**Supporting Information for**

# An Iridium(IV) Species, [Cp*Ir(NHC)Cl]$^{+}$, Related to a Water-Oxidation Catalyst

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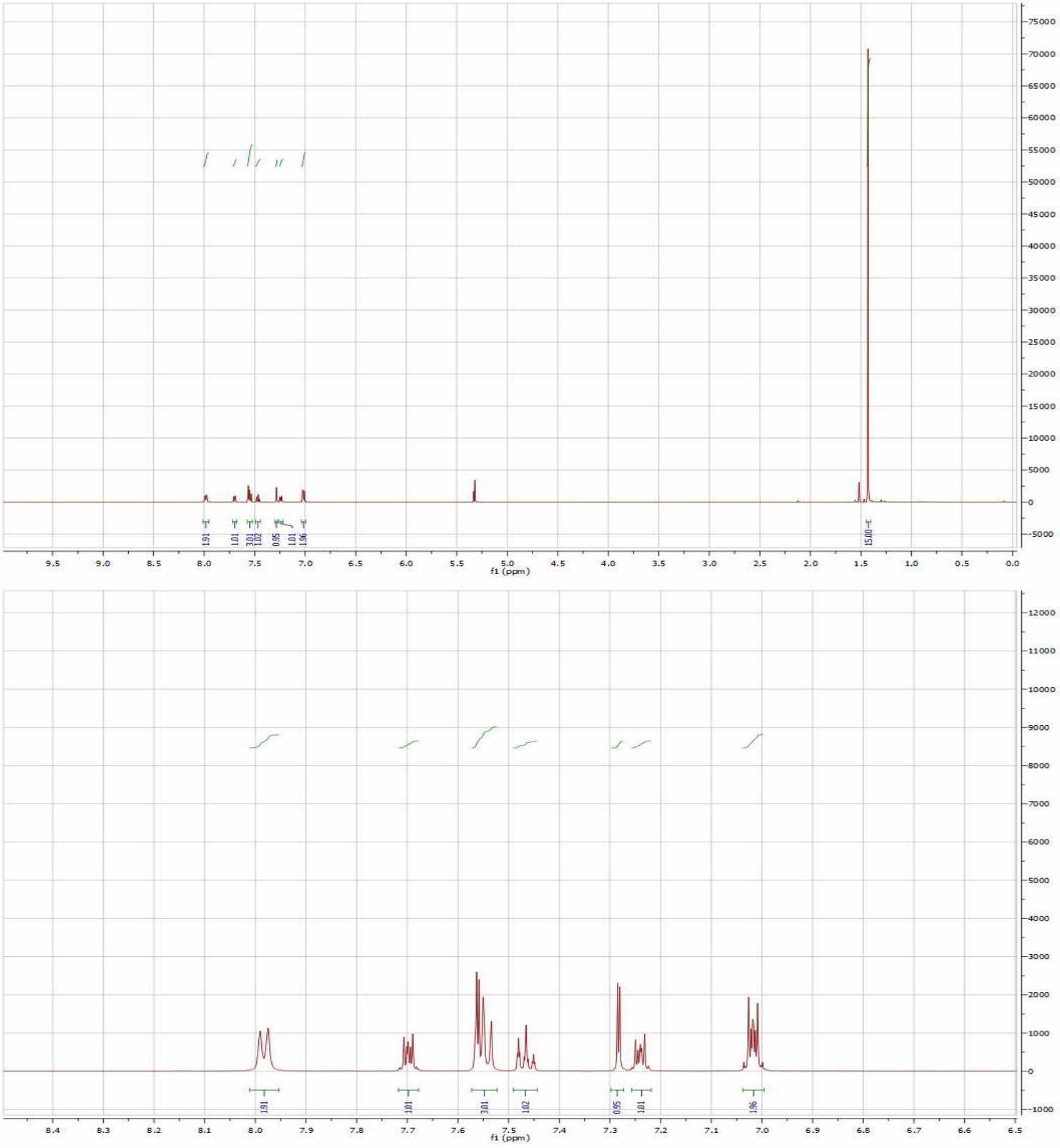



**Figure S1** $^{1}$H Spectra of **3** referenced to residual solvent peak ($CD_2Cl_2$). Top: Full spectrum with solvent peaks at δ = 5.32 ($CD_2Cl_2$) and δ = 1.52 (water). Bottom: Enlarged spectrum of aromatic protons (δ = 6.5-8.5).

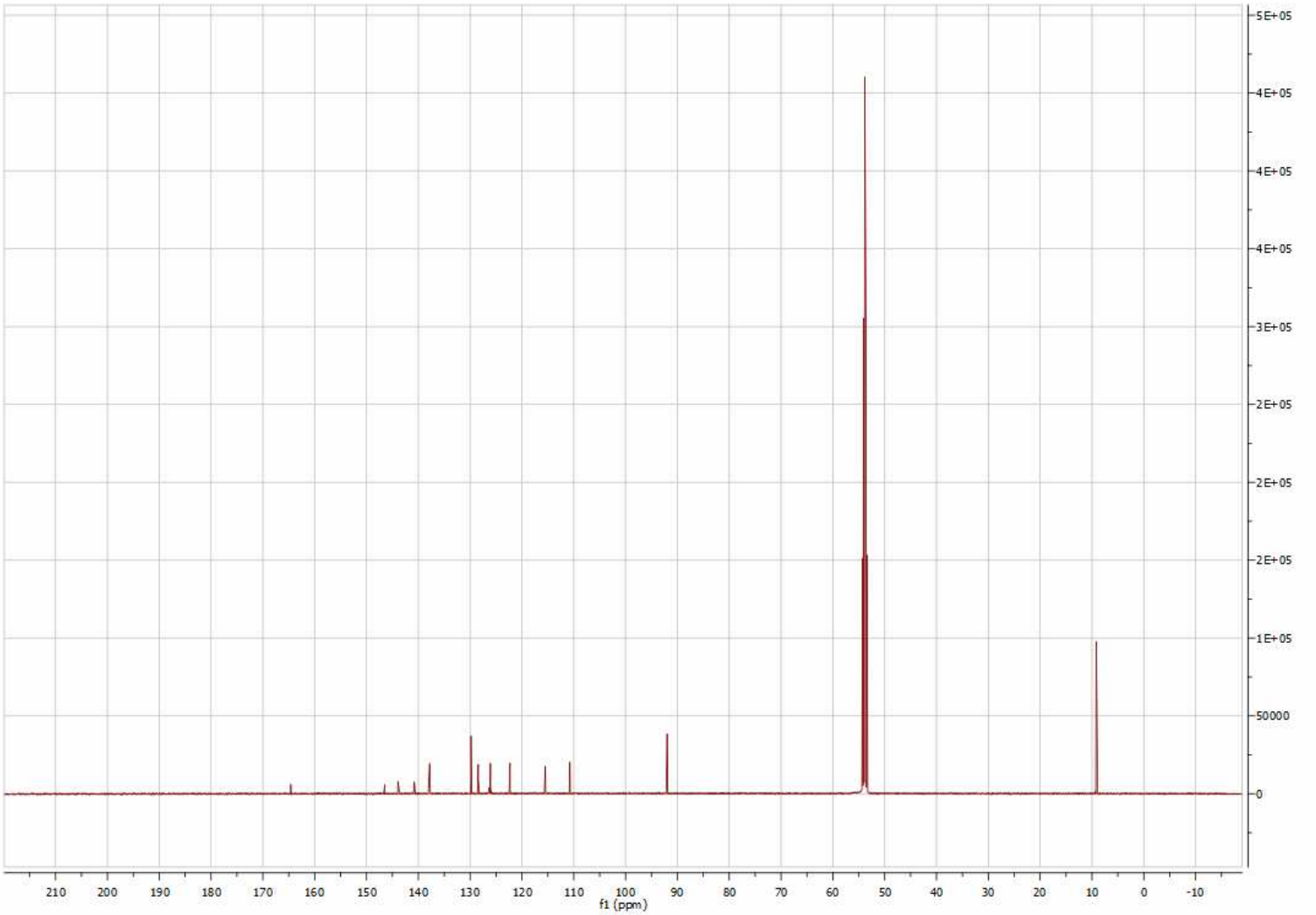



**Figure S2** $^{13}C$ Spectra of **3** referenced to residual solvent peak ($CD_2Cl_2$). Solvent peak for $CD_2Cl_2$ at $\delta = 53.84$.

