Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information for:

A Full Set of Iridium(IV) Pyridine-Alkoxide Stereoisomers: Highly Geometry-Dependent Redox Properties

Dimitar Y. Shopov,[a] Benjamin Rudshteyn,[a,b] Jesús Campos,[a,c] David J. Vinyard,[a,d] Victor S. Batista,[a,b,*] Gary W. Brudvig,[a,b,*] Robert H. Crabtree[a,b,*]

[a] Department of Chemistry, Yale University, 225 Prospect St., New Haven, CT 06520, United States

[b] Energy Sciences Institute, Yale University, 520 West Campus Dr., West Haven, CT 06516, United States

[c] Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA). Universidad de Sevilla and Consejo Superior de Investigaciones Científicas (CSIC). Avenida Américo Vespucio 49, 41092 Sevilla (Spain)

[d] Department of Biological Sciences, Louisiana State University, Baton Rouge, LA 70803, USA.

Section I. Experimental

Methods

NMR spectroscopy. ^{1}H and proton-decoupled ^{13}C NMR spectra were collected on an Agilent Technologies DD2 600 MHz spectrometer equipped with a cold probe.

High-resolution mass spectroscopy (HRMS). Mass spectra were taken on a 9.4 T Bruker Qe FT-ICR MS instrument in positive ion mode.

Electrochemistry. Cyclic voltammograms were collected using a Princeton Applied Research VersaStat 4 potentiostat. Aqueous measurements were done in a 0.1 M KNO_3 solution with a glassy carbon working electrode, saturated aqueous Ag/AgCl reference electrode, and a platinum wire counter electrode. A scan rate of 100 mV/s was used. Organic measurements were done in 0.1 M NBu_4PF_6 dichloromethane solution with a glassy carbon working electrode, platinum wire counter electrode, and an AgCl-coated silver wire pseudo-reference electrode. Ferrocene was added to solutions as an internal reference. Reported reduction potentials were referenced against a normal hydrogen electrode (NHE) potential using the standard accepted value of 0.197 V for saturated Ag/AgCl electrodes (aqueous measurements), and the reported value of 0.704 V for ferrocene (organic measurements).[1]

UV-visible spectroscopy. Absorption spectra in the range 300-1000 nm were collected using a Cary 50 spectrophotometer on volumetric solutions of 0.10 mM of each $\mathbf{3^{IV}}$-$\mathbf{8^{IV}}$. The latter complex was dissolved in a 1:1 mixture of ethyl acetate and dichloromethane, while all others were dissolved in pure dichloromethane. The appropriate blank solvent spectra have been subtracted from the sample spectra.

EPR. Differential spectra were recorded on a Bruker EXELSYS E500 spectrometer equipped with a super-high Q resonator and an Oxford ESR-900 helium-flow cryostat at 4.5-7 K. Instrument parameters were microwave frequency, 9.4 GHz; microwave power 0.002-1 mW; modulation frequency, 100 kHz; modulation amplitude, 19.5 G; sweep time, 84 s; conversion time, 41 ms; time constant, 10 ms. Samples of approximately 0.3 mM were dissolved in glassing solvent mixtures (Table S1). Simulations were performed using the 'pepper' function in EasySpin version 5.0.5.[2] Line broadening was simulated using the HStrain function accounting for unresolved hyperfine couplings.

Table S1. Solvent conditions and instrument parameters.

	solvent	ν, GHz	microwave power, mW	T, K
1	DCM/toluene	9.3884	0.01	4.8
3	DCM/toluene	9.3891	0.002	4.8
4	DCM/toluene	9.3884	0.01	4.8
5	DCM/ethyl acetate	9.3717	1	7.0
8	Ethyl acetate/toluene	9.3887	0.05	4.8

DFT. Geometries, thermochemistry,[3] orbital analysis, and time dependent-DFT UV-visible absorptions[4-10] were optimized using the B3LYP functional[4,11] and the def2SVP pseudopotential[12] for the Ir centers and the 6-31+G(d,p)[13-18] basis set for the other atoms directly in the dielectric continuum of dichloromethane (ε = 8.93)[19] using the SMD model.[20] Such an approach is useful when the structure changes significantly upon solvation,[21,22] as expected here due to the Ir-Cl bonds. To calculate the potentials for oxidation (free energy) of Ir(III) (d^6) to Ir(IV) (d^5), electronic energies from single point calculation with triple zeta basis sets, i.e., 6-311+G(d,p)[13] and def2TZV[12] were used. The Ir(III) structures were treated as singlets (with a charge of -2 for the monopyalk and a charge of -1 for the dipyalk) and the Ir(IV) structures were treated as doublets (with a charge of -1 for for the monopyalk and a charge of 0 for the dipyalk). Spin contamination was found to be minimal. The UV-visible spectra were generated with a broadening factor of 0.222 eV or 1790.55 cm^{-1}. 60 excited states were computed, half of them doublet and half of them quartet. The integration grid consisted of an "ultrafine" pruned grid of 99 radial shells with 590 angular points each. The optimization criteria were "tight" i.e. maximum step size = 0.000015 au, RMS step size = 0.000010 au, maximum force = 0.000060 au, and RMS force threshold = 0.000040 au.

X-ray crystallography. See Section IV.

Synthesis

General. Solvents and reagents were purchased from commercial sources and used as received. The ligand pyalk was prepared according to prior literature.[23] The preparations of $\mathbf{1}^{III/IV}$, $\mathbf{2}^{III/IV}$,[24] and Na[$\mathbf{8}^{IV}$][25] have been reported in our previous works. Reactions below were carried out under ambient atmosphere. Pressurized high-temperature reactions were carried out in a Biotage Initiator microwave synthesizer. Complexes $\mathbf{3}^{IV}$-$\mathbf{7}^{IV}$ were prepared simultaneously via a single route, detailed below.

Formation of $\mathbf{3}^{IV}$-$\mathbf{7}^{IV}$. The starting material for this process was an unseparated mixture of [$\mathbf{1}^{IV}$]Cl and [$\mathbf{2}^{IV}$]Cl, prepared in a manner similar to the previously reported procedure, omitting the oxidation state-setting and separation steps, as well as the introduction of $NaPF_6$. After oxidizing the crude reaction mixture with $NaIO_4$, the solution was saturated with NaCl, the products were extracted into dichloromethane, and then the solution was evaporated to dryness, in the same manner as originally described. The use of PF_6^- as a counterion was avoided due to decomposition concerns during the following high-temperature acid treatment.

A total of 5 20 mL solutions each containing 640 mg (1 mmol) of the above mixture of [$\mathbf{1}^{IV}$]Cl and [$\mathbf{2}^{IV}$]Cl was dissolved in 16 mL acetone and 4 mL 1M HCl, then loaded into 20 mL pressure vials. Each was heated in the microwave reactor for 30 minutes at 130 ^{o}C, and then cooled to room temperature. Solutions changed color from dark, nearly black, orange to clear yellow. The combined products were evaporated until no more acetone remained, and then diluted with water to 100 mL. An excess of sodium periodate (3 g) was added and the solution stirred for 10 minutes. **CAUTION:** This reaction produces chlorine vapors. Most chlorine remains dissolved in solution, however. The solution turned very dark wine-red, with solid dark precipitate forming. The oxidized products (along with chlorine) were repeatedly extracted with dichloromethane, until the aqueous layer became red-orange (leftover starting material) and the organic layer was lighter than the former. The extract was evaporated under static reduced pressure (to prevent chlorine release and damage to equipment); chlorine condensed along with the solvent, giving it a light orange-green tint.

Separation of **3^{IV}**-**7^{IV}**. The dried products were washed with hexane to remove any free ligand, redissolved in a minimal amount of dichloromethane (approx. 30 mL) and filtered. The solids, containing mostly undissolved **3^{IV}** along with inorganic salts, were washed with water to give pure solid **3^{IV}**. The remaining solution was loaded onto a large (7 x 30 cm) silica gel column presoaked with dichloromethane, and eluted using a solution of 25% ethyl acetate in dichloromethane. Complex **3^{IV}** eluted first as a purple band, followed by **5^{IV}** as an orange band, **7^{IV}** as a dark maroon band, **4^{IV}** as a very dark green band, merging into **6^{IV}**, a very dark and broad red band; at this point the ethyl acetate content was increased to 50% to accelerate the remaining elution. Transitions between bands were monitored by TLC; major overlap occurred between **4^{IV}** and **6^{IV}**, and lesser overlaps between the remaining adjacent bands. Pure product fractions were evaporated to dryness; the mixed fraction of **4^{IV}** and **6^{IV}** was separated by dissolving the solid in dichloromethane and precipitating by adding hexane until the solution was mostly green, and then decanting the solvent. This step was repeated until the red solid gave off no more green color; the wash solutions were concentrated and the process repeated. The purity of the solid **6^{IV}** thus obtained was confirmed by TLC. The remaining dissolved portion, enriched in **4^{IV}**, was allowed to stand at room temperature for several days, resulting in the reduction of leftover **6^{IV}**. This portion was removed by filtering through a short silica gel column using 1:1 ethyl acetate/dichloromethane. All matching fractions of pure products were combined, and individual yields described below. Cumulative yield: 1.54 g, 2.88 mmol, 58% (not including impure product fractions).

trans-Cl, trans-O, trans-N-bis(2-{pyridin-2-yl}propan-2-olato)-dichloro-iridium(IV) (**3^{IV}**) Yield: 82 mg, 3%. Crystals suitable for crystallography were grown by slow diffusion of a dichloromethane solution layered with hexane. HRMS (FT-ICR): calcd. for $[IrN_2O_2C_{16}H_{21}Cl_2]$ $(M+H^+)$: 536.058971 (z = 1). Found: m/z = 536.06127 (z = 1).

cis-Cl, cis-O, trans-N-bis(2-{pyridin-2-yl}propan-2-olato)-dichloro-iridium(IV) (**4^{IV}**) Yield: 150 mg, 6%. Crystals suitable for crystallography were grown by slow diffusion of an ethyl acetate solution layered with hexane (crystallization from dichloromethane results in friable crystals which disintegrate on drying). HRMS (FT-ICR): calcd. for $[IrN_2O_2C_{16}H_{21}Cl_2]$ $(M+H^+)$: 536.058971 (z = 1). Found: m/z = 536.06137 (z = 1). Reduced-state crystals (H**4^{III}**) were obtained by refluxing approx. 3 mg of **4^{IV}** in isopropanol until the solution became yellow (approx. 5 min), then evaporating the solvent and redissolving in 0.5 mL dichloromethane. Yellow crystals precipitated spontaneously after several hours.

cis-Cl, trans-O, cis-N-bis(2-{pyridin-2-yl}propan-2-olato)-dichloro-iridium(IV) (**5^{IV}**) Yield: 138 mg, 5%. Crystals suitable for crystallography were grown by slow diffusion of a dichloromethane solution layered with hexane. HRMS (FT-ICR): calcd. for $[IrN_2O_2C_{16}H_{21}Cl_2]$ $(M+H^+)$: 536.058971 (z = 1). Found: m/z = 536.0592 (z = 1).

cis-Cl, cis-O, cis-N-bis(2-{pyridin-2-yl}propan-2-olato)-dichloro-iridium(IV) (**6^{IV}**) Yield: 1.05 g, 39%. Crystals suitable for crystallography were grown by slow diffusion of a dichloromethane solution layered with hexane, kept at -20 °C for several days. HRMS (FT-ICR): calcd. for $[Ir^{III}N_2O_2C_{16}H_{22}Cl_2]$ ($M^{-}+2H^{+}$, reduced from ionizing conditions): 537.06879 (z = 1). Found: m/z =537.0676 (z = 1).). Reduced-state crystals (H**6**$^{\mathbf{III}}$) were grown by the same method, except for keeping the sample at room temperature. The compound reduces slowly at room temperature, building up enough material to precipitate yellow crystals, which were collected.

trans-Cl, cis-O, cis-N-bis(2-{pyridin-2-yl}propan-2-olato)-dichloro-iridium(IV) (**7**$^{\mathbf{IV}}$) Yield: 120 mg, 5%. Crystals suitable for crystallography were grown by slow diffusion of a dichloromethane solution layered with hexane. HRMS (FT-ICR): calcd. for $[Ir^{III}N_2O_2C_{16}H_{22}Cl_2]$ ($M^{-}+2H^{+}$, reduced from ionizing conditions): 537.06879 (z = 1). Found: m/z = 537.0678 (z = 1).

Section II. TLC Separation Example

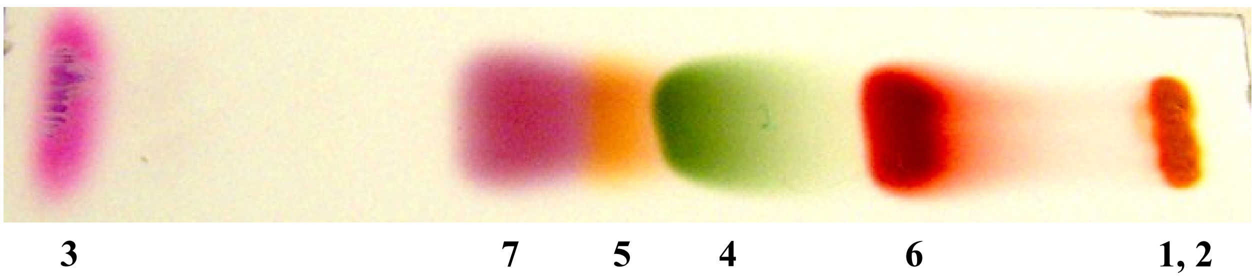


Figure S1. TLC separation of the *bis*-pyalk Ir(IV) species using 25% ethyl acetate in dichloromethane. Elution is from right to left (tris-pyalk starting material remaining at the starting position). Note that the elution order of **5** and **7** is reversed in column chromatography when using the same eluent.

Section III. NMR Spectra

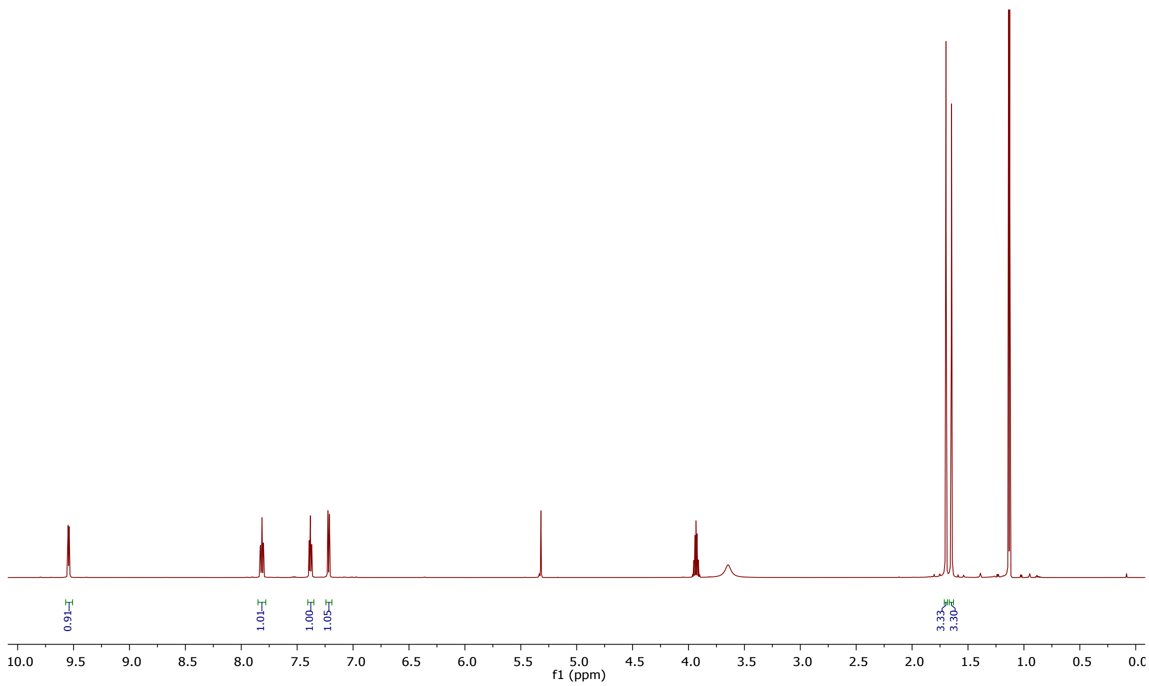


Figure S2. ^{1}H NMR spectrum (CD_2Cl_2) of $\mathbf{4^{III}}$ reduced with isopropanol. Major peaks without integration are from isopropanol, water, or solvent residual.

