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Supporting Information

Alkenyl-functionalized NHC Iridium-based catalysts for hydrosilylation.

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Summary: A family of alkene-functionalized N-heterocyclic carbene iridium complexes has been synthesized, providing a series of monocoordinated, bischelate 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.

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 $SiMe_4$ (δ 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 ºC and the desolvation temperature to 150ºC. 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 1×10^{-4} M) in dichlormethane: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 ºC 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 = $HSiMe_2Ph$).

Entry	Catalyst[a]	Substrate	Conv (%)[b]	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[c]	**1a**	Phenylacetylene	92	--	28	72
9	**1c**	Phenylacetylene	45	--	20	80
10	**3**	Phenylacetylene	18	--	7	93
11	**4**	Phenylacetylene	0			
12[c]	**5**	Phenylacetylene	80	--	20	80

Aerobic conditions, Temp 25 ºC, Time 1 h, Solvent $CHCl_3$. [a]Catalyst loading (1 mol%); [b]Yields determined by ^1H NMR. [c]Catalyst active at least for three runs.

Table 2 Hydrosilylation of phenylacetylene at 60ºC (hydrosilane = $HSiMe_2Ph$).

Entry	Catalyst[a]	Time (h)	Conv (%)[b]	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**[c]	2	85	--	30	70
14	**1a**[d]	2	45[e]	--	35	65

Aerobic conditions, Temp 60 ºC, Solvent $CHCl_3$. [a]Catalyst loading (1 mol%) unless otherwise stated; [b]Yields determined by ^{1}H NMR. [c]Catalyst loading (0.1 mol%). [d]Catalyst loading (0.01 mol%). [e]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 monocromated Mo-Kα radiation (λ=0.71073 A) 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=-28°) at values ϕ=0, 90 and 180 with the detector at 2θ= 28° At each of these runs, frames (606, 435 and 230 respectively) were collected at 0.3° 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.

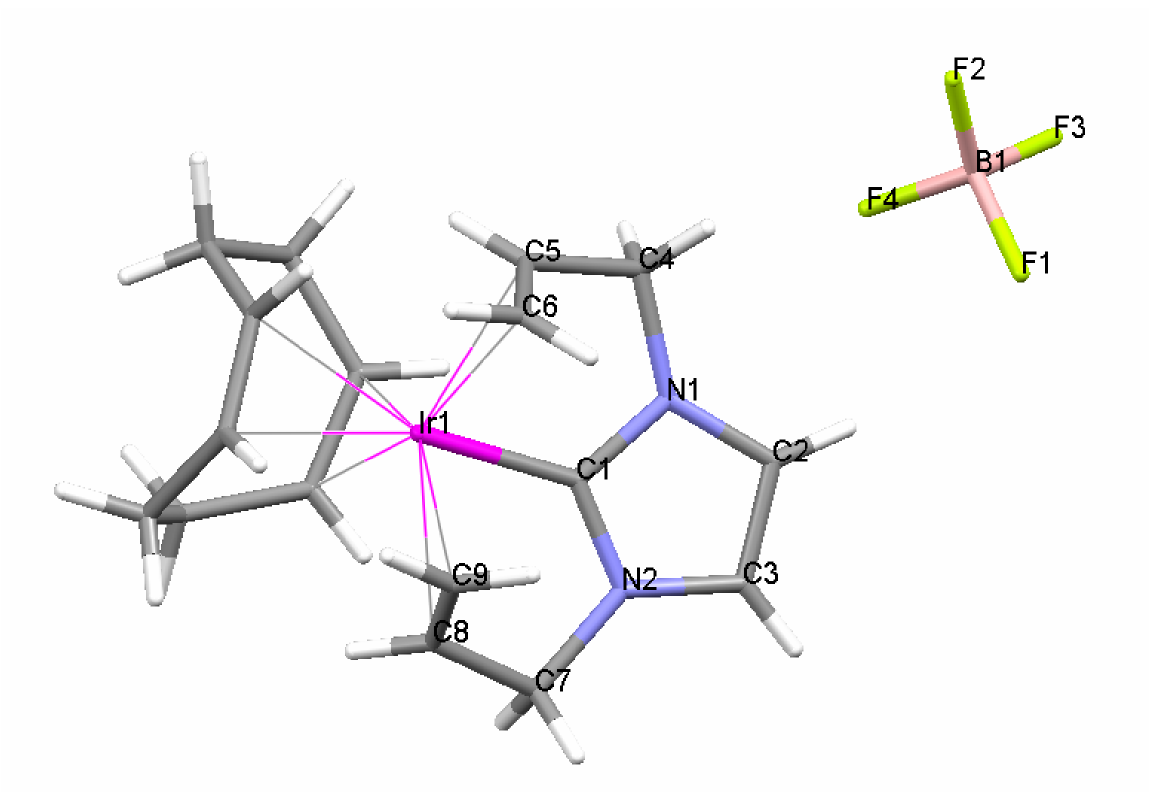


Figure 1. ORTEP diagram of complex **2a** showing 50% probability ellipsoids. Hydrogen atoms and the counterion (BF_4^-) have been omitted for clarity.

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

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	α = 90°.
	b = 36.568(2) Å	β= 99.5350(10)°.
	c = 12.0502(6) Å	γ = 90°.
Volume	3532.0(3) $Å^3$	
Z	8	
Density (calculated)	2.014 Mg/m^3	

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**.

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)

Ir(31)-C(40)	2.284(9)
Ir(31)-C(41)	2.294(8)
Ir(31)-C(38)	2.309(10)
N(31)-C(31)	1.341(11)
N(31)-C(32)	1.392(11)
N(31)-C(34)	1.444(11)
C(31)-N(32)	1.333(11)
F(31)-B(31)	1.376(12)
B(31)-F(34)	1.330(14)
B(31)-F(33)	1.360(12)
B(31)-F(32)	1.370(13)
N(32)-C(33)	1.378(11)
N(32)-C(37)	1.458(11)
C(32)-C(33)	1.345(13)
C(34)-C(35)	1.544(14)
C(35)-C(36)	1.389(14)
C(37)-C(38)	1.523(14)
C(38)-C(39)	1.352(15)
C(40)-C(41)	1.384(13)
C(40)-C(47)	1.508(14)
C(41)-C(42)	1.506(13)
C(42)-C(43)	1.520(13)
C(43)-C(44)	1.503(12)
C(44)-C(45)	1.391(13)
C(45)-C(46)	1.510(12)
C(46)-C(47)	1.507(14)
C(1)-Ir(1)-C(5)	76.8(3)
C(1)-Ir(1)-C(6)	85.4(4)
C(5)-Ir(1)-C(6)	36.9(3)
C(1)-Ir(1)-C(15)	91.2(4)
C(5)-Ir(1)-C(15)	88.3(3)
C(6)-Ir(1)-C(15)	124.3(4)
C(1)-Ir(1)-C(9)	83.7(4)
C(5)-Ir(1)-C(9)	119.3(4)
C(6)-Ir(1)-C(9)	85.3(4)
C(15)-Ir(1)-C(9)	149.5(4)
C(1)-Ir(1)-C(14)	96.4(3)
C(5)-Ir(1)-C(14)	124.1(3)
C(6)-Ir(1)-C(14)	160.0(3)
C(15)-Ir(1)-C(14)	35.9(3)
C(9)-Ir(1)-C(14)	114.7(4)
C(1)-Ir(1)-C(11)	164.6(4)
C(5)-Ir(1)-C(11)	118.2(3)
C(6)-Ir(1)-C(11)	104.7(3)
C(15)-Ir(1)-C(11)	92.5(3)
C(9)-Ir(1)-C(11)	85.6(4)
C(14)-Ir(1)-C(11)	78.2(3)
C(1)-Ir(1)-C(10)	160.0(3)
C(5)-Ir(1)-C(10)	85.9(3)
C(6)-Ir(1)-C(10)	86.6(4)
C(15)-Ir(1)-C(10)	78.3(3)
C(9)-Ir(1)-C(10)	113.9(4)
C(14)-Ir(1)-C(10)	85.0(3)
C(11)-Ir(1)-C(10)	34.9(3)
C(1)-Ir(1)-C(8)	73.9(4)
C(5)-Ir(1)-C(8)	142.5(3)
C(6)-Ir(1)-C(8)	117.2(4)
C(15)-Ir(1)-C(8)	114.9(4)
C(9)-Ir(1)-C(8)	35.0(3)
C(14)-Ir(1)-C(8)	82.3(3)
C(11)-Ir(1)-C(8)	91.1(4)
C(10)-Ir(1)-C(8)	126.0(3)
N(2)-C(1)-N(1)	106.7(8)
N(2)-C(1)-Ir(1)	128.9(7)
N(1)-C(1)-Ir(1)	123.9(7)
F(2)-B(1)-F(3)	110.8(9)
F(2)-B(1)-F(1)	111.7(9)
F(3)-B(1)-F(1)	109.0(9)
F(2)-B(1)-F(4)	110.0(9)
F(3)-B(1)-F(4)	108.4(9)
F(1)-B(1)-F(4)	106.8(9)
C(1)-N(1)-C(2)	110.3(7)
C(1)-N(1)-C(4)	116.3(7)
C(2)-N(1)-C(4)	133.3(8)
C(1)-N(2)-C(3)	110.6(7)
C(1)-N(2)-C(7)	114.1(7)