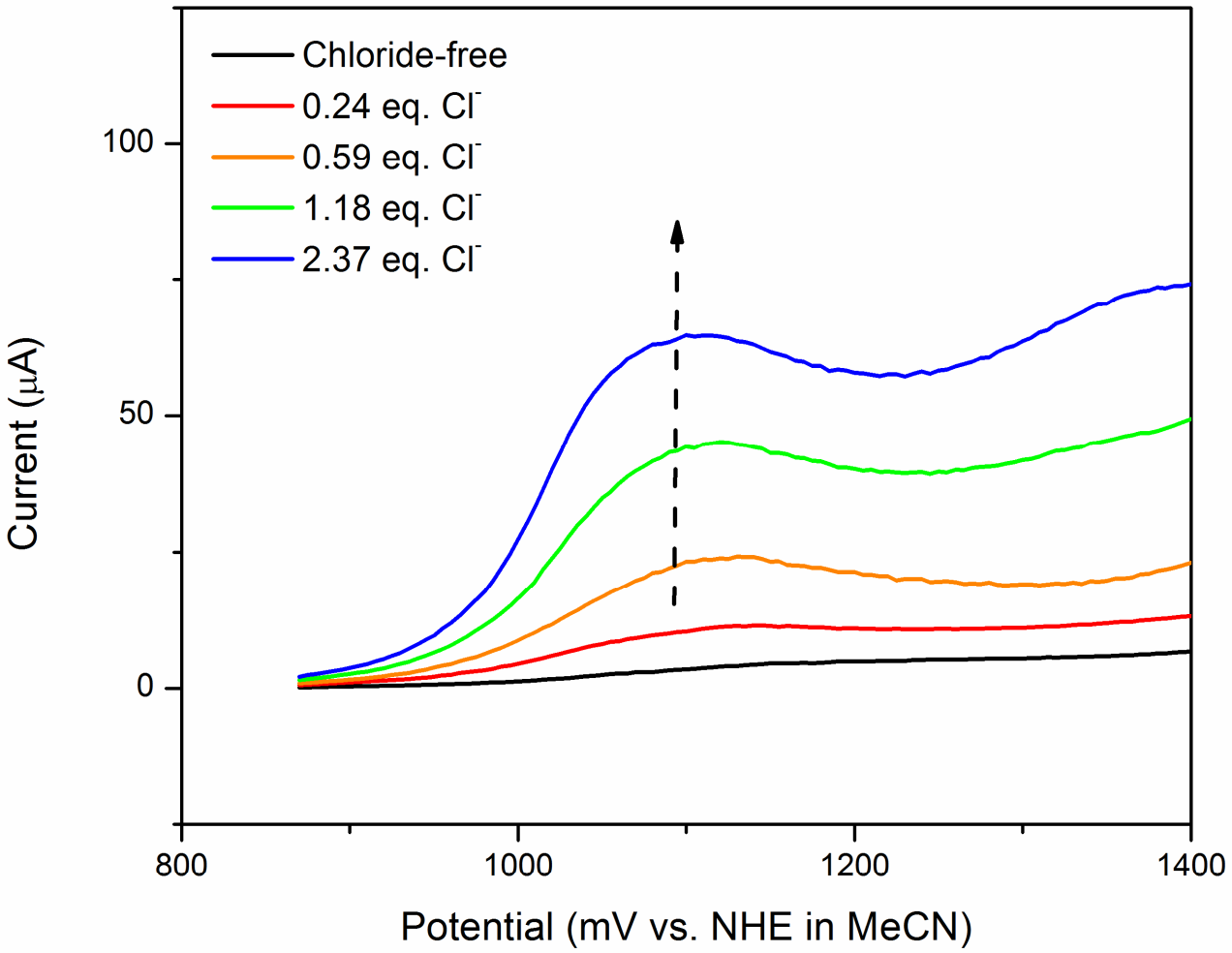



**Figure S3**

Linear polarization voltammograms of solutions containing catalyst precursor **2** and 0.24 (red line), 0.59 (orange line), 1.18 (green line), or 2.37 (blue line) equivalents of chloride. In each case, oxidation process at 1.1 V is completely irreversible, as observed by cyclic voltammetry (not shown). Conditions: 2-3 mM **2** in 0.1 M tetrabutylammonium perchlorate; 100 mV/s scan rate.