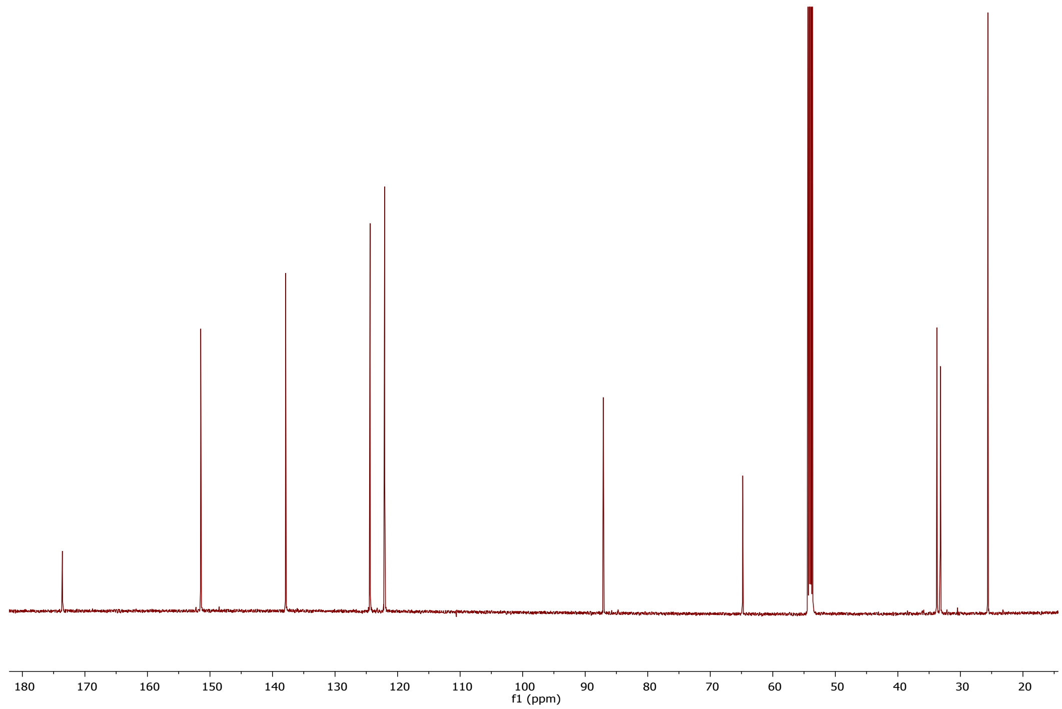


Figure S3. ^{13}C NMR spectrum of $\mathbf{4^{III}}$ (same sample as above). Peaks at 25 and 65 ppm are from isopropanol; solvent residual is at 53 ppm

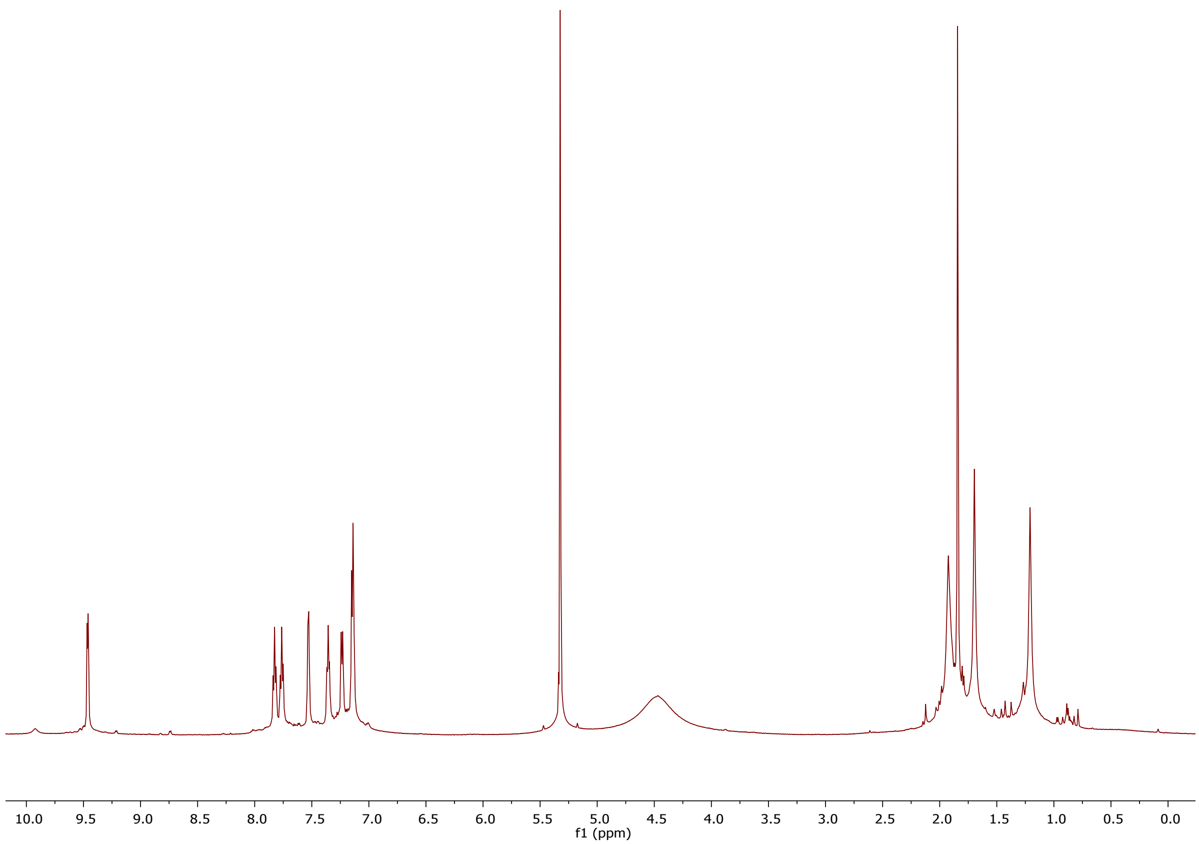


Figure S4. ^{1}H NMR spectrum (CD_2Cl_2) of **6** incompletely reduced with isopropanol.

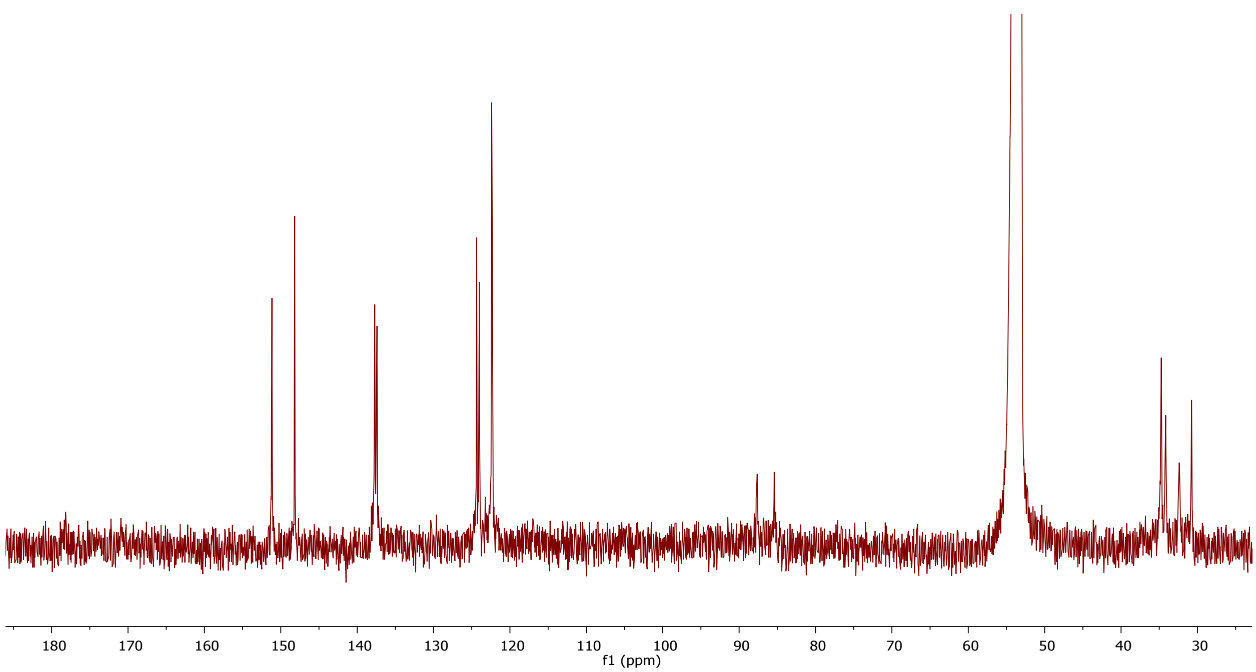


Figure S5. ^{13}C NMR spectrum of above sample.

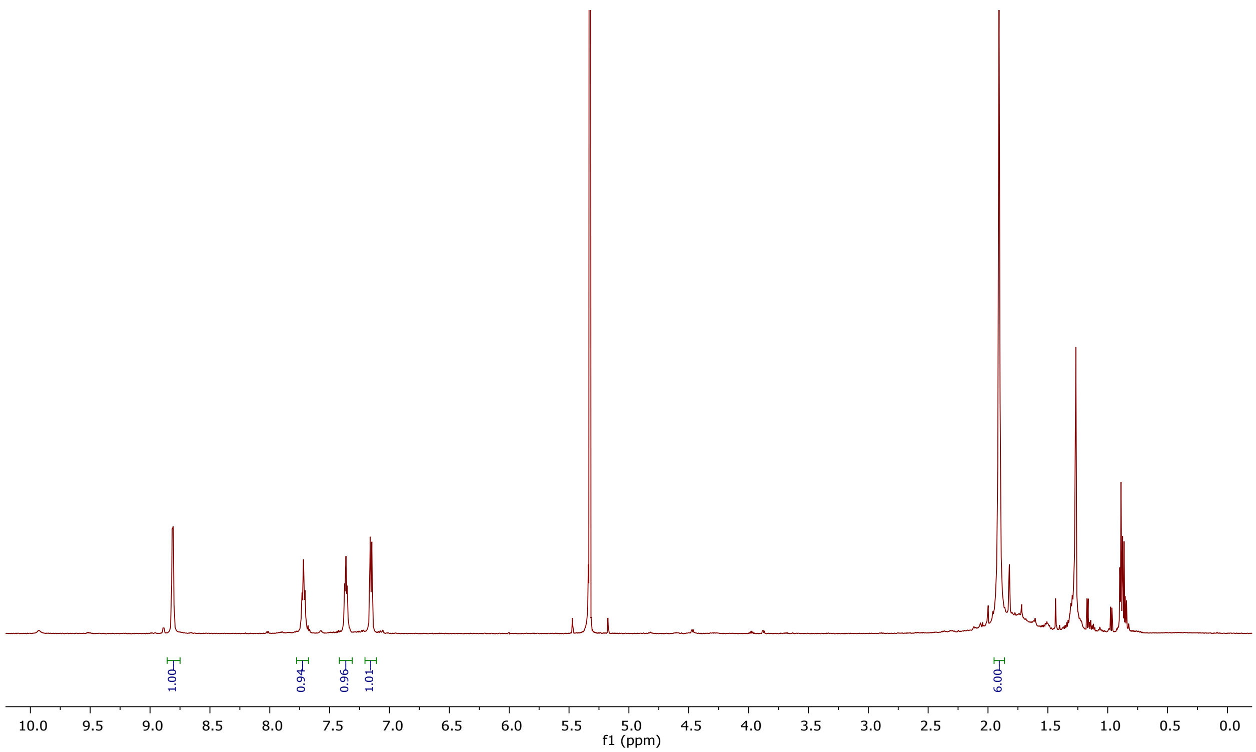


Figure S6. ^{1}H NMR spectrum (CD_2Cl_2) of **7^{III}** reduced with isopropanol.

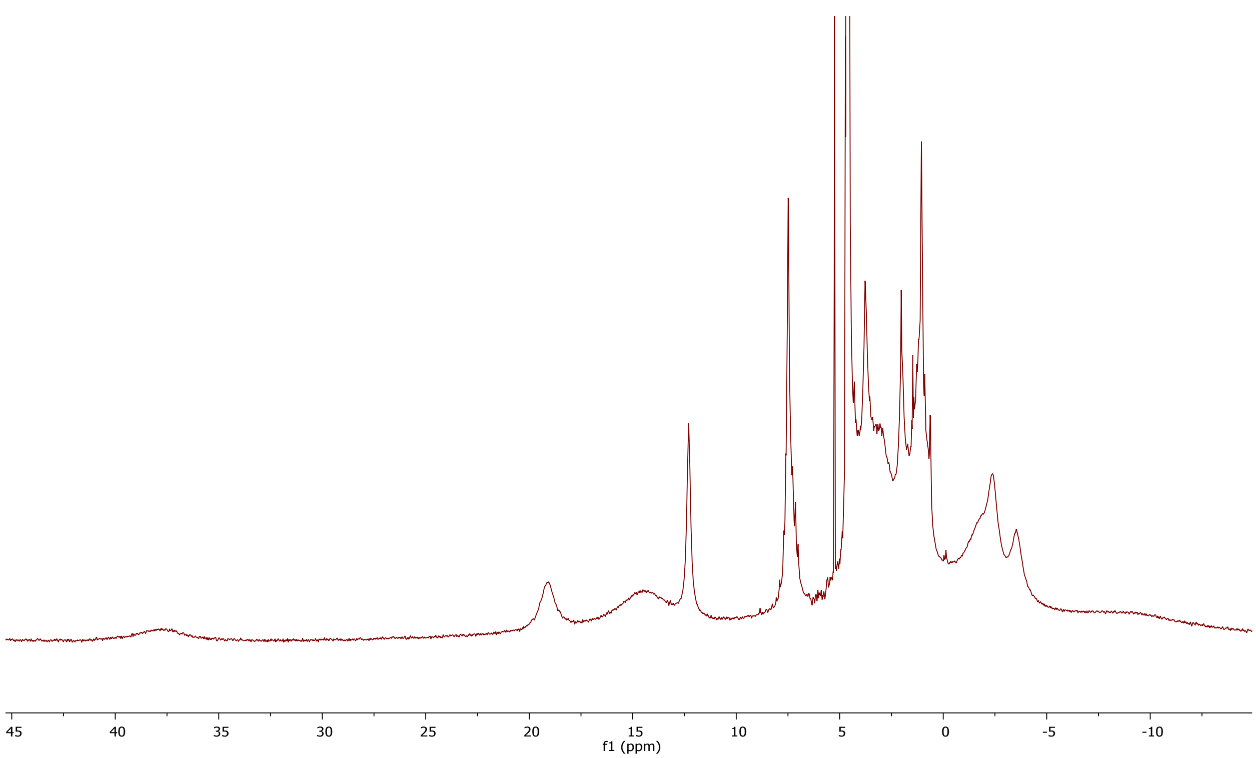


Figure S7. Paramagnetic ^{1}H NMR spectrum of **[1^{IV}]**$^+$ in D_2O.

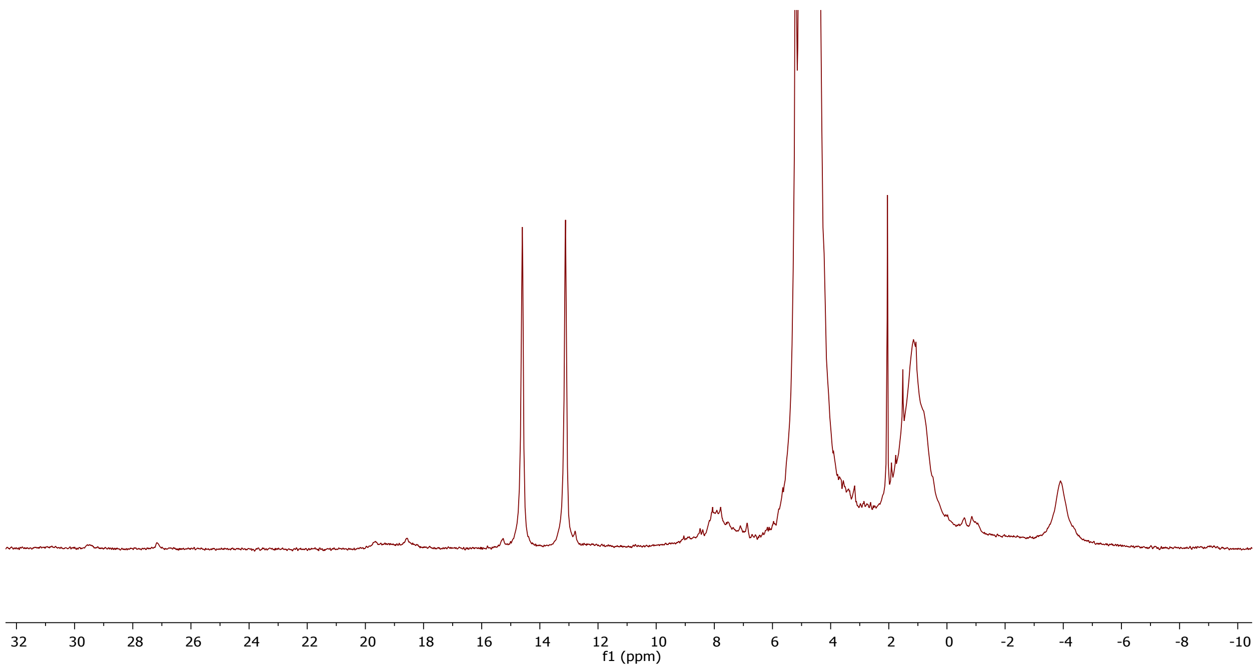


Figure S8. Paramagnetic ^{1}H NMR spectrum of $\mathbf{[2^{IV}]^+}$ in D_2O.

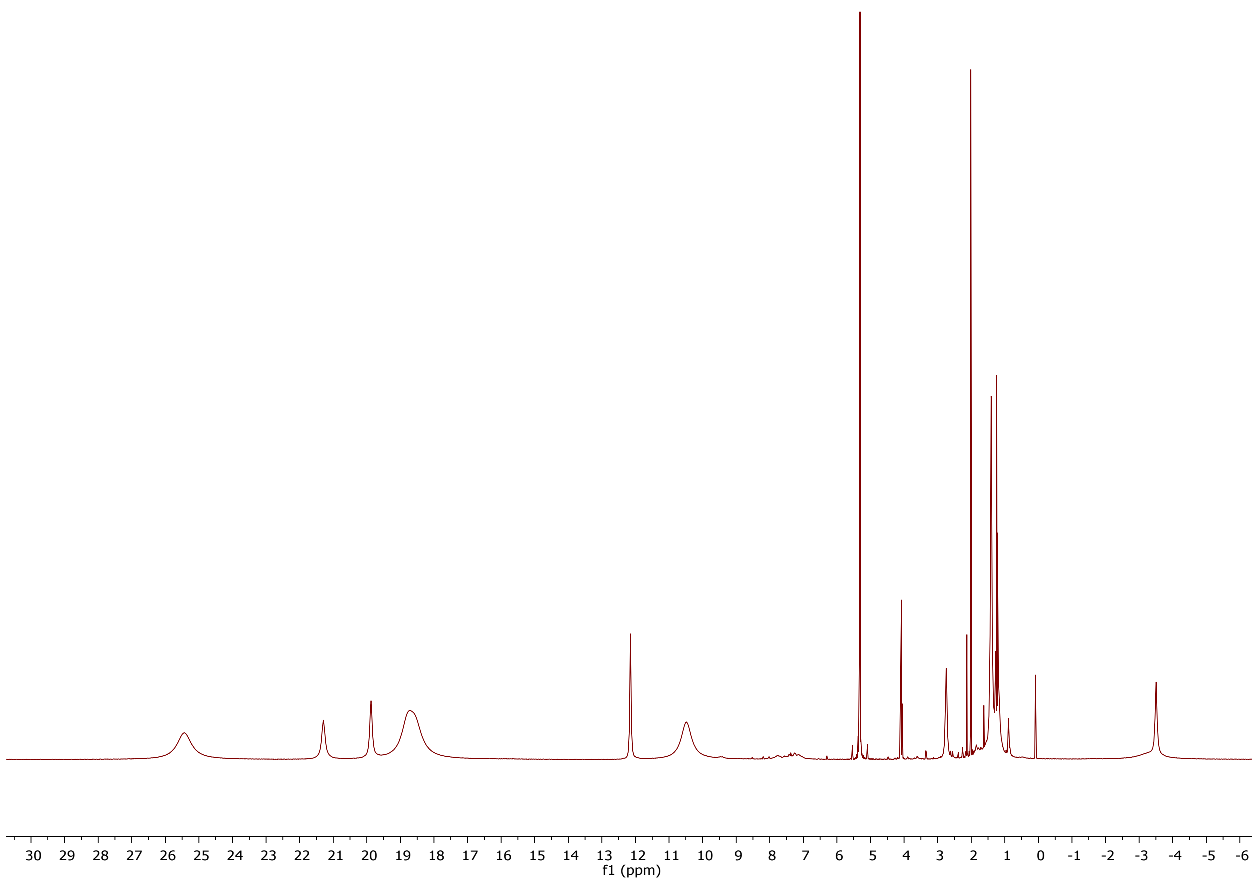


Figure S9. Paramagnetic ^{1}H NMR spectrum of **6** in CD_2Cl_2.