C(3)-N(2)-C(7)	135.3(8)
C(3)-C(2)-N(1)	105.4(8)
C(2)-C(3)-N(2)	107.0(8)
N(1)-C(4)-C(5)	107.7(7)
C(6)-C(5)-C(4)	121.1(8)
C(6)-C(5)-Ir(1)	72.0(5)
C(4)-C(5)-Ir(1)	110.6(6)
C(5)-C(6)-Ir(1)	71.2(5)
N(2)-C(7)-C(8)	109.2(7)
C(9)-C(8)-C(7)	122.2(9)
C(9)-C(8)-Ir(1)	70.7(6)
C(7)-C(8)-Ir(1)	109.1(6)
C(8)-C(9)-Ir(1)	74.4(5)
C(11)-C(10)-C(17)	124.8(9)
C(11)-C(10)-Ir(1)	71.8(5)
C(17)-C(10)-Ir(1)	111.7(6)
C(10)-C(11)-C(12)	126.0(9)
C(10)-C(11)-Ir(1)	73.3(5)
C(12)-C(11)-Ir(1)	110.8(6)
C(11)-C(12)-C(13)	113.0(7)
C(14)-C(13)-C(12)	114.6(7)
C(15)-C(14)-C(13)	124.2(8)
C(15)-C(14)-Ir(1)	70.6(5)
C(13)-C(14)-Ir(1)	112.9(6)
C(14)-C(15)-C(16)	125.8(9)
C(14)-C(15)-Ir(1)	73.5(5)
C(16)-C(15)-Ir(1)	111.7(6)
C(15)-C(16)-C(17)	112.8(8)
C(10)-C(17)-C(16)	114.9(8)
C(31)-Ir(31)-C(36)	83.7(4)
C(31)-Ir(31)-C(35)	76.3(4)
C(36)-Ir(31)-C(35)	37.1(4)
C(31)-Ir(31)-C(44)	93.2(4)
C(36)-Ir(31)-C(44)	127.0(4)
C(35)-Ir(31)-C(44)	90.7(4)
C(31)-Ir(31)-C(45)	98.2(4)
C(36)-Ir(31)-C(45)	162.6(4)
C(35)-Ir(31)-C(45)	126.5(4)
C(44)-Ir(31)-C(45)	35.9(3)
C(31)-Ir(31)-C(39)	82.8(4)
C(36)-Ir(31)-C(39)	86.6(5)
C(35)-Ir(31)-C(39)	120.9(4)
C(44)-Ir(31)-C(39)	145.7(4)
C(45)-Ir(31)-C(39)	110.8(4)
C(31)-Ir(31)-C(40)	164.8(4)
C(36)-Ir(31)-C(40)	103.7(4)
C(35)-Ir(31)-C(40)	117.6(4)
C(44)-Ir(31)-C(40)	92.7(4)
C(45)-Ir(31)-C(40)	78.7(3)
C(39)-Ir(31)-C(40)	84.5(4)
C(31)-Ir(31)-C(41)	159.9(4)
C(36)-Ir(31)-C(41)	87.9(4)
C(35)-Ir(31)-C(41)	86.1(4)
C(44)-Ir(31)-C(41)	77.3(3)
C(45)-Ir(31)-C(41)	84.5(3)
C(39)-Ir(31)-C(41)	115.0(4)
C(40)-Ir(31)-C(41)	35.2(3)
C(31)-Ir(31)-C(38)	73.0(4)
C(36)-Ir(31)-C(38)	117.2(5)
C(35)-Ir(31)-C(38)	142.3(4)
C(44)-Ir(31)-C(38)	112.1(4)
C(45)-Ir(31)-C(38)	79.6(4)
C(39)-Ir(31)-C(38)	34.3(4)
C(40)-Ir(31)-C(38)	91.9(4)
C(41)-Ir(31)-C(38)	126.9(4)
C(31)-N(31)-C(32)	109.1(8)
C(31)-N(31)-C(34)	115.8(8)
C(32)-N(31)-C(34)	135.0(8)
N(32)-C(31)-N(31)	106.9(8)
N(32)-C(31)-Ir(31)	127.9(7)
N(31)-C(31)-Ir(31)	124.5(7)
F(34)-B(31)-F(33)	111.5(10)
F(34)-B(31)-F(32)	113.8(11)
F(33)-B(31)-F(32)	110.4(10)
F(34)-B(31)-F(31)	107.1(10)
F(33)-B(31)-F(31)	108.9(10)

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 2bPF$_6$.

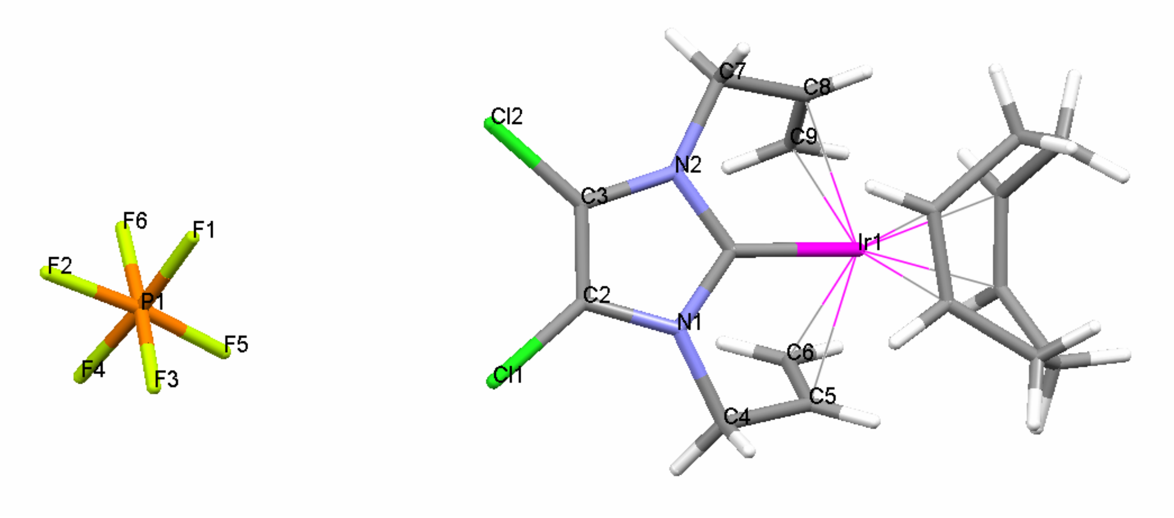


Figure 2. ORTEP diagram of complex **2bPF$_6$** showing 50% probability ellipsoids. Hydrogen atoms and the counterion (PF$_6^-$) have been omitted for clarity.