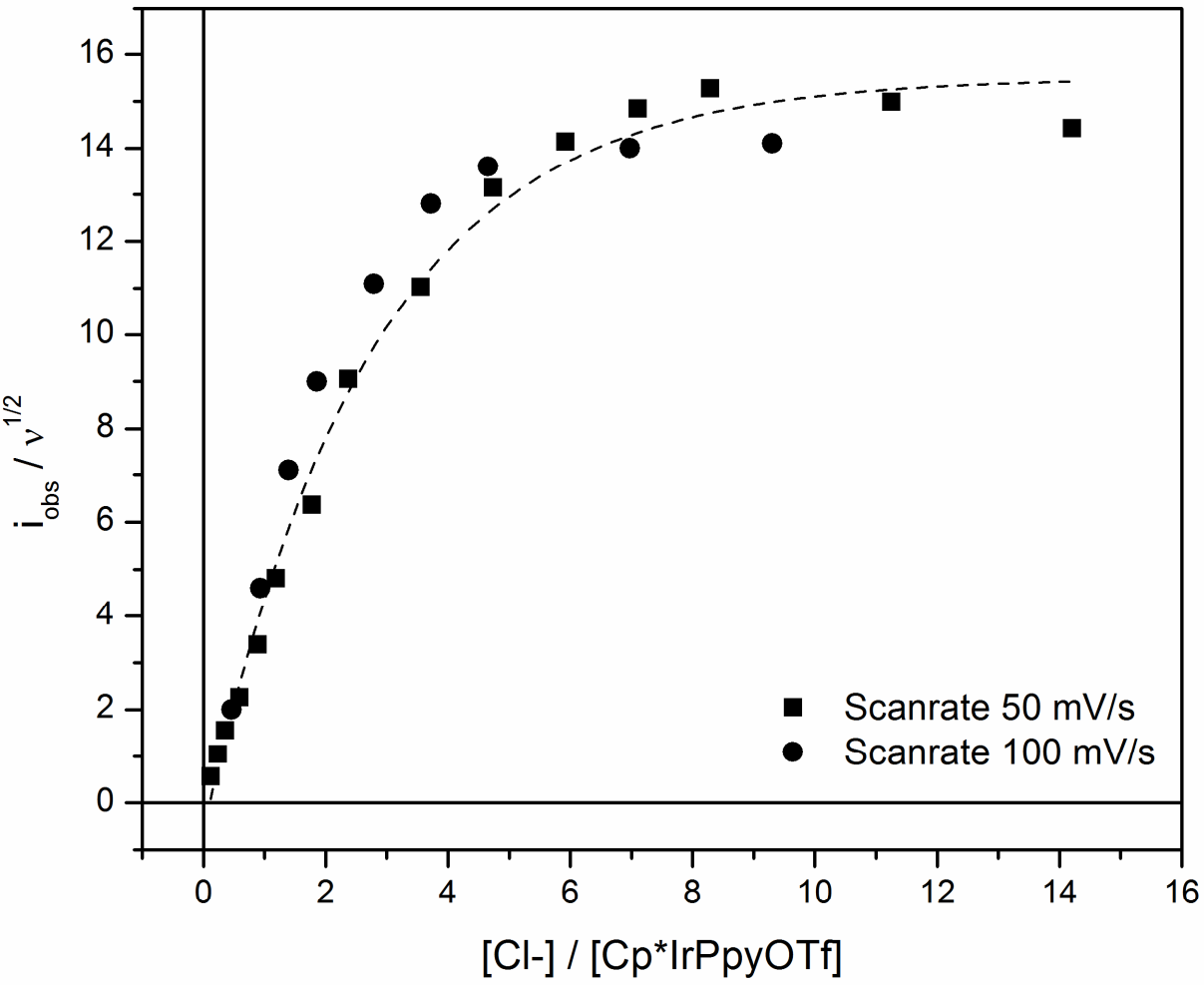



**Figure S4**

Comparison of observed peak current for irreversible oxidation process at 1.1 V for solutions containing **2** and varying equivalents of chloride (in linear polarization voltammetry). Peak current plateaus at *ca.* 10 equivalents of chloride to catalyst. Conditions: 2-3 mM **2** in 0.1 M tetrabutylammonium perchlorate. Data were collected at two scan rates, as noted.

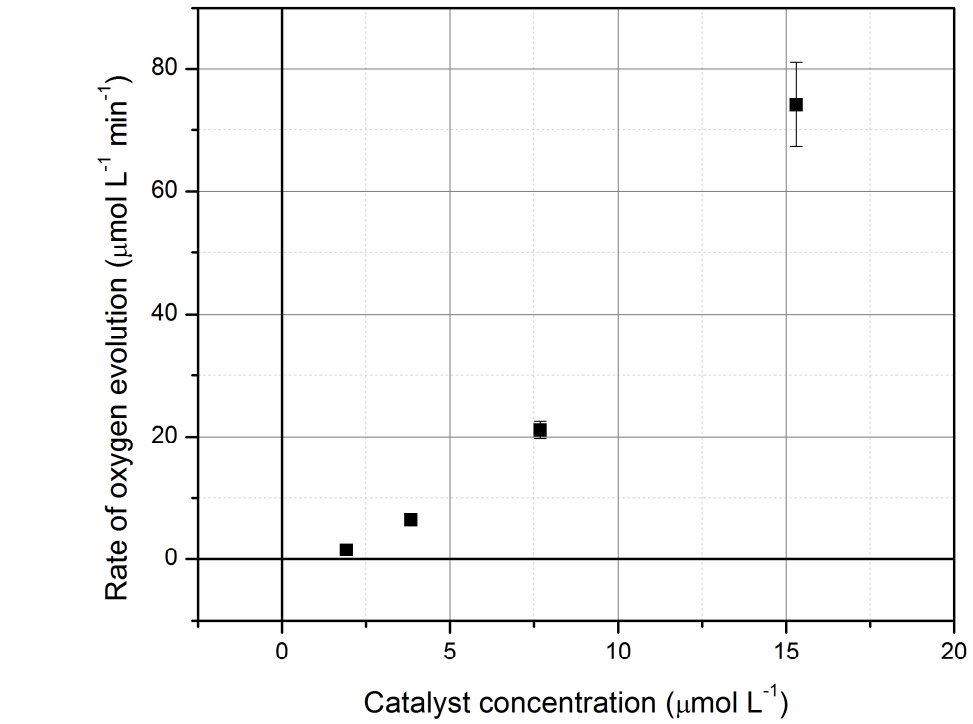



**Figure S5**: Dependence of the rate of oxygen evolution on concentration of catalyst **3** with cerium(IV) as primary oxidant.

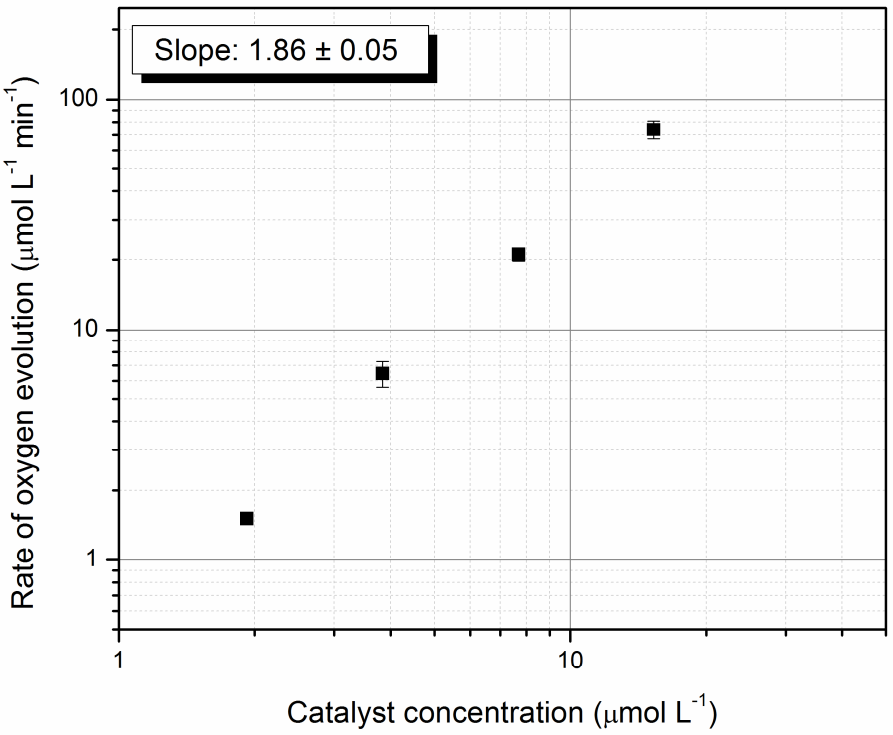



**Figure S6**: Log-log plot for catalyst **3** with cerium(IV).

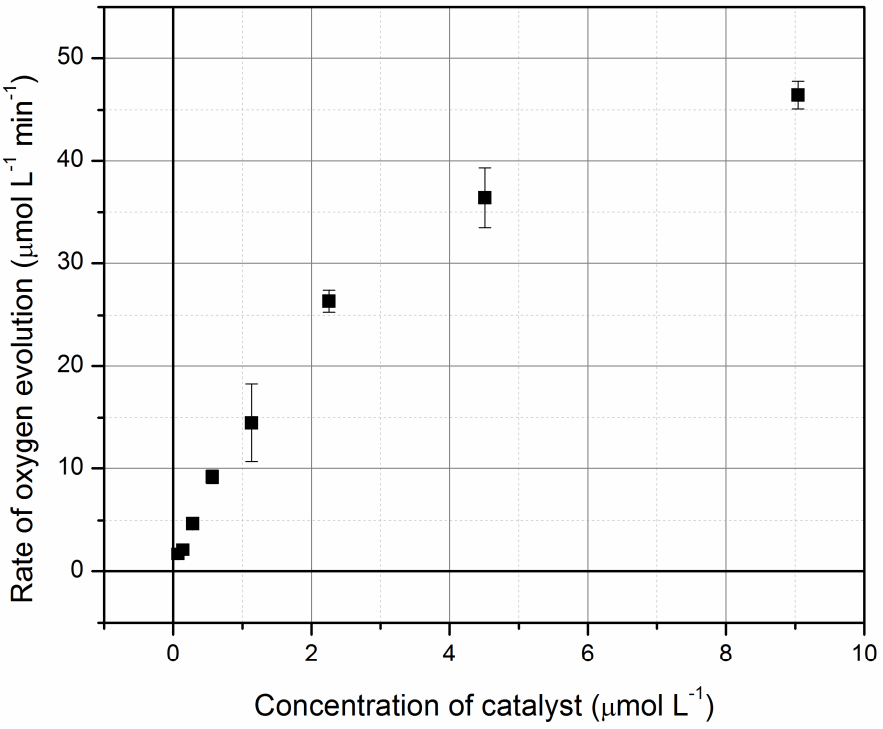



**Figure S7:** Dependence of the rate of oxygen evolution on concentration of catalyst **3** with periodate as primary oxidant.

