Supporting Information for

Surprisingly Big Linker-Dependence of Activity and Selectivity in CO_2 Reduction by an Iridium(I) Pincer Complex

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Table of Contents

General Methods S2
Synthesis S3
Characterization Data S5
General Computational Details S17
Crystal Data S38
References S65

General Methods

All air and/or moisture sensitive chemicals were handled in a nitrogen-filled glovebox. All solvents were used as received unless otherwise noted. Milipore water was used in all cases. ^{1}H and ^{31}P NMR spectra were acquired at room temperature using a Bruker 400 MHz NMR spectrometer. Chemical shifts for ^{1}H NMR spectra were referenced to the residual ^{1}H resonances of the deuterated solvents. Reflection FT-IR spectra of neat solid films were measured using an Agilent Cary 660 FT-IR spectrometer. Absorption spectra were measured using a Shimadzu UV-2600 UV-visible spectrophotometer. XPS measurements were performed using a PHI Versa Probe II system with a monochromatic 1486.7 eV Al Kα X-ray source. SEM and EDS measurements were made on a Hitachi SU8230 field emission SEM.

Electrochemistry experiments were carried out using a Pine Wavenow potentiostat. Cyclic voltammetry measurements were made in a single compartment electrochemical cell under argon or CO_2 atmosphere using a glassy carbon electrode (3.0 mm diameter) as the working electrode and a platinum wire as the counter electrode. A Ag/AgCl wire in saturated KCl (aq) closed by a piece of fritted glass was dipped into the solutions, serving as the reference electrode (hereafter named Ag/AgCl). The potential of the Ag/AgCl electrode $E_{Ag/AgCl}$ was calibrated using the ferrocene/ferrocenium redox couple (Fc/Fc^+, 0.5 mM) in anhydrous DMF with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) before each set of experiments, which was measured to be –0.38 V *vs.* Fc/Fc^+. The glassy carbon electrode was polished with 0.05 μm alumina, sonicated in water for 30 s, and dried with a nitrogen stream before each measurement. The Pt wire was flamed with a propane torch before each experiment. All experiments were performed in either anhydrous DMF or DMF with 5 M water with 0.1 M $TBAPF_6$ as the supporting electrolyte. The concentrations of iridium complexes were 0.5 mM.

The overpotential here was defined as the difference between the half-wave potential $E_{cat/2}$ (the potential at which the current reaches half of the maximum current) and the thermodynamic potentials of CO_2-to-CO conversion E^0 (–1.51 V *vs.* Fc/Fc^+ in a 5 M solution of water in DMF) estimated in the literature.[1]

$E_{cat/2}$ = –1.78 V *vs.* Ag/AgCl; $E_{Ag/AgCl}$ = –0.38 V *vs.* Fc/Fc^+. So,

$E_{cat/2}$ = –2.26 V *vs.* Fc/Fc^+

Accordingly, the overpotential $\eta = E^0 - E_{cat/2}$ = –1.51 V – (–2.26 V) = 0.75 V

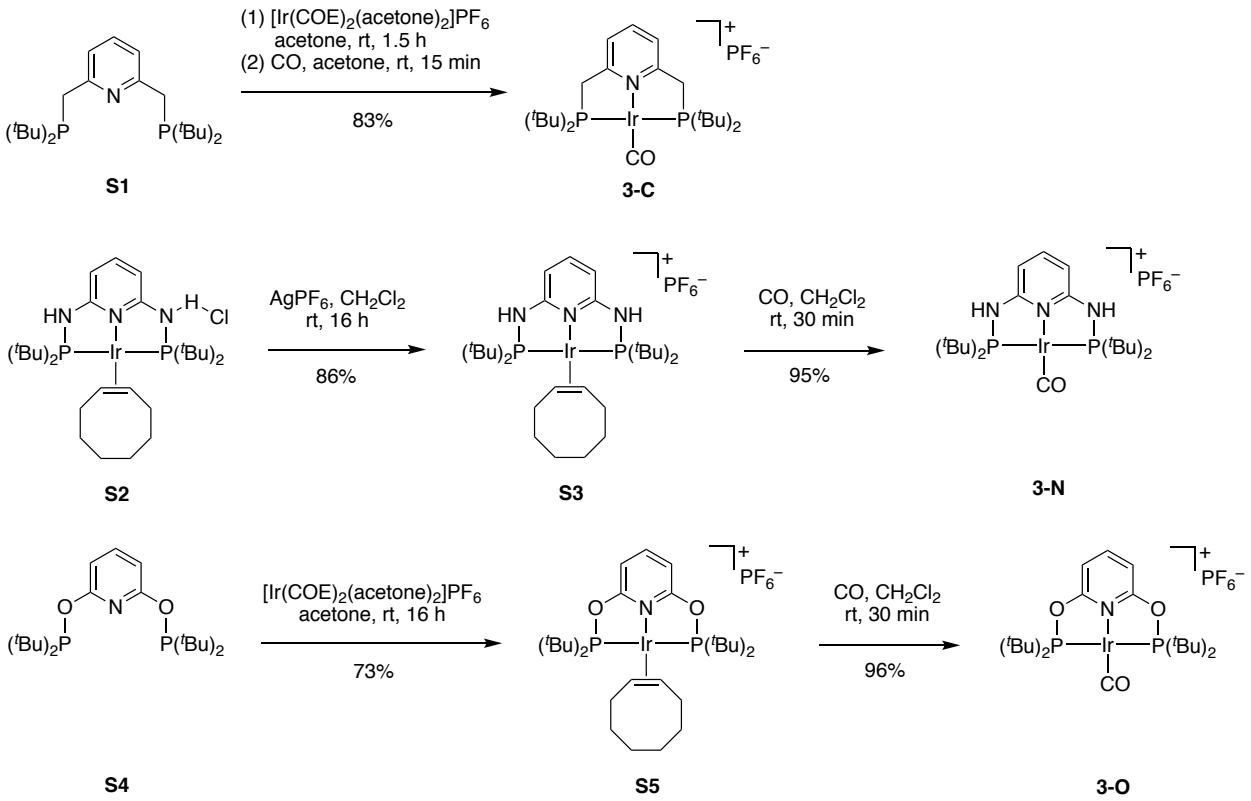
Controlled-potential electrolysis measurements were conducted in a two-compartment H-cell, separated with an anion-exchange membrane (Selemion DSV). The cathodic chamber held the working and reference electrodes in 12 mL of 0.1 M $TBAPF_6$ solution in DMF with 5 M water. The anodic chamber held the counter electrode in 12 mL of 0.1 M $TBAPF_6$ solution in DMF with 5 M water. The volume of the headspace of the cathodic chamber was measured to be 30 mL. Carbon paper electrodes (1 cm × 1 cm, DGS 3250, Fuel Cell Store) and a graphite electrode were used as the working and counter electrodes, respectively. A Ag/AgCl (in saturated KCl aqueous solution) electrode was used as the reference electrode. The cathodic solution was first deaerated by bubbling with argon for 30 min, then with CO_2 for 15 min, and kept under constant CO_2 bubbling (flow rate = 10 mL/min) to maintain the concentration of CO_2 in the electrolyte. The headspace sample of the cathodic chamber was delivered into the sample loop of an SRI gas chromatograph (multiple gas analyzer MG#5) through the CO_2 stream. The gas chromatograph was equipped with a 0.5 m Hayesep D column, a 2 m Molesieve column, a TCD detector (for H_2 detection), a methanizer, and an FID detector (for CO detection). N_2 was used as the carrier gas. The system was calibrated with a mixture of gas calibration standards and nitrogen in various ratios. 1.0 mL of the gas sample was injected from the sample loop in each measurement. CO and

H_2 were detected simultaneously in one measurement with the FID detector and the TCD detector, respectively. The retention time for CO and H_2 were 6 min and 0.5 min, respectively. Faradaic efficiencies were determined by dividing the measured CO or H_2 by the amount expected based on the charge passed during the bulk electrolysis experiment. Bulk electrolysis at each potential was repeated at least twice.

Low-temperature diffraction data (ω-scans) were collected on a Rigaku MicroMax-007HF diffractometer coupled to a Dectris Pilatus3R detector with Mo Kα (λ = 0.71073 Å) for the structures of **3-N** and **3-O**. The diffraction images were processed and scaled using Rigaku Oxford Diffraction software (CrysAlisPro; Rigaku OD: The Woodlands, TX, 2015). These data were refined as a 2-component twin. The fractional volume contribution of the minor twin component was freely refined to a converged value of 0.239(3). The structure was solved with SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL (Sheldrick, G. M. Acta Cryst. 2008, A64, 112–122). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. 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). The full numbering scheme of compounds **3-N** and **3-O** can be found in the full details of the X-ray structure determination (CIF). CCDC number 007c-18031 (compound **3-N**) and 007c-18033 (compound **3-O**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis

$[Ir(COE)_2(acetone)_2]PF_6$[2] was prepared according to literature procedures.



Scheme S1. Synthetic routes for complexes **3-N** and **3-O**.

[{C$_6$H$_3$N-2,6-[CH$_2$P(^{t}Bu)$_2$]$_2$}Ir(CO)]PF$_6$ (3-C). Following a reported procedure,[3] in a glovebox, a solution of **S1** (57 mg, 0.14 mmol) in anhydrous acetone (1.5 mL) was treated dropwise with a solution of [Ir(COE)$_2$(acetone)$_2$]PF$_6$ (102 mg, 0.14 mmol) in acetone (1.5 mL). The resulting solution turned dark red immediately. The solution was stirred in the glovebox at room temperature for 1.5 h, and then taken out of the glovebox and bubbled with CO at room temperature for 15 min. The resulting yellow solution was dried *in vacuo*. Pentane (6.0 mL) was added to the solid sample. The suspension was sonicated for 30 s (benchtop sonicator), and then centrifuged (3245 *g*, 15 min). The supernatant was discarded. This washing procedure was repeated three times to afford the title compound as a yellow powder (92 mg, 83%): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (t, J = 8.0 Hz, 1H), 7.74 (d, J = 7.8 Hz, 2H), 3.89 (t, J = 3.9 Hz, 4H), 1.43–1.39 (m, 36H); ^{31}P NMR ($CDCl_3$, 167 MHz) d 73.5 (s, P-Ir), –144 (sept, J = 733 Hz, PF$_6$).

[{C$_6$H$_3$N-2,6-[NHP(^{t}Bu)$_2$]$_2$}Ir(COE)]PF$_6$ (S3). A solution of complex **S2**[4] (74 mg, 0.10 mmol) in dichloromethane (4.0 mL) was treated with AgPF$_6$ (25 mg, 0.10 mmol) in one portion, and stirred for 16 h at room temperature. The reaction mixture was then centrifuged (4200 rpm, 15 min). The supernatant was separated and concentrated to afford a reddish residue. The resulting sample was suspended in hexanes, sonicated for 30 s (benchtop sonicator), and then centrifuged (3245 *g*, 15 min). The supernatant was discarded. The washing procedure was repeated three times to afford the title compound as a reddish powder (73 mg, 86%): ^{1}H NMR (acetone-d_6, 400 MHz) δ 7.42 (t, J = 8.0 Hz, 1H), 6.47 (d, J = 8.0 Hz, 2H), 5.72 (br, 2H), 5.23 (m, 2H), 4.15 (m, 2H), 2.36 (m, 2H), 1.69 (m, 4H), 1.22–1.52 (m, 40H); ^{31}P NMR (acetone-d_6, 167 MHz) δ 95 (br, P-Ir), –144 (sept, J = 723 Hz, PF$_6$). FT-IR 2969, 2910, 2848, 1617, 1562, 1478, 1175, 828, 557, 473 cm^{-1}.

[{C$_6$H$_3$N-2,6-[NHP(^{t}Bu)$_2$]$_2$}Ir(CO)]PF$_6$ (3-N). A solution of complex **S3** (25 mg, 0.030 mmol) in dichloromethane (10 mL) was bubbled with carbon monoxide for 30 min at room

temperature. The color of the solution changed from orange to dark yellow. The yellow solution was dried by mild argon gas flow. The resulting sample was suspended in hexanes, sonicated for 30 s (benchtop sonicator), and then centrifuged (3245 *g*, 15 min). The supernatant was discarded. The washing procedure was repeated three times to afford the title compound as a yellow powder (21 mg, 95%): ^{1}H NMR (CD_3OD, 400 MHz) δ 7.58 (t, J = 8.0 Hz, 1H), 6.52 (d, J = 8.0 Hz, 2H), 4.85 (s, 2H), 1.46 (d, J = 8.0 Hz, 18H), 1.44 (d, J = 8.0 Hz, 18H); FT-IR 2976, 2954, 2873, 1962, 1617, 1572, 1473, 1398, 1368, 1177, 1056, 839, 630, 552, 479 cm^{-1}; λ_{abs}[DMF/H_2O (5 M)] 355, 418, 472 nm.