Table 5. Crystal data and structure refinement for **2bPF$_6$**.

Identification code	str862mm	
Empirical formula	C17 H22 Cl2 F6 Ir N2 P	
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^3	
Z	4	
Density (calculated)	2.127 Mg/m^3	
Absorption coefficient	6.848 mm^{-1}	
F(000)	1272	
Crystal size	0.12 x 0.11 x 0.08 mm^3	
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	Full-matrix least-squares on F^2
Data / restraints / parameters	3109 / 36 / 262
Goodness-of-fit on F^2	1.117
Final R indices [I>2sigma(I)]	R1 = 0.0525, wR2 = 0.1315
R indices (all data)	R1 = 0.0750, wR2 = 0.1743
Largest diff. peak and hole	2.075 and -2.127 e.$Å^{-3}$

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

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)
P(1)-F(4)	1.576(17)	C(1)-Ir(1)-C(8)	75.4(5)
Cl(1)-C(2)	1.685(17)	C(15)-Ir(1)-C(8)	89.2(6)
N(1)-C(1)	1.320(18)	C(9)-Ir(1)-C(8)	36.8(6)
N(1)-C(2)	1.407(19)	C(5)-Ir(1)-C(8)	142.6(5)
N(1)-C(4)	1.454(18)	C(1)-Ir(1)-C(6)	83.7(6)
C(1)-N(2)	1.336(16)	C(15)-Ir(1)-C(6)	151.4(6)
Cl(2)-C(3)	1.694(13)	C(9)-Ir(1)-C(6)	83.3(6)
N(2)-C(3)	1.408(19)	C(5)-Ir(1)-C(6)	35.9(5)
N(2)-C(7)	1.44(2)	C(8)-Ir(1)-C(6)	116.7(6)
C(2)-C(3)	1.35(2)	C(1)-Ir(1)-C(11)	166.0(5)
C(4)-C(5)	1.567(19)	C(15)-Ir(1)-C(11)	91.2(5)
C(5)-C(6)	1.38(2)	C(9)-Ir(1)-C(11)	104.1(6)
C(7)-C(8)	1.52(2)	C(5)-Ir(1)-C(11)	90.2(5)
C(8)-C(9)	1.41(2)	C(8)-Ir(1)-C(11)	118.4(5)

C(6)-Ir(1)-C(11)	87.1(6)	N(2)-C(1)-Ir(1)	125.1(10)
C(1)-Ir(1)-C(14)	97.4(6)	C(1)-N(2)-C(3)	108.6(12)
C(15)-Ir(1)-C(14)	33.8(6)	C(1)-N(2)-C(7)	116.1(12)
C(9)-Ir(1)-C(14)	158.0(7)	C(3)-N(2)-C(7)	135.2(12)
C(5)-Ir(1)-C(14)	84.6(6)	C(3)-C(2)-N(1)	106.1(13)
C(8)-Ir(1)-C(14)	122.8(6)	C(3)-C(2)-Cl(1)	129.3(11)
C(6)-Ir(1)-C(14)	118.7(7)	N(1)-C(2)-Cl(1)	124.6(11)
C(11)-Ir(1)-C(14)	77.9(6)	C(2)-C(3)-N(2)	107.1(11)
C(1)-Ir(1)-C(10)	160.0(7)	C(2)-C(3)-Cl(2)	130.9(11)
C(15)-Ir(1)-C(10)	79.5(7)	N(2)-C(3)-Cl(2)	122.0(11)
C(9)-Ir(1)-C(10)	84.9(6)	N(1)-C(4)-C(5)	106.0(11)
C(5)-Ir(1)-C(10)	123.8(6)	C(6)-C(5)-C(4)	117.8(13)
C(8)-Ir(1)-C(10)	86.4(6)	C(6)-C(5)-Ir(1)	73.1(9)
C(6)-Ir(1)-C(10)	112.4(8)	C(4)-C(5)-Ir(1)	110.0(9)
C(11)-Ir(1)-C(10)	33.8(6)	C(5)-C(6)-Ir(1)	71.0(9)
C(14)-Ir(1)-C(10)	85.5(6)	N(2)-C(7)-C(8)	108.3(11)
F(5)-P(1)-F(3)	88.4(17)	C(9)-C(8)-C(7)	121.1(15)
F(5)-P(1)-F(1)	102(2)	C(9)-C(8)-Ir(1)	69.9(7)
F(3)-P(1)-F(1)	87.4(10)	C(7)-C(8)-Ir(1)	109.9(9)
F(5)-P(1)-F(2)	174(2)	C(8)-C(9)-Ir(1)	73.3(7)
F(3)-P(1)-F(2)	90.5(13)	C(11)-C(10)-C(17)	122.8(15)
F(1)-P(1)-F(2)	84.3(17)	C(11)-C(10)-Ir(1)	72.6(11)
F(5)-P(1)-F(6)	94.0(16)	C(17)-C(10)-Ir(1)	110.6(11)
F(3)-P(1)-F(6)	177.4(14)	C(10)-C(11)-C(12)	127.7(16)
F(1)-P(1)-F(6)	93.3(10)	C(10)-C(11)-Ir(1)	73.7(9)
F(2)-P(1)-F(6)	87.1(13)	C(12)-C(11)-Ir(1)	111.4(10)
F(5)-P(1)-F(4)	82.3(17)	C(11)-C(12)-C(13)	113.9(13)
F(3)-P(1)-F(4)	94.7(10)	C(12)-C(13)-C(14)	117.6(14)
F(1)-P(1)-F(4)	175.7(14)	C(15)-C(14)-C(13)	129.6(18)
F(2)-P(1)-F(4)	91.8(16)	C(15)-C(14)-Ir(1)	70.1(8)
F(6)-P(1)-F(4)	84.5(9)	C(13)-C(14)-Ir(1)	111.2(10)
C(1)-N(1)-C(2)	109.8(12)	C(14)-C(15)-C(16)	120.1(16)
C(1)-N(1)-C(4)	117.7(12)	C(14)-C(15)-Ir(1)	76.1(9)
C(2)-N(1)-C(4)	132.5(14)	C(16)-C(15)-Ir(1)	111.6(10)
N(1)-C(1)-N(2)	108.4(12)	C(17)-C(16)-C(15)	114.1(17)
N(1)-C(1)-Ir(1)	124.5(9)	C(16)-C(17)-C(10)	118.5(16)

3.3.- Experimental crystallographic data collection for compound 3.

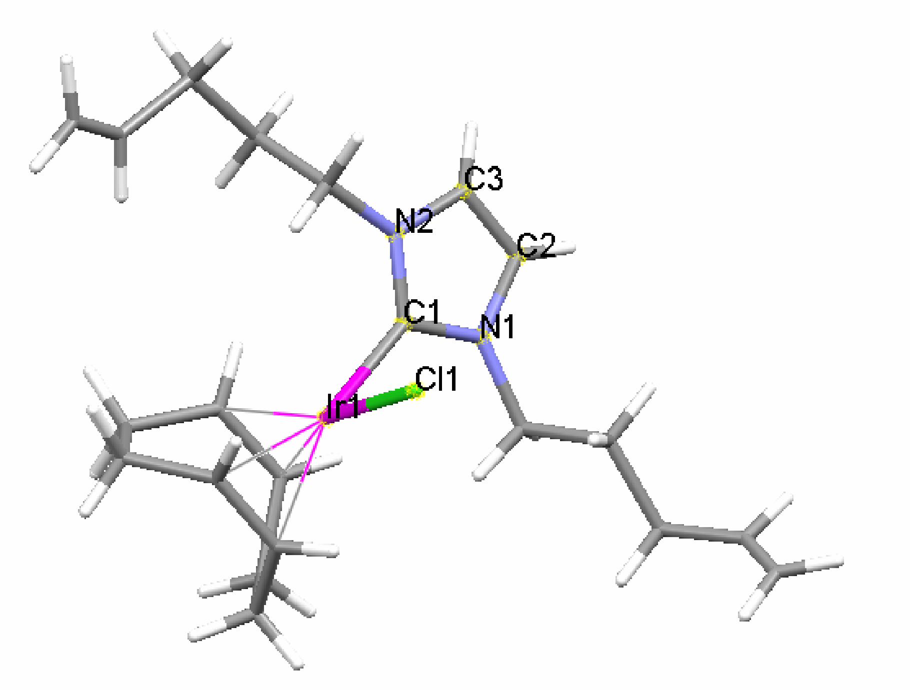


Figure 3. ORTEP diagram of complex **3** showing 35% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 7. Crystal data and structure refinement for **3**.