Section IV. Crystallographic Details

Low-temperature diffraction data (ω scans) were collected on a Rigaku R-AXIS RAPID diffractometer coupled to a RAXIS RAPID imaging plate detector at 93 K or on a Rigaku Mercury275R CCD (SCX mini) at 223 K, both with Mo Kα radiation (λ = 0.71073 Å), and on a Rigaku MicroMax-007HF diffractometer coupled to a Saturn994+ CCD detector with Cu Kα (λ = 1.54178 Å) at 93 K. The data frames were processed and scaled using the Rigaku *CrystalClear*[26] software. The data were corrected for Lorentz and polarization effects. All structures were solved by direct methods using SHELXS-2013 or SHELXT-2014 and refined against F^2 on all data by full-matrix least squares with SHELXL-2014.[27] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model, except for those bound to oxygen or nitrogen which were located in the Fourier difference electron density map. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). In structures $\mathbf{4^{III}}$, $\mathbf{4^{IV}}$ and $\mathbf{5^{IV}}$, solvent molecules were disordered while being located at special positions. Those were modelled using a number of geometrical restraints. Complete details of the X-ray analyses reported herein have been deposited at The Cambridge Crystallographic Data Centre (CCDC 1497501 ($\mathbf{3^{IV}}$), CCDC 1497502 ($\mathbf{7^{IV}}$), CCDC 1497503 ($\mathbf{6^{III}}$), CCDC 1497504 ($\mathbf{4^{IV}}$), CCDC 1497505 ($\mathbf{6^{IV}}$), CCDC 1497506 ($\mathbf{4^{III}}$), CCDC 1497507 ($\mathbf{8^{IV}}$), CCDC 1497508 ($\mathbf{5^{IV}}$)).

Table S2. Summary of data collection, structure solution and refinement details for **3**[IV], **4**[IV], **5**[IV] and **6**[IV].

Compound	**3**[IV]	**4**[IV]	**5**[IV]	**6**[IV]
Formula	$C_{16}H_{20}Cl_2IrN_2O_2$	$C_{16}H_{20}Cl_2IrN_2O_2\cdot 0.5(C_4H_8O_2)$	$2(C_{16}H_{20}Cl_2IrN_2O_2)\cdot CH_2Cl_2$	$C_{16}H_{20}Cl_2IrN_2O_2\cdot CH_2Cl_2$
Formula weight	535.44	579.49	1155.80	620.36
T [K]	93	93	93	93
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	*P-1*	*P2₁/n*	*Pbca*	*P2₁/n*
Unit cell				
a [Å]	7.8768 (1)	7.9001 (1)	14.9782 (4)	8.7599 (2)
b [Å]	8.0811 (1)	18.4626 (3)	15.0278 (3)	15.6388 (3)
c [Å]	8.6738 (6)	14.3136 (10)	17.4463 (12)	15.6017 (11)
α [°]	68.100 (5)	90	90	90
β [°]	66.086 (5)	95.040 (7)	90	98.373 (7)
γ [°]	61.433 (4)	90	90	90
V [$Å^3$]	432.10 (4)	2079.66 (15)	3927.0 (3)	2114.56 (17)
Z	1	4	4	4
ρ_{cald} [g cm^{-3}]	2.058	1.851	1.955	1.949
μ [mm^{-1}]	17.89	14.96	7.22	6.83
F(000)	257	1124	2224	1196
Crystal size [mm]	0.05 x 0.05 x 0.05	0,20 x 0,20 x 0,20	0.20 x 0.18 x 0.06	0.20 x 0.20 x 0.20
$\theta_{min} – \theta_{mac}$ [°]	5.7 – 68.3	2.4 – 68.2	3.0 – 27.5	3.1 – 27.5
Collected reflections	15649	60998	119682	63497
Indep. reflections	1549	3812	4503	4846
R_{int}	0.114	0.054	0.097	0.045
Restraints/param.	0/112	42/269	16/239	0/239
GooF (F^2)	1.06	1.06	0.90	1.06
R_1, wR_2 (I>2σ(I))	0.033/0.082	0.028/0.068	0.037/0.096	0.020/0.041
R_1, wR_2 (all data)	0.033/0.082	0.031/0.070	0.044/0.101	0.024/0.042
Residual e^- ρ [e $Å^{-3}$]	1.41/-2.04	0.90/-0.95	1.95/-2.06	0.83/-0.77

Table S3. Summary of data collection, structure solution and refinement details for **7^{IV}**, **Na[8^{IV}]**, **H[4^{III}]** and **H[6^{III}]**.

Compound	**7^{IV}**	**Na[8^{IV}]**	**H[4^{III}]**	**H[6^{III}]**
Formula	$16(C_{16}H_{20}Cl_2IrN_2O_2)$	$C_{16}H_{30}Cl_8Ir_2N_2Na_2O_7$	$2(C_{16}H_{21}Cl_2IrN_2O_2)\cdot CH_2Cl_2\cdot 2(H_2O)$	$C_{16}H_{23}Cl_2IrN_2O_3$
Formula weight	8567.53	1076.40	1193.85	554.46
T [K]	93	93	223	93
Crystal system	Tetragonal	Triclinic	Monoclinic	Triclinic
Space group	*$I4_1/a$*	*P-1*	*$P2_1/c$*	*P-1*
Unit cell				
a [Å]	16.9129 (3)	8.4303 (2)	9.044 (7)	8.8884 (3)
b [Å]	16.9129 (3)	13.4446 (3)	13.823 (9)	9.6675 (3)
c [Å]	25.3688 (18)	14.3559 (10)	17.039 (13)	12.5862 (9)
α [°]	90	74.431 (5)	90	95.132 (7)
β [°]	90	85.859 (6)	227 (13)	109.482 (8)
γ [°]	90	81.771 (6)	90	110.349 (8)
V [$Å^3$]	7256.6 (6)	1550.31 (13)	2121 (3)	929.79 (10)
Z	1	2	2	2
ρ_{cald} [g cm^{-3}]	1.960	2.306	1.869	1.980
μ [mm^{-1}]	17.04	9.33	6.69	7.48
F(000)	4062	1016	1156	536
Crystal size [mm]	0.10 x 0.08 x 0.03	0.25 x 0.20 x 0.18	0.20 x 0.20 x 0.20	0.10 x 0.08 x 0.06
$\theta_{min} – \theta_{mac}$ [°]	3.1 – 68.2	3.1 – 30.5	1.9 – 27.5	3.2 – 30.5
Collected reflections	96480	86738	29122	16078
Indep. reflections	3317	9438	3748	3227
R_{int}	0.073	0.056	0.102	0.026
Restraints/param.	0/211	10/368	3/257	2/233
GooF (F^2)	1.04	1.09	1.17	0.82
R_1, wR_2 (I>2σ(I))	0.023/0.052	0.031/0.056	0.045/0.133	0.018/0.050
R_1, wR_2 (all data)	0.024/0.052	0.035/0.059	0.055/0.146	0.020/0.065
Residual e^- ρ [e $Å^{-3}$]	0.75/-0.63	1.79/-2.05	2.17 / -2.61	0.69/-0.73

Geometric parameters (Å, º) for ***3***[IV]

Ir1—Cl1^{i}	2.3473 (15)	N1—C5	1.348 (8)
Ir1—Cl1	2.3473 (15)	C1—C2	1.364 (9)
Ir1—O1	1.943 (4)	C8—C6	1.538 (9)
Ir1—O1^{i}	1.943 (4)	C6—C5	1.526 (8)
Ir1—N1	2.031 (5)	C6—C7	1.533 (9)
Ir1—N1^{i}	2.031 (5)	C5—C4	1.392 (9)
O1—C6	1.432 (7)	C4—C3	1.373 (9)
N1—C1	1.349 (8)	C3—C2	1.402 (9)

Cl1—Ir1—Cl1^{i}	180.0	C1—N1—Ir1	124.5 (4)
O1—Ir1—Cl1	90.68 (13)	C5—N1—Ir1	114.7 (4)
O1—Ir1—Cl1^{i}	89.32 (13)	C5—N1—C1	120.7 (5)
O1^{i}—Ir1—Cl1^{i}	90.68 (13)	N1—C1—C2	121.3 (6)
O1^{i}—Ir1—Cl1	89.32 (13)	O1—C6—C8	107.5 (5)
O1—Ir1—O1^{i}	180.0 (2)	O1—C6—C5	109.9 (5)
O1—Ir1—N1	81.86 (18)	O1—C6—C7	107.8 (5)
O1^{i}—Ir1—N1^{i}	81.86 (18)	C5—C6—C8	111.5 (5)
O1^{i}—Ir1—N1	98.14 (18)	C5—C6—C7	109.1 (5)
O1—Ir1—N1^{i}	98.14 (18)	C7—C6—C8	111.1 (5)
N1^{i}—Ir1—Cl1^{i}	90.05 (14)	N1—C5—C6	115.5 (5)
N1^{i}—Ir1—Cl1	89.95 (14)	N1—C5—C4	119.9 (5)
N1—Ir1—Cl1	90.05 (14)	C4—C5—C6	124.5 (5)
N1—Ir1—Cl1^{i}	89.95 (14)	C3—C4—C5	119.8 (6)
N1—Ir1—N1^{i}	180.0	C4—C3—C2	119.1 (6)
C6—O1—Ir1	117.5 (3)	C1—C2—C3	119.1 (6)

Symmetry code: (i) -*x*+2, -*y*, -*z*+1.

Geometric parameters (Å, º) for ***4***[iv]

Ir1—O2	1.937 (3)	C7—H7B	0.9800
Ir1—O1	1.950 (3)	C7—H7C	0.9800
Ir1—N1	2.032 (4)	C2AA—C2	1.377 (8)
Ir1—N2	2.048 (4)	C2AA—C1AA	1.386 (7)
Ir1—Cl2	2.3604 (11)	C2AA—H2AA	0.9500
Ir1—Cl1	2.3630 (11)	C11—C10	1.377 (8)
O1—C6	1.425 (5)	C11—H11	0.9500
C15—C14	1.526 (8)	C1AA—H1AA	0.9500

C15—H15A	0.9800	C8—H8A	0.9800
C15—H15B	0.9800	C8—H8B	0.9800
C15—H15C	0.9800	C8—H8C	0.9800
O2—C14	1.423 (6)	C16—H16A	0.9800
N1—C1	1.340 (6)	C16—H16B	0.9800
N1—C5	1.353 (6)	C16—H16C	0.9800
N2—C9	1.340 (6)	C10—H10	0.9500
N2—C13	1.352 (6)	C2—H2	0.9500
C13—C12	1.388 (7)	C50A—C51A	1.54 (2)
C13—C14	1.518 (7)	C50A—H50A	0.9800
C5—C1AA	1.385 (7)	C50A—H50B	0.9800
C5—C6	1.519 (7)	C50A—H50C	0.9800
C14—C16	1.516 (7)	C51A—O1A	1.210 (17)
C6—C7	1.527 (7)	C51A—O2A	1.50 (4)
C6—C8	1.530 (7)	C52A—O2A	1.49 (4)
C1—C2	1.366 (7)	C52A—C53A	1.54 (2)
C1—H1	0.9500	C52A—H52A	0.9900
C12—C11	1.374 (8)	C52A—H52B	0.9900
C12—H12	0.9500	C53A—H53A	0.9800
C9—C10	1.366 (7)	C53A—H53B	0.9800
C9—H9	0.9500	C53A—H53C	0.9800
C7—H7A	0.9800		

O2—Ir1—O1	92.01 (14)	C6—C7—H7A	109.5
O2—Ir1—N1	91.41 (14)	C6—C7—H7B	109.5
O1—Ir1—N1	82.70 (14)	H7A—C7—H7B	109.5
O2—Ir1—N2	82.51 (14)	C6—C7—H7C	109.5
O1—Ir1—N2	92.81 (14)	H7A—C7—H7C	109.5
N1—Ir1—N2	172.33 (15)	H7B—C7—H7C	109.5
O2—Ir1—Cl2	178.00 (10)	C2—C2AA—C1AA	119.9 (5)
O1—Ir1—Cl2	89.72 (10)	C2—C2AA—H2AA	120.0
N1—Ir1—Cl2	87.82 (11)	C1AA—C2AA—H2AA	120.0
N2—Ir1—Cl2	98.41 (11)	C12—C11—C10	119.4 (5)
O2—Ir1—Cl1	89.14 (10)	C12—C11—H11	120.3
O1—Ir1—Cl1	178.76 (10)	C10—C11—H11	120.3
N1—Ir1—Cl1	96.84 (11)	C5—C1AA—C2AA	119.2 (5)
N2—Ir1—Cl1	87.78 (11)	C5—C1AA—H1AA	120.4
Cl2—Ir1—Cl1	89.12 (4)	C2AA—C1AA—	120.4

		H1AA	
C6—O1—Ir1	116.0 (3)	C6—C8—H8A	109.5
C14—C15—H15A	109.5	C6—C8—H8B	109.5
C14—C15—H15B	109.5	H8A—C8—H8B	109.5
H15A—C15—H15B	109.5	C6—C8—H8C	109.5
C14—C15—H15C	109.5	H8A—C8—H8C	109.5
H15A—C15—H15C	109.5	H8B—C8—H8C	109.5
H15B—C15—H15C	109.5	C14—C16—H16A	109.5
C14—O2—Ir1	117.1 (3)	C14—C16—H16B	109.5
C1—N1—C5	120.7 (4)	H16A—C16—H16B	109.5
C1—N1—Ir1	125.9 (3)	C14—C16—H16C	109.5
C5—N1—Ir1	113.4 (3)	H16A—C16—H16C	109.5
C9—N2—C13	121.0 (4)	H16B—C16—H16C	109.5
C9—N2—Ir1	126.2 (3)	C9—C10—C11	119.2 (5)
C13—N2—Ir1	112.7 (3)	C9—C10—H10	120.4
N2—C13—C12	119.1 (5)	C11—C10—H10	120.4
N2—C13—C14	116.8 (4)	C1—C2—C2AA	118.7 (5)
C12—C13—C14	124.2 (5)	C1—C2—H2	120.7
N1—C5—C1AA	119.7 (4)	C2AA—C2—H2	120.7
N1—C5—C6	116.2 (4)	C51A—C50A—H50A	109.5
C1AA—C5—C6	124.0 (4)	C51A—C50A—H50B	109.5
O2—C14—C16	106.6 (4)	H50A—C50A—H50B	109.5
O2—C14—C13	110.4 (4)	C51A—C50A—H50C	109.5
C16—C14—C13	111.6 (4)	H50A—C50A—H50C	109.5
O2—C14—C15	107.6 (4)	H50B—C50A—H50C	109.5
C16—C14—C15	111.4 (5)	O1A—C51A—O2A	128 (2)
C13—C14—C15	109.2 (4)	O1A—C51A—C50A	126.5 (16)
O1—C6—C5	110.9 (4)	O2A—C51A—C50A	105 (3)
O1—C6—C7	108.5 (4)	O2A—C52A—C53A	99 (2)
C5—C6—C7	109.3 (4)	O2A—C52A—H52A	112.0
O1—C6—C8	106.6 (4)	C53A—C52A—H52A	112.0
C5—C6—C8	110.4 (4)	O2A—C52A—H52B	112.0
C7—C6—C8	111.1 (4)	C53A—C52A—H52B	112.0
N1—C1—C2	121.7 (5)	H52A—C52A—H52B	109.6
N1—C1—H1	119.2	C52A—C53A—H53A	109.5
C2—C1—H1	119.2	C52A—C53A—H53B	109.5
C11—C12—C13	120.0 (5)	H53A—C53A—H53B	109.5
C11—C12—H12	120.0	C52A—C53A—H53C	109.5
C13—C12—H12	120.0	H53A—C53A—H53C	109.5

N2—C9—C10	121.2 (5)	H53B—C53A—H53C	109.5
N2—C9—H9	119.4	C52A—O2A—C51A	105 (4)
C10—C9—H9	119.4		

*Geometric parameters (Å, º) for **5**[iv]*

Ir1—O2	1.952 (3)	C3—C2	1.381 (8)
Ir1—O1	1.962 (4)	C12—C11	1.375 (8)
Ir1—N1	2.040 (5)	C9—C10	1.377 (7)
Ir1—N2	2.050 (4)	C4—C5	1.390 (8)
Ir1—Cl2	2.3266 (12)	C5—C6	1.522 (8)
Ir1—Cl1	2.3372 (13)	C10—C11	1.391 (8)
N2—C9	1.354 (7)	O2—C14	1.435 (6)
N2—C13	1.352 (6)	C16—C14	1.534 (8)
N1—C1	1.338 (7)	C14—C15	1.530 (7)
N1—C5	1.357 (6)	O1—C6	1.436 (7)
C13—C12	1.387 (7)	C6—C7	1.533 (8)
C13—C14	1.518 (7)	C6—C8	1.530 (8)
C1—C2	1.369 (8)	Cl3—C50	1.609 (13)
C3—C4	1.373 (9)	C50—Cl4	1.622 (13)