{C_6H_3N-2,6-[OP(^{t}Bu)$_2$]$_2$}Ir(COE)]PF_6 (S5). A solution of pincer ligand **S4**[4] (100 mg, 0.10 mmol) in acetone (2.0 mL) was treated with a freshly prepared solution of [Ir(COE)$_2$(acetone)$_2$]PF_6[3] (325 mg, 0.10 mmol) in one portion, and stirred for 16 h at room temperature. The color changed from yellow to red. The red solution was dried by mild nitrogen gas flow. The resulting sample was suspended in hexanes, sonicated for 30 s (benchtop sonicator), and then centrifuged (3245 *g*, 15 min). The supernatant was discarded. The washing procedure was repeated three times to afford the title compound as a reddish powder (154 mg, 73%): ^{1}H NMR (acetone-d_6, 400 MHz) δ 8.31 (t, J = 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 4.69 (m, 2H), 2.67 (m, 2H), 1.47–1.56 (m, 46H); ^{31}P NMR (acetone-d_6, 167 MHz) δ 207 (s, *P*-Ir), –144 (sept, J = 723 Hz, *P*F_6). FT-IR 2964, 2918, 2865, 1610, 1462, 1055, 833, 548 cm^{-1}.

{C_6H_3N-2,6-[OP(^{t}Bu)$_2$]$_2$}Ir(CO)]PF_6 (3-O). A solution of complex **S5** (100 mg, 0.118 mmol) in dichloromethane (20 mL) was bubbled with carbon monoxide for 30 min at room temperature. The color of the solution changed from red to dark yellow. The yellow solution was dried by mild argon gas flow. The resulting sample was suspended in hexanes, sonicated for 30 s (benchtop sonicator), and then centrifuged (3245 *g*, 15 min). The supernatant was discarded. The washing procedure was repeated three times to afford the title compound as a yellow powder (87 mg, 96%): ^{1}H NMR (acetone-d_6, 400 MHz) δ 8.35 (t, J = 8.0 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 1.54 (d, J = 8.0 Hz, 18H), 1.52 (d, J = 8.0 Hz, 18H); ^{31}P NMR (acetone-d_6, 167 MHz) δ 181 (br, *P*-Ir), –141 (sept, J = 752 Hz, *P*F_6); FT-IR 2954, 2924, 2865, 1980, 1621, 1445, 1369, 1333, 1038, 833, 638, 552, 482 cm^{-1}; λ_{abs} [DMF/H_2O (5 M)] 340, 415, 470 nm.

Characterization Data

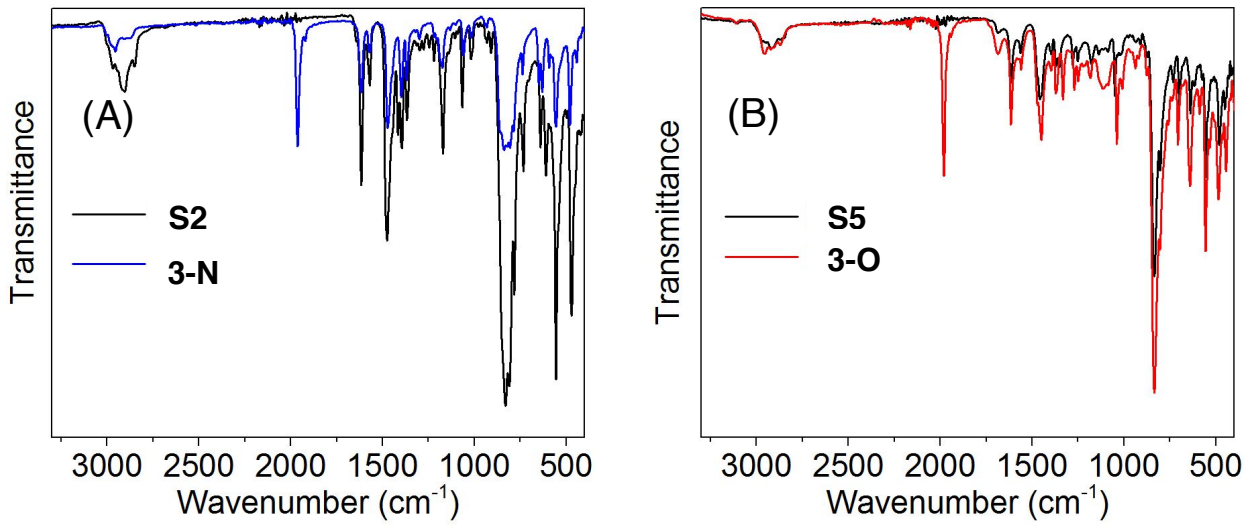


Figure S1. FT-IR spectra of iridium complexes **3-N** and **3-O** before and after COE substitution with CO.

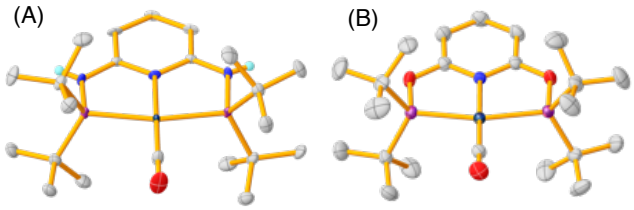


Figure S2. (A) X-ray crystal structure of **3-N**. The Ir-C distance refined to a value of 1.822(10) Å; Ir-P distances are 2.2846(8) Å and 2.2892(8) Å; Ir-N distance is 2.076(8) Å. (B) X-ray crystal structure of **3-O**. The model lies on the crystallographic 2-fold axis that contains the N-Ir-C-O atoms. The Ir-C distance refined to a value of 1.822(10) Å; both Ir-P distances are 2.2858(17) Å; Ir-N distance is 2.076(8). The counter ion (PF_6^-) is omitted from both images. All hydrogen atoms are omitted except for those on nitrogen in **3-N**. All omissions are intended to enhance the clarity of the models.

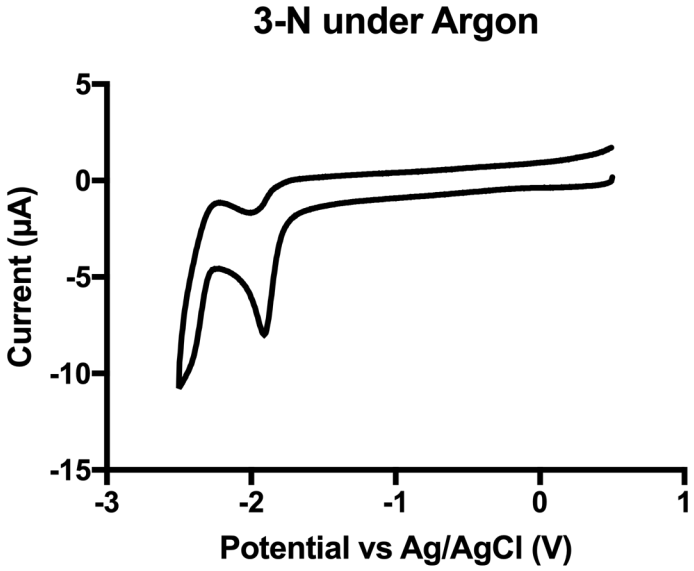


Figure S3. Cyclic voltammetry of a 0.5 mM solution of **3-N** in DMF under argon. Scan rate = 0.1 V/s.

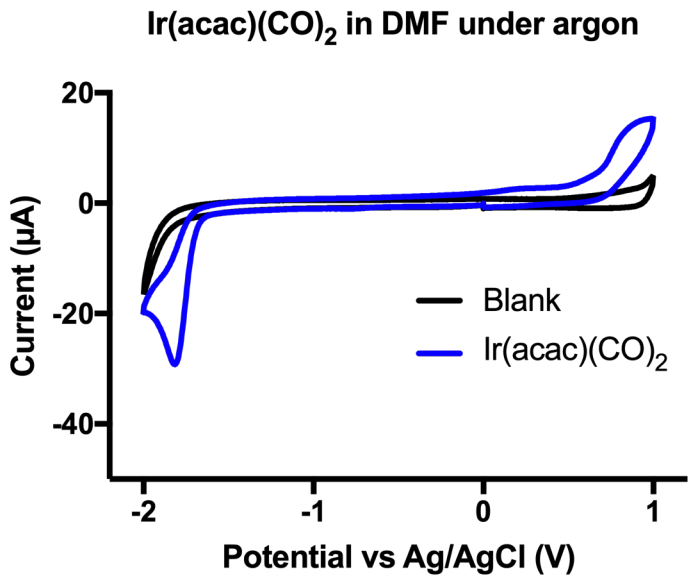


Figure S4. Cyclic voltammetry of a 1.0 mM solution of $Ir(acac)(CO)_2$ in DMF under argon. Scan rate = 0.1 V/s. One irreversible reduction event was observed at –1.81 V *vs.* Ag/AgCl.

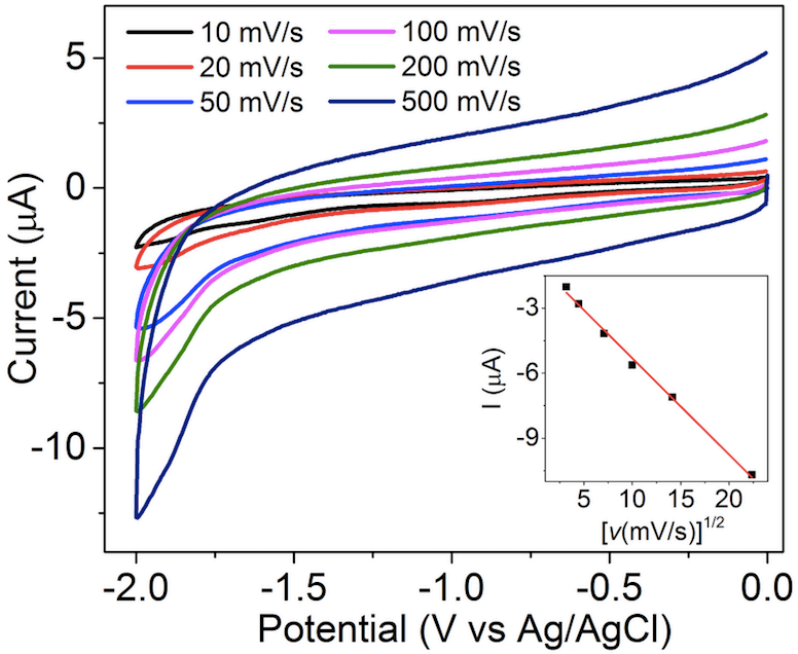


Figure S5. Scan-rate-dependent CV of 0.5 mM **3-N** in DMF with 5 M H_2O. Inset: square root of scan rate versus current for the 1st reduction peak.

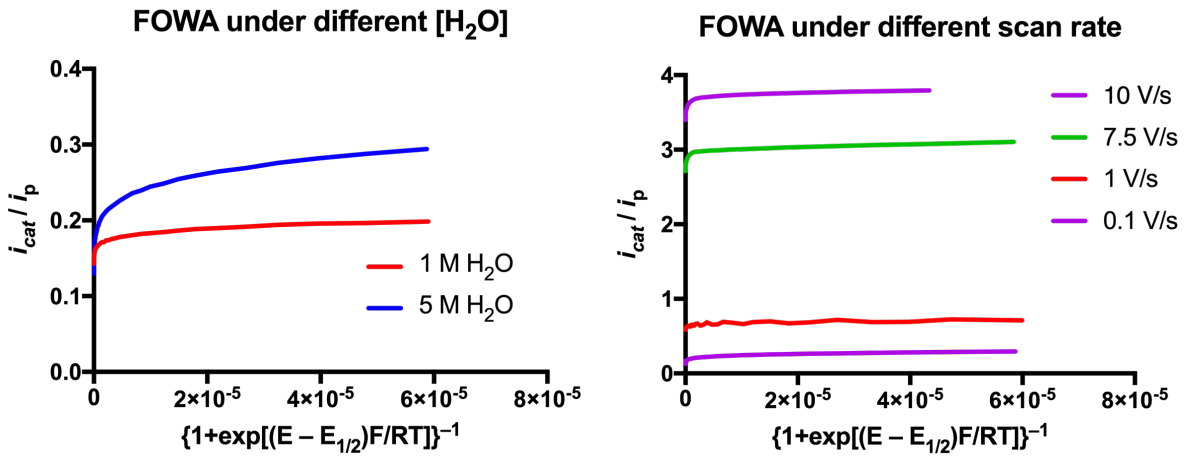


Figure S6. Left: Foot-of-wave analysis of 0.5 mM **3-N** in CO_2-saturated DMF in the presence of 1 M or 5 M water. Scan rate = 0.1 V/s. Right: Foot-of-wave analysis of **3-N** with different scan rates.