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	α= 64.168(2)°.
	b = 13.9740(14) Å	β= 85.560(3)°.
	c = 14.7666(15) Å	γ = 89.213(2)°.
Volume	2225.8(4) Å^3	
Z	4	
Density (calculated)	1.612 Mg/m^3	
Absorption coefficient	6.124 mm^{-1}	
F(000)	1064	
Crystal size	0.13 x 0.11 x 0.09 mm^3	
Theta range for data collection	1.62 to 25.00°.	
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 F^2	
Data / restraints / parameters	7842 / 32 / 448	
Goodness-of-fit on F^2	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**.

Ir(1)-C(1)	2.030(10)
Ir(1)-C(15)	2.108(10)
Ir(1)-C(14)	2.110(11)
Ir(1)-C(18)	2.171(10)
Ir(1)-C(19)	2.190(12)
Ir(1)-Cl(1)	2.358(3)
N(1)-C(2)	1.366(12)
N(1)-C(1)	1.376(12)
N(1)-C(4)	1.478(12)
C(1)-N(2)	1.329(12)
N(2)-C(3)	1.377(13)
N(2)-C(9)	1.430(12)
C(2)-C(3)	1.327(14)
C(4)-C(5)	1.504(12)
C(5)-C(6)	1.537(12)
Cl(31)-Ir(31)	2.360(3)
C(6)-C(7)	1.420(19)
C(7)-C(8)	1.009(18)
C(9)-C(10)	1.489(15)
C(10)-C(11)	1.53(2)
C(11)-C(12)	1.521(10)
C(12)-C(13)	0.97(3)
C(14)-C(15)	1.399(15)
C(14)-C(21)	1.525(18)
C(15)-C(16)	1.529(15)
C(16)-C(17)	1.423(15)
C(17)-C(18)	1.486(16)
C(18)-C(19)	1.392(16)
C(19)-C(20)	1.541(19)
C(20)-C(21)	1.449(19)
Ir(31)-C(31)	2.020(10)
Ir(31)-C(45)	2.103(10)
Ir(31)-C(44)	2.137(11)
Ir(31)-C(49)	2.180(10)
Ir(31)-C(48)	2.180(9)
N(31)-C(32)	1.365(12)
N(31)-C(31)	1.379(12)
N(31)-C(34)	1.447(13)
C(31)-N(32)	1.353(11)
N(32)-C(33)	1.387(12)
N(32)-C(39)	1.454(11)
C(32)-C(33)	1.323(14)
C(44)-C(45)	1.436(15)
C(44)-C(51)	1.485(15)
C(45)-C(46)	1.513(15)
C(46)-C(47)	1.528(16)
C(47)-C(48)	1.506(15)
C(48)-C(49)	1.389(14)
C(49)-C(50)	1.529(16)
C(50)-C(51)	1.575(17)
C(34)-C(35)	1.496(12)
C(35)-C(36)	1.580(15)
C(36)-C(37)	1.386(19)
C(37)-C(38)	1.016(18)
C(39)-C(40)	1.489(11)
C(40)-C(41)	1.640(18)
C(41)-C(42)	1.43(2)
C(42)-C(43)	1.04(2)
C(1)-Ir(1)-C(15)	93.4(4)
C(1)-Ir(1)-C(14)	93.6(4)
C(15)-Ir(1)-C(14)	38.7(4)
C(1)-Ir(1)-C(18)	162.1(4)
C(15)-Ir(1)-C(18)	81.4(4)
C(14)-Ir(1)-C(18)	92.9(5)
C(1)-Ir(1)-C(19)	160.6(5)
C(15)-Ir(1)-C(19)	94.6(5)
C(14)-Ir(1)-C(19)	81.8(5)
C(18)-Ir(1)-C(19)	37.2(4)
C(1)-Ir(1)-Cl(1)	87.0(3)
C(15)-Ir(1)-Cl(1)	160.4(3)
C(14)-Ir(1)-Cl(1)	160.8(4)
C(18)-Ir(1)-Cl(1)	92.2(3)

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(2)-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)

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.