O2—Ir1—O1	166.42 (16)	C4—C3—C2	119.8 (6)
O2—Ir1—N1	90.13 (16)	C11—C12—C13	119.6 (5)
O1—Ir1—N1	80.69 (16)	N2—C9—C10	122.1 (5)
O2—Ir1—N2	79.84 (17)	C3—C4—C5	119.4 (5)
O1—Ir1—N2	90.77 (16)	N1—C5—C4	120.1 (5)
N1—Ir1—N2	93.98 (17)	N1—C5—C6	116.2 (5)
O2—Ir1—Cl2	92.90 (11)	C4—C5—C6	123.7 (5)
O1—Ir1—Cl2	96.68 (12)	C9—C10—C11	117.8 (5)
N1—Ir1—Cl2	87.68 (12)	C1—C2—C3	118.8 (5)
N2—Ir1—Cl2	172.54 (13)	C12—C11—C10	120.2 (5)
O2—Ir1—Cl1	95.96 (12)	C14—O2—Ir1	117.4 (3)
O1—Ir1—Cl1	93.54 (11)	O2—C14—C13	108.5 (4)
N1—Ir1—Cl1	173.76 (12)	O2—C14—C15	106.0 (4)
N2—Ir1—Cl1	88.44 (13)	C13—C14—C15	111.1 (4)
Cl2—Ir1—Cl1	90.64 (5)	O2—C14—C16	110.3 (4)
C9—N2—C13	119.9 (5)	C13—C14—C16	110.6 (5)
C9—N2—Ir1	125.3 (4)	C15—C14—C16	110.3 (4)
C13—N2—Ir1	114.7 (4)	C6—O1—Ir1	116.9 (3)

C1—N1—C5	120.0 (5)	O1—C6—C5	108.3 (4)
C1—N1—Ir1	125.8 (4)	O1—C6—C7	106.4 (5)
C5—N1—Ir1	114.2 (4)	C5—C6—C7	110.2 (5)
N2—C13—C12	120.3 (5)	O1—C6—C8	110.8 (5)
N2—C13—C14	115.5 (4)	C5—C6—C8	110.3 (5)
C12—C13—C14	124.2 (5)	C7—C6—C8	110.7 (5)
N1—C1—C2	122.0 (5)	Cl3—C50—Cl4	125.2 (16)

Geometric parameters (Å, º) for ***6^{IV}***

Ir1—Cl1	2.3345 (7)	N1—C5	1.345 (4)
Ir1—Cl2	2.3447 (7)	C4—C5	1.393 (4)
Ir1—O1	1.9499 (19)	C12—C13	1.389 (4)
Ir1—O2	1.9550 (19)	C12—C11	1.381 (4)
Ir1—N1	2.037 (2)	N2—C13	1.351 (4)
Ir1—N2	2.068 (2)	N2—C9	1.346 (4)
Cl4—C17	1.754 (4)	C13—C14	1.520 (4)
Cl5—C17	1.749 (4)	C5—C6	1.516 (4)
O1—C6	1.425 (3)	C6—C7	1.527 (4)
O2—C14	1.427 (3)	C6—C8	1.525 (4)
C3—C2	1.387 (5)	C14—C16	1.527 (4)
C3—C4	1.383 (4)	C14—C15	1.529 (4)
C2—C1	1.376 (4)	C11—C10	1.382 (5)
N1—C1	1.344 (4)	C9—C10	1.384 (4)

Cl1—Ir1—Cl2	92.45 (3)	C9—N2—Ir1	125.9 (2)
O1—Ir1—Cl1	92.83 (6)	C9—N2—C13	120.1 (2)
O1—Ir1—Cl2	91.65 (6)	N1—C1—C2	122.1 (3)
O1—Ir1—O2	90.76 (8)	C12—C13—C14	123.7 (3)
O1—Ir1—N1	82.47 (9)	N2—C13—C12	120.2 (3)
O1—Ir1—N2	171.87 (9)	N2—C13—C14	116.1 (2)
O2—Ir1—Cl1	173.51 (6)	N1—C5—C4	120.1 (3)
O2—Ir1—Cl2	92.85 (7)	N1—C5—C6	116.3 (2)
O2—Ir1—N1	85.53 (9)	C4—C5—C6	123.5 (3)
O2—Ir1—N2	81.12 (9)	O1—C6—C5	111.1 (2)
N1—Ir1—Cl1	89.58 (7)	O1—C6—C7	108.0 (2)
N1—Ir1—Cl2	173.87 (7)	O1—C6—C8	106.8 (2)
N1—Ir1—N2	96.35 (9)	C5—C6—C7	110.1 (2)
N2—Ir1—Cl1	95.21 (7)	C5—C6—C8	109.3 (2)

N2—Ir1—Cl2	89.22 (7)	C8—C6—C7	111.5 (3)
C6—O1—Ir1	116.38 (16)	O2—C14—C13	110.3 (2)
C14—O2—Ir1	117.95 (17)	O2—C14—C16	109.1 (2)
C4—C3—C2	119.4 (3)	O2—C14—C15	106.4 (2)
C1—C2—C3	118.5 (3)	C13—C14—C16	108.8 (2)
C1—N1—Ir1	125.9 (2)	C13—C14—C15	111.7 (2)
C1—N1—C5	120.3 (2)	C16—C14—C15	110.4 (3)
C5—N1—Ir1	113.66 (18)	C12—C11—C10	119.1 (3)
C3—C4—C5	119.6 (3)	N2—C9—C10	121.5 (3)
C11—C12—C13	120.0 (3)	C11—C10—C9	119.1 (3)
C13—N2—Ir1	113.94 (18)	Cl5—C17—Cl4	111.7 (2)

Geometric parameters (Å, º) for ***7***^{IV}

Ir1—Cl1	2.3358 (9)	C13—C14	1.524 (5)
Ir1—Cl2	2.3195 (9)	C5—C6	1.508 (5)
Ir1—O1	1.937 (3)	C5—C4	1.384 (5)
Ir1—N2	2.083 (3)	C12—C11	1.376 (6)
Ir1—O2	1.958 (2)	C14—C16	1.534 (5)
Ir1—N1	2.084 (3)	C14—C15	1.523 (5)
O1—C6	1.429 (4)	C3—C4	1.376 (6)
N2—C13	1.361 (5)	C3—C2	1.377 (6)
N2—C9	1.352 (5)	C1—C2	1.375 (6)
O2—C14	1.417 (4)	C10—C9	1.377 (5)
N1—C5	1.348 (5)	C10—C11	1.376 (6)
N1—C1	1.355 (5)	C6—C8	1.524 (5)
C13—C12	1.376 (5)	C6—C7	1.520 (5)

Cl2—Ir1—Cl1	170.32 (3)	C14—C13—C12	123.6 (3)
O1—Ir1—Cl1	94.35 (8)	C6—C5—N1	117.1 (3)
O1—Ir1—Cl2	93.72 (8)	C4—C5—N1	120.6 (3)
N2—Ir1—Cl1	84.72 (9)	C4—C5—C6	122.3 (3)
N2—Ir1—Cl2	88.46 (9)	C11—C12—C13	120.4 (4)
N2—Ir1—O1	168.22 (11)	C13—C14—O2	110.4 (3)
O2—Ir1—Cl1	93.15 (8)	C16—C14—O2	107.9 (3)
O2—Ir1—Cl2	92.56 (8)	C16—C14—C13	108.5 (3)
O2—Ir1—O1	87.27 (10)	C15—C14—O2	107.2 (3)
O2—Ir1—N2	81.07 (11)	C15—C14—C13	111.3 (3)
N1—Ir1—Cl1	86.41 (8)	C15—C14—C16	111.6 (3)

N1—Ir1—Cl2	89.60 (8)	C2—C3—C4	119.1 (4)
N1—Ir1—O1	80.95 (11)	C2—C1—N1	121.4 (4)
N1—Ir1—N2	110.66 (12)	C11—C10—C9	118.9 (4)
N1—Ir1—O2	168.14 (11)	C5—C6—O1	109.9 (3)
C6—O1—Ir1	118.6 (2)	C8—C6—O1	107.4 (3)
C13—N2—Ir1	113.1 (2)	C8—C6—C5	110.1 (3)
C9—N2—Ir1	127.6 (3)	C7—C6—O1	107.3 (3)
C9—N2—C13	119.1 (3)	C7—C6—C5	110.6 (3)
C14—O2—Ir1	118.5 (2)	C7—C6—C8	111.4 (4)
C5—N1—Ir1	112.9 (2)	C3—C4—C5	119.9 (4)
C1—N1—Ir1	127.5 (3)	C10—C9—N2	122.0 (4)
C1—N1—C5	119.6 (3)	C1—C2—C3	119.4 (4)
C12—C13—N2	120.3 (3)	C10—C11—C12	119.2 (4)
C14—C13—N2	116.0 (3)		

*Geometric parameters (Å, º) for **8**[iv]*

O3—Na2	2.395 (4)	Na1—O1	2.437 (4)
O3—H3A	0.84 (2)	Na1—Na2^{ii}	3.814 (3)
O3—H3B	0.84 (2)	O2—C14	1.446 (5)
Ir1—O1	1.930 (3)	N2—C9	1.345 (5)
Ir1—N1	2.025 (3)	N2—C13	1.346 (5)
Ir1—Cl3	2.3281 (10)	O6—H6A	0.85 (2)
Ir1—Cl2	2.3295 (10)	O6—H6B	0.845 (19)
Ir1—Cl4	2.3355 (10)	O5—Na1^{i}	2.365 (4)
Ir1—Cl1	2.3504 (10)	O5—H5A	0.839 (19)
Ir1—Na1	3.622 (2)	O5—H5B	0.833 (19)
Ir2—O2	1.934 (3)	O1—C6	1.437 (5)
Ir2—N2	2.030 (3)	C13—C12	1.381 (6)
Ir2—Cl6	2.3195 (10)	C13—C14	1.519 (5)
Ir2—Cl8	2.3312 (10)	C11—C12	1.379 (6)
Ir2—Cl7	2.3401 (11)	C11—C10	1.384 (6)
Ir2—Cl5	2.3574 (10)	C11—H11	0.9500
Ir2—Na2	3.7020 (19)	C10—C9	1.381 (6)
Cl1—Na2	2.819 (2)	C10—H10	0.9500
Cl1—Na1	2.908 (2)	C14—C15	1.524 (6)
Cl5—Na2	2.819 (2)	C14—C16	1.531 (6)
N1—C1	1.340 (5)	C6—C8	1.529 (6)
N1—C5	1.345 (5)	C6—C7	1.535 (6)

C1—C2	1.376 (6)	C9—H9	0.9500
C1—H1	0.9500	C12—H12	0.9500
C4—C3	1.376 (6)	C15—H15A	0.9800
C4—C5	1.390 (6)	C15—H15B	0.9800
C4—H4	0.9500	C15—H15C	0.9800
C3—C2	1.397 (6)	O4—H4A	0.84 (2)
C3—H3	0.9500	O4—H4B	0.831 (19)
C2—H2	0.9500	O7—H7D	0.85 (2)
C5—C6	1.512 (6)	O7—H7E	0.85 (2)
Na2—O5	2.381 (4)	C16—H16A	0.9800
Na2—O4	2.409 (4)	C16—H16B	0.9800
Na2—O2	2.596 (3)	C16—H16C	0.9800
Na2—Na1^{i}	3.814 (3)	C8—H8A	0.9800
Na2—H5B	2.68 (6)	C8—H8B	0.9800
Na2—H4B	2.66 (6)	C8—H8C	0.9800
Na1—O7	2.285 (5)	C7—H7A	0.9800
Na1—O6	2.297 (4)	C7—H7B	0.9800
Na1—O5^{ii}	2.365 (4)	C7—H7C	0.9800

Na2—O3—H3A	114 (5)	O3—Na2—H4B	101.4 (11)
Na2—O3—H3B	113 (4)	O4—Na2—H4B	18.0 (7)
H3A—O3—H3B	104 (6)	O2—Na2—H4B	60.4 (9)
O1—Ir1—N1	82.74 (13)	Cl1—Na2—H4B	92.4 (13)
O1—Ir1—Cl3	91.41 (9)	Cl5—Na2—H4B	79.9 (12)
N1—Ir1—Cl3	89.75 (10)	Ir2—Na2—H4B	64.0 (8)
O1—Ir1—Cl2	178.31 (9)	Na1^{i}—Na2—H4B	146.4 (11)
N1—Ir1—Cl2	97.18 (10)	H5B—Na2—H4B	140.2 (18)
Cl3—Ir1—Cl2	90.27 (4)	O7—Na1—O6	162.8 (2)
O1—Ir1—Cl4	88.85 (9)	O7—Na1—O5^{ii}	84.35 (17)
N1—Ir1—Cl4	88.49 (10)	O6—Na1—O5^{ii}	105.75 (15)
Cl3—Ir1—Cl4	178.18 (4)	O7—Na1—O1	85.23 (15)
Cl2—Ir1—Cl4	89.47 (4)	O6—Na1—O1	97.20 (14)
O1—Ir1—Cl1	91.66 (9)	O5^{ii}—Na1—O1	132.91 (15)
N1—Ir1—Cl1	174.39 (10)	O7—Na1—Cl1	89.04 (15)
Cl3—Ir1—Cl1	90.41 (4)	O6—Na1—Cl1	75.95 (12)
Cl2—Ir1—Cl1	88.43 (4)	O5^{ii}—Na1—Cl1	155.27 (14)
Cl4—Ir1—Cl1	91.38 (4)	O1—Na1—Cl1	69.85 (9)
O1—Ir1—Na1	38.75 (9)	O7—Na1—Ir1	89.20 (14)
N1—Ir1—Na1	121.17 (10)	O6—Na1—Ir1	84.81 (11)

Cl3—Ir1—Na1	95.77 (5)	O5^{ii}—Na1—Ir1	162.31 (13)
Cl2—Ir1—Na1	141.10 (5)	O1—Na1—Ir1	29.72 (7)
Cl4—Ir1—Na1	85.56 (5)	Cl1—Na1—Ir1	40.36 (3)
Cl1—Ir1—Na1	53.24 (5)	O7—Na1—Na2^{ii}	114.37 (14)
O2—Ir2—N2	82.71 (12)	O6—Na1—Na2^{ii}	71.20 (11)
O2—Ir2—Cl6	178.32 (9)	O5^{ii}—Na1—Na2^{ii}	36.66 (10)
N2—Ir2—Cl6	95.61 (9)	O1—Na1—Na2^{ii}	149.44 (12)
O2—Ir2—Cl8	89.03 (9)	Cl1—Na1—Na2^{ii}	130.21 (8)
N2—Ir2—Cl8	87.66 (10)	Ir1—Na1—Na2^{ii}	155.92 (7)
Cl6—Ir2—Cl8	90.94 (4)	C14—O2—Ir2	116.7 (2)
O2—Ir2—Cl7	90.69 (9)	C14—O2—Na2	134.5 (2)
N2—Ir2—Cl7	90.39 (10)	Ir2—O2—Na2	108.73 (12)
Cl6—Ir2—Cl7	89.28 (4)	C9—N2—C13	120.3 (3)
Cl8—Ir2—Cl7	178.05 (4)	C9—N2—Ir2	125.7 (3)
O2—Ir2—Cl5	91.18 (8)	C13—N2—Ir2	113.8 (2)
N2—Ir2—Cl5	173.79 (10)	Na1—O6—H6A	109 (5)
Cl6—Ir2—Cl5	90.50 (4)	Na1—O6—H6B	125 (5)
Cl8—Ir2—Cl5	91.19 (4)	H6A—O6—H6B	104 (6)
Cl7—Ir2—Cl5	90.75 (4)	Na1^{i}—O5—Na2	106.96 (16)
O2—Ir2—Na2	41.61 (9)	Na1^{i}—O5—H5A	109 (4)
N2—Ir2—Na2	124.27 (10)	Na2—O5—H5A	108 (4)
Cl6—Ir2—Na2	140.07 (4)	Na1^{i}—O5—H5B	124 (5)
Cl8—Ir2—Na2	89.03 (4)	Na2—O5—H5B	102 (5)
Cl7—Ir2—Na2	92.04 (4)	H5A—O5—H5B	105 (6)
Cl5—Ir2—Na2	49.58 (4)	C6—O1—Ir1	116.6 (2)
Ir1—Cl1—Na2	110.68 (6)	C6—O1—Na1	131.4 (2)
Ir1—Cl1—Na1	86.39 (6)	Ir1—O1—Na1	111.53 (14)
Na2—Cl1—Na1	160.15 (8)	N2—C13—C12	120.4 (4)
Ir2—Cl5—Na2	90.87 (5)	N2—C13—C14	116.4 (3)
C1—N1—C5	120.9 (4)	C12—C13—C14	123.2 (4)
C1—N1—Ir1	125.3 (3)	C12—C11—C10	119.1 (4)
C5—N1—Ir1	113.8 (3)	C12—C11—H11	120.5
N1—C1—C2	121.2 (4)	C10—C11—H11	120.5
N1—C1—H1	119.4	C9—C10—C11	119.0 (4)
C2—C1—H1	119.4	C9—C10—H10	120.5
C3—C4—C5	119.7 (4)	C11—C10—H10	120.5
C3—C4—H4	120.1	O2—C14—C13	109.9 (3)
C5—C4—H4	120.1	O2—C14—C15	107.6 (3)
C4—C3—C2	119.1 (4)	C13—C14—C15	110.6 (3)

C4—C3—H3	120.4	O2—C14—C16	107.6 (3)
C2—C3—H3	120.4	C13—C14—C16	109.2 (3)
C1—C2—C3	118.9 (4)	C15—C14—C16	111.9 (4)
C1—C2—H2	120.5	O1—C6—C5	110.4 (3)
C3—C2—H2	120.5	O1—C6—C8	107.1 (3)
N1—C5—C4	120.1 (4)	C5—C6—C8	111.0 (4)
N1—C5—C6	116.3 (3)	O1—C6—C7	107.0 (3)
C4—C5—C6	123.6 (4)	C5—C6—C7	109.8 (3)
O5—Na2—O3	114.71 (14)	C8—C6—C7	111.5 (4)
O5—Na2—O4	156.40 (15)	N2—C9—C10	121.2 (4)
O3—Na2—O4	87.85 (14)	N2—C9—H9	119.4
O5—Na2—O2	79.23 (12)	C10—C9—H9	119.4
O3—Na2—O2	154.54 (14)	C11—C12—C13	119.9 (4)
O4—Na2—O2	77.23 (12)	C11—C12—H12	120.1
O5—Na2—Cl1	93.58 (10)	C13—C12—H12	120.1
O3—Na2—Cl1	107.98 (11)	C14—C15—H15A	109.5
O4—Na2—Cl1	85.31 (10)	C14—C15—H15B	109.5
O2—Na2—Cl1	91.44 (9)	H15A—C15—H15B	109.5
O5—Na2—Cl5	81.25 (10)	C14—C15—H15C	109.5
O3—Na2—Cl5	91.14 (11)	H15A—C15—H15C	109.5
O4—Na2—Cl5	91.97 (10)	H15B—C15—H15C	109.5
O2—Na2—Cl5	69.19 (8)	Na2—O4—H4A	120 (5)
Cl1—Na2—Cl5	160.53 (9)	Na2—O4—H4B	98 (5)
O5—Na2—Ir2	78.69 (9)	H4A—O4—H4B	101 (6)
O3—Na2—Ir2	128.46 (11)	Na1—O7—H7D	117 (5)
O4—Na2—Ir2	81.73 (9)	Na1—O7—H7E	120 (4)
O2—Na2—Ir2	29.66 (6)	H7D—O7—H7E	115 (6)
Cl1—Na2—Ir2	121.09 (7)	C14—C16—H16A	109.5
Cl5—Na2—Ir2	39.55 (3)	C14—C16—H16B	109.5
O5—Na2—Na1^{i}	36.38 (10)	H16A—C16—H16B	109.5
O3—Na2—Na1^{i}	81.34 (10)	C14—C16—H16C	109.5
O4—Na2—Na1^{i}	155.51 (12)	H16A—C16—H16C	109.5
O2—Na2—Na1^{i}	103.96 (9)	H16B—C16—H16C	109.5
Cl1—Na2—Na1^{i}	118.90 (7)	C6—C8—H8A	109.5
Cl5—Na2—Na1^{i}	66.50 (6)	C6—C8—H8B	109.5
Ir2—Na2—Na1^{i}	87.88 (5)	H8A—C8—H8B	109.5
O5—Na2—H5B	17.7 (8)	C6—C8—H8C	109.5
O3—Na2—H5B	118.4 (14)	H8A—C8—H8C	109.5
O4—Na2—H5B	151.2 (12)	H8B—C8—H8C	109.5

O2—Na2—H5B	81.6 (14)	C6—C7—H7A	109.5
Cl1—Na2—H5B	75.9 (8)	C6—C7—H7B	109.5
Cl5—Na2—H5B	98.5 (8)	H7A—C7—H7B	109.5
Ir2—Na2—H5B	89.4 (12)	C6—C7—H7C	109.5
Na1^{i}—Na2—H5B	49.7 (10)	H7A—C7—H7C	109.5
O5—Na2—H4B	139.4 (8)	H7B—C7—H7C	109.5

Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*-1, *y*, *z*.