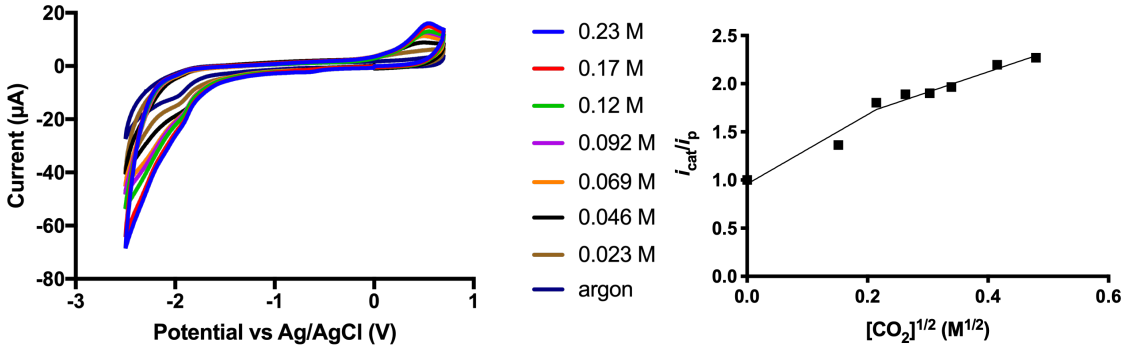


Figure S7. Left: CV scans of a 0.5 mM solution of **3-N** in DMF/H_2O (5 M) with different concentrations of CO_2. Scan rate = 0.1 V/s. Right: plot of the normalized current at –1.9 V *vs* Ag/AgCl against the square root of the CO_2 concentration.

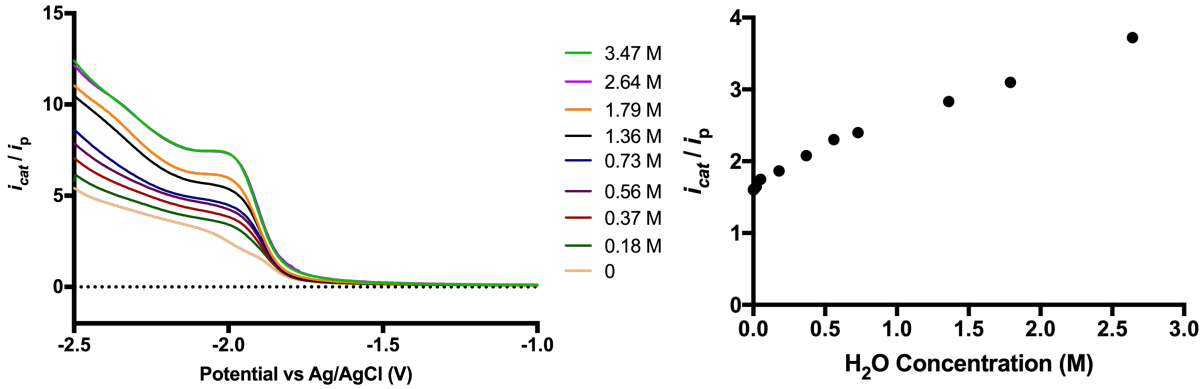


Figure S8. Left: CV scans of a 0.5 mM solution of **3-N** in CO_2-saturated DMF with different concentrations of water. Scan rate = 0.1 V/s. Right: the plot of the normalized current at –1.9 V *vs* Ag/AgCl against different water concentrations.

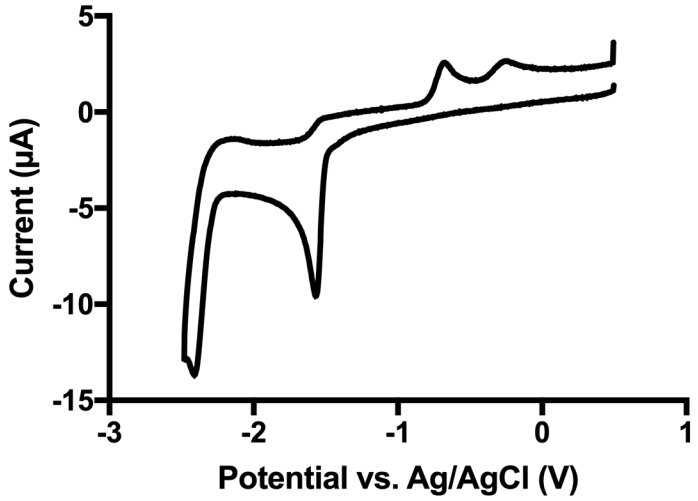


Figure S9. Cyclic voltammetry of a 0.5 mM solution of **3-C** in DMF under argon. Scan rate = 0.1 V/s.

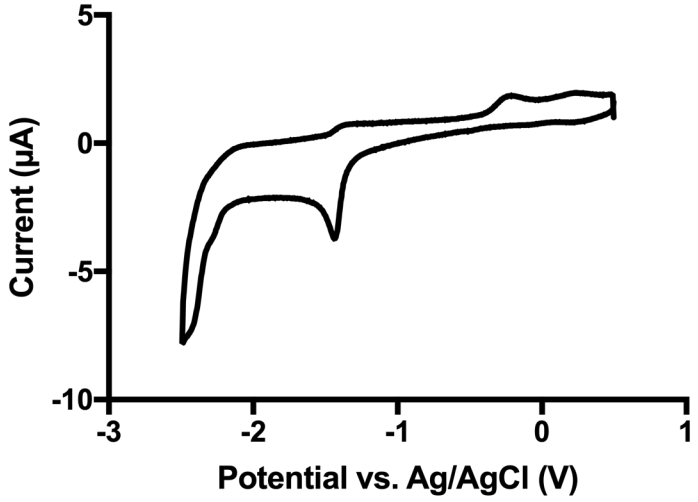


Figure S10. Cyclic voltammetry of a 0.5 mM solution of **3-O** in DMF under argon. Scan rate = 0.1 V/s.

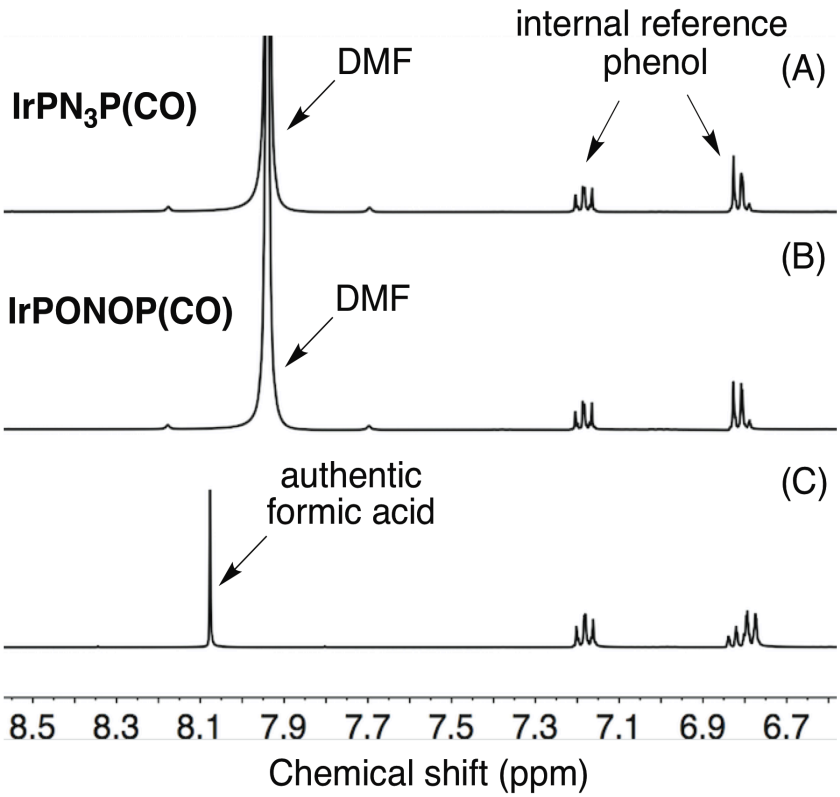


Figure S11. ^{1}H NMR spectra of the electrolyte solutions of **3-N** (A) and **3-O** (B) after CPE, and the electrolyte solution after CPE with authentic formic acid added (C). Phenol is used as an internal reference for the quantification of any liquid products.

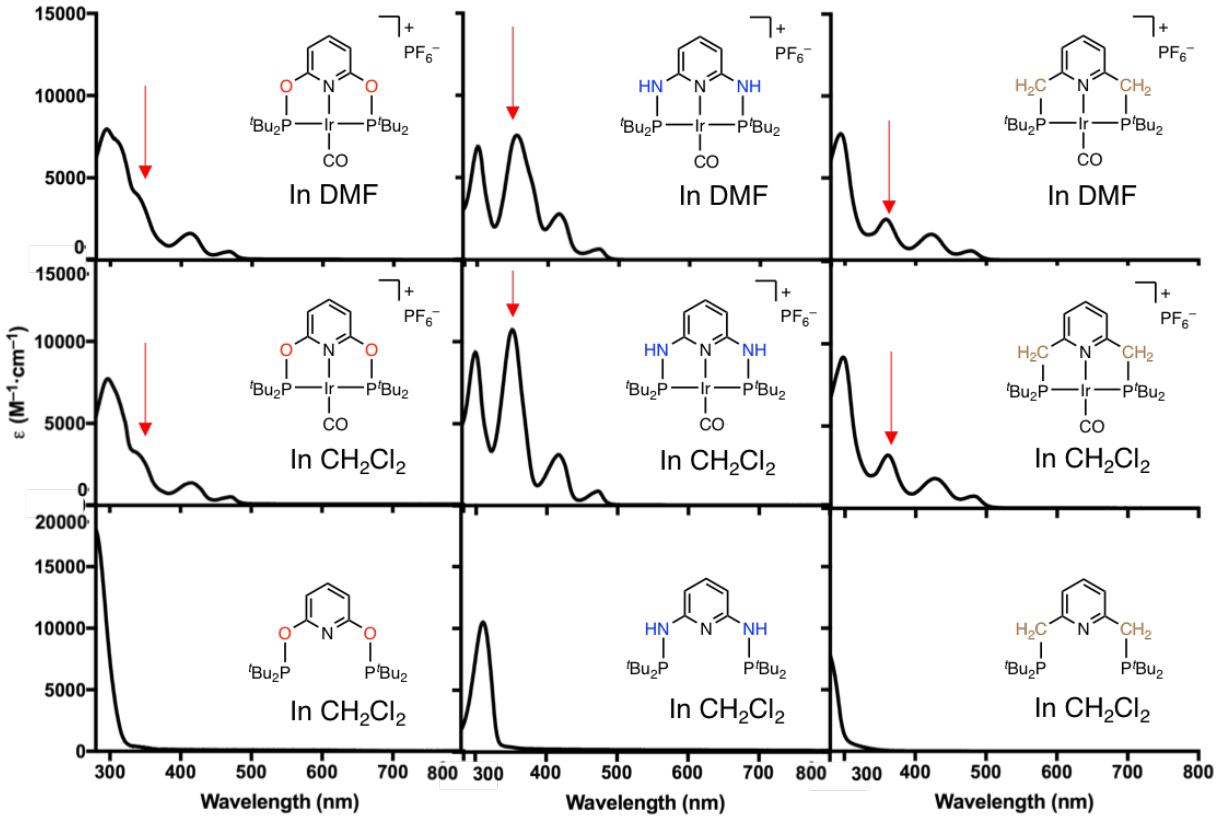


Figure S12. Absorption spectra of **3-N**, **3-O**, and **3-C** in DMF or CH_2Cl_2, and spectra of the corresponding ligands in CH_2Cl_2.

Table S1. Current densities (j) and Faradaic efficiencies (FE) from controlled-potential electrolyses with the studied compounds or the blank solution.

Potential *vs.* Ag/AgCl (V)		–1.5	–1.6	–1.7	–1.8	–1.9	–2.0
3-N	j (mA/cm^2)	0.28	0.46	0.83	2.0	5.0	7.8
	FE(CO)	0	7.5	23	71	98	100
	FE(H_2)	0.25	0.75	1.3	1.7	1.8	1.3
3-C	j (mA/cm^2)		0.86	3.6	3.7	3.4	3.8
	FE(CO)		5.1	47	44	39	43
	FE(H_2)		62	48	47	54	47
3-O	j (mA/cm^2)		0.6	0.78	1.0	1.26	1.85
	FE(CO)		0	0	0	14	20
	FE(H_2)		0.5	0	0.1	0.4	0.1
Blank	j (mA/cm^2)	0.19	0.73	0.80	0.88	0.95	1.3
	FE(CO)	0	0	0	0	4	11
	FE(H_2)	0.31	1.1	0.56	1.4	1.1	1.3

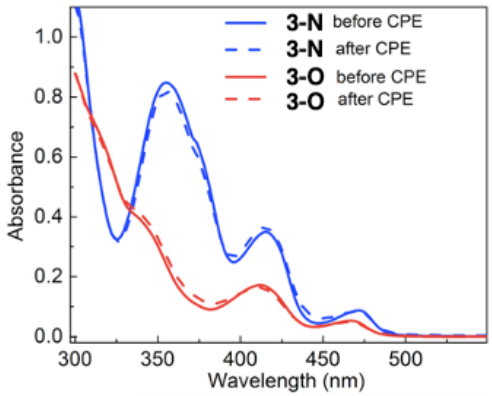


Figure S13. Absorption spectra of the electrolyte solutions of **3-N** (blue) and **3-O** (red) before (solid) and after (dash) 1 hour of CPE. The same amounts of aliquots from the electrolyte solution were used.

