 2001.
13. W. Z. Chen and F. H. Liu, J. Organomet. Chem., 2003, 673, 5-12.