*Geometric parameters (Å, º) for **4**[iii]*

Ir1—O2	2.022 (6)	C8—H8A	0.9600
Ir1—N2	2.024 (6)	C8—H8B	0.9600
Ir1—N1	2.050 (6)	C8—H8C	0.9600
Ir1—O1	2.079 (5)	C9—C10	1.378 (11)
Ir1—Cl1	2.340 (2)	C9—C14	1.514 (11)
Ir1—Cl2	2.408 (2)	C10—C11	1.403 (12)
N1—C5	1.360 (10)	C10—H10	0.9300
N1—C1	1.363 (10)	C11—C12	1.386 (12)
N2—C13	1.354 (9)	C11—H11	0.9300
N2—C9	1.393 (9)	C12—C13	1.356 (10)
O1—C6	1.475 (8)	C12—H12	0.9300
O1—H1	0.82 (2)	C13—H13	0.9300
O2—C14	1.435 (10)	C14—C16	1.522 (12)
C1—C2	1.399 (11)	C14—C15	1.533 (12)
C1—C6	1.527 (11)	C15—H15A	0.9600
C2—C3	1.393 (12)	C15—H15B	0.9600
C2—H2	0.9300	C15—H15C	0.9600
C3—C4	1.371 (12)	C16—H16A	0.9600
C3—H3	0.9300	C16—H16B	0.9600
C4—C5	1.385 (10)	C16—H16C	0.9600
C4—H4	0.9300	C50—Cl3	1.64 (3)
C5—H5	0.9300	C50—Cl4	1.78 (3)
C6—C8	1.519 (11)	C50—H50A	0.9700
C6—C7	1.540 (11)	C50—H50B	0.9700
C7—H7A	0.9600	O3—H3A	0.82 (2)
C7—H7B	0.9600	O3—H3B	0.82 (2)
C7—H7C	0.9600		

O2—Ir1—N2	81.3 (2)	C6—C7—H7C	109.5

O2—Ir1—N1	92.5 (2)	H7A—C7—H7C	109.5
N2—Ir1—N1	173.3 (2)	H7B—C7—H7C	109.5
O2—Ir1—O1	87.6 (2)	C6—C8—H8A	109.5
N2—Ir1—O1	96.6 (2)	C6—C8—H8B	109.5
N1—Ir1—O1	80.7 (2)	H8A—C8—H8B	109.5
O2—Ir1—Cl1	91.40 (17)	C6—C8—H8C	109.5
N2—Ir1—Cl1	86.79 (18)	H8A—C8—H8C	109.5
N1—Ir1—Cl1	95.78 (18)	H8B—C8—H8C	109.5
O1—Ir1—Cl1	176.27 (14)	C10—C9—N2	120.4 (7)
O2—Ir1—Cl2	176.87 (15)	C10—C9—C14	124.7 (7)
N2—Ir1—Cl2	96.89 (18)	N2—C9—C14	114.9 (7)
N1—Ir1—Cl2	89.25 (19)	C9—C10—C11	119.8 (7)
O1—Ir1—Cl2	90.11 (15)	C9—C10—H10	120.1
Cl1—Ir1—Cl2	91.03 (8)	C11—C10—H10	120.1
C5—N1—C1	119.4 (7)	C12—C11—C10	119.6 (7)
C5—N1—Ir1	124.5 (5)	C12—C11—H11	120.2
C1—N1—Ir1	116.0 (5)	C10—C11—H11	120.2
C13—N2—C9	117.6 (6)	C13—C12—C11	118.1 (8)
C13—N2—Ir1	126.9 (5)	C13—C12—H12	121.0
C9—N2—Ir1	115.0 (5)	C11—C12—H12	121.0
C6—O1—Ir1	115.2 (4)	N2—C13—C12	124.6 (8)
C6—O1—H1	111 (7)	N2—C13—H13	117.7
Ir1—O1—H1	112 (6)	C12—C13—H13	117.7
C14—O2—Ir1	114.9 (5)	O2—C14—C9	110.4 (7)
N1—C1—C2	120.5 (7)	O2—C14—C16	107.4 (7)
N1—C1—C6	117.9 (7)	C9—C14—C16	110.9 (7)
C2—C1—C6	121.6 (7)	O2—C14—C15	110.1 (7)
C3—C2—C1	119.5 (8)	C9—C14—C15	107.8 (7)
C3—C2—H2	120.2	C16—C14—C15	110.3 (8)
C1—C2—H2	120.2	C14—C15—H15A	109.5
C4—C3—C2	119.2 (8)	C14—C15—H15B	109.5
C4—C3—H3	120.4	H15A—C15—H15B	109.5
C2—C3—H3	120.4	C14—C15—H15C	109.5
C3—C4—C5	119.9 (8)	H15A—C15—H15C	109.5
C3—C4—H4	120.1	H15B—C15—H15C	109.5
C5—C4—H4	120.1	C14—C16—H16A	109.5
N1—C5—C4	121.5 (8)	C14—C16—H16B	109.5
N1—C5—H5	119.3	H16A—C16—H16B	109.5
C4—C5—H5	119.3	C14—C16—H16C	109.5

O1—C6—C8	106.6 (6)	H16A—C16—H16C	109.5
O1—C6—C1	109.8 (6)	H16B—C16—H16C	109.5
C8—C6—C1	111.0 (7)	Cl3—C50—Cl4	113.8 (13)
O1—C6—C7	108.0 (6)	Cl3—C50—H50A	108.8
C8—C6—C7	111.8 (7)	Cl4—C50—H50A	108.8
C1—C6—C7	109.4 (6)	Cl3—C50—H50B	108.8
C6—C7—H7A	109.5	Cl4—C50—H50B	108.8
C6—C7—H7B	109.5	H50A—C50—H50B	107.7
H7A—C7—H7B	109.5	H3A—O3—H3B	110 (10)

*Geometric parameters (Å, º) for **6**[iii]*

Ir1—N1	1.997 (4)	C7—H7C	0.9800
Ir1—O2	2.010 (3)	C8—H8A	0.9800
Ir1—N2	2.013 (4)	C8—H8B	0.9800
Ir1—O1	2.072 (3)	C8—H8C	0.9800
Ir1—Cl1	2.3506 (11)	C9—C10	1.389 (7)
Ir1—Cl2	2.3790 (12)	C9—C14	1.525 (7)
N1—C1	1.337 (7)	C10—C11	1.355 (8)
N1—C5	1.361 (7)	C10—H10	0.9500
N2—C9	1.337 (6)	C11—C12	1.391 (8)
N2—C13	1.357 (6)	C11—H11	0.9500
O1—C14	1.458 (6)	C12—C13	1.369 (7)
O1—H1	0.85 (2)	C12—H12	0.9500
O2—C6	1.434 (6)	C13—H13	0.9500
C1—C2	1.389 (7)	C14—C15	1.505 (8)
C1—C6	1.519 (8)	C14—C16	1.528 (8)
C2—C3	1.387 (9)	C15—H15A	0.9800
C2—H2	0.9500	C15—H15B	0.9800
C3—C4	1.376 (9)	C15—H15C	0.9800
C3—H3	0.9500	C16—H16A	0.9800
C4—C5	1.367 (8)	C16—H16B	0.9800
C4—H4	0.9500	C16—H16C	0.9800
C6—C7	1.527 (9)	O3—H3A	0.83 (2)
C6—C8	1.549 (8)	O3—H3B	0.77 (8)
C7—H7A	0.9800	C5—H5	0.9500
C7—H7B	0.9800		

N1—Ir1—O2	82.45 (16)	C6—C7—H7C	109.5

N1—Ir1—N2	98.32 (16)	H7A—C7—H7C	109.5
O2—Ir1—N2	89.89 (15)	H7B—C7—H7C	109.5
N1—Ir1—O1	170.35 (16)	C6—C8—H8A	109.5
O2—Ir1—O1	88.17 (14)	C6—C8—H8B	109.5
N2—Ir1—O1	79.32 (15)	H8A—C8—H8B	109.5
N1—Ir1—Cl1	86.43 (12)	C6—C8—H8C	109.5
O2—Ir1—Cl1	89.06 (10)	H8A—C8—H8C	109.5
N2—Ir1—Cl1	174.96 (12)	H8B—C8—H8C	109.5
O1—Ir1—Cl1	95.71 (10)	N2—C9—C10	120.6 (4)
N1—Ir1—Cl2	98.20 (13)	N2—C9—C14	118.3 (4)
O2—Ir1—Cl2	179.23 (10)	C10—C9—C14	121.1 (4)
N2—Ir1—Cl2	89.61 (12)	C11—C10—C9	121.4 (5)
O1—Ir1—Cl2	91.17 (10)	C11—C10—H10	119.3
Cl1—Ir1—Cl2	91.39 (4)	C9—C10—H10	119.3
C1—N1—C5	119.3 (5)	C10—C11—C12	117.9 (5)
C1—N1—Ir1	115.3 (4)	C10—C11—H11	121.1
C5—N1—Ir1	125.2 (4)	C12—C11—H11	121.1
C9—N2—C13	118.7 (4)	C13—C12—C11	119.3 (5)
C9—N2—Ir1	117.2 (3)	C13—C12—H12	120.4
C13—N2—Ir1	124.1 (3)	C11—C12—H12	120.4
C14—O1—Ir1	116.2 (3)	N2—C13—C12	122.2 (5)
C14—O1—H1	111 (5)	N2—C13—H13	118.9
Ir1—O1—H1	120 (5)	C12—C13—H13	118.9
C6—O2—Ir1	114.2 (3)	O1—C14—C15	107.8 (4)
N1—C1—C2	121.1 (5)	O1—C14—C9	107.1 (4)
N1—C1—C6	116.6 (4)	C15—C14—C9	111.5 (4)
C2—C1—C6	122.2 (5)	O1—C14—C16	108.9 (4)
C3—C2—C1	119.3 (6)	C15—C14—C16	112.7 (5)
C3—C2—H2	120.4	C9—C14—C16	108.7 (4)
C1—C2—H2	120.4	C14—C15—H15A	109.5
C2—C3—C4	119.0 (5)	C14—C15—H15B	109.5
C2—C3—H3	120.5	H15A—C15—H15B	109.5
C4—C3—H3	120.5	C14—C15—H15C	109.5
C5—C4—C3	119.5 (6)	H15A—C15—H15C	109.5
C5—C4—H4	120.2	H15B—C15—H15C	109.5
C3—C4—H4	120.2	C14—C16—H16A	109.5
O2—C6—C1	111.2 (4)	C14—C16—H16B	109.5
O2—C6—C7	108.1 (5)	H16A—C16—H16B	109.5
C1—C6—C7	110.4 (5)	C14—C16—H16C	109.5

O2—C6—C8	106.9 (5)	H16A—C16—H16C	109.5
C1—C6—C8	109.3 (5)	H16B—C16—H16C	109.5
C7—C6—C8	110.8 (6)	H3A—O3—H3B	107 (7)
C6—C7—H7A	109.5	N1—C5—C4	121.7 (5)
C6—C7—H7B	109.5	N1—C5—H5	119.2
H7A—C7—H7B	109.5	C4—C5—H5	119.2

Section V. The Frontier t_{2g} Orbitals of the Ir(III) species.

3^{III}

MO

HOMO

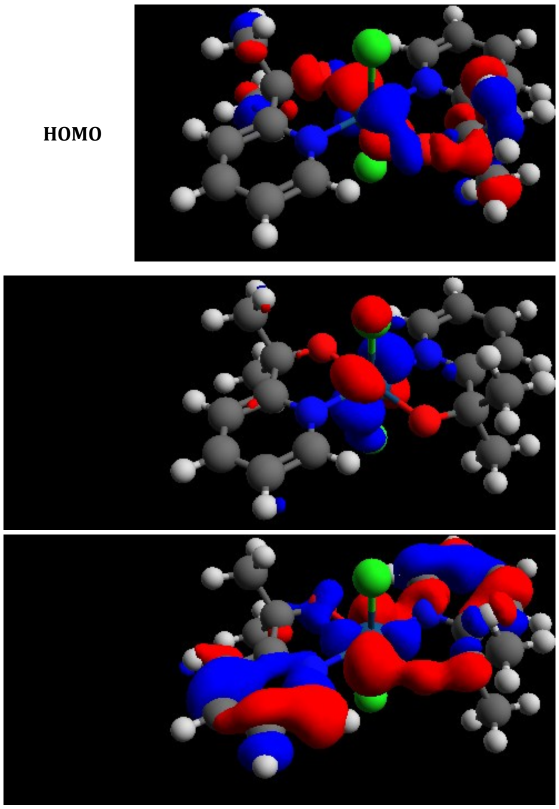


Figure S10. Isosurfaces of the three frontier HOMO orbitals of $\mathbf{3^{III}}$, calculated with an isovalue of 0.05. The energies of the orbitals become more negative going down along a column.

4^{III}

MO

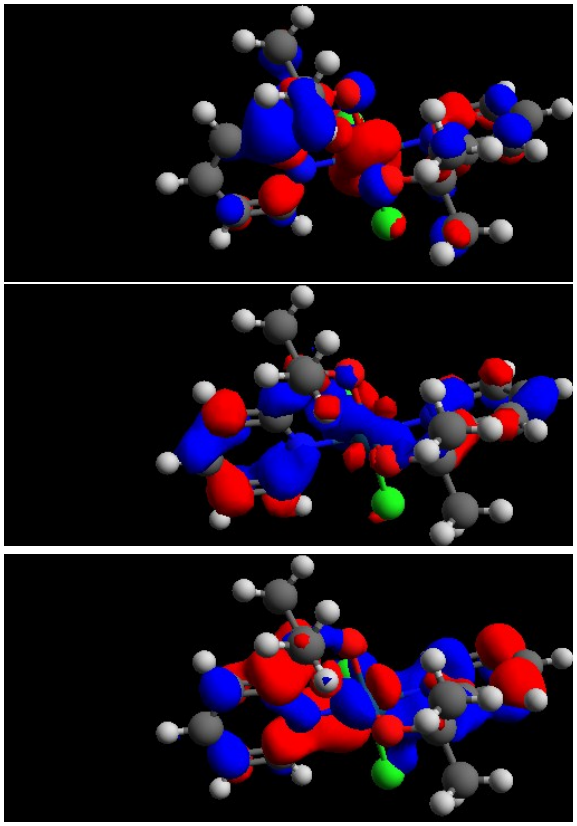


Figure S11. Isosurfaces of the three frontier HOMO orbitals of **4^{III}**, calculated with an isovalue of 0.05. The energies of the orbitals become more negative going down along a column.

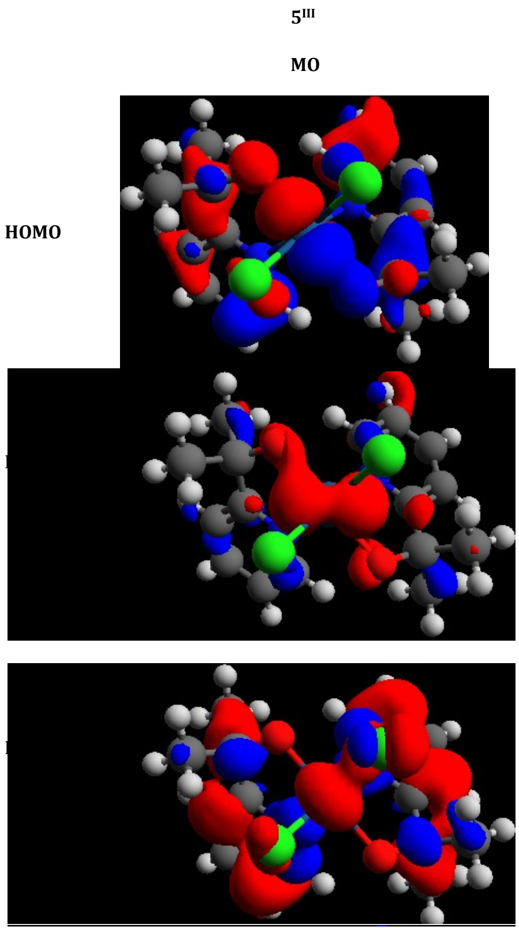


Figure S12. Isosurfaces of the three frontier HOMO orbitals of $\mathbf{5^{III}}$, calculated with an isovalue of 0.05. The energies of the orbitals become more negative going down along a column.