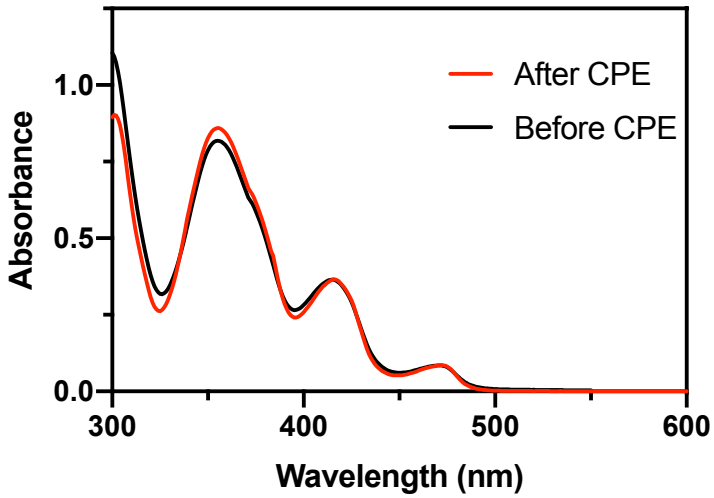


Figure S14. Absorption spectra of the electrolyte solutions of **3-N** before (black) and after (red) the 67 hours of CPE. The same amounts of aliquots from the electrolyte solution were used.

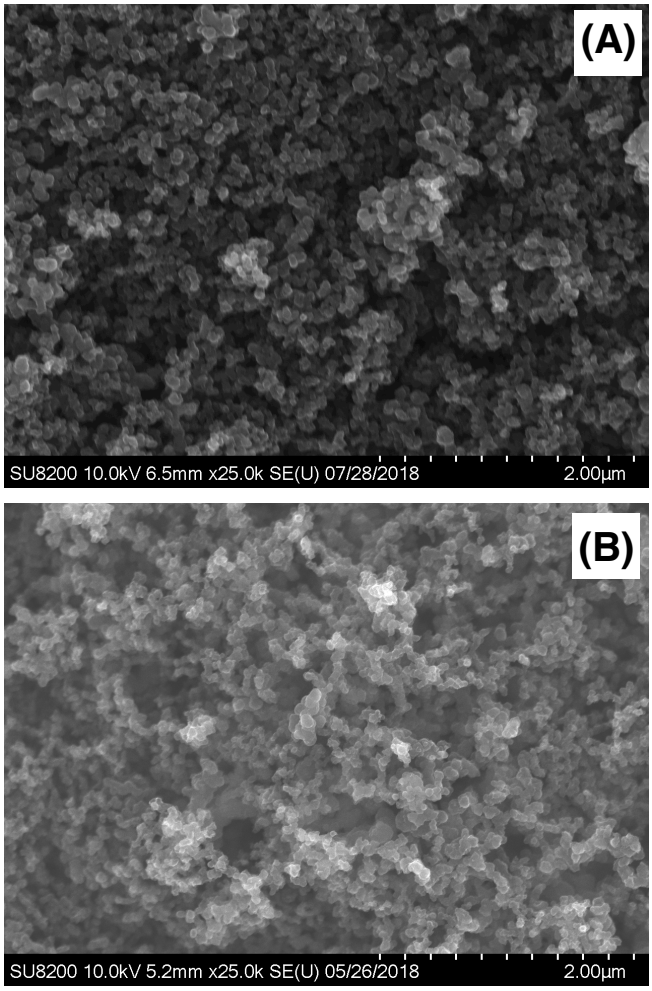


Figure S15. SEM image of the carbon paper electrode (A) before and (B) after 1 hour electrolysis with **3-N**.

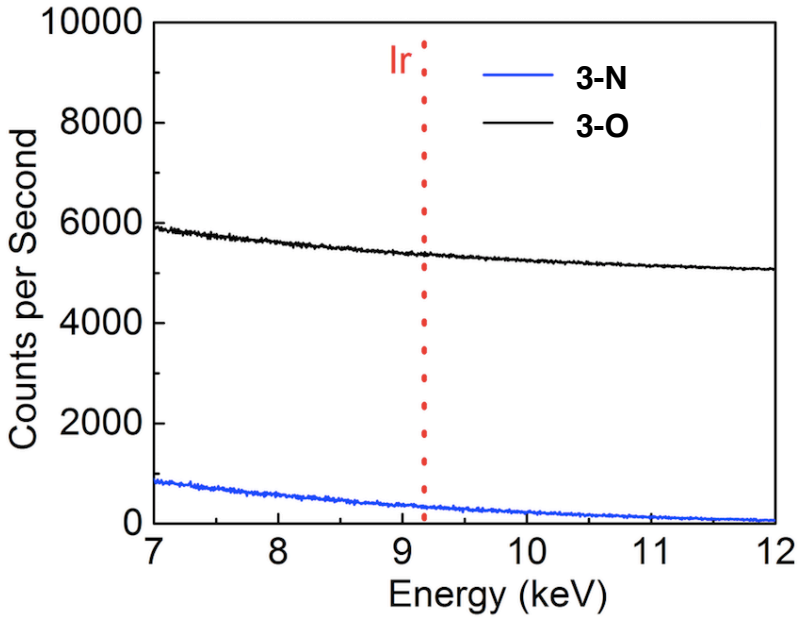


Figure S16. Absence of iridium signal in the EDS spectra of the electrode after 1 hour of electrolysis. A carbon paper electrode was used as the electrode.

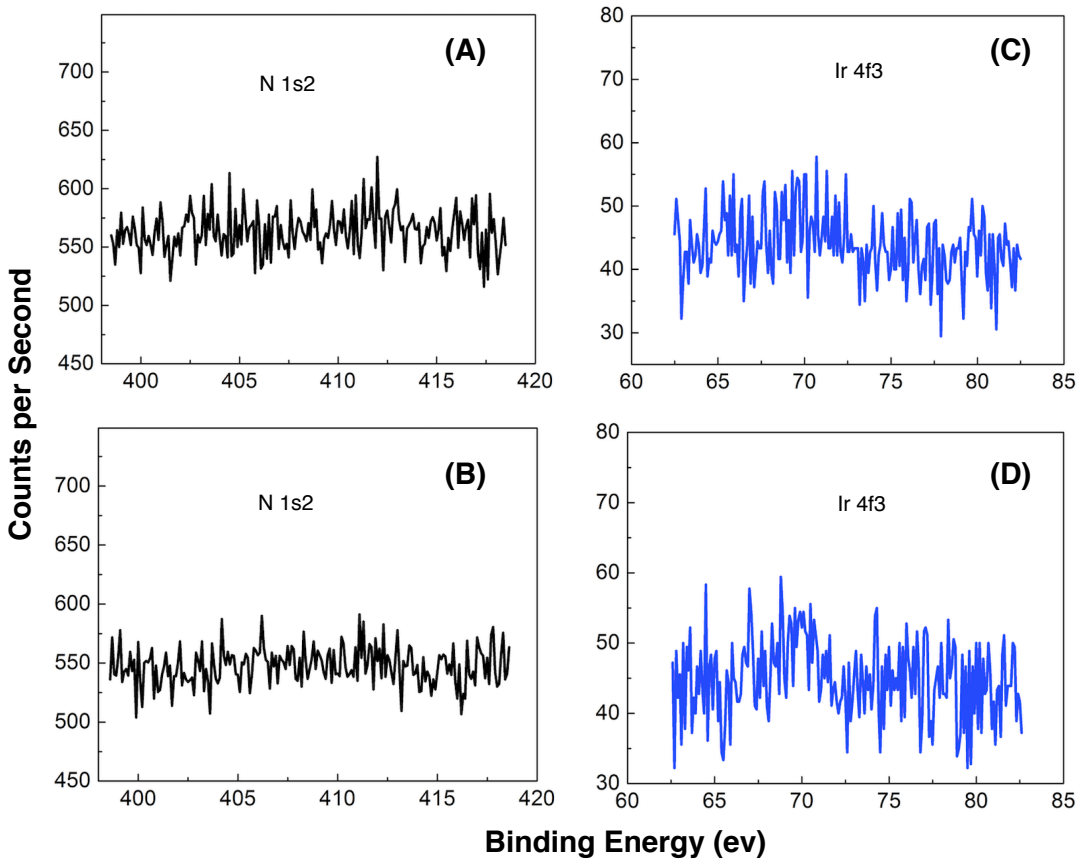


Figure S17. Absence of nitrogen and iridium signals in the XPS spectra of the electrode after 1 hour of electrolysis. (A) N signal of **3-N**, (B) N signal of **3-O**, (C) Ir signal of **3-N**, and (D) Ir signal of **3-O**. A carbon paper electrode was used as the electrode.

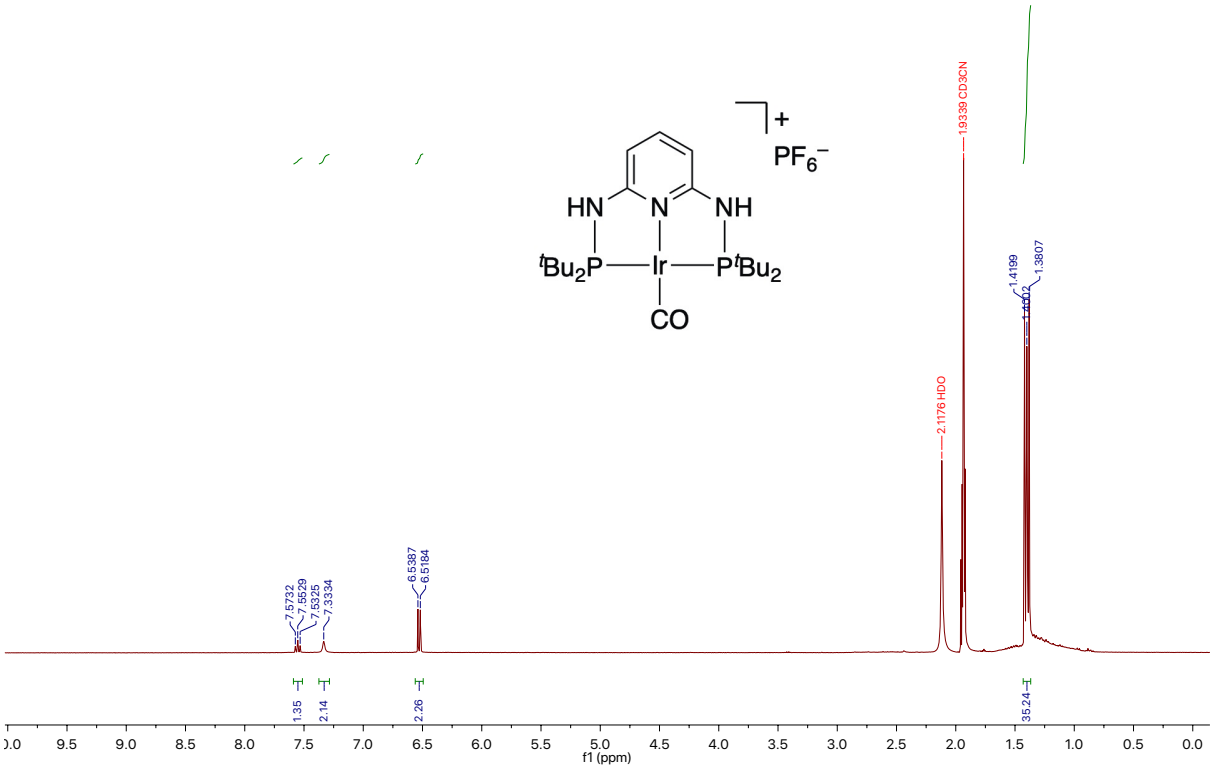


Figure S18. The ^{1}H NMR spectrum of compound **3-N**.

