• Supporting Information

Base-Free Hydrogenation of CO_2 to Formic Acid in Water with An Iridium Complex Bearing a *N,N'*-Diimine Ligand

Sheng-Mei Lu,[†,‡] Zhijun Wang,[†,∥,§,‡] Jun Li,[†] Jianliang Xiao,[∥] Can Li*[,†]

[†] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China.

[∥] Liverpool Centre for Materials & Catalysis, Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, U.K.

[§] Graduate University of Chinese Academy of Sciences, Beijing 100049, China

General: ^{1}H NMR spectra were recorded on a BrukerAvance 400 NMR spectrometer and chemical shifts are given in ppm. The concentration of the produced formic acid (FA) was measured on SHINEHA CIC-100 ion chromatograph with a Shodex IC SI-52 4E column using Na_2CO_3 solution (3.6 mM) as the eluent. $NaHCO_3$, Na_2CO_3, KOH，$KHCO_3$ were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. Sodium formate was purchased from Sinopharm Chemical Reagent Co., Ltd. $[IrCp^*Cl_2]_2$ was purchased from J&K. 3-(Trimethylsilyl)-1-propane sulfonic acid sodium salt (DSS) was purchased from Aladdin. Deionized water used in this work was obtained from PURELAB Ultra water purification system. Ligand **L3** and **L6** was purchased from J&K. Ligands **L1**,[1] **L2**,[2] **L4**[3], **L5**[1] and **L7**[4] were synthesized according to literature procedure. The synthesis and characterization information for **L1** and complex **1** can be found in our previous work.[5]

L2 (2-(pyridin-2-yl)-1,4,5,6-tetrahydropyrimidine)[2]: white solid, ^{1}H NMR (400 MHz, d6-DMSO) δ, 9.94 (s, 1H), 8.79 (d, *J* = 4.8 Hz, 1H), 8.17~8.10 (m, 2H), 7.77~7.74 (m, 1H), 3.52 (t, *J* = 5.6 Hz, 4H), 1.96 (m, 2H); ^{13}C {^{1}H} NMR (100 MHz, d6-DMSO) δ 155.8, 150.2, 145.0, 138.9, 128.5, 122.6, 39.4, 18.3.

L4 (4,4',6,6'-tetrahydroxybipyrimidine)[3]: white solid, ^{1}H NMR (400 MHz, d6-DMSO) δ, 11.71 (b, 2H), 5.60 (s, 1H); ^{13}C {^{1}H} NMR (100 MHz, d6-DMSO) δ 168.4, 153.8, 91.3.

L7 (2,3,4,6,7,9,10,11-Octahydro-pyrazino[1,2-a:4,3-a0]dipyrimidine)[4] light yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ, 1.82-1.86 (m, 4H), 3.20 (t, 4H, *J* = 4.0 Hz), 3.22 (s, 4H), 3.53 (t, 4H, J = 4 Hz); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ, 147.9, 47.9, 47.5, 44.8, 21.4.

Product detection by ^{1}H NMR for CO_2 hydrogenation in water without base

After the reaction, 0.3 mL of product solution was transferred into an NMR tube and then 0.2 mL of D_2O was added to the tube for the ^{1}H NMR measurement.

Figure S1 shows that only *H*-COOH peak was found, no other product was detected. Reaction conditions: complex **1** (0.25 μmol), H_2O (10.0 mL), 5.0 MPa of CO_2/H_2 (1/1), 40 °C, 30 min.

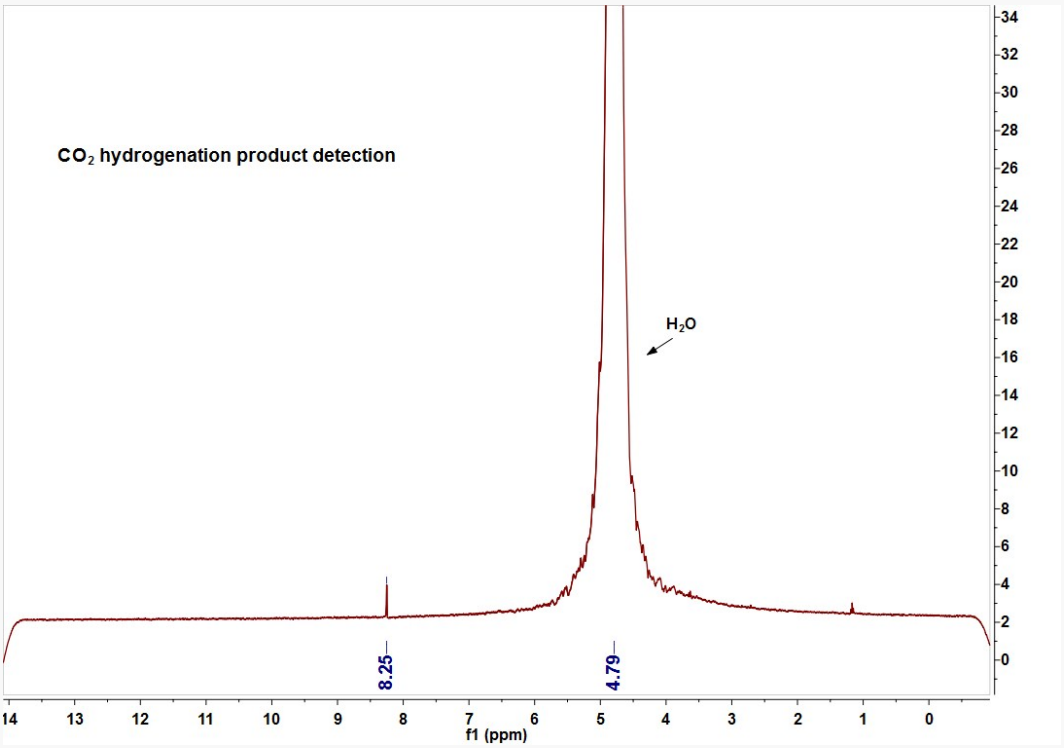


Figure **S1**. CO_2 hydrogenation product detection with ^{1}H NMR

Ea Measurement for CO_2 hydrogenation with complex 1 in the absence of a base

Table **S1** Temperature effect on the CO_2 hydrogenation in water without base[a]

Entry	Temp. (°C)	HCOOH (mmol)[b]	Time (min)	TOF (h^{-1})[c]
1	20	0.0371	15	594
2	30	0.0715	15	1144
3	40	0.1359	15	2174
4	50	0.1646	10	3950
5	60	0.1971	8	5913
6	70	0.2095	6	8380
7	80	0.2731	5	13109

[a] Reaction conditions: complex **1** as the catalyst (0.25 μmol), H_2O (50.0 mL), CO_2/H_2 = 1/1 (5.0 MPa). [b:] Measured on SHINEHA CIC-100 ion chromatograph with the Shodex column (IC SI-52 4E); averaged value from two runs with a reproducibility less than 5%; [c] TOF calculated based on the indicated reaction time.

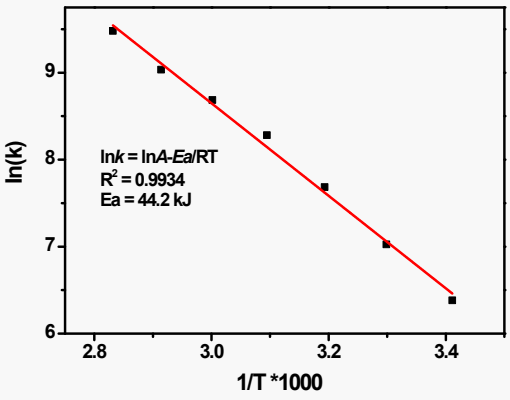


Figure **S2**. Arrhenius plot of initial TOF values for hydrogenation of CO_2 using complex **1**. At all conditions, the conversion is less than 10%.