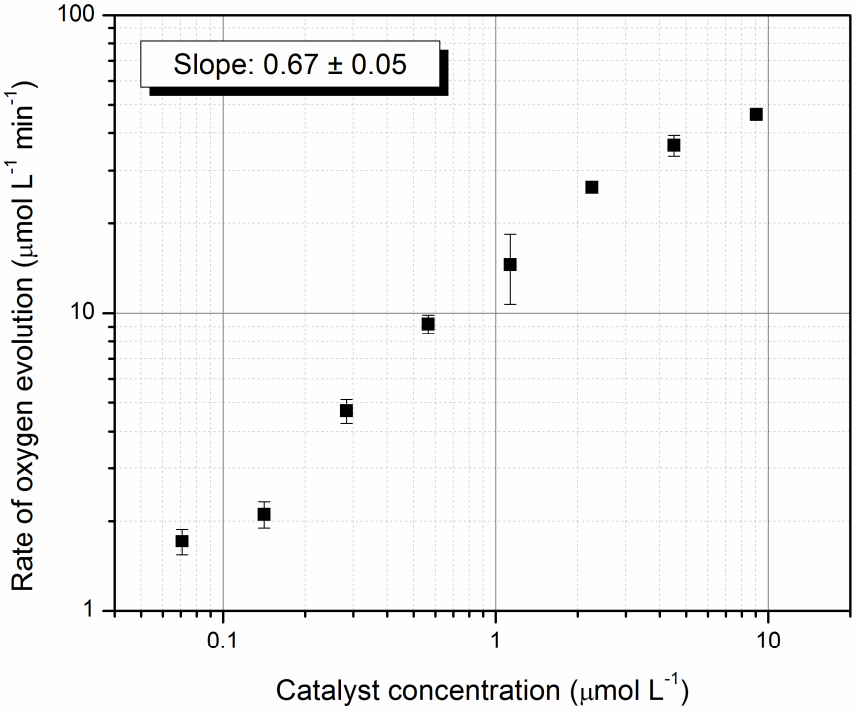



**Figure S8:** Log-log plot for catalyst **3** with periodate.

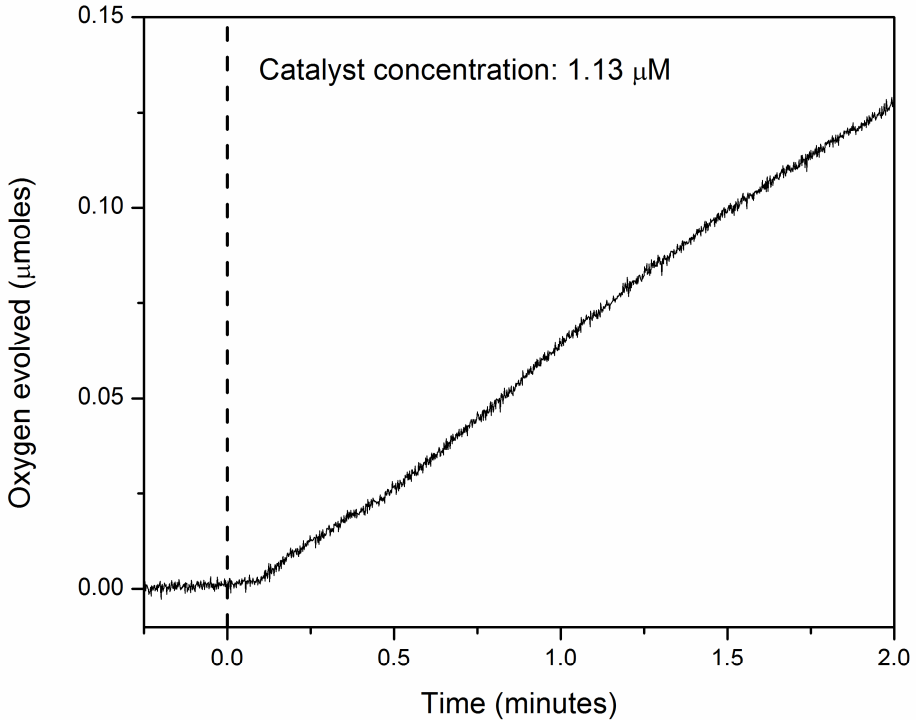



**Figure S9**: Oxygen evolution trace for catalyst **3** driven with periodate.

## S10. Details of Additional DFT Calculations

Experimental observations suggest that the single electron oxidation of **3** to $[Cp^*Ir^{IV}(NHC)Cl]^+$, is easier than the oxidation of **1** to $[Cp^*Ir^{IV}(ppy)Cl]^+$. The oxidation potentials for the conversion of $Ir^{III}$ to $Ir^{IV}$ using the two different ligand systems were calculated using DFT. The procedure outlined by Green and Dilworth was utilized to calculate the potentials (Holland, J. P.; Green, J. C.; Dilworth, J. R. *Dalton Trans*. **2006**, 783). The structures were first optimized in the gas phase using the procedure described in the experimental section of the main paper and then corrections for zero-point energy and entropy were obtained from a frequency calculation. Solvent corrections (in acetonitrile) were then applied by calculating the single point solvation energy of the optimized gas phase molecule using the IEPCM model as implemented in Gaussian 09 Revision A.02. The computed absolute one-electron oxidation potentials, E°, were then compared with experiment by subtraction of 4.1888V. The calculated values were 0.82 V versus SCE for the oxidation of **3** to $[Cp^*Ir^{IV}(NHC)Cl]^+$ and 0.94 V for the oxidation of **1** to $[Cp^*Ir^{IV}(ppy)Cl]^+$. These results are in fairly good agreement with the experimental values and support the hypothesis that **3** is easier to oxidize than **1**. Optimized coordinates for the structures are given below.

*Optimized xyz coordinates of **3***

| | | | |
|---|---|---|---|
| Ir | 0.48041900 | -0.37373000 | -0.11167600 |
| Cl | 0.25361800 | -0.14319600 | -2.55832600 |
| N | 0.50876800 | 2.49388600 | 0.25079600 |