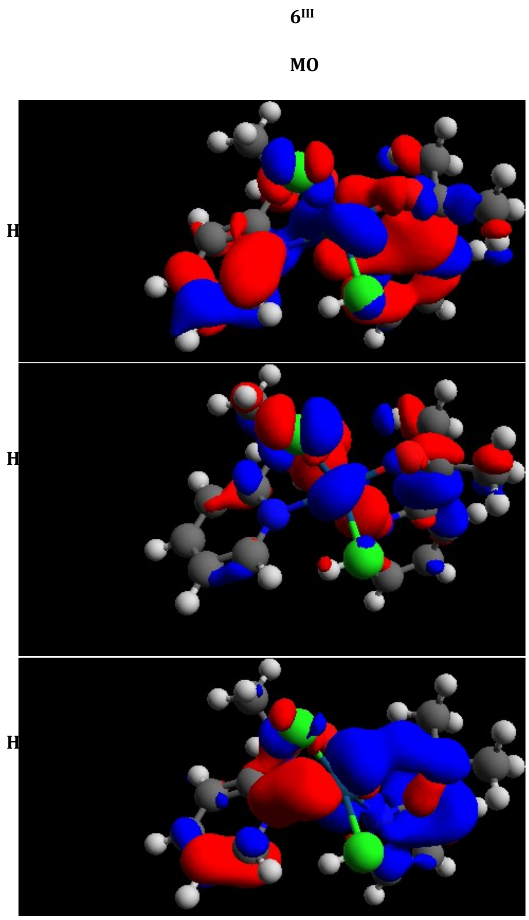


Figure S13. Isosurfaces of the three frontier HOMO orbitals of $\mathbf{6^{III}}$, calculated with an isovalue of 0.05. The energies of the orbitals become more negative going down along a column.

$\mathbf{7^{III}}$

MO

HO

HO

HO

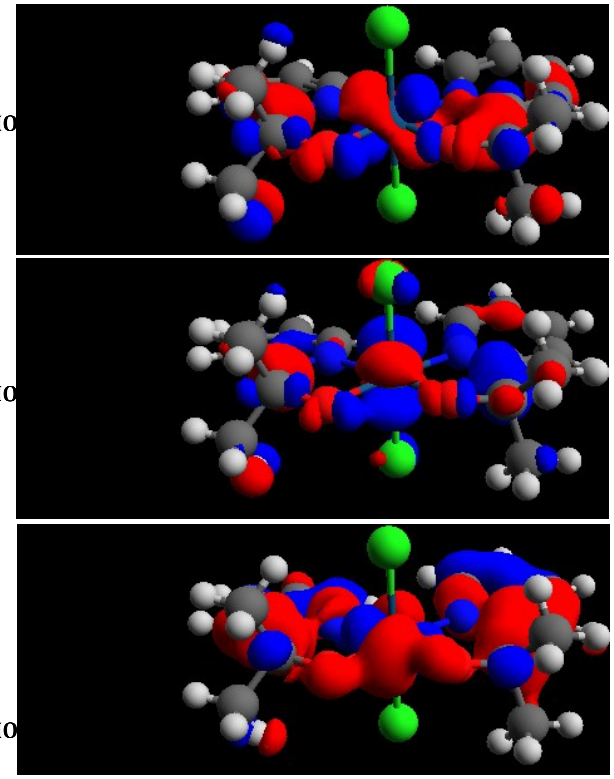


Figure S14. Isosurfaces of the three frontier HOMO orbitals of $\mathbf{7^{III}}$, calculated with an isovalue of 0.05. The energies of the orbitals become more negative going down along a column.

8^{III}

MO

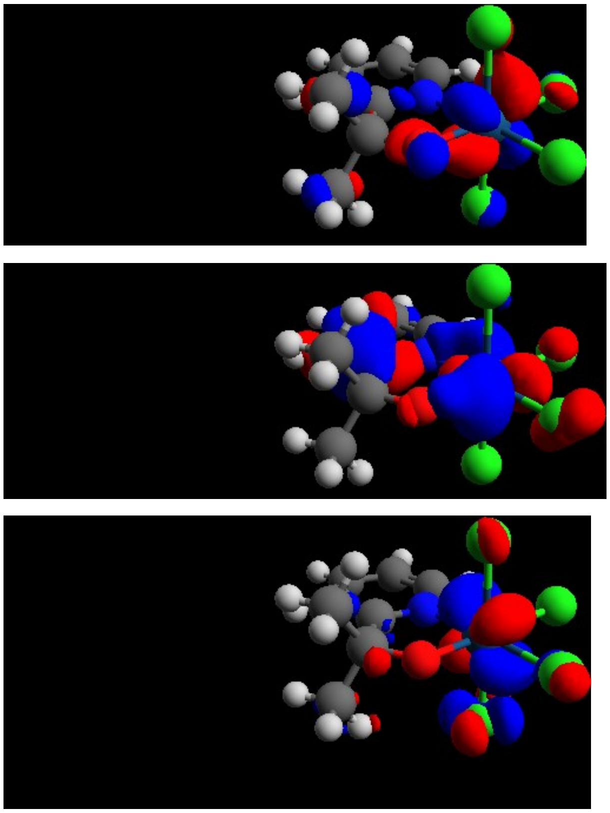


Figure S15. Isosurfaces of the three frontier HOMO orbitals of $\mathbf{8^{III}}$, calculated with an isovalue of 0.05. The energies of the orbitals become more negative going down along a column.

Section VI. The Frontier t_{2g} Orbitals of the Ir(III) species.

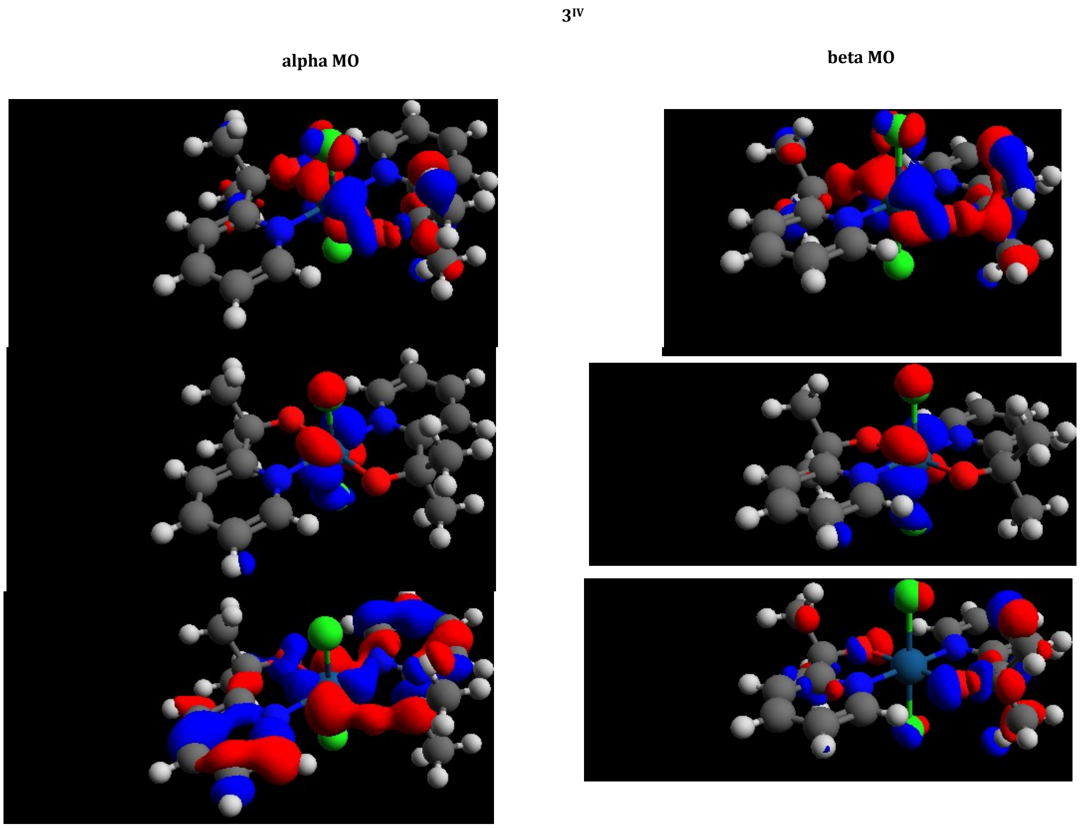


Figure S16. Isosurfaces of the frontier t_{2g} orbitals of $\mathbf{3}^{IV}$, including the occupied SOMO (alpha) and its accompanying unoccupied SOMO (beta) level, calculated with an isovalue of 0.05. The energies of the orbitals become more negative going down along a column.

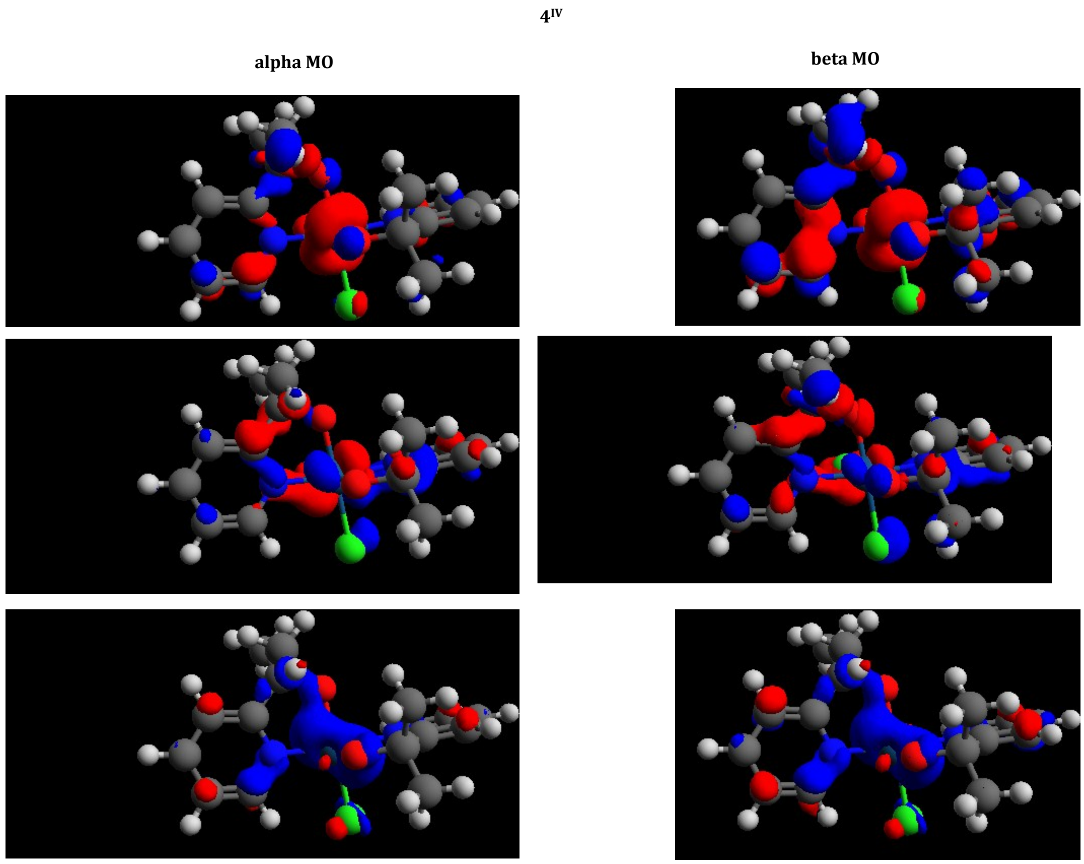


Figure S17. Isosurfaces of the frontier t_{2g} orbitals of $\mathbf{4^{IV}}$, including the occupied SOMO (alpha) and its accompanying unoccupied SOMO (beta) level, calculated with an isovalue of 0.05. The energies of the orbitals become more negative going down along a column.

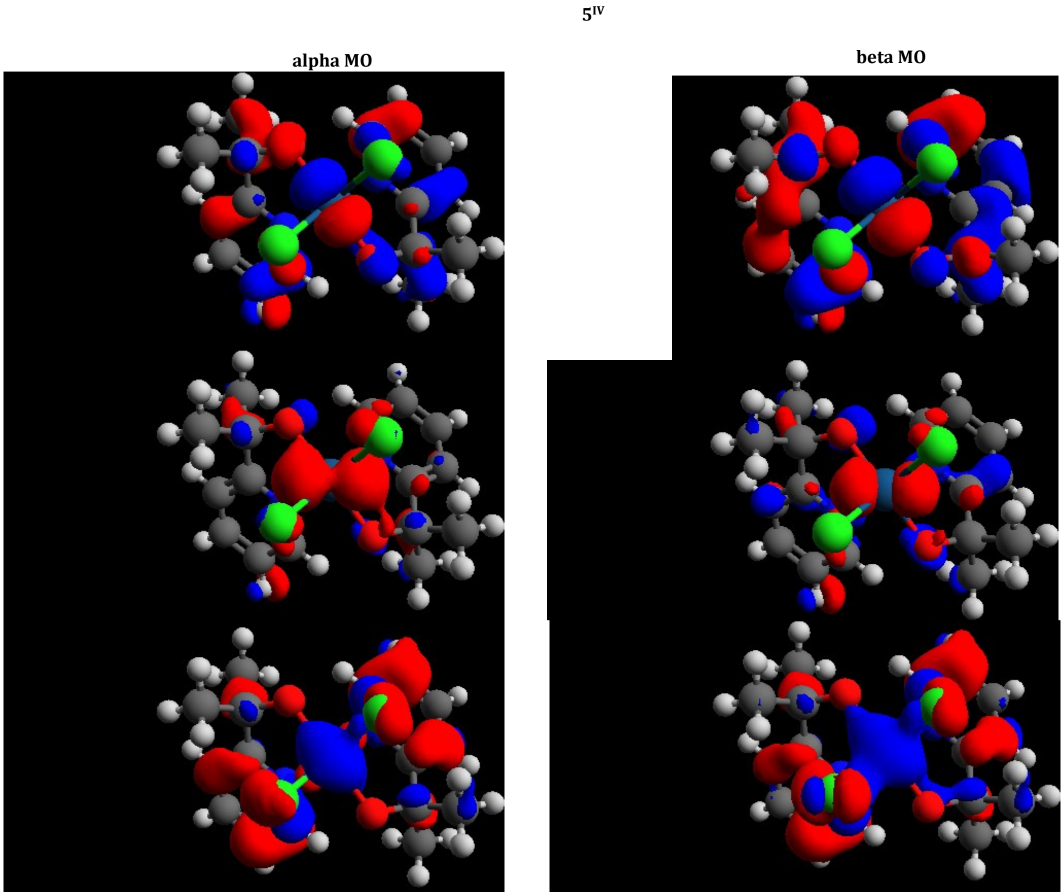


Figure S18. Isosurfaces of the frontier t_{2g} orbitals of $\mathbf{5^{IV}}$, including the occupied SOMO (alpha) and its accompanying unoccupied SOMO (beta) level, calculated with an isovalue of 0.05. The energies of the orbitals become more negative going down along a column.

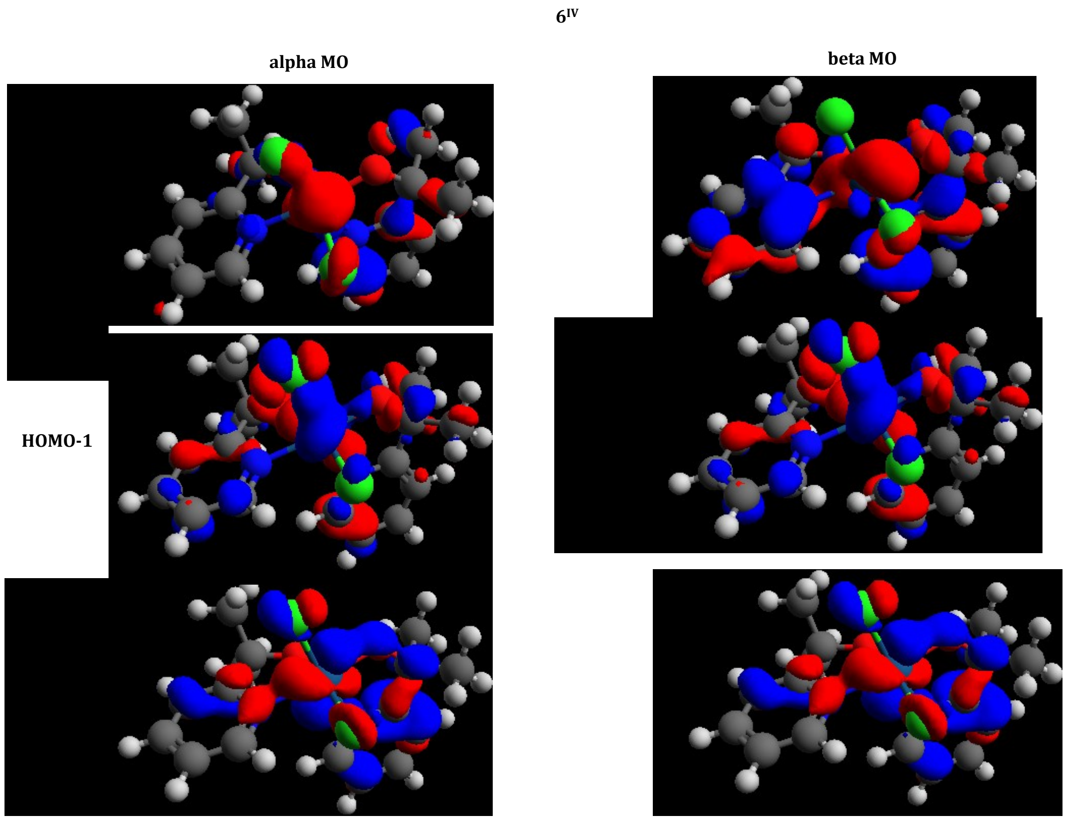


Figure S19. Isosurfaces of the frontier t_{2g} orbitals of $\mathbf{6^{IV}}$, including the occupied SOMO (alpha) and its accompanying unoccupied SOMO (beta) level, calculated with an isovalue of 0.05. The energies of the orbitals become more negative going down along a column.