Table S2 Additive effect on the Hydrogenation of CO_2[a]

Entry	Catalyst	Additive (eqv. to cat.)	HCO_2H (mmol)[b]	TOF (h^{-1})[c]
1	**2**	/	0.128	1024
2	**1**	NaCl (60)	0.089	712
3	**1**	NaCl (200)	0.074	592
4	**1**	NaCl (568)	0.043	344
5	**1**	NaI (2)	0.025	200
6	**1**	NaI (5)	0.010	80
7	**1**	NaI (100)	0	/
8[d]	**2**	PPh_3 (5)	0	/
9[d]	**2**	/	0.125	1000

[a:] General reaction conditions: catalyst **1** or **2** (0.25 μmol), H_2O (10.0 mL), CO_2/H_2 = 1/1 (5.0 MPa), at 40 °C, 30 min; [b:] Measured on SHINEHA CIC-100 ion chromatograph with the Shodex column (IC SI-52 4E); [c] TOF calculated based on the indicated reaction time. [d:] H_2O (9.5 mL)/MeOH (0.5 ml), methanol was used to dissolve PPh_3.

^{1}H NMR detection of Ir-H and *H*-COOH during the hydrogenation of CO_2 using complex 1 in the absence of base

Heavy-walled NMR tube was used for the following measurement at room temperature. Unless otherwise noted, complex **1** (3.0 μmol) was used and H_2 (1.5 MPa) or H_2/CO_2 (1/1, 1.2 MPa) was pressurized into the NMR tube. All the manipulation was carried out under inert gas protection.

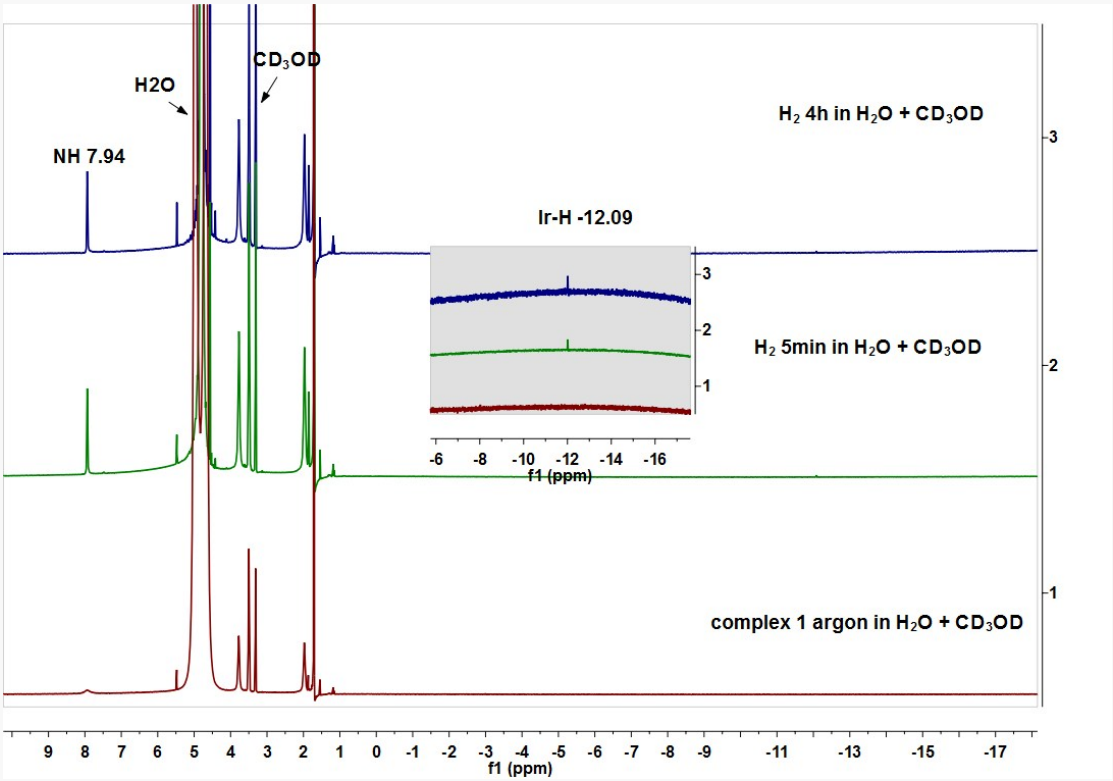


Figure (**S3-1**) ^{1}H NMR spectrum of complex **1** in CD_3OD/H_2O (0.1 mL CD_3OD + 0.03 mL H_2O) shows a weak broad peak of the NH proton at δ = 7.94 ppm; ^{1}H NMR was conducted in Wilmad thick-wall NMR tube.

(**S3-2**) ^{1}H NMR spectrum of complex **1** in CD_3OD/H_2O after pressurized with H_2 (1.5 MPa) for 5 min: N-H signal at δ = 7.94 ppm was detected as a singlet peak; Ir-H signal at δ = -12.09 ppm appeared.

(**S3-3**) ^{1}H NMR spectrum of complex **1** in CD_3OD/H_2O after pressurized with H_2 for 4 h.

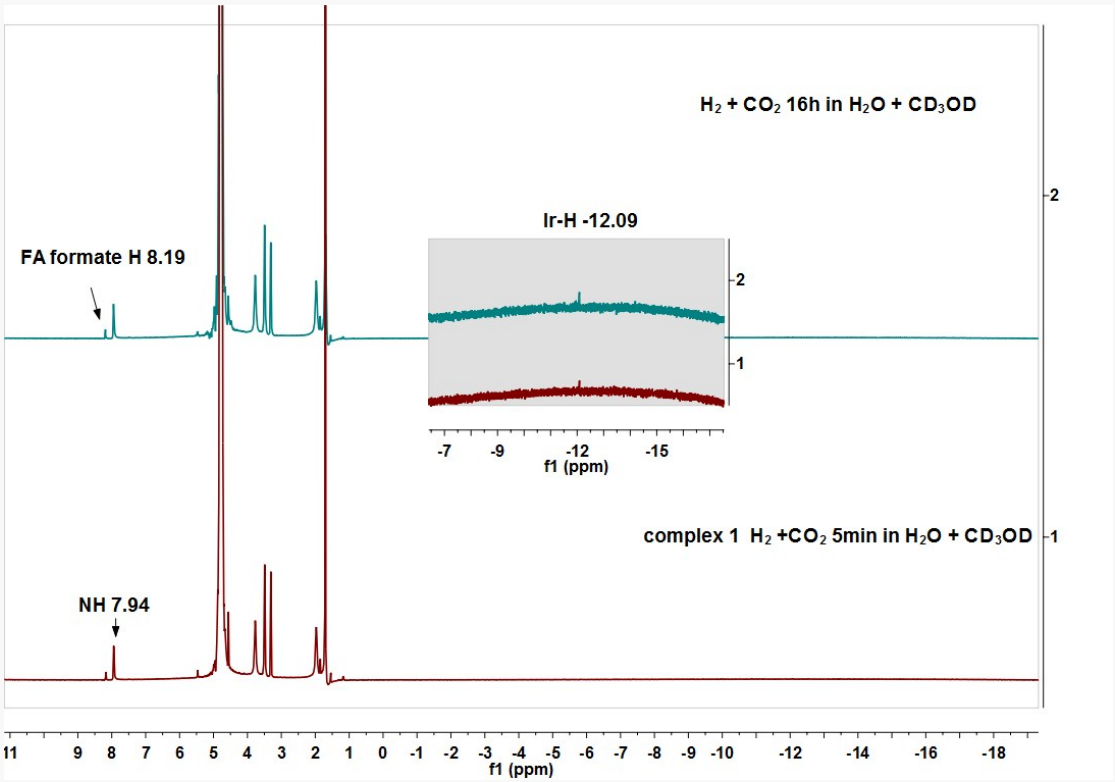


Figure (**S4-1**) ^{1}H NMR spectrum of complex **1** in CD_3OD/H_2O (0.1 mL CD_3OD + 0.03 mL H_2O) after pressurized with H_2/CO_2 (1:1, total 1.2 MPa) for 5 min: NH signal at δ = 7.94 ppm, Ir-H signal at δ = -12.09 ppm and *H*-COOH signal at δ = 8.19 ppm were detectable. ^{1}H NMR was conducted in Wilmad thick-wall NMR tube.