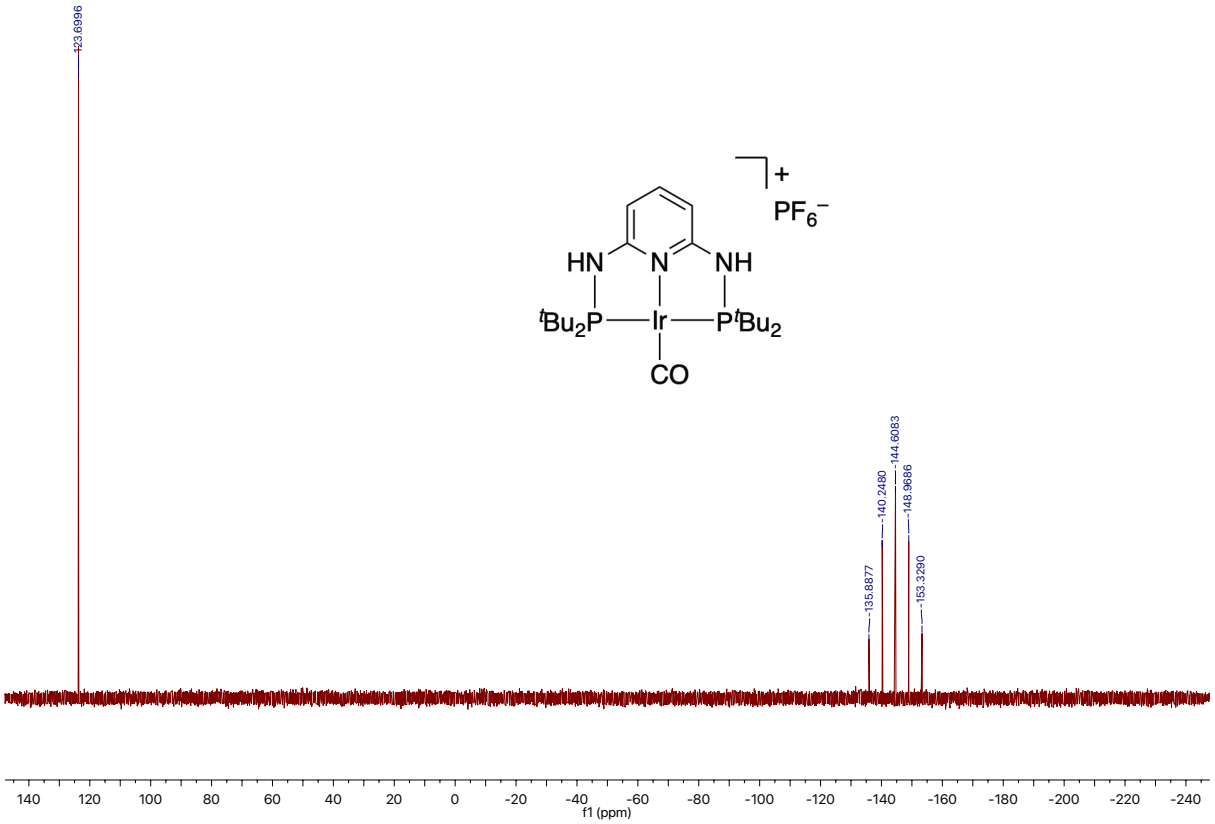


Figure S19. The ^{31}P NMR spectrum of compound **3-N**.

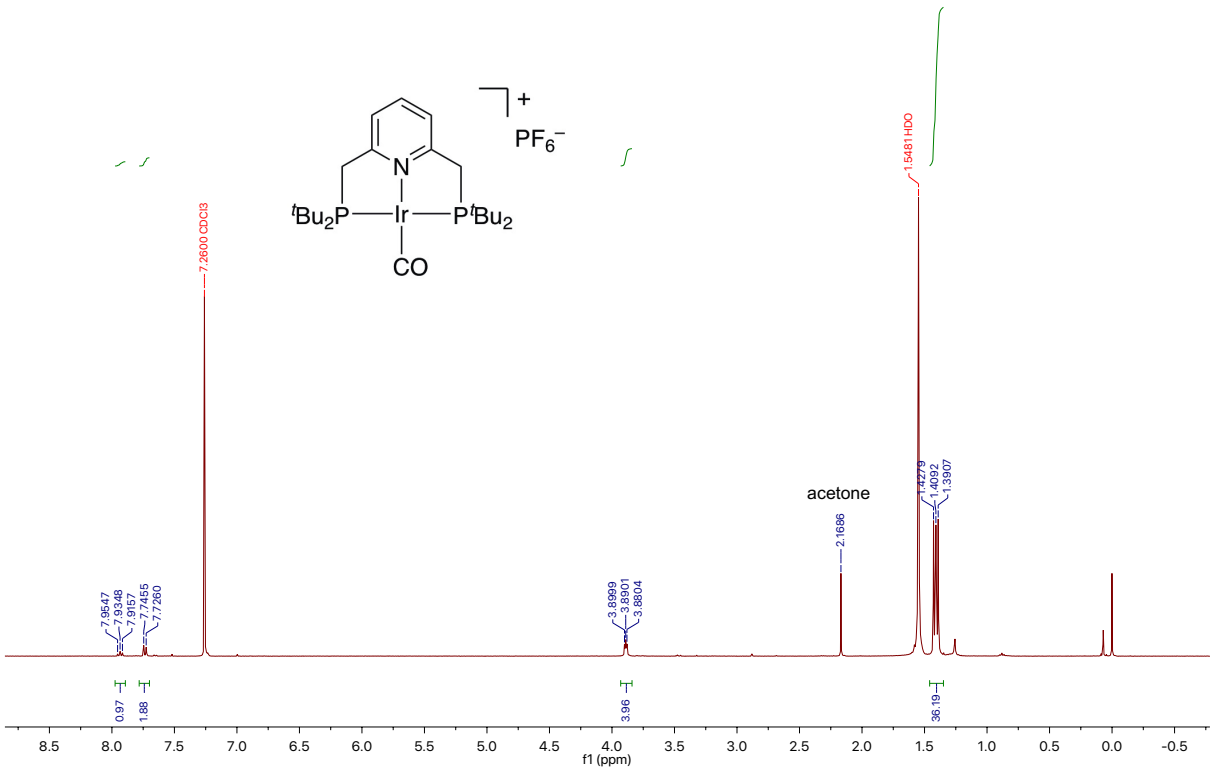


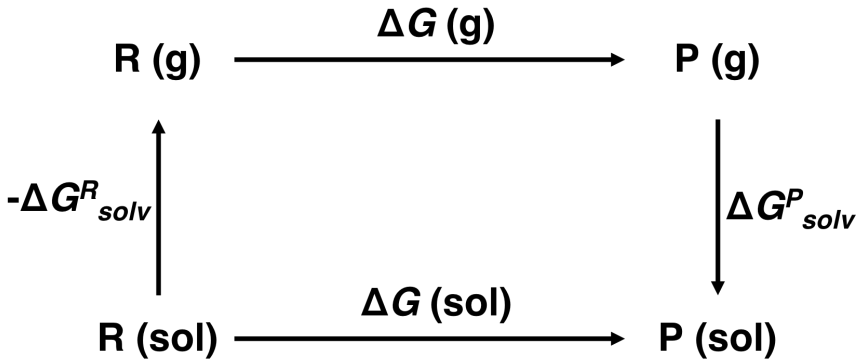
Figure S20. The ^{1}H NMR spectrum of compound **3-C**.

General Computational Details

Density functional theory (DFT) calculations were performed using the B3LYP functional[6] as implemented in Gaussian 2016, revision A.03.[7] All optimizations were performed using the default "ultrafine" integration grid (99 radial shells and 590 angular points per shell) and "tight" convergence criteria (0.000015 a.u. for maximum force, 0.000010 a.u. for RMS force, 0.000060 a.u. for maximum displacement, 0.000040 a.u. for RMS displacement). Stationary points were verified by the absence of imaginary frequencies. All geometry optimizations and frequency calculations were performed with the 6-31+G(d,p)[8] basis set for all nonmetal atoms (C, H, N, O, P) and the DEF2SVP[8a,9] basis set and effective core potential for the Ir center. Single point calculations employed the 6-311+G(2df,p)[8c,10-12] basis set for nonmetal atoms and the DEF2TZVP[8a,9] basis set and effective core potential for Ir. The 5 M water in DMF mixture was modeled using a generic SMD[13] solvent with a dielectric constant of 46.21 (keyword "Eps") and square of the index of refraction at high frequency of 4.28 (keyword "EpsInf"). These parameters were experimentally determined for the 5 M water in DMF mixture at 298 K.[14] All reported orbital energies, density plots, and population analyses were obtained from the single point calculations performed in solvent. Vibrational frequencies reported in Table S2 were scaled such that the CO stretching frequency of **3-O** matched the experimental value (scaling factor of 0.9572) as there was no reference scaling factor for the chosen functional and mixed basis set. All molecular orbital surfaces were plotted with an isovalue of 0.03. Visualization of molecular geometries and isosurfaces was performed in GaussView 6.[15]

Calculation of Reduction Potentials

Reduction potentials were computed according to our previously reported methodology.[16] The Born-Haber thermodynamic cycle in Scheme S2 was used to obtain the change in free energy in solution, ΔG(sol), where reactant R is reduced to form product P. Optimization and frequency calculations were performed to obtain Gibbs free energies in the gas phase, while single point energies were computed in solution.



Scheme S2. Thermodynamic cycle utilized for calculation of reduction potentials.

The Nernst equation was then used to convert the change in free energy in solution to the absolute reduction potential as follows

$$E_{abs} = \frac{-\Delta G(sol)}{nF}$$

where n is the number of electrons transferred in the reaction and F is Faraday's constant. In order to compare the computed reduction potential with measurements, it is necessary to use a reference redox couple. It has been shown that using a reference complex with a metal center in the same row as that of the complex of interest greatly reduces systematic DFT error.[16] Thus, we used the $Ir(acac)(CO)_2^{0/-}$ redox couple as a reference. Relative reduction potentials *vs.* $Ir(acac)(CO)_2^{0/-}$ were computed for each complex of interest. The reported values *vs.* Ag/AgCl (Table S2) were determined by shifting the relative potentials by the experimentally measured reference potential for $Ir(acac)(CO)_2^{0/-}$, –1.80 V *vs.* Ag/AgCl (Figure S4).

Table S2. Comparison of Experimental and Computed CO Stretching Frequencies.[a]

Complex	Experimental (cm^{-1})	Computed (cm^{-1})	Computed After Reduction (cm^{-1})
3-N	1962	1967	1875
3-C	1959	1961	1881
3-O	1980	1980	1890

[a]Computed frequencies were scaled by 0.9572 as explained in General Computational Details.

Table S3. Comparison of Experimental and Computed Reduction Potentials (V *vs.* Ag/AgCl).

Complex	Experimental	Computed 1st Reduction	Computed 2nd Reduction
3-N	–1.91	–1.93	–2.39
3-C	–1.57	–1.81	–2.29
3-O	–1.44	–1.67	–2.60

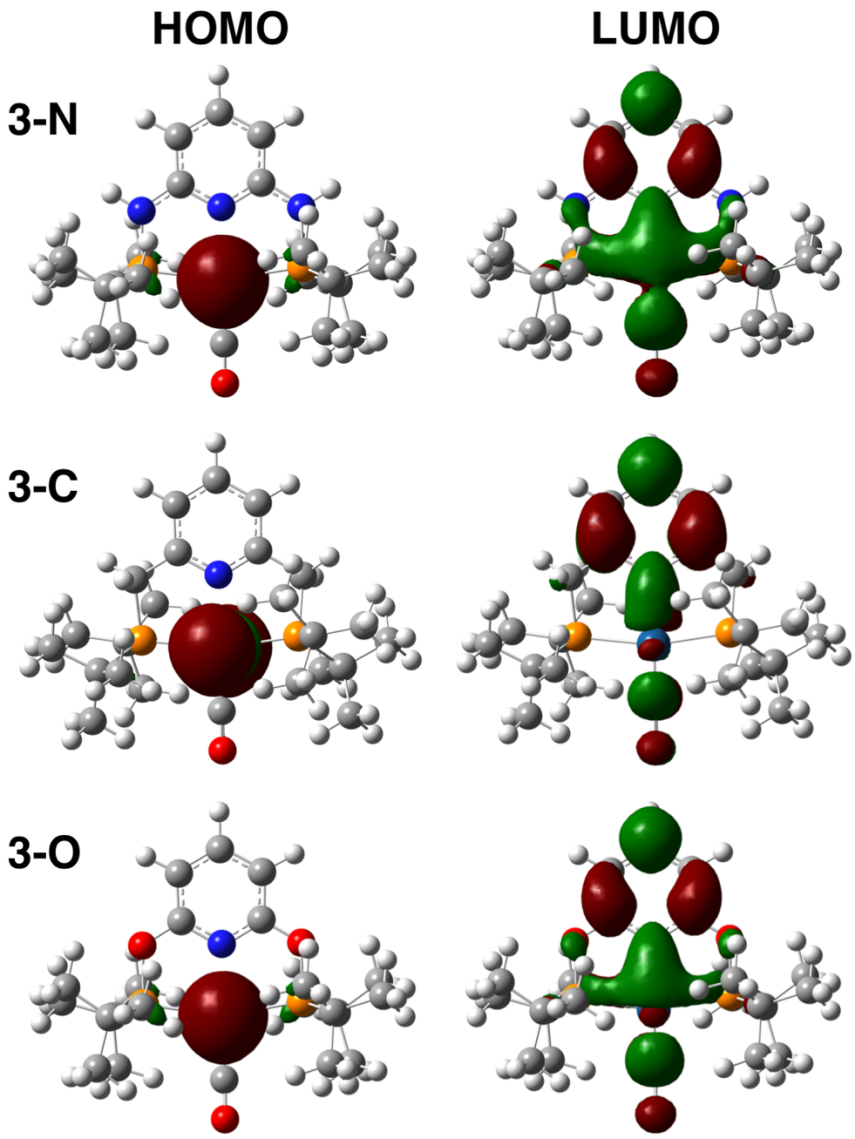


Figure S21. HOMOs (left) and LUMOs (right) of **3-C** (top), **3-N** (middle), and **3-O** (bottom).