| | | | |
|---|---|---|---|
| N | -1.59472300 | 1.98720700 | 0.20752600 |
| C | 0.43866000 | -1.47500600 | 1.79771800 |
| C | 1.47832700 | -2.10804500 | 0.99958000 |
| C | 0.86677600 | -2.65724200 | -0.15849200 |
| C | -0.58616400 | -2.48691900 | -0.02810500 |
| C | -0.84719600 | -1.81441800 | 1.18516400 |
| C | 0.62032200 | -0.95028700 | 3.19418700 |
| C | 2.91657100 | -2.21895300 | 1.40959300 |
| C | 1.52336700 | -3.40481900 | -1.28152900 |
| C | -1.57718300 | -3.02064500 | -1.01835900 |
| C | -2.18305900 | -1.56084300 | 1.81781500 |
| C | -0.34352900 | 1.43111900 | 0.12765400 |
| C | -0.17722800 | 3.68459800 | 0.41796500 |
| C | -1.49704800 | 3.37169900 | 0.39580700 |
| C | 1.88646800 | 2.21132100 | 0.07222900 |
| C | 2.11998400 | 0.84694900 | -0.19234000 |
| C | 3.44599400 | 0.50531600 | -0.49346600 |
| C | 4.47232600 | 1.45930100 | -0.47178700 |
| C | 4.19943500 | 2.79478200 | -0.16087600 |
| C | 2.88327700 | 3.18383200 | 0.10477100 |
| C | -2.85104200 | 1.33438500 | -0.00353500 |
| C | -3.04502600 | 0.53961600 | -1.13772000 |
| C | -4.29792800 | -0.04122900 | -1.35102800 |
| C | -5.34909500 | 0.17762800 | -0.45449600 |
| C | -5.14519900 | 0.98147200 | 0.67109400 |
| C | -3.89415100 | 1.55801000 | 0.90215400 |
| H | 1.59358000 | -0.46777700 | 3.31501100 |
| H | 0.55566900 | -1.76353500 | 3.93116700 |
| H | -0.14651800 | -0.21321700 | 3.44763400 |
| H | 3.55719300 | -2.51192700 | 0.57512300 |
| H | 3.01737700 | -2.98514800 | 2.18966400 |
| H | 3.30089500 | -1.27792300 | 1.81072600 |
| H | 1.17137200 | -3.03781200 | -2.25044900 |
| H | 1.29780800 | -4.47780100 | -1.22022100 |
| H | 2.60979500 | -3.29070000 | -1.26055000 |
| H | -2.59315900 | -2.69334700 | -0.78731900 |
| H | -1.56822000 | -4.11852800 | -1.02000500 |
| H | -1.33401800 | -2.68138800 | -2.03090200 |
| H | -2.19959500 | -0.61030900 | 2.35651100 |
| H | -2.40832400 | -2.35319400 | 2.54477000 |
| H | -2.99032800 | -1.54026400 | 1.08362200 |
| H | 0.31436200 | 4.63801800 | 0.52079700 |
| H | -2.37266500 | 3.99675000 | 0.45799400 |
| H | 3.68997600 | -0.51638200 | -0.76668100 |
| H | 5.48963100 | 1.15748000 | -0.70779600 |
| H | 4.99643700 | 3.53199600 | -0.14315000 |
| H | 2.65099600 | 4.22378700 | 0.31758700 |
| H | -2.22656500 | 0.38773000 | -1.83589000 |
| H | -4.45344900 | -0.65518000 | -2.23341200 |
| H | -6.32191100 | -0.27073100 | -0.63418000 |
| H | -5.95460400 | 1.15506400 | 1.37413900 |
| H | -3.72371500 | 2.16853900 | 1.78419100 |

*Optimized xyz coordinates of [Cp*Ir$^{IV}$(NHC)Cl]$^{+}$*

| | | | |
|---|---|---|---|
| Ir | 0.47809900 | -0.37161900 | -0.21715200 |
| Cl | 0.16068000 | -0.29158200 | -2.56207900 |

| | | | |
|---|---|---|---|
| N | 0.44819700 | 2.49468000 | 0.21441800 |
| N | -1.64527000 | 1.94121500 | 0.15861200 |
| C | 0.60314600 | -1.28208700 | 1.81362100 |
| C | 1.59397700 | -2.00104600 | 1.03199700 |
| C | 0.91294400 | -2.70570500 | -0.01126100 |
| C | -0.51297600 | -2.51856500 | 0.17643800 |
| C | -0.70879700 | -1.66967900 | 1.31039300 |
| C | 0.86843000 | -0.57614500 | 3.11118600 |
| C | 3.04401200 | -2.10723400 | 1.38302000 |
| C | 1.52095600 | -3.58476500 | -1.06121500 |
| C | -1.57082800 | -3.17647200 | -0.65339400 |
| C | -2.01075600 | -1.38111700 | 1.98907600 |
| C | -0.38727700 | 1.42703500 | 0.06162600 |
| C | -0.26213400 | 3.66676600 | 0.40978400 |
| C | -1.57386900 | 3.32094100 | 0.37523800 |
| C | 1.82549100 | 2.23821000 | 0.05284900 |
| C | 2.09410500 | 0.87881300 | -0.20311700 |
| C | 3.41983000 | 0.53155700 | -0.49439700 |
| C | 4.42391800 | 1.50468200 | -0.50680300 |
| C | 4.12630500 | 2.84028300 | -0.21093500 |
| C | 2.81123700 | 3.22138900 | 0.06373000 |
| C | -2.90577100 | 1.26698100 | -0.01819200 |
| C | -3.15282800 | 0.53284100 | -1.18065700 |
| C | -4.40316200 | -0.06983900 | -1.34803600 |
| C | -5.39740400 | 0.07687100 | -0.37605600 |
| C | -5.14318600 | 0.83130500 | 0.77391400 |
| C | -3.89403700 | 1.42728200 | 0.95880500 |
| H | 1.83361200 | -0.06543000 | 3.09791500 |
| H | 0.88074000 | -1.29542300 | 3.93992300 |
| H | 0.09905200 | 0.16780700 | 3.32970200 |
| H | 3.65253800 | -2.44682500 | 0.54315300 |
| H | 3.15412700 | -2.84554100 | 2.18799000 |
| H | 3.45174000 | -1.16178800 | 1.74578900 |
| H | 1.07804600 | -3.39142400 | -2.04231900 |
| H | 1.34549300 | -4.64010600 | -0.81787400 |
| H | 2.59901800 | -3.43626700 | -1.14365800 |
| H | -2.54795900 | -2.71214600 | -0.51136500 |
| H | -1.65623600 | -4.23485400 | -0.37475800 |
| H | -1.32345700 | -3.13545200 | -1.71779800 |
| H | -1.99640400 | -0.41926300 | 2.50447700 |
| H | -2.19502700 | -2.15550200 | 2.74543100 |
| H | -2.85164800 | -1.38463300 | 1.29506800 |
| H | 0.20768400 | 4.62819500 | 0.53739300 |
| H | -2.46429700 | 3.92433400 | 0.44669600 |
| H | 3.67782300 | -0.49019000 | -0.74840700 |
| H | 5.44210100 | 1.22066500 | -0.75449700 |
| H | 4.91323700 | 3.58738100 | -0.21053600 |
| H | 2.57069600 | 4.26122000 | 0.26068800 |
| H | -2.38864600 | 0.45013700 | -1.94520700 |
| H | -4.60461300 | -0.63438800 | -2.25328100 |
| H | -6.37022200 | -0.38302300 | -0.51950000 |
| H | -5.91375200 | 0.95529600 | 1.52831100 |
| H | -3.68729600 | 2.00365800 | 1.85581700 |