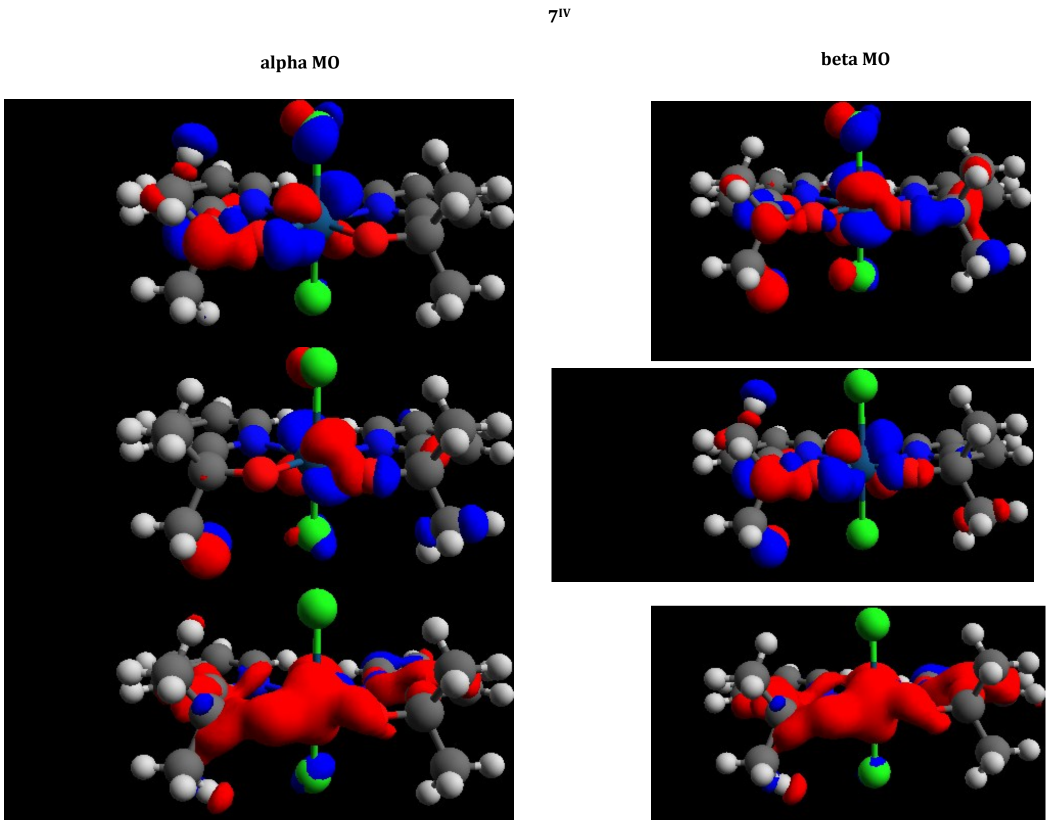


Figure S20. Isosurfaces of the frontier t_{2g} orbitals of $\mathbf{7^{IV}}$, including the occupied SOMO (alpha) and its accompanying unoccupied SOMO (beta) level, calculated with an isovalue of 0.05. The energies of the orbitals become more negative going down along a column.

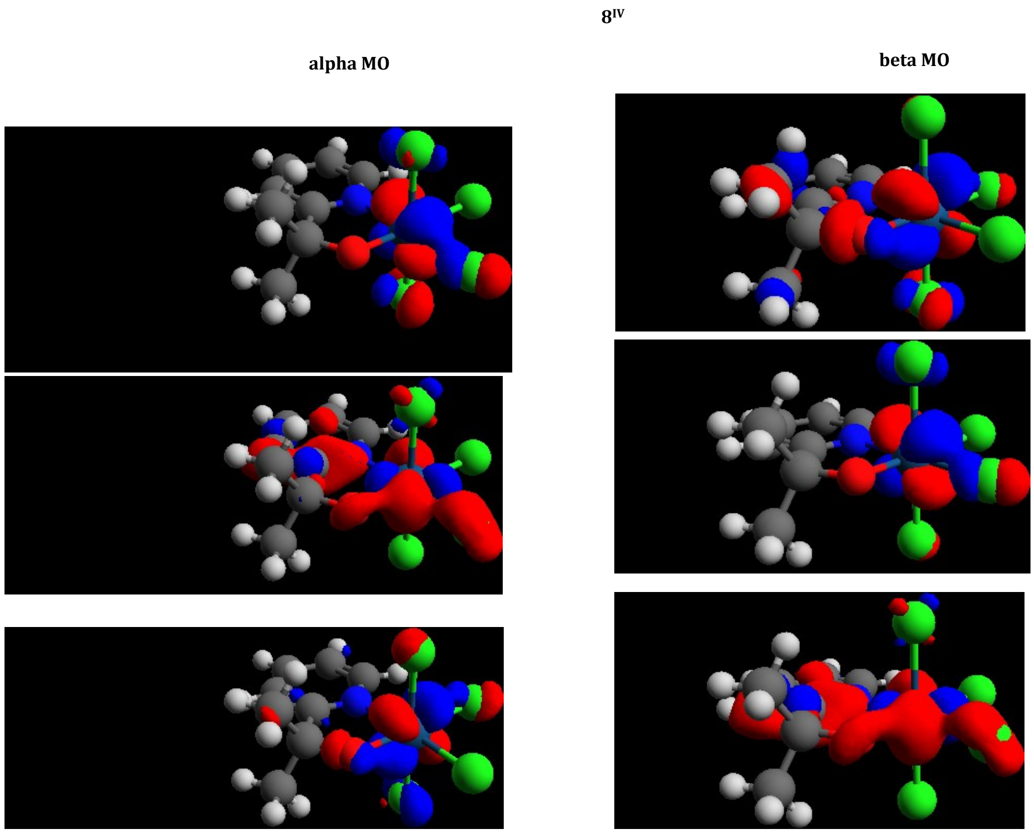


Figure S21. Isosurfaces of the frontier t_{2g} orbitals of $\mathbf{8^{IV}}$, including the occupied SOMO (alpha) and its accompanying unoccupied SOMO (beta) level, calculated with an isovalue of 0.05. The energies of the orbitals become more negative going down along a column.

Section VII: Selected Natural Transition Orbitals

3^{IV}

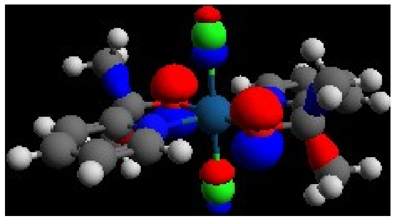
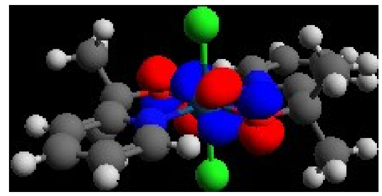
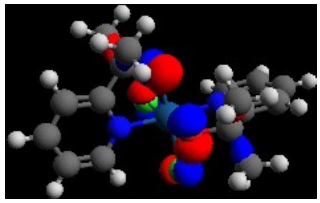
	Initial NTO	**Final NTO**
579.45 nm		

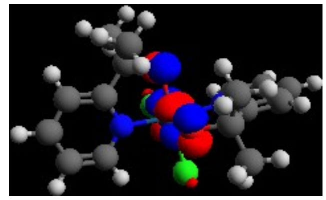
Figure S22. Isosurfaces of the natural transition orbital of $\mathbf{3^{IV}}$, from the ground (left) to the excited (right) state, calculated with an isovalue of 0.05. The wavelength of the transition is indicated.

4^{IV}

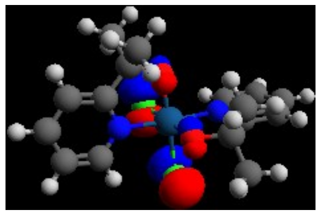
Initial NTO **Final NTO**

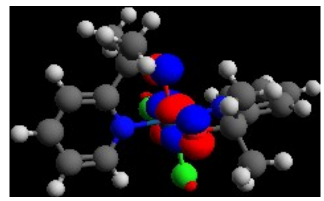
651.16 nm



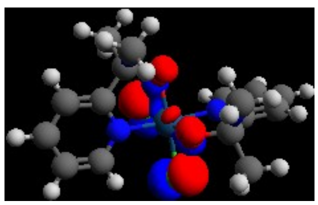


493.66 nm





476.52 nm



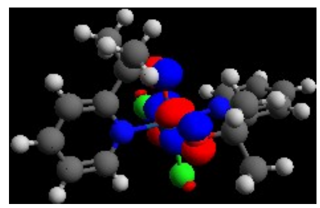


Figure S23. Isosurfaces of the natural transition orbital of **4^{IV}**, from the ground (left) to the excited (right) state, calculated with an isovalue of 0.05. The wavelength of the transition is indicated.

5^{IV}

Initial NTO | **Final NTO**

498.53 nm

413.48 nm

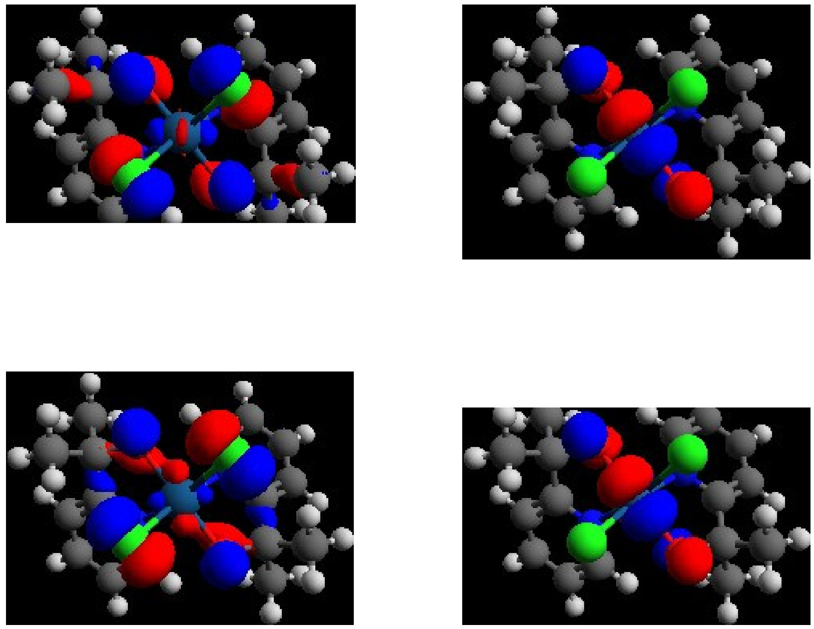


Figure S24. Isosurfaces of the natural transition orbital of **5^{IV}**, from the ground (left) to the excited (right) state, calculated with an isovalue of 0.05. The wavelength of the transition is indicated.

6^{IV}

Initial NTO **Final NTO**

546.45 nm

311.41 nm

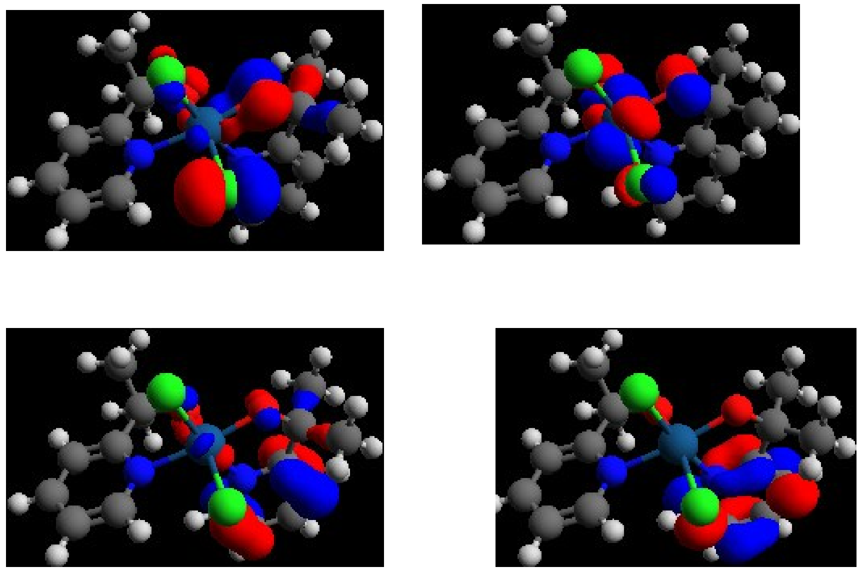


Figure S25. Isosurfaces of the natural transition orbital of **6^{IV}**, from the ground (left) to the excited (right) state, calculated with an isovalue of 0.05. The wavelength of the transition is indicated.

$\mathbf{7^{IV}}$

Initial NTO **Final NTO**

609.85 nm

373.03 nm

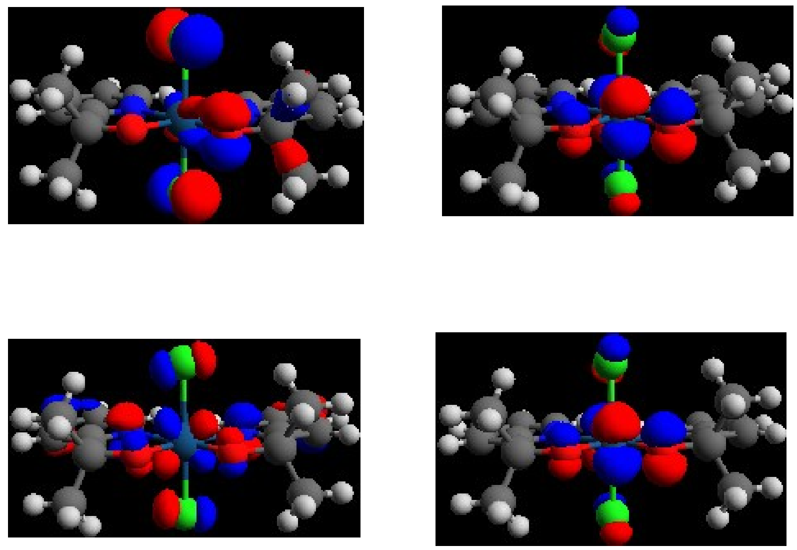


Figure S26. Isosurfaces of the natural transition orbital of **$\mathbf{7^{IV}}$**, from the ground (left) to the excited (right) state, calculated with an isovalue of 0.05. The wavelength of the transition is indicated.

$\mathbf{8^{IV}}$

Initial NTO **Final NTO**

552.79 nm

Figure S27. Isosurfaces of the natural transition orbital of **$\mathbf{8^{IV}}$**, from the ground (left) to the excited (right) state, calculated with an isovalue of 0.05. The wavelength of the transition is indicatedI.

Section VIII. Coordinates for Theoretical Structures

The coordinates for theoretical structures (optimized in dielectric continuum of DCM) are included below in .xyz format labeled with their name and electronic energy (SCF) in Hartrees.

43
3(III) SCF Energy: -1906.83027390 a.u.

Ir	0.00000	0.00000	0.00000
C	-2.91050	-0.11740	-0.00143
C	-2.14125	2.10340	-0.00047
C	-4.23506	0.33868	-0.00217
C	-3.43417	2.60807	-0.00117
H	-1.26180	2.73863	0.00023
C	-4.50289	1.70564	-0.00207
H	-5.04762	-0.38000	-0.00284
H	-3.59418	3.68109	-0.00103
H	-5.52874	2.06301	-0.00267
N	-1.89317	0.77664	-0.00062
C	-2.50849	-1.59810	-0.00130
O	-1.11351	-1.75227	-0.00088
C	-3.09623	-2.27609	1.26301
H	-4.19188	-2.23250	1.29664
H	-2.79442	-3.32945	1.26402
H	-2.69472	-1.80388	2.16467
C	-3.09538	-2.27627	-1.26589
H	-2.79352	-3.32961	-1.26656
H	-4.19100	-2.23274	-1.30025
H	-2.69329	-1.80417	-2.16735
O	1.11351	1.75228	0.00089
C	2.50849	1.59810	0.00130
C	2.91050	0.11740	0.00143
C	3.09539	2.27628	1.26589
C	3.09623	2.27609	-1.26302
C	4.23506	-0.33868	0.00216
N	1.89317	-0.77664	0.00063
H	4.19102	2.23274	1.30023
H	2.79353	3.32962	1.26655
H	2.69331	1.80418	2.16735
H	2.79441	3.32945	-1.26402
H	4.19187	2.23249	-1.29666
H	2.69470	1.80388	-2.16467
C	4.50288	-1.70564	0.00206
H	5.04762	0.38000	0.00282
C	2.14125	-2.10340	0.00047

C	3.43417	-2.60807	0.00117
H	5.52873	-2.06301	0.00265
H	1.26179	-2.73863	-0.00022
H	3.59418	-3.68109	0.00104
Cl	-0.00079	-0.00059	2.43709
Cl	0.00079	0.00060	-2.43709

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4(III) SCF Energy: -1906.83172548 a.u.

Ir	0.01636	-0.43480	0.02631
C	2.67634	0.69105	0.21881
C	2.66894	-1.07656	-1.32438
C	4.04620	0.88041	0.00366
C	4.02670	-0.93043	-1.57653
H	2.06483	-1.83194	-1.81339
C	4.73031	0.06806	-0.89796
H	4.56862	1.66335	0.54222
H	4.51441	-1.58955	-2.28706
H	5.79380	0.21054	-1.06750
N	2.01188	-0.28377	-0.45160
C	1.83056	1.55673	1.15707
O	0.57249	0.96446	1.39379
C	2.52939	1.71737	2.52458
H	3.48001	2.25779	2.45084
H	1.86648	2.28612	3.18542
H	2.71162	0.73989	2.98178
C	1.65545	2.94868	0.49502
H	1.06790	3.58634	1.16576
H	2.61781	3.44118	0.30637
H	1.11075	2.83843	-0.44586
O	-0.53077	1.04965	-1.25848
C	-1.90108	1.38253	-1.26806
C	-2.67699	0.61135	-0.19769
C	-2.49325	1.04796	-2.66039
C	-2.04151	2.90164	-1.00312
C	-4.04097	0.80301	0.05324
N	-1.97543	-0.30055	0.52086
H	-3.54967	1.33026	-2.74508
H	-1.92780	1.59804	-3.42096
H	-2.39210	-0.02173	-2.86319
H	-1.44437	3.44142	-1.74583
H	-3.07943	3.24539	-1.08520
H	-1.66610	3.15580	-0.00733
C	-4.68082	0.06088	1.04269
H	-4.59232	1.53316	-0.52917
C	-2.58979	-1.02355	1.48217

C	-3.93876	-0.87149	1.77297
H	-5.73883	0.20653	1.24106
H	-1.95882	-1.73119	2.00737
H	-4.39036	-1.47461	2.55362
Cl	-0.59842	-2.17630	-1.65819
Cl	0.65879	-2.21412	1.65233

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5(III) SCF Energy: -1906.82586028 a.u.