(**S4-2**) ^{1}H NMR spectrum of complex **1** in CD_3OD/H_2O after pressurized with H_2/CO_2 for 16 h.

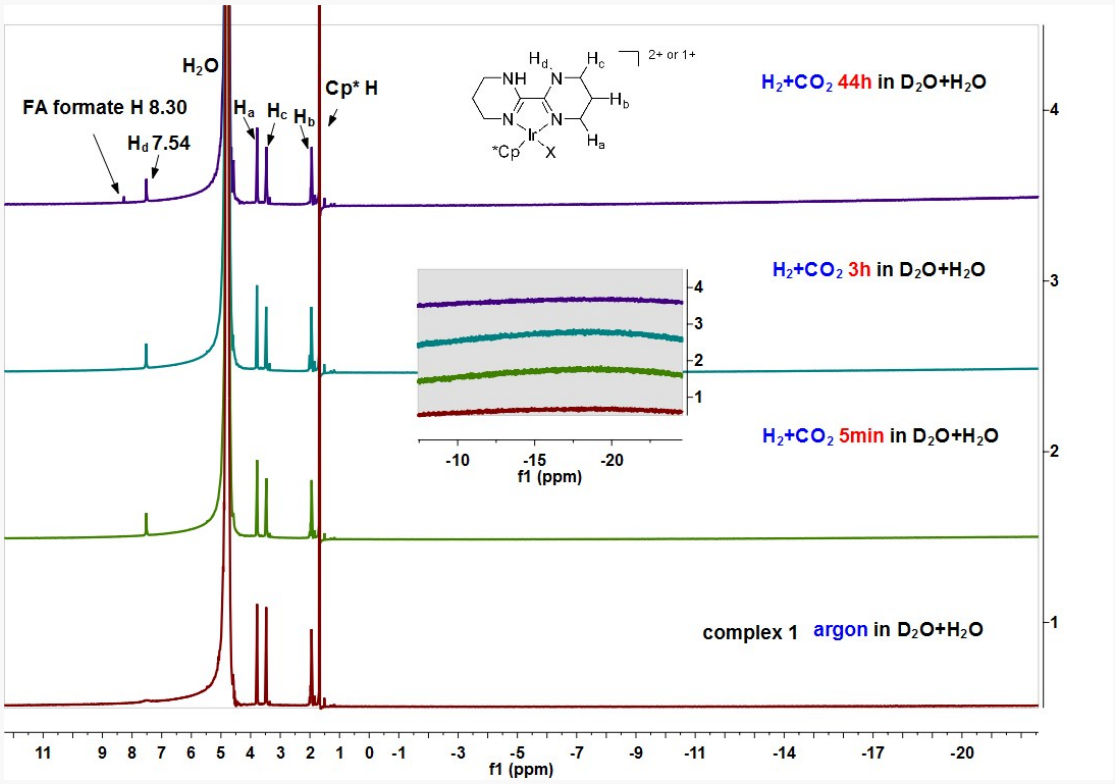


Figure (**S5-1**) ^{1}H NMR spectrum of complex **1** in D_2O/H_2O (0.05 mL D_2O + 0.15 mL H_2O) shows a weak broad peak of NH proton at δ = 7.54 ppm; ^{1}H NMR was conducted in Wilmad thick-wall NMR tube.

(**S5-2**) ^{1}H NMR spectrum of complex **1** in D_2O/H_2O after pressurized with H_2/CO_2 (1:1, total 1.2 MPa) for 5 min: NH signal at δ = 7.54 ppm was detected as a singlet peak; *H*-COOH signal was also detected but very tiny. No Ir-H signal was detected;

(**S5-3**) ^{1}H NMR spectrum of complex **1** in D_2O/H_2O after pressurized with H_2/CO_2 for 3 h;

(**S5-4**) ^{1}H NMR spectrum of complex **1** in D_2O/H_2O after pressurized with H_2/CO_2 for 44 h. A peak at δ = 8.30 ppm (*H*-COOH) was obviously observed.

The ^{1}H NMR monitoring of the catalyst structure during the reaction process

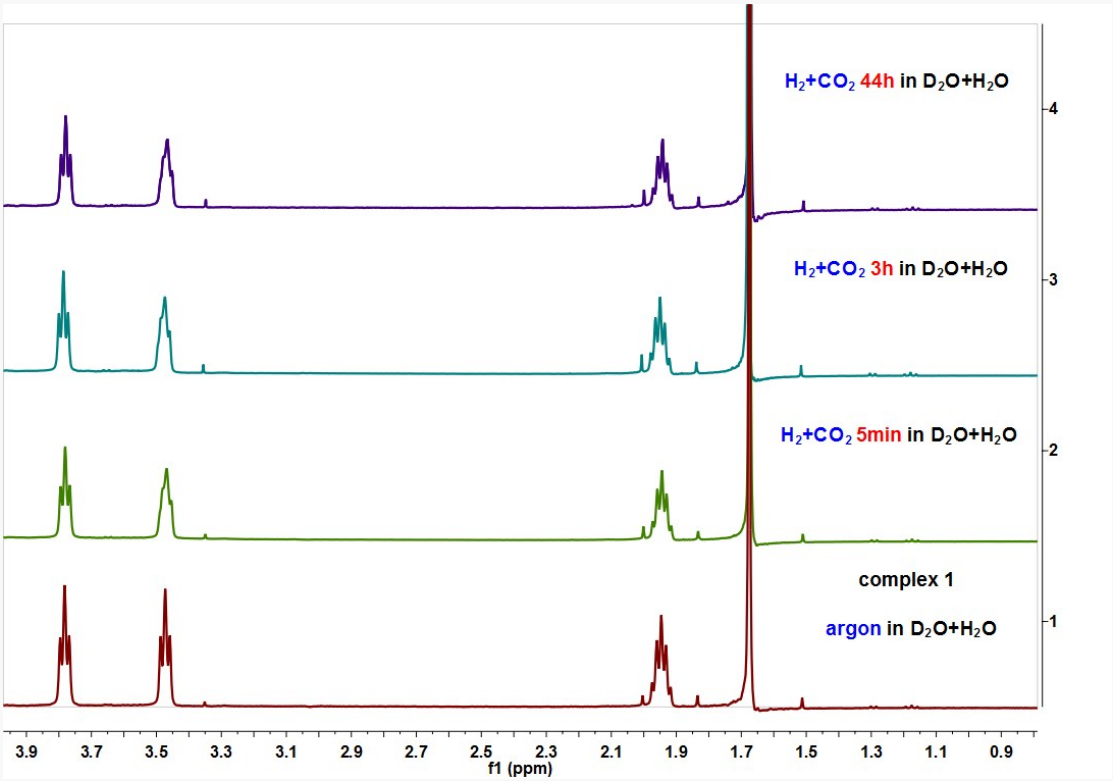


Figure **S6** Partial enlargement of **Figure S5**: the signals of the complex **1** in water remain the same during the reaction.