*Optimized xyz coordinates of **1***

| | | | |
|---|---|---|---|
| Ir | -0.37673400 | -0.01704700 | -0.15402000 |

| | | | |
|---|---|---|---|
| Cl | -0.03172300 | 0.10086700 | -2.57469400 |
| C | -1.57400500 | 0.29601800 | 1.67941100 |
| C | -1.73089700 | -1.06936300 | 1.23248800 |
| C | -2.33413300 | -1.03287700 | -0.07781900 |
| C | -2.70653000 | 0.36136700 | -0.35184800 |
| C | -2.25442900 | 1.16446200 | 0.71177200 |
| C | -1.08941300 | 0.73344400 | 3.03181300 |
| C | -1.43123600 | -2.29083900 | 2.04831600 |
| C | -2.78368300 | -2.20404000 | -0.90230300 |
| C | -3.41684200 | 0.80223000 | -1.59515800 |
| C | -2.45289700 | 2.64277000 | 0.88236100 |
| C | 2.47147200 | -0.68617300 | 0.15542500 |
| C | 1.19730300 | -1.28113500 | -0.03748100 |
| C | 1.15725800 | -2.68111200 | -0.15238600 |
| C | 2.31057600 | -3.45681000 | -0.02457900 |
| C | 3.55491600 | -2.85433700 | 0.21065600 |
| C | 3.63358400 | -1.46812800 | 0.28771900 |
| H | -0.37003700 | 0.02313600 | 3.44616900 |
| H | -1.92626900 | 0.81682700 | 3.73904900 |
| H | -0.59839600 | 1.70986600 | 2.98561900 |
| H | -1.24499700 | -3.16530400 | 1.42274200 |
| H | -2.28940300 | -2.51960000 | 2.69414100 |
| H | -0.55553200 | -2.14967000 | 2.68626600 |
| H | -2.65170400 | -2.00293100 | -1.96884400 |
| H | -3.84446200 | -2.42866000 | -0.72450300 |
| H | -2.21008800 | -3.10397400 | -0.66532000 |
| H | -3.54321000 | 1.88681100 | -1.62822400 |
| H | -4.41234900 | 0.34415200 | -1.64864600 |
| H | -2.85385400 | 0.50208700 | -2.48556800 |
| H | -1.59515200 | 3.11302100 | 1.37269700 |
| H | -3.33018700 | 2.84489300 | 1.51131400 |
| H | -2.61125300 | 3.14583000 | -0.07513800 |
| H | 0.21556700 | -3.17718000 | -0.36588500 |
| H | 2.24362000 | -4.53827200 | -0.11676400 |
| H | 4.45010600 | -3.46050900 | 0.31265700 |
| H | 4.60140700 | -0.99834800 | 0.44154900 |
| C | 2.47450900 | 0.77138300 | 0.14164400 |
| C | 3.60444900 | 1.60220300 | 0.23252500 |
| C | 3.46475800 | 2.98051700 | 0.14812800 |
| H | 4.58491000 | 1.15739100 | 0.35579900 |
| C | 1.10816700 | 2.65929200 | -0.13051600 |
| C | 2.18955400 | 3.52516200 | -0.04614300 |
| H | 4.33647700 | 3.62447200 | 0.21704300 |
| H | 0.10267900 | 3.02290400 | -0.30379400 |
| H | 2.03375700 | 4.59406500 | -0.14125300 |
| N | 1.23732300 | 1.32466900 | -0.01370700 |

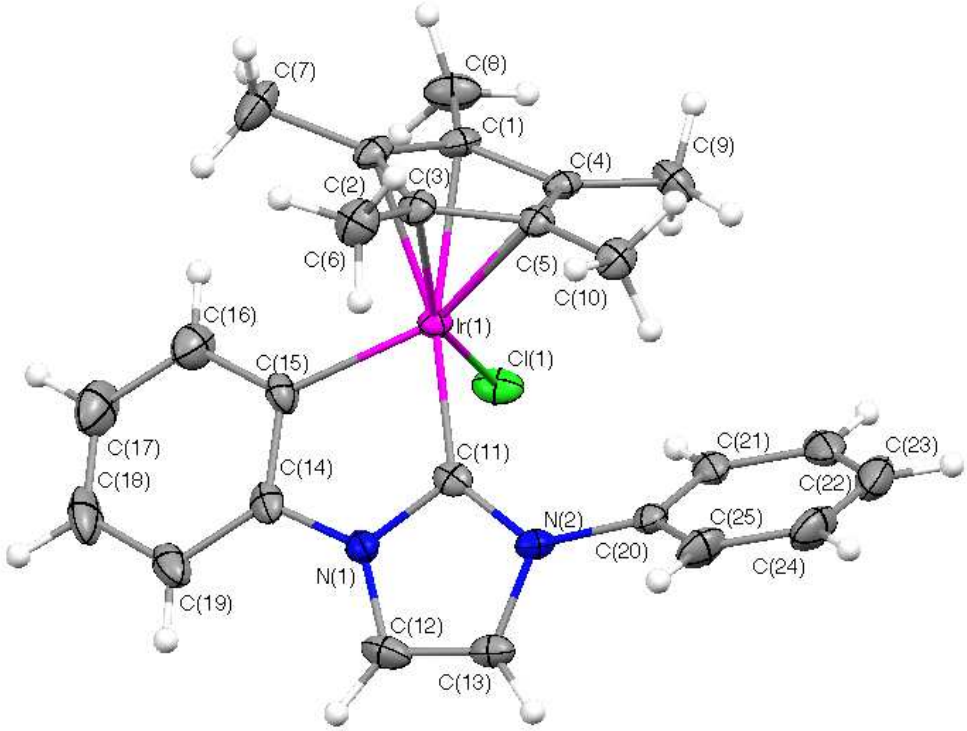
*Optimized xyz coordinates of [Cp*Ir$^{IV}$(ppy)Cl]$^{+}$*

| | | | |
|---|---|---|---|
| Ir | 0.37078400 | 0.02171100 | -0.25261200 |
| Cl | 0.32265700 | -0.49498300 | -2.55787300 |
| C | 1.29669600 | 0.17311300 | 1.76274600 |
| C | 1.80612000 | 1.27880600 | 0.97608500 |
| C | 2.55069100 | 0.72697800 | -0.12627400 |
| C | 2.64111100 | -0.71482600 | 0.06543000 |
| C | 1.87102200 | -1.05398800 | 1.21037400 |
| C | 0.59701700 | 0.28149100 | 3.08527100 |

| | | | |
|---|---|---|---|
| C | 1.73041700 | 2.72265700 | 1.36056900 |
| C | 3.28687800 | 1.48760100 | -1.18598700 |
| C | 3.42627400 | -1.63645200 | -0.81407600 |
| C | 1.73153000 | -2.40936300 | 1.83114300 |
| C | -2.45339600 | 0.74160400 | 0.10832100 |
| C | -1.17306700 | 1.31532700 | -0.11961300 |
| C | -1.08623000 | 2.70313400 | -0.30984800 |
| C | -2.23208000 | 3.49981100 | -0.26819200 |
| C | -3.48441400 | 2.92847000 | -0.00810900 |
| C | -3.59616900 | 1.55044300 | 0.17151300 |
| H | -0.00656400 | 1.18927900 | 3.14540600 |
| H | 1.33053500 | 0.31080000 | 3.90097100 |
| H | -0.06257400 | -0.57114700 | 3.26373600 |
| H | 1.88534100 | 3.38805200 | 0.50934100 |
| H | 2.52703200 | 2.93026800 | 2.08650300 |
| H | 0.77890900 | 2.97633200 | 1.83148700 |
| H | 3.21542000 | 0.98525300 | -2.15385600 |
| H | 4.34952200 | 1.56376600 | -0.92279700 |
| H | 2.89717900 | 2.50034000 | -1.30373500 |
| H | 3.20945000 | -2.68590500 | -0.60709100 |
| H | 4.49962600 | -1.47849600 | -0.65001900 |
| H | 3.22262600 | -1.44752500 | -1.87179000 |
| H | 0.73781500 | -2.56217200 | 2.25857500 |
| H | 2.45478500 | -2.50812000 | 2.65075400 |
| H | 1.93170400 | -3.21401600 | 1.12057100 |
| H | -0.13282200 | 3.17076100 | -0.52517600 |
| H | -2.14993100 | 4.56880300 | -0.44070600 |
| H | -4.37007000 | 3.55393400 | 0.03770600 |
| H | -4.57601500 | 1.11347700 | 0.33638000 |
| C | -2.47483500 | -0.71418200 | 0.15764300 |
| C | -3.60039400 | -1.53048100 | 0.33868000 |
| C | -3.47148900 | -2.91212600 | 0.27024100 |
| H | -4.56777400 | -1.07733200 | 0.51939400 |
| C | -1.13030000 | -2.61950700 | -0.15133800 |
| C | -2.21515100 | -3.46982800 | 0.00746100 |
| H | -4.33983600 | -3.54923800 | 0.40436200 |
| H | -0.14071900 | -2.99515800 | -0.37885700 |
| H | -2.07601100 | -4.54087500 | -0.08502500 |
| N | -1.25351100 | -1.28145500 | -0.05192100 |