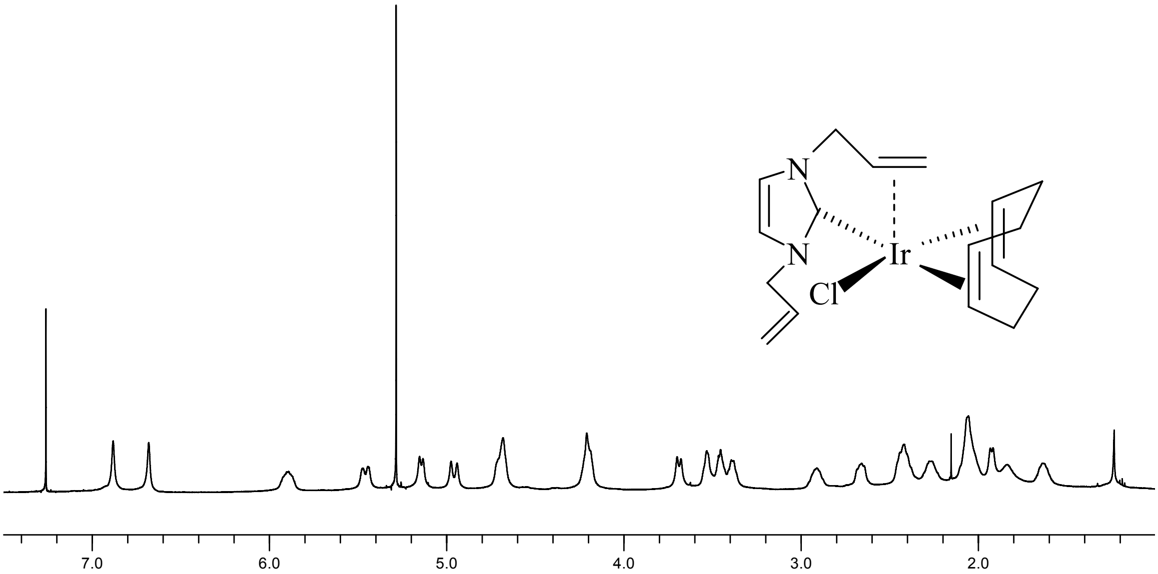


Figure 4: Proton NMR of complex **1a** at 25 ºC

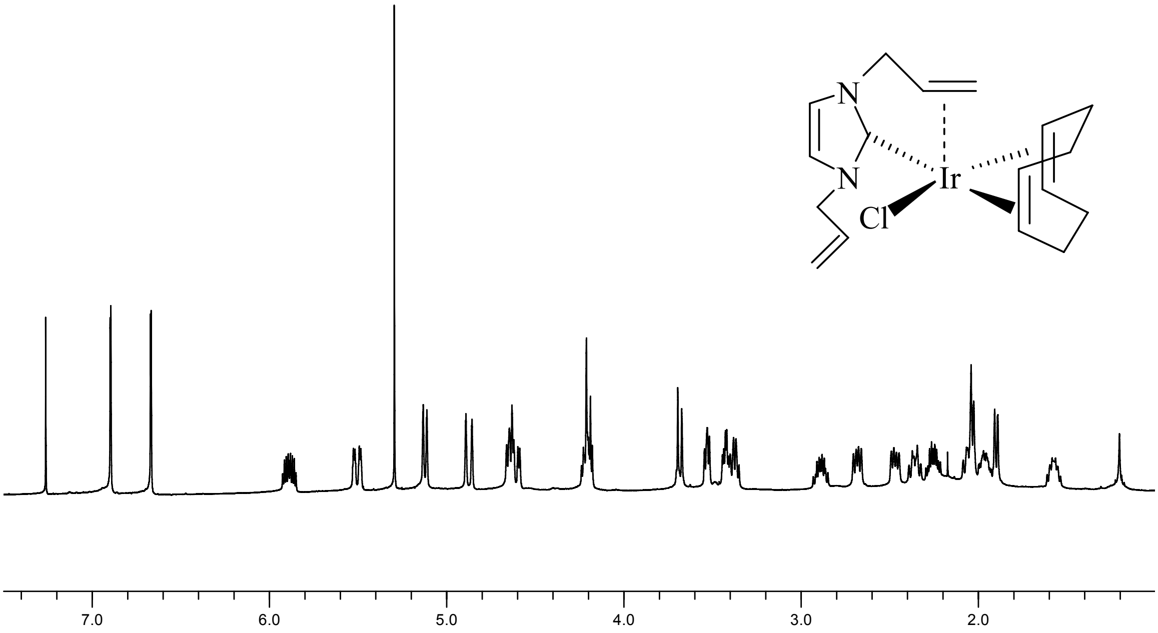


Figure 5: Proton NMR of complex **1a** at -15 ºC

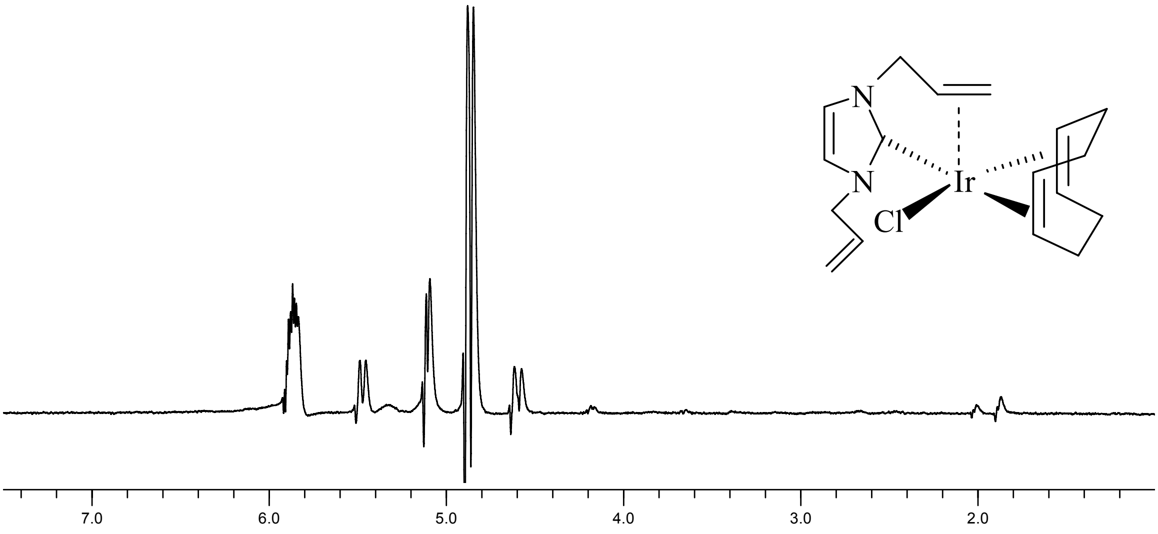


Figure 6: TOCSY 1D NMR of complex **1a** at -10 ºC

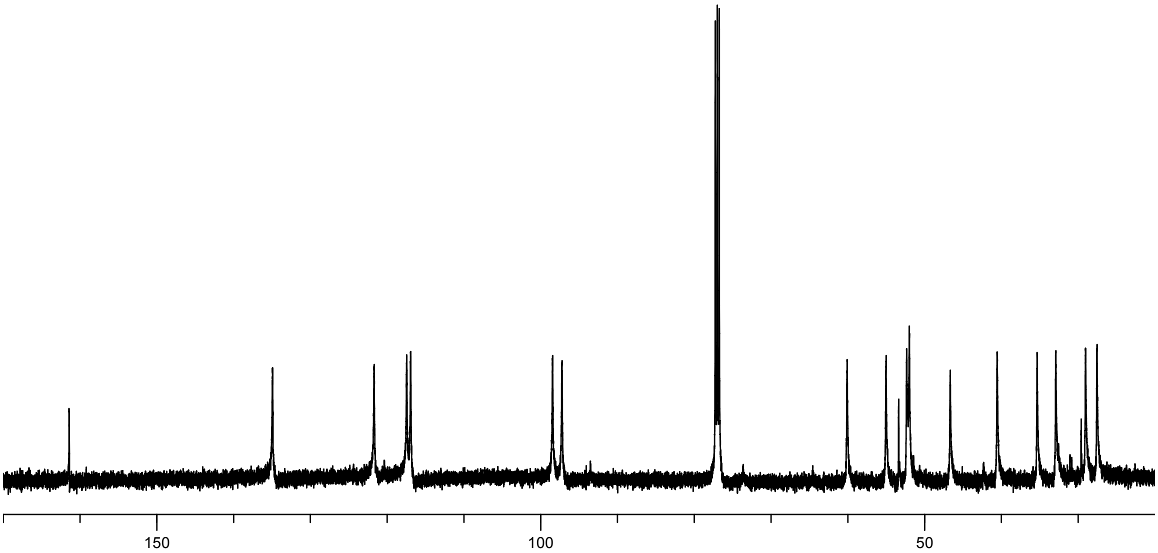


Figure 7: ^{13}C NMR of complex **1a** at 25 ºC

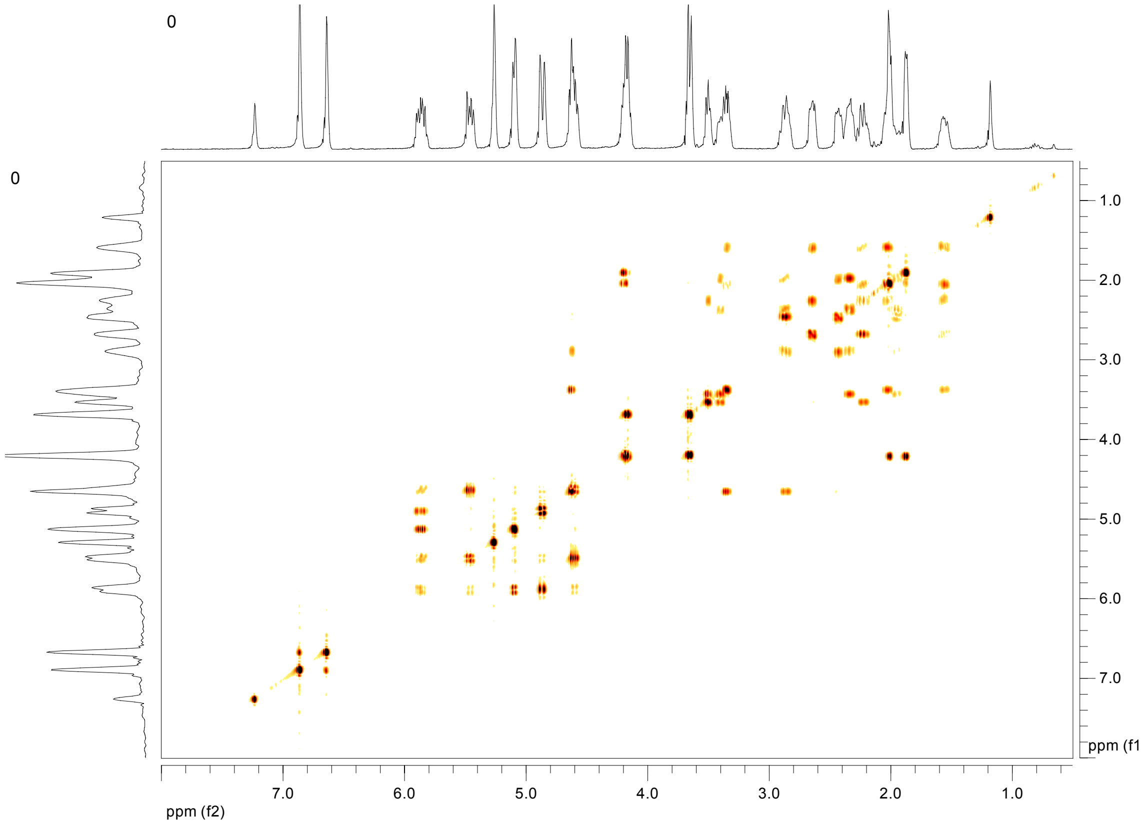
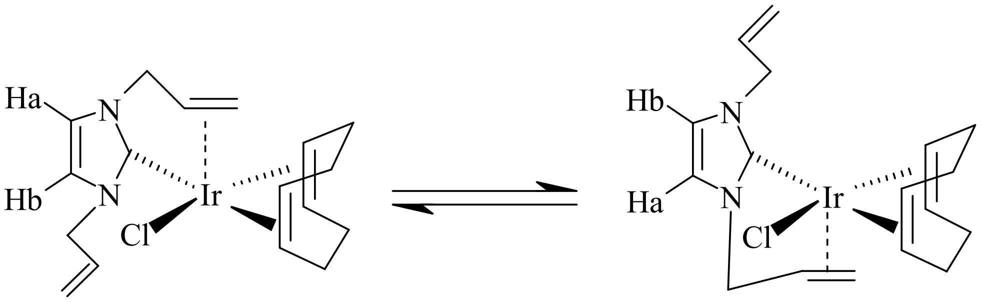


Figure 8: Cosy NMR experiment of complex **1a** at -5 ºC

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. Dynamic process for complex **1a**.

Compound **1a** shows a sharp AB pattern for the azole-ring protons at -15 ºC. 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 ºC. The rate constant (k = 253 s^{-1}) and the free energy ($\Delta G^{\neq}$ = 15.4 