UV-Vis absorption spectra and pKa measurement of complex 1

The structure of complex **1** in water was investigated by UV-Vis absorption spectra measured in aqueous solutions at various pH values (Figure S9a). The pH of the solutions was adjusted by mixing the stock solution of complex **1** (0.15 mM) in H_2SO_4 (0.02 M) and NaOH (0.1 M). The UV/Vis spectra were recorded right after testing the pH value.

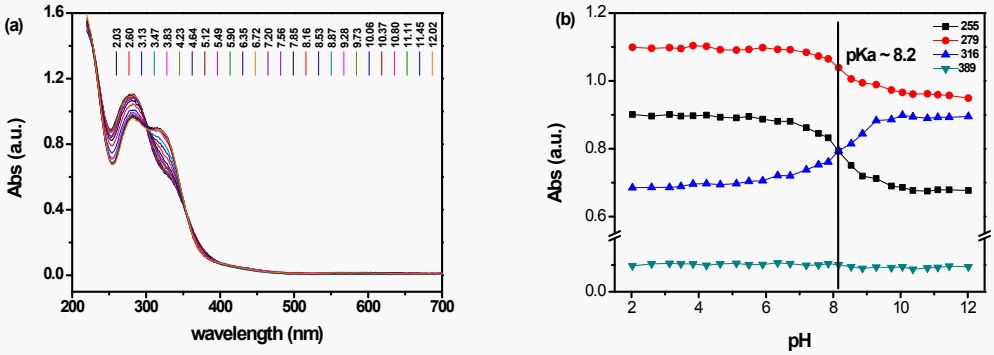


Figure **S7**. (**a**) The UV-Vis absorption spectra of complex **1** measured at pH values in the range from 2.0 to12.0; (**b**) Absorbance changes at 255 nm, 279 nm, 316 nm and 389 nm as a function of pH change.

As shown in Figure S7b, the complex remains unchanged structurally below pH 6 (under our reaction conditions, the pH of the reaction solution is below 4) and loses the NH proton on the ligand under basic solution. The pKa value of complex **1** for the deprotonation of NH group in water is estimated to be 8.2.

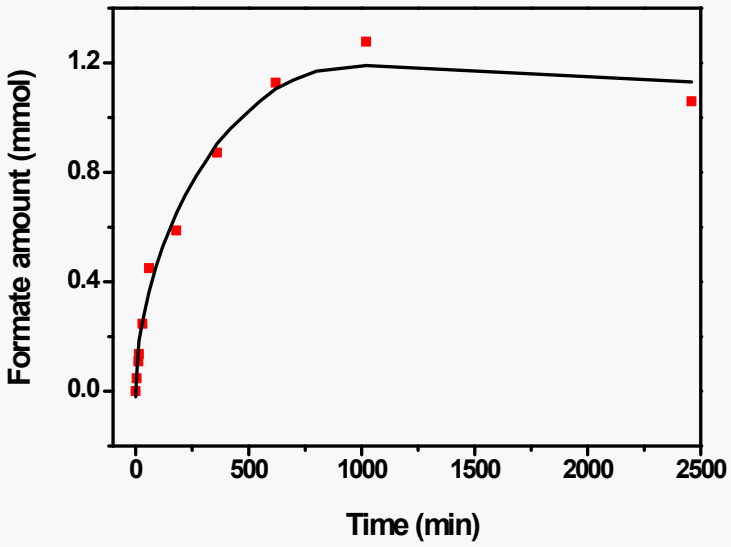
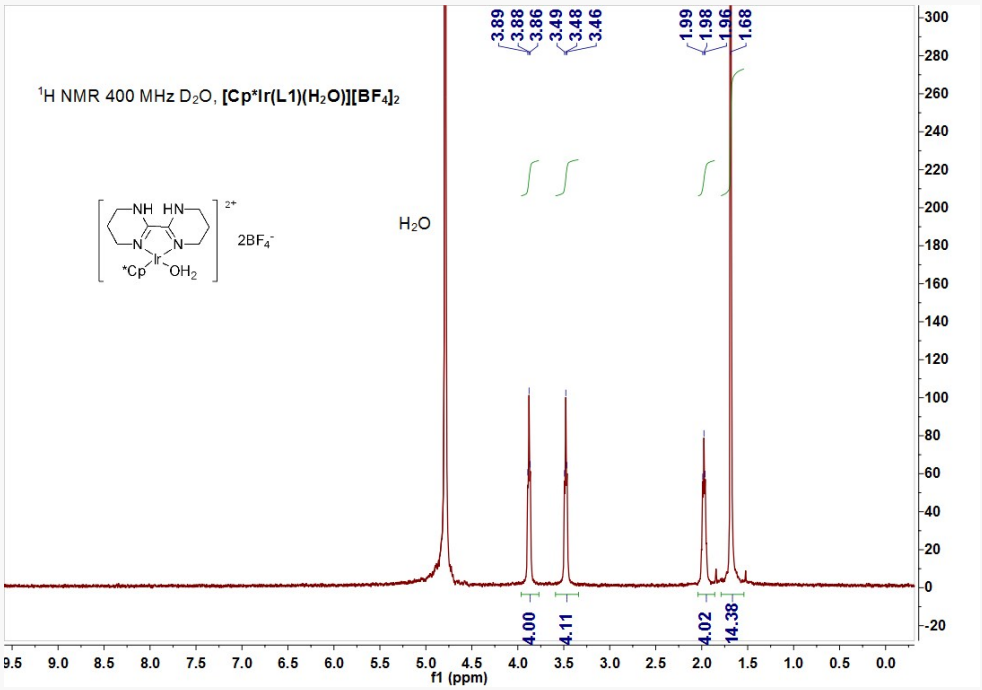
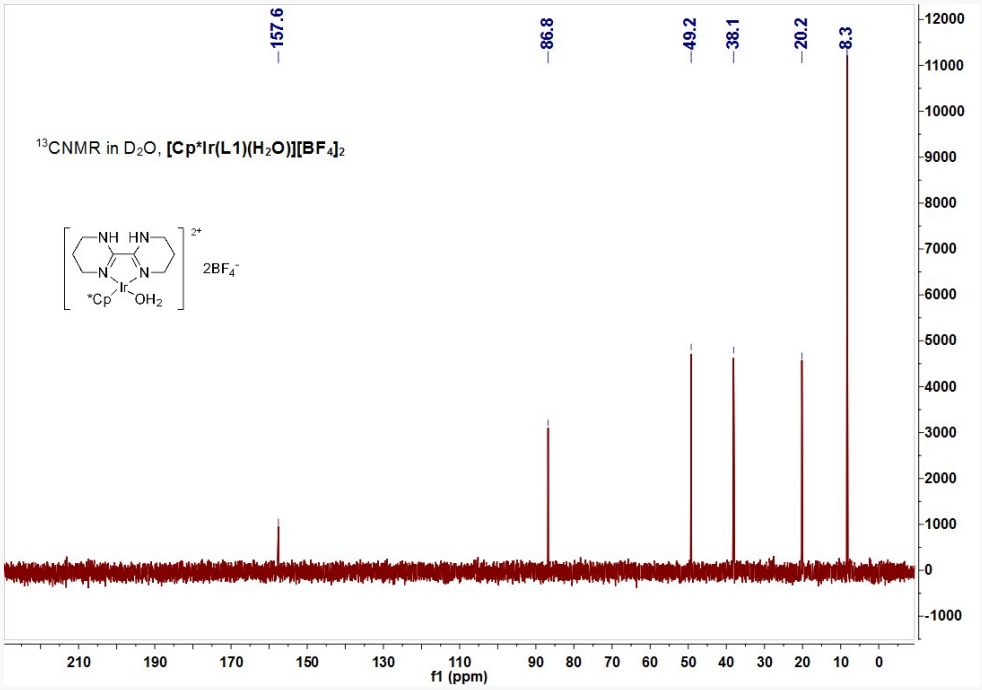