**S11**

X-ray Crystal structure of Cp*Ir($\kappa^2$-$C^2$,$C^{2'}$-NHC)(Cl)



*EXPERIMENTAL DETAILS*

A. Crystal Data

| | |
|---|---|
| Empirical Formula | $IrClN_2C_{25}H_{26}$ |
| Formula Weight | 582.17 |
| Crystal Color, Habit | yellow, block |
| Crystal Dimensions | 0.15 X 0.12 X 0.10 mm |
| Crystal System | monoclinic |
| Lattice Type | Primitive |
| Indexing Images | 6 images @ 20.0 seconds |
| Detector Position | 49.90 mm |
| Pixel Size | 0.146 mm |
| Lattice Parameters | a = 8.5206(10) Å<br>b = 10.4823(12) Å<br>c = 23.856(3) Å<br>$\beta$= 96.247(3) $^o$<br>V = 2118.0(4) $Å^3$ |
| Space Group | $P2_1/n$ (#14) |
| Z value | 4 |
| $D_{calc}$ | 1.826 $g/cm^3$ |
| $F_{000}$ | 1136.00 |
| $\mu$(MoK$\alpha$) | 64.612 $cm^{-1}$ |

B. Intensity Measurements

| | |
|---|---|
| Diffractometer | RigakuSCXmini |
| Radiation | MoK$\alpha$ ($\lambda$ = 0.71075 Å) |
| Detector Aperture | 75 mm round |
| Data Images | 360 exposures |
| $\omega$oscillation Range ($\chi$=54.0, $\phi$=0.0) | -120.0 - 60.0$^{o}$ |
| Exposure Rate | 30.0 sec./$^{o}$ |
| Detector Swing Angle | -28.40$^{o}$ |
| $\omega$oscillation Range ($\chi$=54.0, $\phi$=120.0) | -120.0 - 60.0$^{o}$ |
| Exposure Rate | 30.0 sec./$^{o}$ |
| Detector Swing Angle | -28.40$^{o}$ |
| Detector Position | 49.90 mm |
| Pixel Size | 0.146 mm |
| $2\theta_{max}$ | 55.0$^{o}$ |
| No. of Reflections Measured | Total: 14194<br>Unique: 4843 ($R_{int}$ = 0.046) |
| Corrections | Lorentz-polarization<br>Absorption<br>(trans. factors: 0.424 - 0.524) |

C. Structure Solution and Refinement

| | |
|---|---|
| Structure Solution | Direct Methods (SIR92) |
| Refinement | Full-matrix least-squares on $F^2$ |
| Function Minimized | $\Sigma$ w $(Fo^2 - Fc^2)^2$ |
| Least Squares Weights | $w = 1/ [ \sigma^2(Fo^2) + (0.0137 \cdot P)^2 + 2.8595 \cdot P ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$ |
| $2\theta_{max}$ cutoff | $55.0^o$ |
| Anomalous Dispersion | All non-hydrogen atoms |
| No. Observations (All reflections) | 4843 |
| No. Variables | 263 |
| Reflection/Parameter Ratio | 18.41 |
| Residuals: R1 ($I>2.00\sigma(I)$) | 0.0429 |
| Residuals: R (All reflections) | 0.0813 |
| Residuals: wR2 (All reflections) | 0.0584 |
| Goodness of Fit Indicator | 1.094 |
| Max Shift/Error in Final Cycle | 0.001 |
| Maximum peak in Final Diff. Map | 0.96 $e^-/Å^3$ |
| Minimum peak in Final Diff. Map | -0.71 $e^-/Å^3$ |

Table 1. Atomic coordinates and $B_{iso}/B_{eq}$

| atom | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| Ir(1) | 0.34939(2) | 0.25465(2) | 0.616830(8) | 2.050(4) |
| Cl(1) | 0.59309(16) | 0.19607(14) | 0.58239(7) | 3.27(2) |
| N(1) | 0.3866(5) | 0.5124(4) | 0.57951(19) | 2.39(8) |
| N(2) | 0.2691(5) | 0.4195(4) | 0.50727(19) | 2.37(8) |
| C(1) | 0.1287(5) | 0.2243(5) | 0.6500(2) | 2.59(11) |
| C(2) | 0.2481(6) | 0.1668(5) | 0.6888(2) | 2.63(10) |
| C(3) | 0.3226(6) | 0.0718(5) | 0.6605(2) | 2.69(10) |
| C(4) | 0.2435(6) | 0.0607(5) | 0.6039(2) | 2.31(10) |
| C(5) | 0.1221(5) | 0.1513(5) | 0.5984(2) | 2.22(9) |
| C(6) | 0.0090(7) | 0.3185(6) | 0.6642(2) | 3.90(13) |
| C(7) | 0.2781(7) | 0.1984(6) | 0.7500(2) | 4.36(15) |
| C(8) | 0.4552(7) | -0.0120(6) | 0.6836(2) | 4.08(14) |
| C(9) | 0.2840(7) | -0.0362(5) | 0.5625(2) | 3.42(12) |
| C(10) | -0.0021(5) | 0.1676(5) | 0.5507(2) | 2.95(11) |
| C(11) | 0.3273(5) | 0.3989(5) | 0.5618(2) | 2.31(10) |
| C(12) | 0.3671(7) | 0.6021(5) | 0.5373(2) | 3.41(12) |
| C(13) | 0.2952(6) | 0.5452(5) | 0.4929(2) | 2.80(10) |
| C(14) | 0.4701(6) | 0.5147(5) | 0.6336(2) | 2.88(11) |
| C(15) | 0.4700(6) | 0.3985(5) | 0.6607(2) | 2.72(10) |
| C(16) | 0.5572(7) | 0.3922(6) | 0.7134(2) | 4.12(14) |
| C(17) | 0.6352(8) | 0.4983(8) | 0.7359(3) | 5.27(17) |
| C(18) | 0.6312(8) | 0.6110(7) | 0.7079(3) | 4.96(17) |
| C(19) | 0.5494(7) | 0.6209(6) | 0.6556(2) | 4.01(14) |
| C(20) | 0.2034(6) | 0.3295(5) | 0.4668(2) | 2.44(10) |
| C(21) | 0.2771(7) | 0.2146(5) | 0.4610(2) | 2.84(11) |
| C(22) | 0.2133(8) | 0.1316(6) | 0.4198(2) | 3.96(14) |
| C(23) | 0.0822(9) | 0.1636(7) | 0.3856(2) | 4.76(16) |
| C(24) | 0.0092(8) | 0.2786(7) | 0.3918(2) | 4.72(17) |
| C(25) | 0.0696(7) | 0.3613(6) | 0.4328(2) | 3.76(13) |