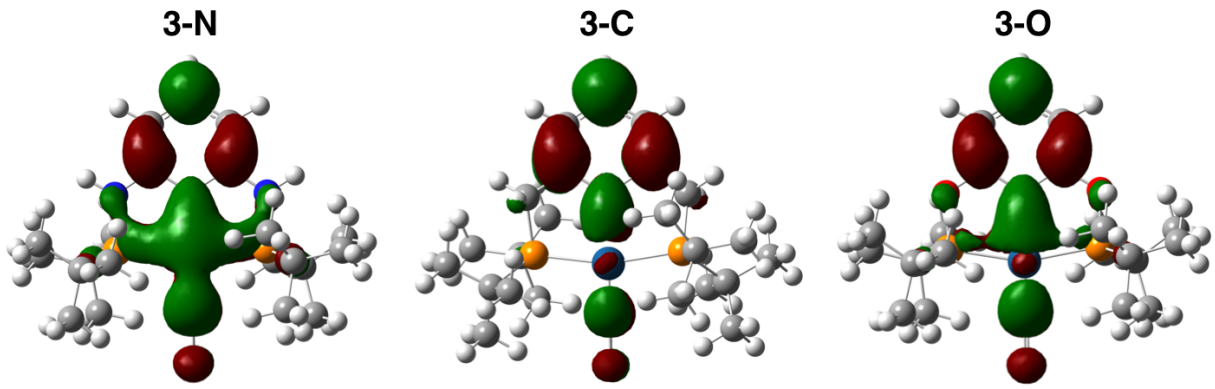


Figure S22. Singly occupied molecular orbitals (SOMOs) of reduced complexes **3-N** (left), **3-C** (middle), and **3-O** (right).

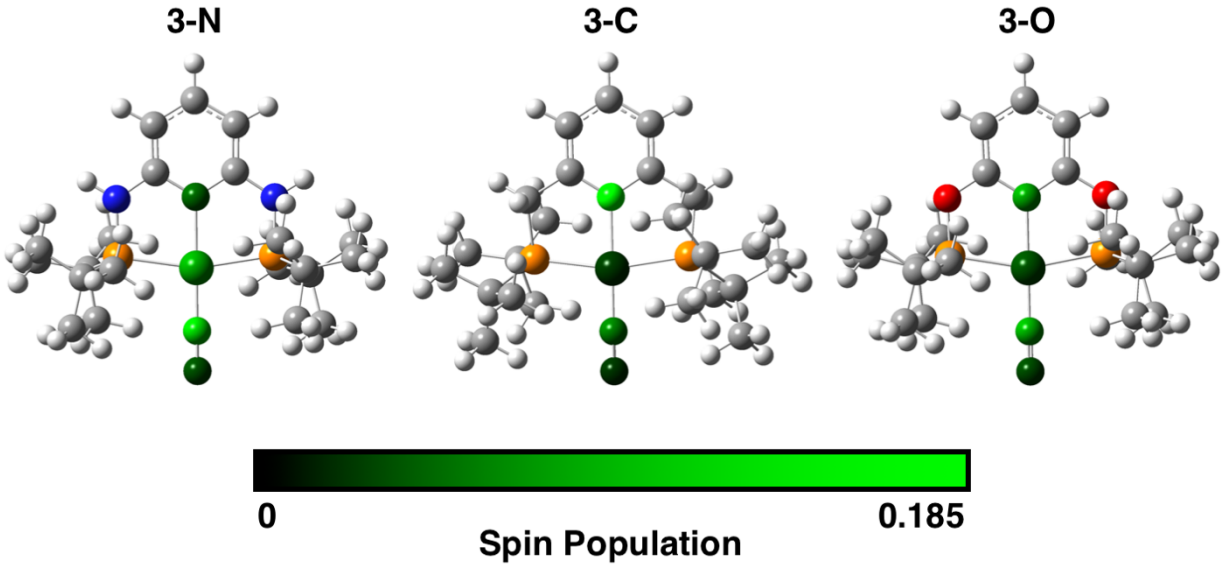
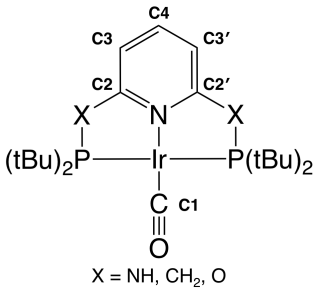


Figure S23. Mulliken spin population on the pyridyl N, Ir center, and CO of **3-N** (left), **3-C** (middle), and **3-O** (right). Lighter green indicates greater spin population according to the indicated scale. Note that the spin population of the C at the C4 position of the pyridyl ring has the largest spin population in all complexes (Table S4), but has been omitted from the color scale for clarity.

Table S4. Mulliken Spin Population by Atom.



Atom	3-N	3-C	3-O
O	0.053	0.037	0.049
C1	0.145	0.085	0.114
Ir	0.113	0.040	0.055
P	0.078	0.030	0.058
N	0.070	0.185	0.110
C2	0.161	0.168	0.196
C3	–0.081	–0.093	–0.112
C4	0.357	0.437	0.418

Note: Mulliken spin populations on other atoms (including the linkers) were negligible in all cases.

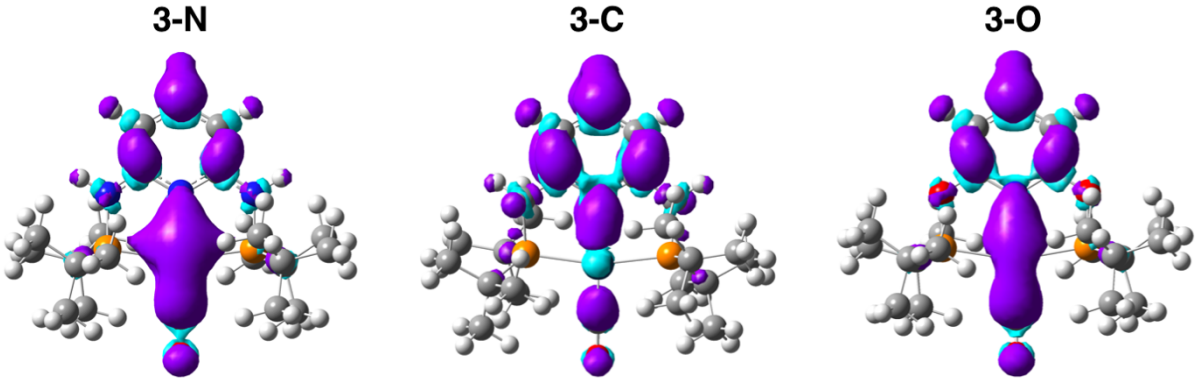


Figure S24. Electron density differences (isovalue = 0.0014) after reduction of **3-N** (left), **3-C** (middle), and **3-O** (right). Purple and light blue surfaces correspond to an increase and decrease in electron density, respectively. Electron densities were computed using the geometry of the oxidized complexes to exclude inconsequential differences due to small changes in geometry.

Table S5. CM5 Partial Charges on Ir Atom Before and After Reduction

Complex	Partial Charge on Ir (*e*)	Partial Charge on Ir After Reduction (*e*)
3-N	0.290	0.197
3-C	0.270	0.213
3-O	0.300	0.226

Table S6. Minimum energy geometries of complexes and corresponding SCF energy (a.u.) in solvent at UB3LYP/DEF2TZVP/6-311+G(2df,p) level.

[3-N]$^+$

Energy: -1890.16329791

Atom	x (Å)	y (Å)	z (Å)
Ir	0.000001	-0.402225	0.000042
C	-0.000015	-2.254531	0.000300
O	-0.000021	-3.415432	0.000461
P	-2.330772	-0.071746	0.012175
P	2.330781	-0.071779	-0.012187
N	0.000014	1.727719	-0.000257
C	1.177122	2.416918	-0.041343
C	-1.177085	2.416944	0.040629
C	1.208998	3.816472	-0.041678
C	-1.208943	3.816499	0.040562
C	0.000032	4.504778	-0.000656
H	2.156792	4.341010	-0.074096
H	-2.156731	4.341059	0.072829
H	0.000039	5.590349	-0.000812
C	-3.294478	-0.559306	1.582811
C	-3.236641	-0.466791	-1.619551
C	3.294473	-0.559794	-1.582689
C	3.236648	-0.466378	1.619648
C	-4.568020	0.285006	1.800551
H	-5.310140	0.161438	1.010612
H	-5.037006	-0.034424	2.738243
H	-4.341566	1.350344	1.911961
C	-2.333732	-0.307525	2.767095
H	-1.431723	-0.921010	2.697457
H	-2.031146	0.742460	2.831898
H	-2.851781	-0.561254	3.699241
C	-3.656308	-2.057781	1.528936
H	-4.428948	-2.273341	0.786454
H	-2.787484	-2.691114	1.323391
H	-4.052887	-2.357744	2.505402
C	-4.732800	-0.098990	-1.605952
H	-5.135584	-0.235940	-2.616144
H	-5.314491	-0.738945	-0.938245
H	-4.910973	0.946742	-1.332246
C	-3.068517	-1.968683	-1.938984
H	-3.547224	-2.175077	-2.902993
H	-2.015580	-2.248227	-2.027031
H	-3.537813	-2.619183	-1.197941
C	-2.520027	0.352690	-2.716771
H	-2.662845	1.429680	-2.590231

H	-1.445702	0.145255	-2.741373
H	-2.939533	0.073909	-3.689957
C	3.656255	-2.058267	-1.528404
H	4.428874	-2.273653	-0.785849
H	2.787405	-2.691516	-1.322706
H	4.052842	-2.358505	-2.504782
C	4.568041	0.284418	-1.800660
H	5.310164	0.161034	-1.010694
H	5.037010	-0.035274	-2.738272
H	4.341623	1.349734	-1.912348
C	2.333736	-0.308309	-2.767042
H	1.431700	-0.921734	-2.697226
H	2.031197	0.741671	-2.832146
H	2.851771	-0.562329	-3.699117
C	4.732820	-0.098640	1.605933
H	5.135606	-0.235316	2.616161
H	5.314480	-0.738811	0.938405
H	4.911033	0.947005	1.331924
C	2.520073	0.353451	2.716633
H	2.662936	1.430398	2.589779
H	1.445739	0.146070	2.741300
H	2.939570	0.074934	3.689898
C	3.068464	-1.968170	1.939518
H	3.547157	-2.174303	2.903590
H	2.015515	-2.247644	2.027637
H	3.537739	-2.618905	1.198667
N	2.330166	1.664722	-0.088746
H	3.195682	2.188972	-0.102700
N	-2.330138	1.664776	0.088244
H	-3.195648	2.189039	0.102046

[3-N]^{0}

Energy: -1890.23890156

Atom	x (Å)	y (Å)	z (Å)
Ir	-0.000002	-0.380173	0.000037
C	-0.000019	-2.235232	0.000283
O	-0.000030	-3.411955	0.000439
P	-2.305266	-0.040740	0.031850
P	2.305270	-0.040788	-0.031874
N	0.000016	1.711688	-0.000256
C	1.175072	2.444823	-0.072777
C	-1.175027	2.444864	0.072053
C	1.206889	3.827943	-0.071297
C	-1.206822	3.827984	0.070174
C	0.000040	4.552657	-0.000666
H	2.163378	4.338666	-0.130861
H	-2.163302	4.338740	0.129589

H	0.000049	5.636375	-0.000822
C	-3.306780	-0.598519	1.569521
C	-3.243301	-0.430700	-1.602470
C	3.306779	-0.599019	-1.569385
C	3.243299	-0.430307	1.602557
C	-4.588335	0.228355	1.804308
H	-5.330321	0.111966	1.012667
H	-5.055485	-0.105108	2.739615
H	-4.366002	1.293738	1.925382
C	-2.371575	-0.381873	2.779910
H	-1.457707	-0.974805	2.692553
H	-2.079672	0.668151	2.880135
H	-2.901273	-0.677310	3.695086
C	-3.654634	-2.096663	1.467258
H	-4.411324	-2.297751	0.703590
H	-2.772972	-2.709233	1.252927
H	-4.063491	-2.435147	2.427482
C	-4.749861	-0.114177	-1.572993
H	-5.158947	-0.232669	-2.584605
H	-5.306851	-0.790366	-0.919019
H	-4.956404	0.917142	-1.264544
C	-3.025287	-1.911457	-1.977308
H	-3.471016	-2.098837	-2.962484
H	-1.960174	-2.150931	-2.038358
H	-3.491138	-2.602656	-1.270606
C	-2.569220	0.446869	-2.680656
H	-2.743439	1.513646	-2.511283
H	-1.488001	0.279901	-2.709071
H	-2.986810	0.186618	-3.661415
C	3.654618	-2.097137	-1.466687
H	4.411308	-2.298011	-0.702962
H	2.772950	-2.709636	-1.252177
H	4.063470	-2.435903	-2.426814
C	4.588341	0.227777	-1.804410
H	5.330327	0.111609	-1.012738
H	5.055485	-0.105960	-2.739622
H	4.366016	1.293127	-1.925791
C	2.371576	-0.382715	-2.779836
H	1.457702	-0.975613	-2.692307
H	2.079682	0.667282	-2.880366
H	2.901270	-0.678423	-3.694926
C	4.749865	-0.113829	1.572987
H	5.158954	-0.232054	2.584629
H	5.306834	-0.790210	0.919194
H	4.956431	0.917401	1.264255
C	2.569240	0.447584	2.680495
H	2.743482	1.514309	2.510815
H	1.488018	0.280648	2.708961