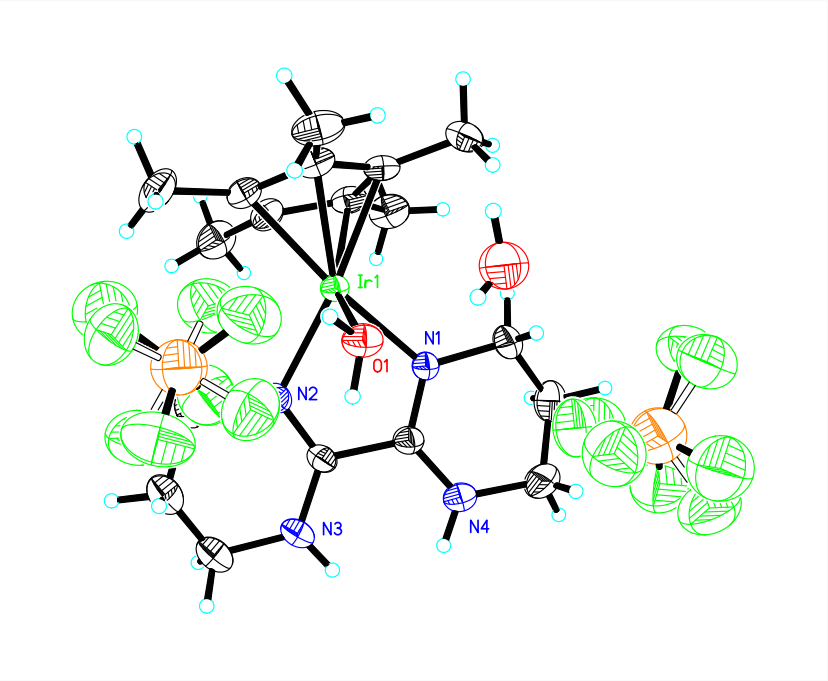
Figure **S8**. Plot of FA amount versus the reaction time: complex **1** (0.25 μmol), H_2O (50.0 mL), at 40 °C, 5.0 MPa CO_2/H_2 (1/1).


^{1}H NMR 400 MHz D_2O, **[Cp*Ir(L1)(H_2O)][BF_4]$_2$**
H_2O
$2BF_4^-$
3.89
3.88
3.86
3.49
3.48
3.46
1.99
1.98
1.96
1.68
4.00
4.11
4.02
14.38
f1 (ppm)


^{13}CNMR in D_2O, **[Cp*Ir(L1)(H_2O)][BF_4]$_2$**
$2BF_4^-$
157.6
86.8
49.2
38.1
20.2
8.3
f1 (ppm)

Crystal structure of $[Cp^*Ir(L1)(H_2O)][BF_4]_2$:

CCDC 1438213 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



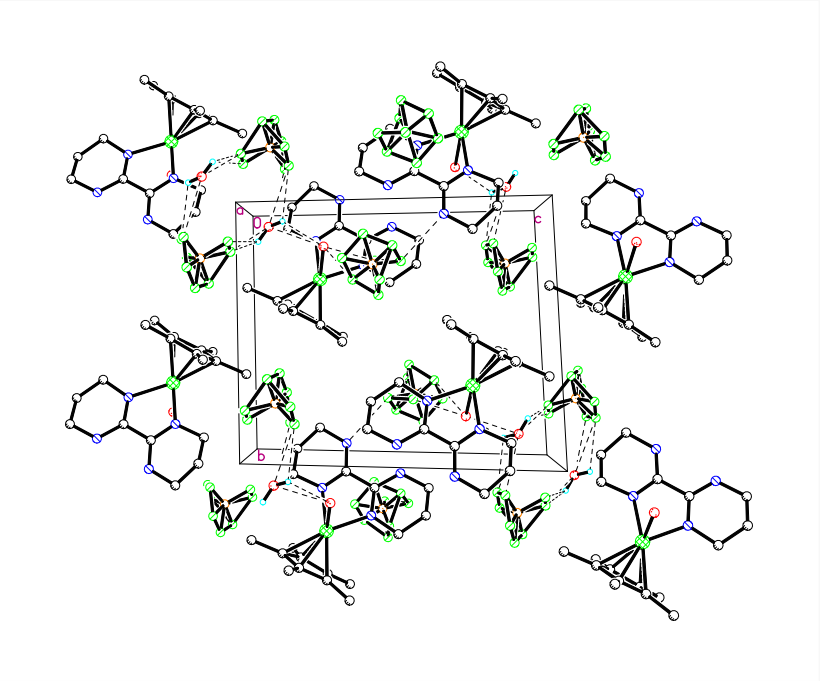


Table 1. Crystal data and structure refinement for mo_dm15855_0m.

Identification code	mo_dm15855_0m	
Empirical formula	C18 H33 B2 F8 Ir N4 O2	
Formula weight	703.30	
Temperature	293 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.6729(15) Å	α= 85.039(3)°.
	b = 11.3034(19) Å	β= 74.421(3)°.
	c = 13.751(2) Å	γ = 78.507(3)°.
Volume	1271.8(4) $Å^3$	
Z	2	
Density (calculated)	1.837 Mg/m^3	
Absorption coefficient	5.331 mm^{-1}	
F(000)	688	
Crystal size	0.33 x 0.28 x 0.25 mm^3	
Theta range for data collection	2.357 to 30.901°.	
Index ranges	-12<=h<=11, -16<=k<=16, -19<=l<=19	
Reflections collected	13116	
Independent reflections	7928 [R(int) = 0.0322]	
Completeness to theta = 26.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.4254	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7928 / 298 / 397	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0486, wR2 = 0.1202	
R indices (all data)	R1 = 0.0680, wR2 = 0.1312	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.859 and -2.302 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for mo_dm15855_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	4217(1)	2896(1)	2538(1)	38(1)
O(1)	6353(6)	1642(4)	2745(4)	56(1)
N(1)	3510(7)	1283(4)	2406(4)	44(1)
N(2)	3316(7)	2325(5)	4023(4)	44(1)
N(3)	2548(11)	702(6)	5041(4)	78(2)
N(4)	2795(9)	-461(5)	3263(5)	62(2)
C(1)	4642(9)	3777(6)	1062(5)	49(1)
C(2)	5561(9)	4206(6)	1639(6)	52(2)
C(3)	4478(9)	4758(6)	2517(6)	53(2)
C(4)	2870(9)	4691(6)	2497(6)	54(2)
C(5)	2967(9)	4083(6)	1599(5)	51(2)
C(6)	5301(13)	3247(8)	59(6)	73(2)
C(7)	7347(10)	4127(8)	1376(8)	77(2)
C(8)	4928(15)	5429(8)	3252(9)	85(3)
C(9)	1318(11)	5238(8)	3209(8)	74(2)
C(10)	1530(10)	3875(8)	1281(7)	69(2)
C(11)	3645(12)	765(7)	1440(5)	65(2)
C(12)	2659(18)	-196(9)	1560(8)	102(4)
C(13)	2854(16)	-1071(7)	2367(7)	88(3)
C(14)	3098(8)	647(6)	3221(5)	44(1)
C(15)	2979(8)	1266(6)	4159(4)	44(1)
C(16)	2335(16)	1266(9)	5967(6)	92(2)
C(17)	3092(16)	2278(9)	5831(7)	94(2)
C(18)	3191(14)	3023(8)	4902(6)	75(2)
F(1)	7396(18)	-2610(16)	1442(11)	145(4)
F(2)	9007(19)	-1468(11)	1740(9)	108(3)
F(3)	8807(19)	-1603(13)	197(9)	123(4)
F(4)	10070(20)	-3171(13)	938(12)	166(5)
F(1')	7479(19)	-1459(15)	1544(13)	167(5)
F(2')	9980(20)	-2149(16)	1654(12)	149(5)
F(3')	8580(20)	-3368(12)	1272(12)	143(4)
F(4')	9440(20)	-1964(14)	166(10)	132(5)