Kcal/mol) at 50 ºC 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 ºC, 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 ºC to 40 ºC 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.[9-11]

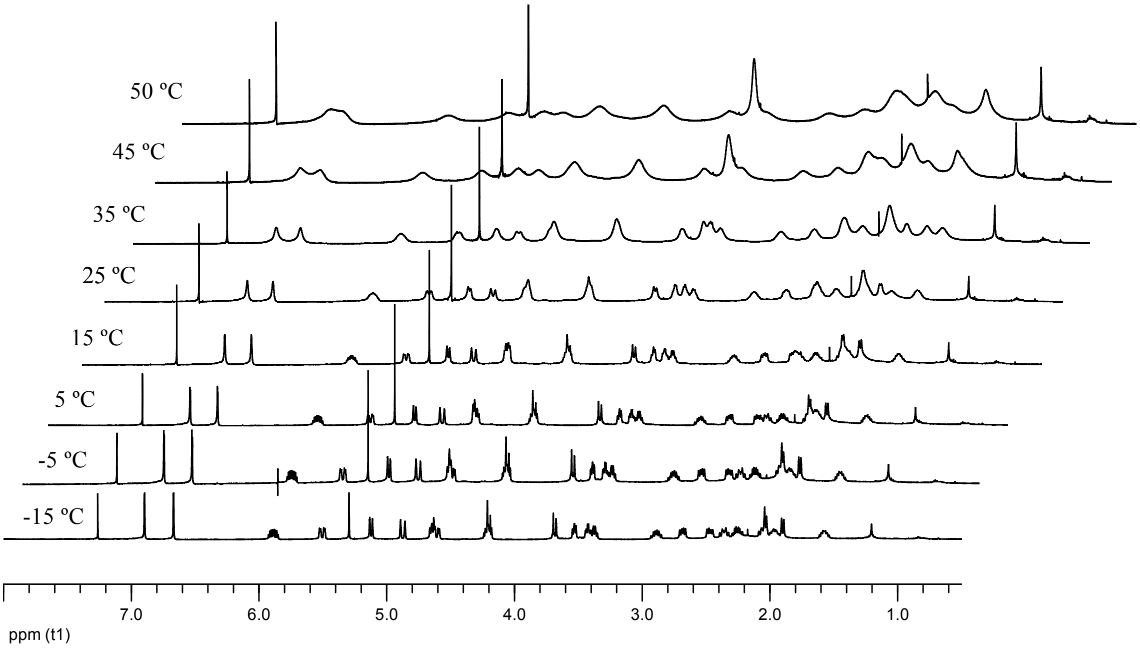


Figure 9. Variable temperature analysis for compound **1a** from -15 °C to 40 °C. Solvent $CDCl_3$, 5 mM, 500 MHz.

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 $\Delta G^{\neq} = 15.5$ Kcal/mol. The results agree well with the ones obtained previously using ^{1}H NMR.

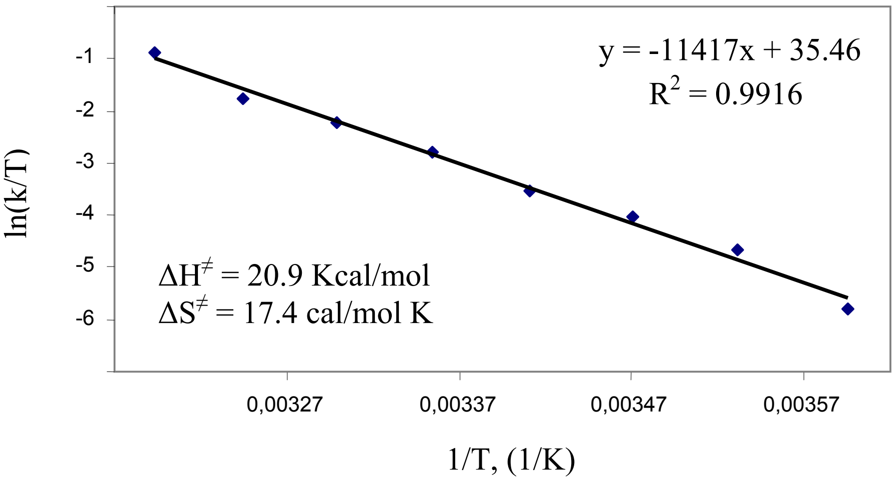


Figure 10. Complex **1a** line shape Analysis. Selected signal at 6.89 ppm, H_{imid}. Linear regression from Eq. $\ln(k/T) = -(\Delta H^{\neq}/T)(1/T) + \Delta S^{\neq}/R + 23.76$. Results: $\Delta H^{\neq} = 20.9$ Kcal/mol; $\Delta S^{\neq} = 17.4$ Kcal/mol.