H	2.986828	0.187604	3.661326
C	3.025247	-1.910953	1.977809
H	3.470953	-2.098065	2.963047
H	1.960128	-2.150387	2.038903
H	3.491099	-2.602361	1.271312
N	2.334653	1.670698	-0.164434
H	3.203193	2.187766	-0.161676
N	-2.334622	1.670784	0.163930
H	-3.203153	2.187865	0.161020

[3-N]$^-$

Energy: -1890.29942423

Atom	x (Å)	y (Å)	z (Å)
Ir	-0.021070	-0.437652	0.900237
C	-0.022173	-1.734853	2.218865
O	-0.052017	-2.660016	2.971097
P	-2.217408	-0.129973	0.238693
P	2.178314	-0.188567	0.194677
N	-0.003854	1.728236	0.466424
C	1.172382	2.376889	0.233054
C	-1.166667	2.405733	0.249618
C	1.225030	3.749163	-0.054846
C	-1.191550	3.776171	-0.044306
C	0.024456	4.457129	-0.171974
H	2.185119	4.237391	-0.196214
H	-2.141739	4.286208	-0.175215
H	0.035587	5.520905	-0.393479
C	-3.654294	-0.550364	1.479452
C	-2.940831	-0.457342	-1.607209
C	3.022102	-0.440875	-1.625385
C	3.551695	-0.668871	1.488158
C	-4.941105	0.286035	1.311225
H	-5.448506	0.125555	0.360188
H	-5.649356	0.013272	2.107235
H	-4.739283	1.357310	1.424829
C	-3.126228	-0.268794	2.902227
H	-2.257015	-0.879343	3.144804
H	-2.829711	0.778840	3.014264
H	-3.927873	-0.482223	3.625979
C	-3.985135	-2.051178	1.362567
H	-4.476778	-2.295218	0.415005
H	-3.081334	-2.663117	1.450923
H	-4.668167	-2.344301	2.172660
C	-4.423588	-0.199216	-1.919593
H	-4.602278	-0.331205	-3.000059
H	-5.089475	-0.896132	-1.401338
H	-4.733228	0.823588	-1.671759

C	-2.596309	-1.920488	-1.943924
H	-2.767003	-2.110274	-3.014834
H	-1.546722	-2.132104	-1.712838
H	-3.210155	-2.631840	-1.380888
C	-2.092488	0.459207	-2.507384
H	-2.389029	1.510273	-2.418326
H	-1.030821	0.385212	-2.251394
H	-2.214063	0.164988	-3.560458
C	3.467887	-1.902692	-1.788093
H	4.383106	-2.127767	-1.231043
H	2.684904	-2.593066	-1.451948
H	3.669568	-2.120699	-2.848763
C	4.167372	0.509769	-2.021902
H	5.066054	0.389670	-1.413620
H	4.459869	0.321997	-3.068856
H	3.856182	1.560381	-1.975207
C	1.852402	-0.185399	-2.591133
H	1.009399	-0.846452	-2.370731
H	1.487764	0.845785	-2.520200
H	2.179131	-0.356627	-3.628279
C	4.994327	-0.272462	1.121257
H	5.655491	-0.494387	1.971886
H	5.379351	-0.827091	0.261567
H	5.091484	0.799970	0.914134
C	3.192895	0.039003	2.812795
H	3.286368	1.126277	2.722891
H	2.166019	-0.182335	3.112533
H	3.881951	-0.303345	3.599366
C	3.488012	-2.193758	1.717032
H	4.170262	-2.468935	2.534606
H	2.481277	-2.510439	1.998648
H	3.790247	-2.760637	0.831455
N	2.300611	1.581633	0.280366
H	3.150323	2.050899	-0.005988
N	-2.316400	1.639195	0.331304
H	-3.153090	2.120261	0.023774

[3-C]$^{+}$

Energy: -1858.01786256

Atom	x (Å)	y (Å)	z (Å)
Ir	-0.000004	-0.345308	0.000013
C	-0.000033	-2.188028	0.000246
O	-0.000048	-3.350108	0.000393
P	-2.345948	-0.050947	0.100616
P	2.345948	-0.051052	-0.100653
N	0.000032	1.818096	-0.000262
C	1.143079	2.505762	-0.282912

C	-1.142991	2.505874	0.282213
C	1.166497	3.901091	-0.276844
C	-1.166361	3.901202	0.275789
C	0.000080	4.609039	-0.000617
H	2.091929	4.420057	-0.501785
H	-2.091775	4.420257	0.500599
H	0.000099	5.694616	-0.000755
C	-3.325661	-0.962890	1.468329
C	-3.213139	-0.072754	-1.603949
C	3.325651	-0.963383	-1.468117
C	3.213121	-0.072438	1.603927
C	-4.626780	-0.233213	1.869366
H	-5.347960	-0.166023	1.053965
H	-5.103611	-0.797172	2.679413
H	-4.443871	0.775704	2.251630
C	-2.401866	-1.038915	2.705814
H	-1.482223	-1.590618	2.498390
H	-2.123975	-0.050795	3.087821
H	-2.937268	-1.556288	3.510277
C	-3.659010	-2.398702	1.011363
H	-4.400610	-2.417289	0.208937
H	-2.773724	-2.949985	0.681784
H	-4.086680	-2.945944	1.859102
C	-4.730395	0.184453	-1.535266
H	-5.117965	0.274363	-2.556875
H	-5.270994	-0.636072	-1.057959
H	-4.979163	1.114576	-1.013623
C	-2.938858	-1.431206	-2.286407
H	-3.384053	-1.418928	-3.288082
H	-1.866167	-1.611839	-2.397667
H	-3.375125	-2.273921	-1.746149
C	-2.553199	1.035213	-2.456359
H	-2.767894	2.040768	-2.081102
H	-1.468358	0.907330	-2.519812
H	-2.955928	0.978854	-3.474060
C	3.658959	-2.399082	-1.010764
H	4.400551	-2.417473	-0.208325
H	2.773656	-2.950255	-0.681049
H	4.086625	-2.946560	-1.858353
C	4.626792	-0.233842	-1.869332
H	5.347963	-0.166451	-1.053940
H	5.103620	-0.798029	-2.679221
H	4.443909	0.774976	-2.251866
C	2.401867	-1.039713	-2.705591
H	1.482211	-1.591342	-2.498033
H	2.124000	-0.051687	-3.087859
H	2.937267	-1.557307	-3.509913
C	4.730383	0.184717	1.535194

H	5.117946	0.274877	2.556784
H	5.270968	-0.635941	1.058100
H	4.979178	1.114702	1.013318
C	2.553197	1.035765	2.456042
H	2.767903	2.041216	2.080516
H	1.468354	0.907911	2.519532
H	2.955927	0.979673	3.473758
C	2.938804	-1.430706	2.286738
H	3.383987	-1.418174	3.288414
H	1.866109	-1.611289	2.398032
H	3.375062	-2.273571	1.746706
C	-2.380575	1.731818	0.664357
H	-2.432961	1.702430	1.758940
H	-3.277853	2.259858	0.327804
C	2.380635	1.731565	-0.664860
H	2.433016	1.701890	-1.759435
H	3.277931	2.259662	-0.328447

[3-C]^{0}

Energy: -1858.09862303

Atom	x (Å)	y (Å)	z (Å)
Ir	0.000006	-0.349399	0.000059
C	0.000023	-2.194098	0.000480
O	0.000033	-3.369843	0.000751
P	-2.326711	-0.035471	0.117615
P	2.326719	-0.035496	-0.117636
N	-0.000008	1.758357	-0.000414
C	1.150361	2.503472	-0.303039
C	-1.150384	2.503595	0.301879
C	1.165012	3.881259	-0.294034
C	-1.165048	3.881377	0.292266
C	-0.000021	4.625507	-0.001048
H	2.092845	4.390789	-0.541504
H	-2.092885	4.391009	0.539510
H	-0.000025	5.709022	-0.001286
C	-3.331001	-0.995215	1.440664
C	-3.209769	-0.028113	-1.586518
C	3.331031	-0.995825	-1.440244
C	3.209763	-0.027355	1.586500
C	-4.627848	-0.271821	1.865742
H	-5.347578	-0.173691	1.051557
H	-5.110786	-0.853803	2.661025
H	-4.431982	0.725340	2.271578
C	-2.423286	-1.132912	2.684810
H	-1.499120	-1.667602	2.455098
H	-2.147180	-0.162650	3.109834
H	-2.968639	-1.689057	3.458324

C	-3.672718	-2.411353	0.932876
H	-4.406136	-2.395803	0.122201
H	-2.785904	-2.951960	0.589833
H	-4.111616	-2.987726	1.756887
C	-4.728692	0.215429	-1.515009
H	-5.117424	0.333175	-2.534674
H	-5.265831	-0.621028	-1.060104
H	-4.979866	1.129223	-0.965899
C	-2.923239	-1.359504	-2.313267
H	-3.340509	-1.309269	-3.327144
H	-1.846995	-1.536533	-2.394632
H	-3.373599	-2.221175	-1.814661
C	-2.562819	1.111669	-2.406628
H	-2.789476	2.101200	-1.999721
H	-1.475346	1.004087	-2.453270
H	-2.956331	1.073883	-3.430246
C	3.672745	-2.411735	-0.931817
H	4.406154	-2.395821	-0.121141
H	2.785928	-2.952190	-0.588540
H	4.111653	-2.988476	-1.755565
C	4.627881	-0.272612	-1.865621
H	5.347601	-0.174122	-1.051470
H	5.110832	-0.854940	-2.660643
H	4.432015	0.724370	-2.271895
C	2.423341	-1.134082	-2.684346
H	1.499163	-1.668656	-2.454413
H	2.147259	-0.164012	-3.109824
H	2.968706	-1.690588	-3.457591
C	4.728683	0.216179	1.514903
H	5.117398	0.334381	2.534522
H	5.265842	-0.620472	1.060378
H	4.979852	1.129736	0.965395
C	2.562785	1.112786	2.406090
H	2.789436	2.102137	1.998740
H	1.475313	1.005212	2.452766
H	2.956284	1.075466	3.429730
C	2.923252	-1.358425	2.313845
H	3.340515	-1.307726	3.327703
H	1.847012	-1.535440	2.395285
H	3.373634	-2.220310	1.815630
C	-2.364041	1.720608	0.735497
H	-2.355639	1.626282	1.830029
H	-3.287934	2.244111	0.468982
C	2.364022	1.720304	-0.736315
H	2.355608	1.625480	-1.830803
H	3.287912	2.243939	-0.470049

[3-C]$^-$

Energy: -1858.15120604

Atom	x (Å)	y (Å)	z (Å)
Ir	0.011507	-0.354084	0.250502
C	0.043461	-2.188445	0.505649
O	0.046162	-3.380012	0.557651
P	-2.288655	-0.045842	0.180460
P	2.295306	-0.028506	-0.069345
N	0.000808	1.750003	0.196884
C	1.120894	2.521732	-0.192521
C	-1.184701	2.505955	0.373863
C	1.082657	3.889916	-0.335780
C	-1.241930	3.873156	0.222136
C	-0.102963	4.638902	-0.125028
H	1.997104	4.392255	-0.649278
H	-2.198828	4.363749	0.396602
H	-0.138414	5.716204	-0.239923
C	-3.427451	-0.992943	1.422364
C	-3.136779	-0.038591	-1.587215
C	3.267690	-0.950741	-1.467020
C	3.341031	-0.064363	1.568912
C	-4.747851	-0.257544	1.741779
H	-5.394611	-0.139540	0.870807
H	-5.306762	-0.836778	2.490493
H	-4.567366	0.733851	2.169749
C	-2.650113	-1.157444	2.748587
H	-1.703069	-1.680107	2.599589
H	-2.413762	-0.194017	3.210658
H	-3.274760	-1.727053	3.454860
C	-3.739623	-2.403804	0.881458
H	-4.398575	-2.377767	0.008797
H	-2.827238	-2.944707	0.612710
H	-4.252689	-2.983632	1.661381
C	-4.655416	0.202192	-1.612599
H	-4.986730	0.324195	-2.655709
H	-5.221544	-0.635235	-1.193624
H	-4.938849	1.115114	-1.076527
C	-2.798372	-1.362995	-2.298679
H	-3.095539	-1.296027	-3.355455
H	-1.720727	-1.554523	-2.249834
H	-3.316329	-2.222498	-1.863409
C	-2.445572	1.103024	-2.363470
H	-2.732784	2.091325	-1.993522
H	-1.355644	1.017523	-2.291644
H	-2.731207	1.040473	-3.423502