B(1)	8848(16)	-2233(11)	1127(9)	129(3)
F(5)	6992(14)	2255(13)	4448(11)	130(4)
F(6)	9416(17)	2220(13)	3420(9)	134(4)
F(7)	8410(20)	3623(11)	4533(12)	154(5)
F(8)	9138(18)	1749(13)	5031(10)	145(4)
F(7')	7770(17)	3010(12)	3708(10)	128(4)
F(6')	9285(16)	1294(10)	4113(11)	127(4)
F(5')	7319(16)	2293(12)	5290(10)	147(4)
F(8')	9542(15)	3060(11)	4595(10)	110(3)
B(2)	8509(14)	2442(10)	4378(9)	114(3)
O(2)	8173(12)	905(7)	985(7)	117(3)

Table 3. Bond lengths [Å] and angles [°] for mo_dm15855_0m.

Ir(1)-O(1)	2.165(4)
Ir(1)-N(1)	2.073(5)
Ir(1)-N(2)	2.076(5)
Ir(1)-C(1)	2.154(6)
Ir(1)-C(2)	2.163(7)
Ir(1)-C(3)	2.158(6)
Ir(1)-C(4)	2.134(6)
Ir(1)-C(5)	2.125(6)
O(1)-H(1A)	0.8885
O(1)-H(1B)	0.8867
N(1)-C(11)	1.464(8)
N(1)-C(14)	1.284(8)
N(2)-C(15)	1.275(8)
N(2)-C(18)	1.468(9)
N(3)-H(3)	0.8600
N(3)-C(15)	1.317(8)
N(3)-C(16)	1.423(10)
N(4)-H(4)	0.8600
N(4)-C(13)	1.446(10)
N(4)-C(14)	1.323(8)
C(1)-C(2)	1.435(10)
C(1)-C(5)	1.429(10)
C(1)-C(6)	1.474(11)
C(2)-C(3)	1.420(11)
C(2)-C(7)	1.479(10)
C(3)-C(4)	1.419(10)
C(3)-C(8)	1.486(11)
C(4)-C(5)	1.439(10)
C(4)-C(9)	1.489(11)
C(5)-C(10)	1.493(9)
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600

C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(11)-C(12)	1.484(13)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(12)-C(13)	1.443(13)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-C(15)	1.490(8)
C(16)-H(16A)	0.9700
C(16)-H(16B)	0.9700
C(16)-C(17)	1.404(14)
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(17)-C(18)	1.461(12)
C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
F(1)-B(1)	1.358(14)
F(2)-B(1)	1.309(13)
F(3)-B(1)	1.415(14)
F(4)-B(1)	1.328(14)
F(1')-B(1)	1.346(14)
F(2')-B(1)	1.391(14)
F(3')-B(1)	1.339(14)
F(4')-B(1)	1.317(15)
F(5)-B(2)	1.350(13)
F(6)-B(2)	1.357(14)
F(7)-B(2)	1.353(14)
F(8)-B(2)	1.299(13)

F(7')-B(2)	1.313(13)
F(6')-B(2)	1.368(13)
F(5')-B(2)	1.415(14)
F(8')-B(2)	1.345(13)
O(2)-H(2A)	0.8499
O(2)-H(2B)	0.8500

N(1)-Ir(1)-O(1)	80.5(2)
N(1)-Ir(1)-N(2)	76.1(2)
N(1)-Ir(1)-C(1)	107.0(2)
N(1)-Ir(1)-C(2)	140.8(2)
N(1)-Ir(1)-C(3)	166.3(2)
N(1)-Ir(1)-C(4)	128.5(3)
N(1)-Ir(1)-C(5)	101.4(2)
N(2)-Ir(1)-O(1)	80.8(2)
N(2)-Ir(1)-C(1)	167.0(2)
N(2)-Ir(1)-C(2)	142.1(3)
N(2)-Ir(1)-C(3)	108.9(2)
N(2)-Ir(1)-C(4)	102.3(3)
N(2)-Ir(1)-C(5)	128.4(3)
C(1)-Ir(1)-O(1)	112.0(2)
C(1)-Ir(1)-C(2)	38.8(3)
C(1)-Ir(1)-C(3)	65.3(3)
C(2)-Ir(1)-O(1)	95.0(2)
C(3)-Ir(1)-O(1)	112.7(2)
C(3)-Ir(1)-C(2)	38.4(3)
C(4)-Ir(1)-O(1)	150.9(3)
C(4)-Ir(1)-C(1)	65.7(3)
C(4)-Ir(1)-C(2)	64.5(3)
C(4)-Ir(1)-C(3)	38.6(3)
C(5)-Ir(1)-O(1)	150.6(3)
C(5)-Ir(1)-C(1)	39.0(3)
C(5)-Ir(1)-C(2)	64.8(3)
C(5)-Ir(1)-C(3)	65.3(3)
C(5)-Ir(1)-C(4)	39.5(3)
Ir(1)-O(1)-H(1A)	112.1
Ir(1)-O(1)-H(1B)	111.1
H(1A)-O(1)-H(1B)	107.0

C(11)-N(1)-Ir(1)	124.0(4)
C(14)-N(1)-Ir(1)	117.0(4)
C(14)-N(1)-C(11)	118.5(5)
C(15)-N(2)-Ir(1)	116.6(4)
C(15)-N(2)-C(18)	119.4(6)
C(18)-N(2)-Ir(1)	123.7(5)
C(15)-N(3)-H(3)	119.1
C(15)-N(3)-C(16)	121.9(7)
C(16)-N(3)-H(3)	119.1
C(13)-N(4)-H(4)	118.9
C(14)-N(4)-H(4)	118.9
C(14)-N(4)-C(13)	122.2(6)
C(2)-C(1)-Ir(1)	70.9(4)
C(2)-C(1)-C(6)	125.9(7)
C(5)-C(1)-Ir(1)	69.4(4)
C(5)-C(1)-C(2)	106.6(6)
C(5)-C(1)-C(6)	127.1(7)
C(6)-C(1)-Ir(1)	129.5(5)
C(1)-C(2)-Ir(1)	70.3(4)
C(1)-C(2)-C(7)	126.8(8)
C(3)-C(2)-Ir(1)	70.6(4)
C(3)-C(2)-C(1)	109.2(6)
C(3)-C(2)-C(7)	124.0(7)
C(7)-C(2)-Ir(1)	126.3(5)
C(2)-C(3)-Ir(1)	71.0(4)
C(2)-C(3)-C(8)	125.9(8)
C(4)-C(3)-Ir(1)	69.8(4)
C(4)-C(3)-C(2)	107.8(6)
C(4)-C(3)-C(8)	125.9(8)
C(8)-C(3)-Ir(1)	130.7(6)
C(3)-C(4)-Ir(1)	71.6(4)
C(3)-C(4)-C(5)	108.0(6)
C(3)-C(4)-C(9)	127.6(7)
C(5)-C(4)-Ir(1)	69.9(3)
C(5)-C(4)-C(9)	124.3(7)
C(9)-C(4)-Ir(1)	128.2(6)
C(1)-C(5)-Ir(1)	71.6(3)
C(1)-C(5)-C(4)	108.4(6)