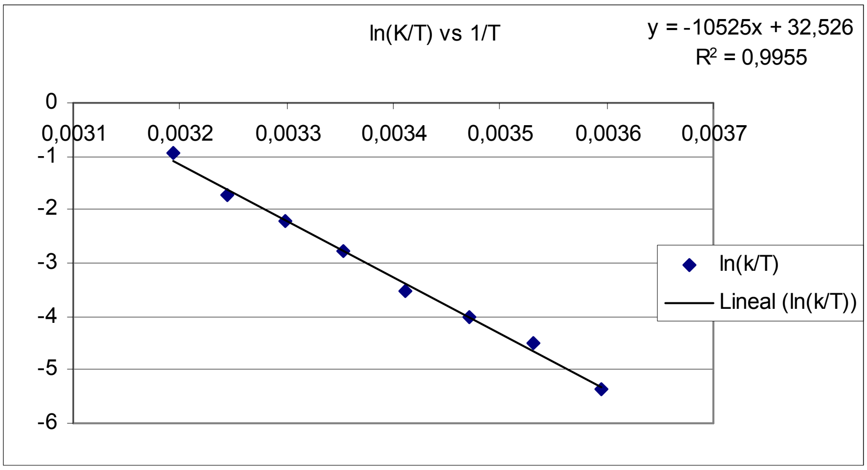
5.1.- Kinetic constant at the coalescence temperature for complex 1a.

Coalescence T (K)	Equation	Δν (Hz)	k (s^{-1})
323.15	k = л Δν / 1.414	113.95	253.13
	k = 2,22[(Δν)^2 + 6*(Jab)^2]^0.5		253.20

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= л (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

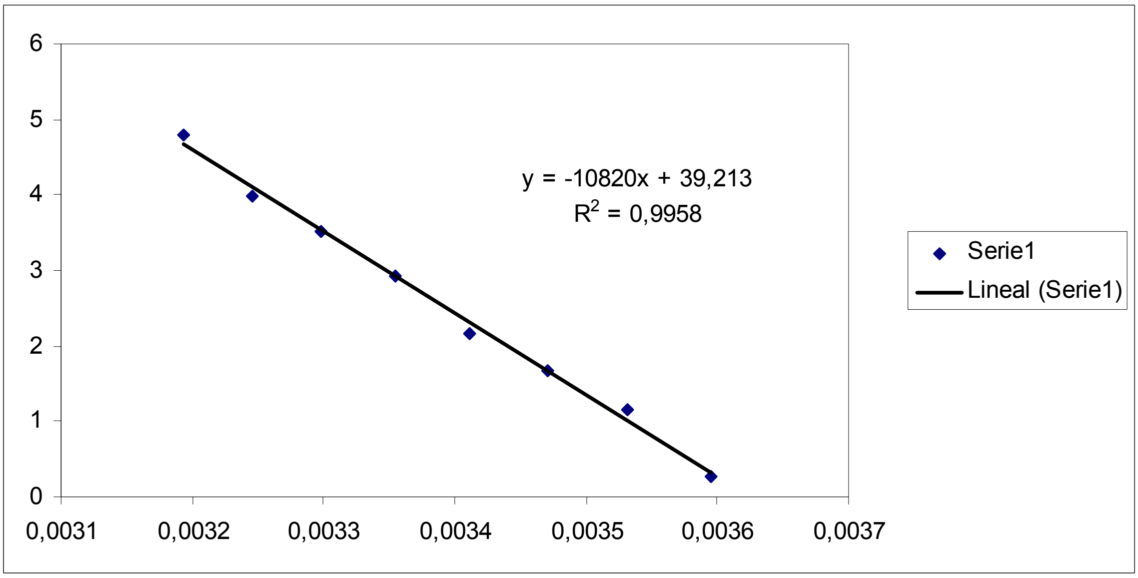


Eyring Equation: ln(k/T) = -(ΔH/R)(1/T) + ΔS/R + 23.76

ΔH = 20.9 Kcal/mol

ΔS = 17.42 cal/mol/K

K (s-1) k= л (w - wo)	ln k	1/T (K)
0,91106185	-0,09314449	0,00380011
0,03141593	-3,46044032	0,00372926
2,07345112	0,72921442	0,00366099
1,31946889	0,2772293	0,00359518
3,1415926	1,14472987	0,0035317
5,27787557	1,66352366	0,00347041
8,79645928	2,17434929	0,00341122
18,7238919	2,92980035	0,00335402
33,3637134	3,50746888	0,0032987
54,2867201	3,99427963	0,00324517
121,139811	4,79694534	0,00319336
385,944651	5,95569397	0,00314317

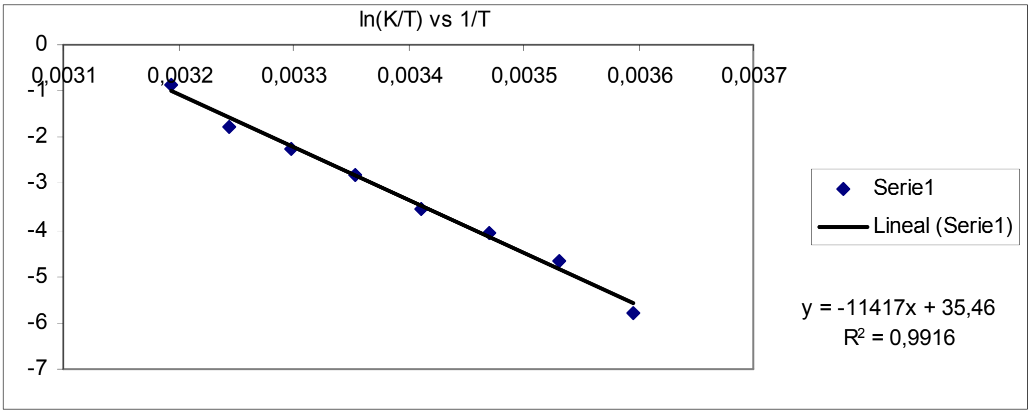


The Arrhenius Activation Energy Ea: ln k = ln k0 - Ea/(RT)

Ea = 21.50 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= π (w - wo)	k/T	1/T	ln(k/T)
258,15	3,55	3,55					
263,15	3,79	3,55	0,24	0,75398222	0,00286522	0,00380011	-5,8551107
268,15	3,53	3,55	-0,02	-0,06283185	-0,00023432	0,00372926	#¡NUM!
273,15	4,08	3,55	0,53	1,66504408	0,00609571	0,00366099	-5,1001695
278,15	3,82	3,55	0,27	0,84823	0,00304954	0,00359518	-5,79276399
283,15	4,41	3,55	0,86	2,70176964	0,00954183	0,0035317	-4,65206981
288,15	5,16	3,55	1,61	5,05796409	0,01755323	0,00347041	-4,04251713
293,15	6,25	3,55	2,7	8,48230002	0,02893502	0,00341122	-3,54270278
298,15	9,3	3,55	5,75	18,0641575	0,06058748	0,00335402	-2,80366699
303,15	13,79	3,55	10,24	32,1699082	0,10611878	0,0032987	-2,24319624
308,15	20,31	3,55	16,76	52,653092	0,17086838	0,00324517	-1,76686171
313,15	45,05	3,55	41,5	130,376093	0,41633752	0,00319336	-0,87625901
318,15	132,85	3,55	129,3	406,207923	1,27678115	0,00314317	0,24434218