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 2. Atomic coordinates and $B_{iso}$ involving hydrogens/$B_{eq}$

| atom | x | y | z | $B_{eq}$ |
|---|---|---|---|---|
| H(1) | 0.0325 | 0.3449 | 0.7032 | 4.68 |
| H(2) | -0.0950 | 0.2798 | 0.6590 | 4.68 |
| H(3) | 0.0112 | 0.3922 | 0.6397 | 4.68 |
| H(4) | 0.3647 | 0.1467 | 0.7673 | 5.23 |
| H(5) | 0.1839 | 0.1810 | 0.7681 | 5.23 |
| H(6) | 0.3053 | 0.2880 | 0.7543 | 5.23 |
| H(7) | 0.4797 | -0.0718 | 0.6548 | 4.90 |
| H(8) | 0.4250 | -0.0585 | 0.7158 | 4.90 |
| H(9) | 0.5474 | 0.0398 | 0.6951 | 4.90 |
| H(10) | 0.2160 | -0.0255 | 0.5275 | 4.10 |
| H(11) | 0.2694 | -0.1209 | 0.5775 | 4.10 |
| H(12) | 0.3933 | -0.0256 | 0.5555 | 4.10 |
| H(13) | -0.0783 | 0.2302 | 0.5605 | 3.54 |
| H(14) | -0.0550 | 0.0867 | 0.5424 | 3.54 |
| H(15) | 0.0452 | 0.1965 | 0.5177 | 3.54 |
| H(16) | 0.3993 | 0.6879 | 0.5398 | 4.09 |
| H(17) | 0.2663 | 0.5828 | 0.4575 | 3.36 |
| H(18) | 0.5629 | 0.3151 | 0.7336 | 4.95 |
| H(19) | 0.6929 | 0.4925 | 0.7717 | 6.32 |
| H(20) | 0.6846 | 0.6823 | 0.7246 | 5.95 |
| H(21) | 0.5473 | 0.6978 | 0.6352 | 4.81 |
| H(22) | 0.3689 | 0.1930 | 0.4846 | 3.41 |
| H(23) | 0.2616 | 0.0521 | 0.4153 | 4.75 |
| H(24) | 0.0406 | 0.1066 | 0.3574 | 5.71 |
| H(25) | -0.0820 | 0.3003 | 0.3680 | 5.67 |
| H(26) | 0.0194 | 0.4397 | 0.4377 | 4.51 |

$B_{eq} = 8/3\ \pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha)$

Table 3. Anisotropic displacement parameters

| atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Ir(1) | 0.02235(9) | 0.02907(10) | 0.02660(10) | -0.00219(15) | 0.00330(6) | 0.00241(15) |
| Cl(1) | 0.0262(7) | 0.0417(7) | 0.0590(10) | 0.0034(6) | 0.0165(7) | 0.0107(7) |
| N(1) | 0.032(2) | 0.030(2) | 0.031(2) | -0.004(2) | 0.009(2) | -0.003(2) |
| N(2) | 0.028(2) | 0.032(2) | 0.031(2) | -0.002(2) | 0.005(2) | 0.008(2) |
| C(1) | 0.027(2) | 0.041(4) | 0.032(2) | -0.003(2) | 0.010(2) | -0.000(2) |
| C(2) | 0.025(2) | 0.049(3) | 0.026(3) | -0.009(2) | 0.004(2) | 0.006(2) |
| C(3) | 0.029(3) | 0.041(3) | 0.032(3) | -0.004(2) | 0.005(2) | 0.014(2) |
| C(4) | 0.023(2) | 0.036(3) | 0.029(3) | -0.007(2) | 0.003(2) | 0.009(2) |
| C(5) | 0.021(2) | 0.036(3) | 0.029(3) | -0.006(2) | 0.006(2) | 0.001(2) |
| C(6) | 0.044(3) | 0.056(4) | 0.049(4) | 0.006(3) | 0.008(3) | -0.002(3) |
| C(7) | 0.045(3) | 0.096(5) | 0.025(3) | -0.005(3) | 0.004(2) | -0.001(3) |
| C(8) | 0.040(3) | 0.051(4) | 0.065(4) | 0.007(3) | 0.011(3) | 0.021(3) |
| C(9) | 0.041(3) | 0.029(3) | 0.061(4) | -0.004(2) | 0.008(3) | -0.007(3) |
| C(10) | 0.019(2) | 0.057(3) | 0.036(3) | -0.005(2) | 0.000(2) | 0.002(2) |
| C(11) | 0.019(2) | 0.031(3) | 0.039(3) | 0.001(2) | 0.011(2) | -0.001(2) |
| C(12) | 0.041(3) | 0.026(3) | 0.065(4) | 0.002(2) | 0.021(3) | 0.007(3) |
| C(13) | 0.034(3) | 0.033(3) | 0.041(3) | 0.003(2) | 0.012(2) | 0.010(2) |
| C(14) | 0.029(3) | 0.043(3) | 0.040(3) | -0.009(2) | 0.017(2) | -0.015(2) |
| C(15) | 0.028(3) | 0.036(3) | 0.040(3) | -0.009(2) | 0.002(2) | -0.010(2) |
| C(16) | 0.040(3) | 0.070(4) | 0.045(4) | -0.014(3) | -0.003(3) | 0.002(3) |
| C(17) | 0.047(4) | 0.102(6) | 0.049(4) | -0.026(4) | -0.005(3) | -0.011(4) |
| C(18) | 0.046(4) | 0.084(5) | 0.060(5) | -0.035(4) | 0.013(3) | -0.038(4) |
| C(19) | 0.050(4) | 0.048(4) | 0.058(4) | -0.022(3) | 0.022(3) | -0.018(3) |
| C(20) | 0.033(3) | 0.036(3) | 0.024(3) | -0.006(2) | 0.008(2) | 0.004(2) |
| C(21) | 0.039(3) | 0.037(3) | 0.035(3) | -0.007(2) | 0.017(2) | -0.002(2) |
| C(22) | 0.065(4) | 0.044(3) | 0.047(4) | -0.016(3) | 0.030(3) | -0.004(3) |
| C(23) | 0.073(5) | 0.076(5) | 0.033(4) | -0.025(4) | 0.013(4) | -0.008(4) |
| C(24) | 0.058(4) | 0.088(6) | 0.030(3) | -0.016(4) | -0.009(3) | 0.013(3) |
| C(25) | 0.041(3) | 0.067(4) | 0.034(3) | 0.002(3) | -0.003(3) | 0.015(3) |

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table 4. Bond lengths (Å)

| atom | atom | distance | atom | atom | distance |
|---|---|---|---|---|---|
| Ir(1) | Cl(1) | 2.3948(14) | Ir(1) | C(1) | 2.142(5) |
| Ir(1) | C(2) | 2.204(5) | Ir(1) | C(3) | 2.205(5) |
| Ir(1) | C(4) | 2.233(5) | Ir(1) | C(5) | 2.221(4) |
| Ir(1) | C(11) | 1.998(5) | Ir(1) | C(15) | 2.048(5) |
| N(1) | C(11) | 1.342(6) | N(1) | C(12) | 1.376(7) |
| N(1) | C(14) | 1.404(7) | N(2) | C(11) | 1.359(7) |
| N(2) | C(13) | 1.385(7) | N(2) | C(20) | 1.421(6) |
| C(1) | C(2) | 1.432(7) | C(1) | C(5) | 1.446(7) |
| C(1) | C(6) | 1.485(8) | C(2) | C(3) | 1.393(8) |
| C(2) | C(7) | 1.492(7) | C(3) | C(4) | 1.447(7) |
| C(3) | C(8) | 1.488(8) | C(4) | C(5) | 1.400(7) |
| C(4) | C(9) | 1.483(8) | C(5) | C(10) | 1.477(6) |
| C(12) | C(13) | 1.308(8) | C(14) | C(15) | 1.380(8) |
| C(14) | C(19) | 1.376(8) | C(15) | C(16) | 1.389(8) |
| C(16) | C(17) | 1.374(10) | C(17) | C(18) | 1.356(11) |
| C(18) | C(19) | 1.367(9) | C(20) | C(21) | 1.372(7) |
| C(20) | C(25) | 1.365(7) | C(21) | C(22) | 1.380(8) |
| C(22) | C(23) | 1.351(9) | C(23) | C(24) | 1.372(11) |
| C(24) | C(25) | 1.365(9) | | | |