C(1)-C(5)-C(10)	127.0(7)
C(4)-C(5)-Ir(1)	70.6(4)
C(4)-C(5)-C(10)	124.6(7)
C(10)-C(5)-Ir(1)	125.7(5)
C(1)-C(6)-H(6A)	109.5
C(1)-C(6)-H(6B)	109.5
C(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(2)-C(7)-H(7A)	109.5
C(2)-C(7)-H(7B)	109.5
C(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(3)-C(8)-H(8A)	109.5
C(3)-C(8)-H(8B)	109.5
C(3)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(4)-C(9)-H(9A)	109.5
C(4)-C(9)-H(9B)	109.5
C(4)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(5)-C(10)-H(10A)	109.5
C(5)-C(10)-H(10B)	109.5
C(5)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(1)-C(11)-H(11A)	109.2
N(1)-C(11)-H(11B)	109.2
N(1)-C(11)-C(12)	112.1(7)
H(11A)-C(11)-H(11B)	107.9

C(12)-C(11)-H(11A)	109.2
C(12)-C(11)-H(11B)	109.2
C(11)-C(12)-H(12A)	108.7
C(11)-C(12)-H(12B)	108.7
H(12A)-C(12)-H(12B)	107.6
C(13)-C(12)-C(11)	114.2(9)
C(13)-C(12)-H(12A)	108.7
C(13)-C(12)-H(12B)	108.7
N(4)-C(13)-H(13A)	109.7
N(4)-C(13)-H(13B)	109.7
C(12)-C(13)-N(4)	109.9(7)
C(12)-C(13)-H(13A)	109.7
C(12)-C(13)-H(13B)	109.7
H(13A)-C(13)-H(13B)	108.2
N(1)-C(14)-N(4)	125.0(6)
N(1)-C(14)-C(15)	114.0(5)
N(4)-C(14)-C(15)	120.9(6)
N(2)-C(15)-N(3)	125.6(6)
N(2)-C(15)-C(14)	115.2(5)
N(3)-C(15)-C(14)	119.2(6)
N(3)-C(16)-H(16A)	109.1
N(3)-C(16)-H(16B)	109.1
H(16A)-C(16)-H(16B)	107.9
C(17)-C(16)-N(3)	112.4(8)
C(17)-C(16)-H(16A)	109.1
C(17)-C(16)-H(16B)	109.1
C(16)-C(17)-H(17A)	107.4
C(16)-C(17)-H(17B)	107.4
C(16)-C(17)-C(18)	119.7(9)
H(17A)-C(17)-H(17B)	106.9
C(18)-C(17)-H(17A)	107.4
C(18)-C(17)-H(17B)	107.4
N(2)-C(18)-H(18A)	109.0
N(2)-C(18)-H(18B)	109.0
C(17)-C(18)-N(2)	112.7(7)
C(17)-C(18)-H(18A)	109.0
C(17)-C(18)-H(18B)	109.0
H(18A)-C(18)-H(18B)	107.8

F(1)-B(1)-F(3)	104.7(9)
F(2)-B(1)-F(1)	112.3(10)
F(2)-B(1)-F(3)	107.4(9)
F(2)-B(1)-F(4)	113.9(10)
F(4)-B(1)-F(1)	110.6(9)
F(4)-B(1)-F(3)	107.4(9)
F(1')-B(1)-F(2')	106.8(9)
F(3')-B(1)-F(1')	109.9(10)
F(3')-B(1)-F(2')	106.8(9)
F(4')-B(1)-F(1')	112.2(10)
F(4')-B(1)-F(2')	108.9(10)
F(4')-B(1)-F(3')	111.9(10)
F(5)-B(2)-F(6)	108.0(9)
F(5)-B(2)-F(7)	108.1(9)
F(7)-B(2)-F(6)	107.4(9)
F(8)-B(2)-F(5)	110.4(9)
F(8)-B(2)-F(6)	111.3(9)
F(8)-B(2)-F(7)	111.4(9)
F(7')-B(2)-F(6')	112.9(9)
F(7')-B(2)-F(5')	108.5(9)
F(7')-B(2)-F(8')	112.9(9)
F(6')-B(2)-F(5')	104.9(8)
F(8')-B(2)-F(6')	110.3(9)
F(8')-B(2)-F(5')	106.8(9)
H(2A)-O(2)-H(2B)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for mo_dm15855_0m. The anisotropic

displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	39(1)	38(1)	38(1)	1(1)	-9(1)	-10(1)
O(1)	46(3)	55(3)	61(3)	9(2)	-11(2)	-5(2)
N(1)	55(3)	42(2)	36(2)	-2(2)	-10(2)	-17(2)
N(2)	46(3)	50(3)	35(2)	-2(2)	-7(2)	-11(2)
N(3)	131(5)	68(3)	34(3)	6(2)	-7(3)	-36(4)
N(4)	84(5)	50(3)	52(3)	5(2)	-9(3)	-30(3)
C(1)	51(4)	43(3)	50(3)	15(3)	-12(3)	-13(3)
C(2)	49(4)	43(3)	67(4)	9(3)	-16(3)	-14(3)
C(3)	54(4)	46(3)	61(4)	2(3)	-14(3)	-20(3)
C(4)	53(4)	37(3)	67(4)	-3(3)	-14(3)	-3(3)
C(5)	53(4)	46(3)	59(4)	15(3)	-23(3)	-15(3)
C(6)	100(7)	65(5)	45(4)	9(3)	-5(4)	-16(5)
C(7)	53(5)	73(5)	104(7)	23(5)	-14(5)	-27(4)
C(8)	113(8)	53(4)	109(8)	-6(4)	-52(7)	-28(5)
C(9)	57(5)	60(4)	94(7)	-8(4)	-7(4)	0(4)
C(10)	65(5)	70(5)	84(6)	15(4)	-44(5)	-16(4)
C(11)	95(6)	66(4)	40(3)	-6(3)	-19(4)	-26(4)
C(12)	174(12)	81(6)	71(6)	-17(5)	-42(7)	-51(7)
C(13)	144(10)	58(5)	76(6)	1(4)	-36(6)	-45(6)
C(14)	45(3)	45(3)	42(3)	2(2)	-8(3)	-14(3)
C(15)	49(3)	49(3)	32(3)	2(2)	-8(2)	-10(3)
C(16)	143(5)	88(4)	40(3)	2(3)	-9(3)	-35(4)
C(17)	137(5)	98(4)	48(3)	-5(3)	-12(3)	-40(4)
C(18)	116(6)	80(4)	38(3)	-10(3)	-18(3)	-35(4)
F(1)	136(7)	143(7)	154(7)	-6(6)	-17(6)	-47(6)
F(2)	134(7)	112(6)	91(6)	-28(5)	-40(5)	-30(5)
F(3)	142(7)	122(7)	107(6)	23(5)	-47(6)	-23(6)
F(4)	162(8)	154(7)	164(7)	-1(7)	-26(6)	-8(6)
F(1')	160(8)	153(7)	167(8)	4(7)	-19(6)	-14(6)
F(2')	151(7)	157(7)	145(7)	-9(6)	-45(6)	-35(6)
F(3')	151(7)	111(6)	163(7)	13(6)	-22(6)	-46(6)
F(4')	140(7)	139(7)	114(7)	9(6)	-25(6)	-31(6)

B(1)	136(4)	125(4)	128(4)	-2(3)	-32(3)	-31(3)
F(5)	105(6)	161(7)	131(7)	-9(6)	-34(6)	-40(6)
F(6)	129(7)	141(7)	116(7)	4(6)	-10(6)	-16(6)
F(7)	162(7)	139(7)	152(7)	-1(6)	-20(6)	-36(6)
F(8)	141(7)	160(7)	129(7)	42(6)	-47(6)	-22(6)
F(7')	138(7)	134(7)	128(6)	23(6)	-70(6)	-24(6)
F(6')	122(7)	110(6)	144(7)	-18(6)	-23(6)	-19(6)
F(5')	144(7)	141(7)	136(7)	15(6)	-13(6)	-24(6)
F(8')	99(6)	114(6)	137(6)	-13(5)	-50(5)	-35(5)
B(2)	114(4)	120(4)	116(4)	2(3)	-41(3)	-30(3)
O(2)	127(7)	81(5)	101(6)	-8(4)	25(5)	5(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for mo_dm15855_0m.