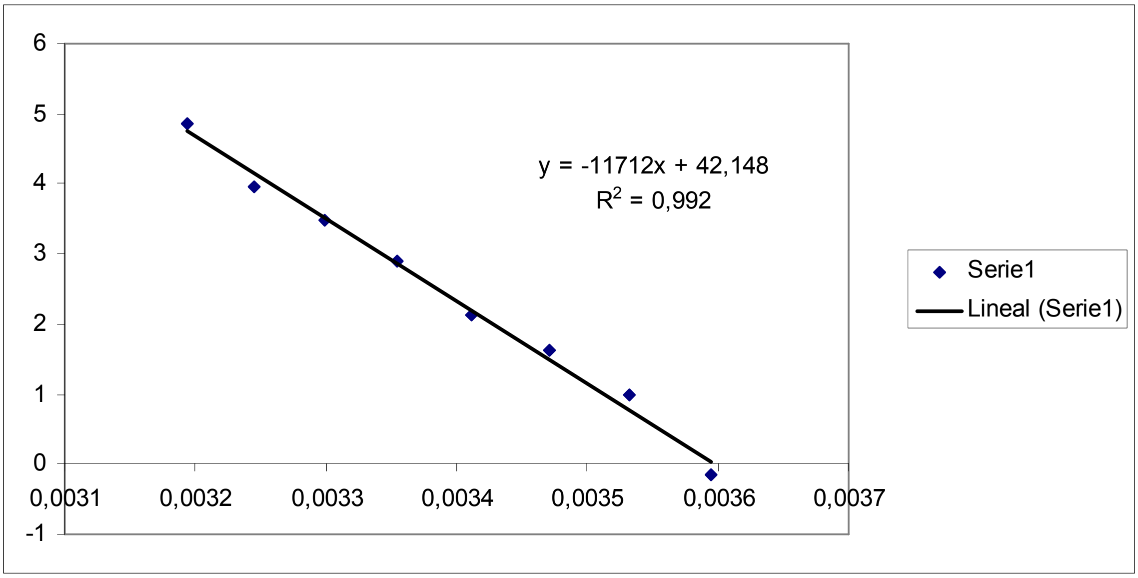


Eyring Equation: $\ln(k/T) = -(\Delta H/R)(1/T) + \Delta S/R + 23.76$

$\Delta H = 22.7$ Kcal/mol

$\Delta S = 23.24$ cal/mol/K

K (s-1) k= π (w - wo)	ln k	1/T (K)
0,75398222	-0,28238649	0,00380011
-0,06283185	#¡NUM!	0,00372926
1,66504408	0,5098516	0,00366099
0,84823	-0,16460345	0,00359518
2,70176964	0,99390698	0,0035317
5,05796409	1,62096405	0,00347041
8,48230002	2,13798164	0,00341122
18,0641575	2,89392972	0,00335402
32,1699082	3,47103149	0,0032987
52,653092	3,96372496	0,00324517
130,376093	4,8704233	0,00319336
406,207923	6,00686515	0,00314317



The Arrhenius Activation Energy Ea: ln k = ln k0 - Ea/(RT)

Ea = 23.27 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_2Cl_2 (3 x 50 ml) and dry over Na_2SO_4. The volatiles were removed under reduced pressure and the crude was purified through a flash silica-gel chromatography with acetone/CH_2Cl_2 (1:1). Yield: 2.34 g, 83%, orange oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (s, 1H, NC*H*N), 7.03 (s, 1H, NC*H*CHN), 6.87 (s, 1H, NCHC*H*N), 5.79 (m, 1H, -C*H*=CH_2), 5.05 (m, 2H, -CH=C*H₂*), 3.94 (m, 2H, NC*H₂*-), 2.07 (m, 2H, -C*H₂*-), 1.90 (m, 2H, -C*H₂*-).

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 ºC. The solid was washed with Et_2O (3 x 50 mL) and dry under vacuum. Yield: 1.8 g, 86%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.59 (s, 1H, NC*H*N), 7.42 (s, 2H, NC*H*C*H*N), 5.76 (m, 2H, -C*H*=CH$_2$), 5.03 (m, 4H, -CH=C*H*$_2$), 4.38 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 4H, NC*H*$_2$-), 2.15 (m, 4H, -C*H*$_2$-), 2.08 (m, 4H, -C*H*$_2$-). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 136.5 (N*C*N), 136.1 (-*C*H=CH$_2$), 122.6 (N*C*H*C*HN), 116.2 (-CH=*C*H$_2$), 49.2 (NCH$_2$-), 30.0 (-CH$_2$-), 29.2 (-CH$_2$-).

1, 3-Bis(2-propenyl)-imidazolium Bromide. This ligand precursor prepared according to literature methodologies.[12] 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. Glyoxal (5.73 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 pale yellow oil. Anion exchange afforded the pure product. Yield (6.9 g, 80%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 10.7 (s, 1H, NC*H*N), 7.53 (s, 2H, C*H*=CH) 5.99 – 5.94 (m, 2H, -C*H*=CH$_2$), 5.43 – 5.40 (m, 4H, -CH=C*H*$_2$), 4.93 (s, 4H, N-C*H*$_2$-). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 137.4 (N*C*N), 130.4 (*C*H=*C*H), 122.6 (-CH=*C*H$_2$), 122.3 (-CH=*C*H$_2$), 52.3 (NCH$_2$-).

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 ºC for 24 hours. After filtration, the volatiles were removed under reduced pressure. The mixture was quenched with water (20 ml), extracted with CH$_2$Cl$_2$ (3 x 50 ml) and dry over Na$_2$SO$_4$. A colourless oil of 4, 5-dichloro-1-(2-propenyl)-imidazole was obtained. Yield (1.07 g, 71 %). ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.36 (s, 1H, NC*H*N), 5.94 (m, 1H, NCH$_2$C*H*=CH$_2$), 5.33 d, J_{HH} = 10.2 HZ, NCH2CH=CH*H*$_{cis}$), 5.17 (d, 1H, NCH$_2$CH=CH*H*$_{trans}$, J_{HH} = 15 Hz), 4.51 (d, 2H, NC*H*$_2$CH=CH$_2$, 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 ºC. The solid was washed with Et$_2$O (3 x 50 mL) and dry under vacuum. Yield: 3.5 g, 85%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.82 (s, 1H, NC*H*N), 6.02 – 5.97 (m, 2H, -C*H*=CH$_2$), 5.54 – 5.47 (m, 4H, -CH=C*H*$_2$), 4.82 (d, 4H,

$^3J_{H-H}$ = 6.3 Hz, N-C*H*$_2$-). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ 136.8 (N*C*N), 128.1 (*C*-Cl), 124.1 (-CH=*C*H$_2$), 123.9 (-CH=*C*H$_2$), 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%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.5 (s, 1H, NC*H*N), 5.99 – 5.90 (m, 2H, -C*H*=CH$_2$), 5.42 (d, 2H, $^3J_{H-H}$ = 10.5 Hz, -CH=C*H*$_2$), 5.27 (d, 2H, $^3J_{H-H}$ = 17.1 Hz, -CH=C*H*$_2$), 4.68 (d, 4H, $^2J_{H-H}$ = 6.0 Hz, N-C*H*$_2$), 2.17 (s, 6H, C-C*H*$_3$).

3-methyl, 1-(2-propenyl)-imidaozolin-2-ylidene [(1, 2, 5, 6-η)-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$_2$Cl$_2$. 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$_2$Cl$_2$/hexanes. The filtrate was cold at -20ºC and compound **5** precipitated as a white solid. Yield: 180 mg (65%). ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.83 (s, 1H, NC*H*CHN), 6.64 (s, 1H, NCHC*H*N), 4.67 (m, 1H, COD), 4.18 – 4.12 (m, 3H, NCH*H*CH=CH$_2$, NCHHC*H*=CH$_2$ COD), 3.92 (s, 3H, -CH$_3$), 3.65 (d, $^3J_{HH}$ = 11.5 Hz, NCH*H*CH=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$_2$CH=CH*H*), 1.93 (m, 1H, COD), 1.90 (d, 1H, $^3J_{HHtrans}$ = 9.3 Hz, NCH$_2$CH=CH*H*), 1.61 – 1.59 (m, 1H, COD). ^{13}C NMR (75 MHz, CDCl$_3$): *δ* 160.88 (*C*-Ir), 123.16 (*C*H imidazole), 117.35 (*C*H imidazole), 98.50 (*C*H cod), 97.62 (*C*H cod), 60.39 (NCH$_2$*C*H=CH$_2$), 55.10 (*C*H cod), 52.59 (NCH$_2$CH=*C*H$_2$), 46.92 (*C*H cod), 40.40 (N*C*H$_2$CH=CH$_2$), 37.26 (N*C*H$_3$), 35.51 (*C*H$_2$ cod), 32.93 (*C*H$_2$ cod), 29.53

*C*H$_2$ cod), 28.02 (*C*H$_2$ cod). Electrospray Ms. Cone 25V. m/z (fragment): $[M-Cl]^+$ = 423.

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