Ir	0.00166	-0.71720	0.00166
O	1.35362	-0.54764	-1.57463
C	2.53120	0.15425	-1.26626
C	2.36774	0.95285	0.03435
C	2.84821	1.11710	-2.43626
C	3.72012	-0.82965	-1.09447
C	3.29701	1.89134	0.49868
N	1.25836	0.68619	0.77167
H	3.81174	1.62506	-2.31385
H	2.88741	0.53266	-3.36171
H	2.06764	1.87752	-2.54374
H	3.83835	-1.39338	-2.02688
H	4.66314	-0.31120	-0.87993
H	3.50663	-1.53641	-0.28934
C	3.08997	2.54329	1.71230
H	4.18162	2.10097	-0.09286
C	1.05612	1.30038	1.95750
C	1.94822	2.23827	2.45886
H	3.81055	3.27129	2.07389
H	0.15498	0.99295	2.47676
H	1.75026	2.71040	3.41558
O	-1.35061	-0.54729	1.57762
C	-2.52950	0.15187	1.26793
C	-2.36794	0.94755	-0.03472
C	-2.84781	1.11727	2.43549
C	-3.71678	-0.83457	1.09927
C	-3.29993	1.88195	-0.50184
N	-1.25760	0.68225	-0.77104
H	-3.81221	1.62331	2.31191
H	-2.88583	0.53523	3.36249
H	-2.06851	1.87930	2.54076
H	-3.83415	-1.39545	2.03352
H	-4.66071	-0.31851	0.88298
H	-3.50197	-1.54356	0.29646
C	-3.09471	2.53097	-1.71733
H	-4.18528	2.09055	0.08896
C	-1.05690	1.29376	-1.95850

C	-1.95183	2.22738	-2.46277
H	-3.81759	3.25551	-2.08127
H	-0.15476	0.98752	-2.47671
H	-1.75521	2.69722	-3.42089
Cl	-1.32815	-2.43076	-1.16718
Cl	1.33323	-2.42818	1.17283

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6(III) SCF Energy: -1906.82772400 a.u.

Ir	0.04262	-0.64195	-0.17763
C	2.51425	0.80772	0.14074
C	0.92396	2.14119	-0.95593
C	3.44193	1.85254	0.06715
C	1.80822	3.20648	-1.05736
H	-0.08244	2.20115	-1.35086
C	3.09480	3.06108	-0.53202
H	4.43477	1.71012	0.47923
H	1.48812	4.12371	-1.54027
H	3.81478	3.87212	-0.59223
N	1.26388	0.97413	-0.36631
C	2.79741	-0.55491	0.78078
O	1.82221	-1.48566	0.38926
C	4.17204	-1.08839	0.32120
H	5.00708	-0.47169	0.67317
H	4.30062	-2.09681	0.72822
H	4.21548	-1.15344	-0.77072
C	2.79853	-0.37992	2.32367
H	3.02360	-1.34913	2.78382
H	3.54917	0.34670	2.66082
H	1.80703	-0.05949	2.65410
O	-0.42233	-0.00194	1.70294
C	-1.70213	0.56908	1.86621
C	-2.40619	0.77373	0.52161
C	-1.53194	1.93409	2.57627
C	-2.57188	-0.36446	2.74646
C	-3.64764	1.40891	0.39488
N	-1.77385	0.28526	-0.57540
H	-2.49191	2.41033	2.80744
H	-0.99505	1.77410	3.51737
H	-0.94208	2.61964	1.95861
H	-2.06335	-0.51301	3.70551
H	-3.56594	0.05491	2.94394
H	-2.68326	-1.33759	2.26106
C	-4.24525	1.53321	-0.85695
H	-4.14154	1.79544	1.27979
C	-2.35646	0.39139	-1.79059

C	-3.58703	1.00864	-1.97270
H	-5.20864	2.02441	-0.95970
H	-1.79623	-0.04027	-2.61225
H	-4.01477	1.06895	-2.96806
Cl	0.56859	-1.26076	-2.54195
Cl	-1.22023	-2.72679	0.14035

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7(III) SCF Energy: -1906.82157111 a.u.

Ir	0.00035	-0.27949	0.00003
C	-2.89361	0.25681	0.02774
C	-1.75943	2.26495	-0.30345
C	-4.11531	0.94143	0.02451
C	-2.93930	2.99621	-0.33093
H	-0.80970	2.75477	-0.46447
C	-4.14813	2.32222	-0.14434
H	-5.03577	0.38094	0.14701
H	-2.90041	4.06762	-0.49758
H	-5.09324	2.85750	-0.14677
N	-1.71947	0.93047	-0.09704
C	-2.79413	-1.26399	0.13456
O	-1.47570	-1.68284	-0.08163
C	-3.28827	-1.72019	1.53247
H	-4.33491	-1.44495	1.71407
H	-3.20330	-2.81107	1.59192
H	-2.66140	-1.28340	2.31337
C	-3.68622	-1.91437	-0.95226
H	-3.54845	-3.00001	-0.90366
H	-4.75185	-1.69820	-0.81259
H	-3.38483	-1.57773	-1.94908
O	1.47937	-1.67972	0.08119
C	2.79692	-1.25805	-0.13483
C	2.89316	0.26294	-0.02784
C	3.29213	-1.71322	-1.53271
C	3.69032	-1.90650	0.95207
C	4.11339	0.95018	-0.02475
N	1.71762	0.93405	0.09740
H	4.33806	-1.43542	-1.71444
H	3.20989	-2.80433	-1.59200
H	2.66407	-1.27814	-2.31361
H	3.55487	-2.99244	0.90352
H	4.75549	-1.68807	0.81246
H	3.38815	-1.57045	1.94885
C	4.14327	2.33101	0.14434
H	5.03502	0.39169	-0.14757

C	1.75476	2.26856	0.30413
C	2.93305	3.00237	0.33142
H	5.08723	2.86832	0.14661
H	0.80400	2.75624	0.46552
H	2.89190	4.07365	0.49828
Cl	0.06622	-0.20961	-2.44299
Cl	-0.06577	-0.21123	2.44305

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8(III) SCF Energy: -2386.52080971 a.u.

Ir	-0.45087	-0.54991	0.00000
O	-1.17216	1.35387	0.00000
C	-0.20089	2.37123	0.00000
C	1.21705	1.79668	0.00000
C	-0.39486	3.24451	1.26508
C	-0.39486	3.24451	-1.26508
C	2.37193	2.58782	0.00000
N	1.32233	0.44286	0.00000
H	0.29853	4.09374	1.30292
H	-1.41835	3.63545	1.26314
H	-0.26306	2.63496	2.16383
H	-1.41835	3.63545	-1.26314
H	0.29853	4.09374	-1.30292
H	-0.26306	2.63496	-2.16383
C	3.63062	1.99171	0.00000
H	2.27515	3.66825	0.00000
C	2.53950	-0.14302	0.00000
C	3.71446	0.59688	0.00000
H	4.52872	2.60279	0.00000
H	2.53068	-1.22652	0.00000
H	4.66993	0.08250	0.00000
Cl	-0.39486	-0.53018	2.43833
Cl	-2.73293	-1.46525	0.00000
Cl	0.50509	-2.86176	0.00000
Cl	-0.39486	-0.53018	-2.43833

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3(IV) SCF Energy: -1906.69368033 a.u.

Ir	0.00000	0.00000	-0.00001
C	-2.89922	-0.14949	-0.00000
C	-2.18954	2.09235	0.00000
C	-4.23506	0.26010	-0.00000
C	-3.49815	2.55340	0.00000
H	-1.33474	2.75929	0.00000
C	-4.53859	1.61956	-0.00000
H	-5.02351	-0.48476	-0.00000

H	-3.69172	3.62041	0.00000
H	-5.57370	1.94745	-0.00000
N	-1.91022	0.77308	-0.00000
C	-2.45040	-1.60821	-0.00000
O	-1.02295	-1.67721	-0.00001
C	-2.95839	-2.32734	1.26635
H	-4.05284	-2.34640	1.29566
H	-2.59430	-3.35951	1.25835
H	-2.58787	-1.83189	2.16756
C	-2.95840	-2.32734	-1.26636
H	-2.59431	-3.35952	-1.25835
H	-4.05285	-2.34641	-1.29566
H	-2.58788	-1.83189	-2.16757
O	1.02295	1.67721	-0.00000
C	2.45040	1.60821	-0.00001
C	2.89922	0.14949	-0.00001
C	2.95840	2.32734	1.26635
C	2.95839	2.32735	-1.26636
C	4.23506	-0.26010	-0.00001
N	1.91022	-0.77308	-0.00001
H	4.05285	2.34640	1.29565
H	2.59430	3.35951	1.25835
H	2.58788	1.83188	2.16756
H	2.59430	3.35952	-1.25835
H	4.05285	2.34641	-1.29566
H	2.58787	1.83190	-2.16757
C	4.53859	-1.61956	-0.00002
H	5.02351	0.48476	-0.00001
C	2.18954	-2.09235	-0.00001
C	3.49815	-2.55340	-0.00002
H	5.57370	-1.94745	-0.00002
H	1.33474	-2.75929	-0.00001
H	3.69173	-3.62041	-0.00002
Cl	0.00000	-0.00001	2.41285
Cl	-0.00000	0.00001	-2.41286

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4(IV) SCF Energy: -1906.69051754 a.u.

Ir	0.00000	-0.41984	0.00000
C	2.67922	0.63514	0.21473
C	2.60701	-0.96526	-1.50441
C	4.03640	0.85716	-0.03136
C	3.95270	-0.78321	-1.79059
H	1.98743	-1.67108	-2.04446
C	4.67972	0.14478	-1.04064
H	4.57730	1.58304	0.56568

H	4.41383	-1.36029	-2.58453
H	5.73422	0.31076	-1.23937
N	1.99388	-0.26869	-0.52547
C	1.88772	1.37183	1.29057
O	0.52928	0.91022	1.31826
C	2.48593	1.11209	2.68617
H	3.51054	1.49131	2.75599
H	1.87545	1.62730	3.43434
H	2.48664	0.04245	2.91147
C	1.85526	2.88333	0.98553
H	1.23938	3.38476	1.73847
H	2.86179	3.31260	1.02105
H	1.42778	3.07281	-0.00288
O	-0.52928	0.91020	-1.31827
C	-1.88771	1.37182	-1.29059
C	-2.67922	0.63515	-0.21474
C	-2.48592	1.11204	-2.68619
C	-1.85526	2.88332	-0.98558
C	-4.03640	0.85718	0.03135
N	-1.99388	-0.26868	0.52548
H	-3.51054	1.49126	-2.75602
H	-1.87544	1.62724	-3.43437
H	-2.48663	0.04240	-2.91147
H	-1.23938	3.38473	-1.73853
H	-2.86179	3.31259	-1.02112
H	-1.42778	3.07282	0.00282
C	-4.67972	0.14481	1.04064
H	-4.57730	1.58305	-0.56570
C	-2.60701	-0.96523	1.50443
C	-3.95270	-0.78317	1.79061
H	-5.73422	0.31080	1.23936
H	-1.98743	-1.67104	2.04448
H	-4.41383	-1.36023	2.58455
Cl	-0.63108	-2.18092	-1.56791
Cl	0.63107	-2.18090	1.56794

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5(IV) SCF Energy: -1906.68238738 a.u.

Ir	-0.00094	0.70235	0.00212
O	1.16247	0.43125	1.57596
C	2.44123	-0.17413	1.37645
C	2.42908	-0.90628	0.03703
C	2.66335	-1.16567	2.53432
C	3.54122	0.90777	1.39208
C	3.44916	-1.75692	-0.39506
N	1.35267	-0.68377	-0.75373

H	3.65812	-1.61940	2.48461
H	2.57985	-0.62534	3.48238
H	1.91492	-1.96377	2.51832
H	3.50470	1.43283	2.35186
H	4.53170	0.45432	1.28097
H	3.38935	1.63136	0.58896
C	3.35422	-2.37166	-1.64152
H	4.30816	-1.92841	0.24400
C	1.25372	-1.26383	-1.96709
C	2.23708	-2.12017	-2.44207
H	4.14340	-3.03300	-1.98620
H	0.37022	-1.00496	-2.53773
H	2.12676	-2.56903	-3.42316
O	-1.16413	0.43460	-1.57250
C	-2.44223	-0.17275	-1.37470
C	-2.42882	-0.90954	-0.03780
C	-2.66359	-1.16053	-2.53589
C	-3.54337	0.90809	-1.38613
C	-3.44748	-1.76330	0.39150
N	-1.35273	-0.68791	0.75365
H	-3.65787	-1.61547	-2.48749
H	-2.58087	-0.61694	-3.48216
H	-1.91435	-1.95793	-2.52271
H	-3.50857	1.43579	-2.34453
H	-4.53330	0.45342	-1.27496
H	-3.39119	1.62960	-0.58122
C	-3.35154	-2.38190	1.63598
H	-4.30625	-1.93403	-0.24809
C	-1.25277	-1.27186	1.96506
C	-2.23477	-2.13125	2.43731
H	-4.13967	-3.04557	1.97856
H	-0.36961	-1.01349	2.53646
H	-2.12368	-2.58316	3.41692
Cl	-1.32512	2.38120	1.09234
Cl	1.32149	2.38579	-1.08298

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6(IV) SCF Energy: -1906.67778550 a.u.

Ir	0.04926	-0.59987	-0.10774
C	2.58980	0.76545	0.03309
C	0.99146	2.17318	-0.95833
C	3.56474	1.75650	-0.10569
C	1.92092	3.19027	-1.12287
H	-0.03718	2.27862	-1.28042
C	3.23122	2.97733	-0.68692
H	4.57448	1.56525	0.24025

H	1.61776	4.12364	-1.58422
H	3.98357	3.75194	-0.80028
N	1.32614	0.99583	-0.39300
C	2.85733	-0.60184	0.65192
O	1.66114	-1.38888	0.63923
C	3.92546	-1.36549	-0.15422
H	4.88575	-0.83987	-0.13427
H	4.06308	-2.35568	0.29075
H	3.61056	-1.49022	-1.19372
C	3.29050	-0.44653	2.12302
H	3.44538	-1.43948	2.55610
H	4.22590	0.11725	2.19978
H	2.51828	0.07062	2.69986
O	-0.47970	0.34026	1.54852
C	-1.85184	0.67153	1.75170
C	-2.54498	0.71204	0.39253
C	-1.86458	2.06688	2.40713
C	-2.53093	-0.35264	2.68432
C	-3.84103	1.19738	0.20249
N	-1.82540	0.24299	-0.65611
H	-2.88334	2.38473	2.65053
H	-1.28849	2.02546	3.33682
H	-1.40937	2.81265	1.74842
H	-1.98595	-0.37858	3.63366
H	-3.56815	-0.06523	2.88791
H	-2.51687	-1.35104	2.24434
C	-4.39569	1.20607	-1.07477
H	-4.40426	1.56346	1.05372
C	-2.35849	0.24791	-1.89719
C	-3.63775	0.72610	-2.14506
H	-5.40297	1.57995	-1.23187
H	-1.73318	-0.15274	-2.68512
H	-4.02632	0.71000	-3.15740
Cl	0.57914	-1.27909	-2.35994
Cl	-1.17396	-2.64870	0.28298

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7(IV) SCF Energy: -1906.66778013 a.u.

Ir	0.00873	-0.25891	0.01047
C	-2.90916	0.18188	-0.01066
C	-1.84723	2.26158	0.08745
C	-4.15812	0.81223	-0.01428
C	-3.05594	2.94132	0.08899
H	-0.91444	2.80253	0.14226
C	-4.23841	2.20002	0.03250

H	-5.05698	0.20742	-0.05212
H	-3.06075	4.02477	0.13546
H	-5.20470	2.69530	0.02938
N	-1.77084	0.91603	0.03023
C	-2.75147	-1.33321	-0.04620
O	-1.38101	-1.68412	0.02662
C	-3.46967	-1.96716	1.16530
H	-4.54989	-1.78686	1.14092
H	-3.29991	-3.04848	1.14483
H	-3.06559	-1.57152	2.10173
C	-3.33617	-1.89255	-1.36272
H	-3.17457	-2.97519	-1.38533
H	-4.41213	-1.70136	-1.44177
H	-2.83194	-1.44828	-2.22531
O	1.37658	-1.64225	0.01865
C	2.76098	-1.30867	0.05656
C	2.92421	0.20408	0.01726
C	3.42545	-1.95963	-1.17343
C	3.34725	-1.88798	1.36020
C	4.17560	0.82629	0.01191
N	1.78523	0.93601	-0.02122
H	4.50661	-1.78707	-1.17497
H	3.24584	-3.03873	-1.14455
H	3.00193	-1.55918	-2.09877
H	3.16997	-2.96771	1.38074
H	4.42645	-1.71145	1.41660
H	2.86749	-1.43703	2.23307
C	4.25909	2.21448	-0.04125
H	5.07241	0.21799	0.04752
C	1.86599	2.27991	-0.08477
C	3.07798	2.95656	-0.09494
H	5.22639	2.70756	-0.04480
H	0.93476	2.82428	-0.13603
H	3.08486	4.03985	-0.14561
Cl	-0.04599	-0.02931	-2.36594
Cl	-0.00894	-0.00876	2.38629

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8(IV) SCF Energy: -2386.38003319 a.u.

Ir	-0.71938	-0.00369	0.00000
O	0.25711	-1.66838	0.00000
C	1.69127	-1.61648	0.00000
C	2.16193	-0.16796	0.00000
C	2.16994	-2.35052	-1.26792
C	2.16994	-2.35052	1.26792
C	3.50767	0.20408	0.00000

N	1.19298	0.77762	0.00000
H	3.26335	-2.39471	-1.29736
H	1.78023	-3.37277	-1.25661
H	1.81016	-1.84608	-2.16809
H	1.78023	-3.37277	1.25661
H	3.26335	-2.39471	1.29736
H	1.81016	-1.84608	2.16809
C	3.84896	1.55465	0.00000
H	4.27389	-0.56361	0.00000
C	1.51098	2.08770	0.00000
C	2.83267	2.51277	0.00000
H	4.89245	1.85466	0.00000
H	0.67642	2.77834	0.00000
H	3.05140	3.57502	0.00000
Cl	-0.71139	0.06292	-2.39802
Cl	-2.82642	-1.18552	0.00000
Cl	-1.90037	2.10637	0.00000
Cl	-0.71139	0.06292	2.39802

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