	x	y	z	U(eq)
H(1A)	6124	1160	3289	84
H(1B)	7104	2031	2820	84
H(3)	2390	-28	5059	94
H(4)	2555	-830	3841	74
H(6A)	6053	2510	107	110
H(6B)	5852	3806	-405	110
H(6C)	4425	3079	-179	110
H(7A)	7762	3756	1932	116
H(7B)	7599	4924	1236	116
H(7C)	7839	3650	790	116
H(8A)	4122	5442	3886	127
H(8B)	4985	6241	2997	127
H(8C)	5969	5036	3345	127
H(9A)	516	4743	3263	111
H(9B)	939	6032	2960	111
H(9C)	1499	5289	3861	111
H(10A)	1886	3303	753	103
H(10B)	995	4624	1038	103
H(10C)	785	3563	1848	103
H(11A)	4778	430	1138	78
H(11B)	3286	1400	986	78
H(12A)	1519	179	1684	122
H(12B)	2956	-616	931	122
H(13A)	3889	-1618	2162	105
H(13B)	1993	-1542	2514	105
H(16A)	1180	1513	6273	110
H(16B)	2783	685	6427	110
H(17A)	4195	1997	5892	113
H(17B)	2532	2801	6390	113
H(18A)	4133	3409	4773	91
H(18B)	2230	3653	4992	91
H(2A)	8618	717	1471	175

H(2B)	8534	1502	645	175

Table 6. Torsion angles [°] for mo_dm15855_0m.

Ir(1)-N(1)-C(11)-C(12)	-164.5(7)
Ir(1)-N(1)-C(14)-N(4)	-171.9(6)
Ir(1)-N(1)-C(14)-C(15)	8.0(8)
Ir(1)-N(2)-C(15)-N(3)	173.1(6)
Ir(1)-N(2)-C(15)-C(14)	-7.0(7)
Ir(1)-N(2)-C(18)-C(17)	-159.3(7)
Ir(1)-C(1)-C(2)-C(3)	-60.1(5)
Ir(1)-C(1)-C(2)-C(7)	121.1(7)
Ir(1)-C(1)-C(5)-C(4)	61.3(4)
Ir(1)-C(1)-C(5)-C(10)	-121.3(7)
Ir(1)-C(2)-C(3)-C(4)	-60.4(5)
Ir(1)-C(2)-C(3)-C(8)	127.1(8)
Ir(1)-C(3)-C(4)-C(5)	-60.8(4)
Ir(1)-C(3)-C(4)-C(9)	124.5(8)
Ir(1)-C(4)-C(5)-C(1)	-62.0(4)
Ir(1)-C(4)-C(5)-C(10)	120.6(6)
N(1)-C(11)-C(12)-C(13)	-47.2(13)
N(1)-C(14)-C(15)-N(2)	-0.7(9)
N(1)-C(14)-C(15)-N(3)	179.3(7)
N(3)-C(16)-C(17)-C(18)	32.8(16)
N(4)-C(14)-C(15)-N(2)	179.3(6)
N(4)-C(14)-C(15)-N(3)	-0.8(10)
C(1)-C(2)-C(3)-Ir(1)	59.9(4)
C(1)-C(2)-C(3)-C(4)	-0.5(7)
C(1)-C(2)-C(3)-C(8)	-173.1(7)
C(2)-C(1)-C(5)-Ir(1)	-61.5(4)
C(2)-C(1)-C(5)-C(4)	-0.2(7)
C(2)-C(1)-C(5)-C(10)	177.1(6)
C(2)-C(3)-C(4)-Ir(1)	61.2(5)
C(2)-C(3)-C(4)-C(5)	0.4(7)
C(2)-C(3)-C(4)-C(9)	-174.3(7)
C(3)-C(4)-C(5)-Ir(1)	61.8(5)
C(3)-C(4)-C(5)-C(1)	-0.1(7)
C(3)-C(4)-C(5)-C(10)	-177.5(6)
C(5)-C(1)-C(2)-Ir(1)	60.5(4)
C(5)-C(1)-C(2)-C(3)	0.4(7)

C(5)-C(1)-C(2)-C(7)	-178.4(6)
C(6)-C(1)-C(2)-Ir(1)	-125.5(7)
C(6)-C(1)-C(2)-C(3)	174.4(6)
C(6)-C(1)-C(2)-C(7)	-4.4(11)
C(6)-C(1)-C(5)-Ir(1)	124.6(7)
C(6)-C(1)-C(5)-C(4)	-174.0(6)
C(6)-C(1)-C(5)-C(10)	3.3(11)
C(7)-C(2)-C(3)-Ir(1)	-121.3(7)
C(7)-C(2)-C(3)-C(4)	178.4(6)
C(7)-C(2)-C(3)-C(8)	5.8(11)
C(8)-C(3)-C(4)-Ir(1)	-126.3(8)
C(8)-C(3)-C(4)-C(5)	173.0(7)
C(8)-C(3)-C(4)-C(9)	-1.8(12)
C(9)-C(4)-C(5)-Ir(1)	-123.2(7)
C(9)-C(4)-C(5)-C(1)	174.8(7)
C(9)-C(4)-C(5)-C(10)	-2.6(11)
C(11)-N(1)-C(14)-N(4)	0.7(11)
C(11)-N(1)-C(14)-C(15)	-179.4(6)
C(11)-C(12)-C(13)-N(4)	45.1(14)
C(13)-N(4)-C(14)-N(1)	-1.9(12)
C(13)-N(4)-C(14)-C(15)	178.2(8)
C(14)-N(1)-C(11)-C(12)	23.4(11)
C(14)-N(4)-C(13)-C(12)	-21.6(14)
C(15)-N(2)-C(18)-C(17)	15.0(12)
C(15)-N(3)-C(16)-C(17)	-18.2(15)
C(16)-N(3)-C(15)-N(2)	3.1(14)
C(16)-N(3)-C(15)-C(14)	-176.9(9)
C(16)-C(17)-C(18)-N(2)	-31.7(15)
C(18)-N(2)-C(15)-N(3)	-1.6(11)
C(18)-N(2)-C(15)-C(14)	178.3(7)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for mo_dm15855_0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

Reference:

1. (a) J. C. Wang and J. E. Bauman, *Inorg. Chem.*, **1965**, *4*, 1613; (b) C. J. Brennan and V. Mckee, *Acta Cryst.* **1999**, *55*, 1492; (c) P. Gogoi and Konwar, D. *Tetrahedron Lett*. **2006**, 47, 79.

2. (a) S. Takahashi and H. Togo, *Heterocycles*, **2010**, 82, 593; (b) H. Prokopcová and C. O. Kappe, *J. Org. Chem*. **2007**, 72, 4440.

3. J. F. Hull, Y. Himeda, W. H. Wang, B. Hashiguchi, R. Periana, D. J. Szalda, J. T. Muckerman, and E. Fujita, *Nat. Chem.* **2012**, 4, 383.

4. J. Li, D. W. Widlicka, K. Fichter, D. P. Reed, G. R. Weisman, E. H. Wong, A. DiPasquale, K. J. Heroux, J. A. Golen, A. L. Rheingold, *Inorganica Chimica Acta* **2010**, 364,185.

5. Z. Wang, S.-M. Lu, J. Li, J. Wang and C. Li, *Chem. Eur. J.* **2015**, 21, 12592.