C	3.618150	-2.379304	-1.004119
H	4.384725	-2.386818	-0.223844
H	2.737079	-2.909307	-0.629247
H	4.013805	-2.949778	-1.856364
C	4.547281	-0.229870	-1.943791
H	5.318168	-0.177760	-1.173014
H	4.973660	-0.777048	-2.797373
H	4.338782	0.788934	-2.287142
C	2.305870	-1.066260	-2.670647
H	1.372169	-1.556915	-2.383543
H	2.040416	-0.086139	-3.080280
H	2.797511	-1.644163	-3.468042
C	4.851269	0.177518	1.398258
H	5.312830	0.291693	2.389862
H	5.355904	-0.657926	0.903485
H	5.065043	1.093119	0.834866
C	2.758065	1.066190	2.447313
H	2.980349	2.060548	2.048122
H	1.670402	0.970165	2.533771
H	3.198039	1.000795	3.452516
C	3.103062	-1.398577	2.303469
H	3.557755	-1.349515	3.303261
H	2.029759	-1.584357	2.418229
H	3.542733	-2.253601	1.781896
C	-2.377122	1.710809	0.811250
H	-2.337577	1.566251	1.904021
H	-3.314063	2.226314	0.573398
C	2.340967	1.744450	-0.620548
H	2.338189	1.684328	-1.719961
H	3.265253	2.256925	-0.329624

[3-O]$^{+}$

Energy: -1929.90308082

Atom	x (Å)	y (Å)	z (Å)
Ir	-0.000001	0.475554	0.000037
C	-0.000020	2.335035	0.000105
O	-0.000032	3.493638	0.000147
P	2.314431	0.087965	0.004094
P	-2.314426	0.087918	-0.004049
N	0.000020	-1.636220	-0.000040
C	1.170896	-2.326329	0.018572
C	-1.170841	-2.326352	-0.018703
C	1.212520	-3.717672	0.018590
C	-1.212438	-3.717695	-0.018823
C	0.000049	-4.406463	-0.000142
H	2.169676	-4.222932	0.033185
H	-2.169582	-4.222974	-0.033455
H	0.000060	-5.491847	-0.000181
C	3.290734	0.444546	1.589083
C	3.242058	0.415352	-1.615494
C	-3.290733	0.444594	-1.589013
C	-3.242061	0.415169	1.615561
C	4.537914	-0.449532	1.749656
H	5.316225	-0.229476	1.018850
H	4.961862	-0.266201	2.743547
H	4.289853	-1.511995	1.686000
C	2.320927	0.155201	2.758712
H	1.421877	0.775740	2.710558
H	2.016390	-0.895952	2.786897
H	2.837665	0.371929	3.700436
C	3.686513	1.936250	1.608698
H	4.450503	2.173451	0.863741
H	2.829917	2.601364	1.456974
H	4.108853	2.170987	2.592040
C	4.715460	-0.032652	-1.592249
H	5.120423	0.059390	-2.606552
H	5.329715	0.595527	-0.942927
H	4.828350	-1.076402	-1.285945
C	3.146850	1.925486	-1.929846
H	3.637918	2.109034	-2.892014
H	2.109794	2.259887	-2.019758
H	3.649204	2.548426	-1.185754
C	2.484939	-0.372980	-2.709407
H	2.579799	-1.454130	-2.575109
H	1.422497	-0.111417	-2.740939
H	2.921235	-0.120267	-3.682104
C	-3.686530	1.936295	-1.608526
H	-4.450526	2.173435	-0.863556
H	-2.829943	2.601409	-1.456753

H	-4.108870	2.171095	-2.591853
C	-4.537901	-0.449488	-1.749649
H	-5.316218	-0.229491	-1.018831
H	-4.961849	-0.266096	-2.743529
H	-4.289829	-1.511952	-1.686063
C	-2.320921	0.155342	-2.758662
H	-1.421879	0.775887	-2.710464
H	-2.016373	-0.895806	-2.786919
H	-2.837660	0.372129	-3.700371
C	-4.715453	-0.032863	1.592283
H	-5.120418	0.059093	2.606593
H	-5.329721	0.595351	0.943008
H	-4.828321	-1.076593	1.285901
C	-2.484926	-0.373224	2.709419
H	-2.579762	-1.454367	2.575044
H	-1.422490	-0.111640	2.740971
H	-2.921229	-0.120590	3.682133
C	-3.146884	1.925283	1.930020
H	-3.637951	2.108753	2.892203
H	-2.109835	2.259701	2.019950
H	-3.649255	2.548264	1.185974
O	-2.321895	-1.629770	-0.041588
O	2.321935	-1.629725	0.041509

[3-O]^{0}

Energy: -1929.98908751

Atom	x (Å)	y (Å)	z (Å)
Ir	-0.000003	0.467001	0.000008
C	0.000028	2.327297	0.000047
O	0.000048	3.501360	0.000071
P	2.288273	0.062632	0.009426
P	-2.288292	0.062709	-0.009426
N	-0.000037	-1.603755	-0.000036
C	1.170828	-2.344177	0.031508
C	-1.170927	-2.344136	-0.031610
C	1.212327	-3.717680	0.030684
C	-1.212473	-3.717638	-0.030843
C	-0.000085	-4.444539	-0.000094
H	2.177845	-4.209500	0.055685
H	-2.178008	-4.209425	-0.055864
H	-0.000103	-5.527663	-0.000116
C	3.301840	0.472127	1.570201
C	3.239843	0.407711	-1.606822
C	-3.301846	0.472307	-1.570183
C	-3.239850	0.407750	1.606838
C	4.553372	-0.413881	1.739357
H	5.331441	-0.196131	1.006794

H	4.978772	-0.228579	2.733685
H	4.303713	-1.476240	1.674972
C	2.355466	0.202945	2.762931
H	1.448953	0.811223	2.706277
H	2.054682	-0.848506	2.809715
H	2.885366	0.442813	3.693455
C	3.689179	1.964414	1.560618
H	4.441112	2.193164	0.799836
H	2.822762	2.614945	1.400648
H	4.120544	2.226426	2.534484
C	4.725452	0.005561	-1.575039
H	5.136084	0.094465	-2.588811
H	5.318876	0.658295	-0.929242
H	4.863896	-1.030537	-1.252172
C	3.099897	1.904809	-1.955085
H	3.562945	2.084509	-2.933225
H	2.050098	2.204175	-2.019677
H	3.598687	2.556369	-1.232379
C	2.519353	-0.423026	-2.693514
H	2.637757	-1.497555	-2.528013
H	1.449817	-0.193936	-2.729473
H	2.957076	-0.179308	-3.669397
C	-3.689133	1.964607	-1.560534
H	-4.441059	2.193349	-0.799743
H	-2.822693	2.615100	-1.400532
H	-4.120486	2.226677	-2.534389
C	-4.553408	-0.413650	-1.739378
H	-5.331470	-0.195906	-1.006805
H	-4.978801	-0.228289	-2.733698
H	-4.303786	-1.476020	-1.675040
C	-2.355481	0.203145	-2.762925
H	-1.448948	0.811389	-2.706244
H	-2.054734	-0.848315	-2.809755
H	-2.885374	0.443072	-3.693438
C	-4.725472	0.005653	1.575037
H	-5.136102	0.094528	2.588813
H	-5.318874	0.658435	0.929268
H	-4.863952	-1.030427	1.252126
C	-2.519388	-0.423059	2.693493
H	-2.637829	-1.497577	2.527944
H	-1.449844	-0.194007	2.729462
H	-2.957104	-0.179369	3.669386
C	-3.099851	1.904828	1.955165
H	-3.562892	2.084502	2.933314
H	-2.050042	2.204155	2.019769
H	-3.598620	2.556437	1.232489
O	-2.337259	-1.622322	-0.072789
O	2.337183	-1.622403	0.072715

[3-O]$^-$

Energy: -1930.05405806

Atom	x (Å)	y (Å)	z (Å)
Ir	0.014364	-0.750440	-0.062446
C	-0.008785	-2.593491	-0.304190
O	-0.003532	-3.782899	-0.338696
P	2.192788	-0.058993	0.236280
P	-2.168306	-0.064982	0.265746
N	0.013267	1.110157	-1.186128
C	1.178279	1.730757	-1.498445
C	-1.155351	1.732664	-1.481710
C	1.219745	2.901924	-2.256703
C	-1.202892	2.903420	-2.242424
C	0.006044	3.477199	-2.652698
H	2.179142	3.341281	-2.504979
H	-2.164494	3.343699	-2.480384
H	0.002939	4.387091	-3.246434
C	3.659086	-1.130080	-0.440623
C	2.909336	1.055050	1.721167
C	-3.021736	1.071612	1.668261
C	-3.556299	-1.213240	-0.445989
C	4.891537	-0.332736	-0.919100
H	5.459351	0.114125	-0.103664
H	5.569349	-1.016765	-1.450065
H	4.603383	0.460115	-1.615254
C	3.128848	-1.910523	-1.662826
H	2.284629	-2.550768	-1.409823
H	2.799674	-1.231426	-2.455586
H	3.943010	-2.534550	-2.060861
C	4.065701	-2.140002	0.651238
H	4.538934	-1.653067	1.510470
H	3.200977	-2.708959	1.009428
H	4.790283	-2.856362	0.238679
C	4.376591	1.510749	1.703240
H	4.552534	2.206554	2.540122
H	5.075205	0.678384	1.832422
H	4.629386	2.040532	0.779410
C	2.634898	0.253521	3.008922
H	2.829908	0.884456	3.889057
H	1.593633	-0.083861	3.044094
H	3.274291	-0.632778	3.089717
C	2.019130	2.311556	1.727324
H	2.271711	2.987024	0.903941
H	0.960809	2.047335	1.643892
H	2.158962	2.859646	2.670672
C	-3.527637	0.157886	2.798035
H	-4.432966	-0.391066	2.519379
H	-2.762730	-0.571883	3.090916

H	-3.770179	0.759475	3.687181
C	-4.124396	2.048792	1.219997
H	-5.062207	1.551058	0.968189
H	-4.342996	2.755921	2.037068
H	-3.805294	2.631511	0.351132
C	-1.850862	1.906565	2.216985
H	-1.019158	1.266320	2.525172
H	-1.470900	2.610003	1.467492
H	-2.188226	2.493673	3.083951
C	-4.977736	-0.622797	-0.473851
H	-5.644285	-1.325410	-0.995319
H	-5.390889	-0.471732	0.526919
H	-5.011327	0.328043	-1.014368
C	-3.165982	-1.555532	-1.900989
H	-3.211542	-0.668348	-2.540681
H	-2.154628	-1.962985	-1.958240
H	-3.875484	-2.298973	-2.293355
C	-3.554803	-2.512657	0.387557
H	-4.253337	-3.233335	-0.061658
H	-2.563682	-2.971974	0.409063
H	-3.875558	-2.341865	1.420372
O	-2.285328	1.191641	-0.996420
O	2.315111	1.181100	-1.032112

$[Ir(acac)(CO)_2]^0$
Energy: -676.604264265

Atom	x (Å)	y (Å)	z (Å)
C	-0.057823	-2.100227	-0.000946
O	-0.080142	-3.254610	-0.041095
Ir	-0.007440	-0.243145	0.019908
C	-0.591749	-0.228837	1.783457
O	-0.954046	-0.191277	2.879832
O	0.643879	-0.207651	-1.940638
O	0.064689	1.821621	-0.005636
C	0.410926	2.587216	-0.977404
C	0.915079	0.819003	-2.663660
C	0.819527	2.157213	-2.249908
H	1.082559	2.920617	-2.971772
C	1.368582	0.489932	-4.064877
H	0.588646	-0.088774	-4.571269
H	1.591754	1.384051	-4.649965
H	2.260543	-0.143888	-4.017415
C	0.351408	4.061116	-0.658905
H	1.004149	4.273783	0.194513
H	0.650890	4.681450	-1.505706
H	-0.668073	4.325862	-0.358642

$[Ir(acac)(CO)_2]^-$

Energy: -676.682004236

Atom	x (Å)	y (Å)	z (Å)
C	-0.237598	-2.037757	-0.183929
O	-0.610160	-3.152130	-0.226377
Ir	0.129604	-0.247917	0.075187
C	-0.890398	-0.118006	1.607556
O	-1.614610	-0.198209	2.530330
O	1.335823	-0.161445	-1.704119
O	0.657561	1.835533	0.160576
C	0.658342	2.595119	-0.896908
C	1.258041	0.827623	-2.547254
C	0.939645	2.153128	-2.201945
H	0.884360	2.883842	-3.004627
C	1.487734	0.447074	-3.995539
H	0.705951	-0.251864	-4.327641
H	1.485105	1.318237	-4.659930
H	2.445984	-0.077617	-4.103093
C	0.269300	4.037152	-0.643425
H	0.353833	4.655190	-1.544110
H	-0.767049	4.086730	-0.277982
H	0.901888	4.468772	0.143101

Crystal Data

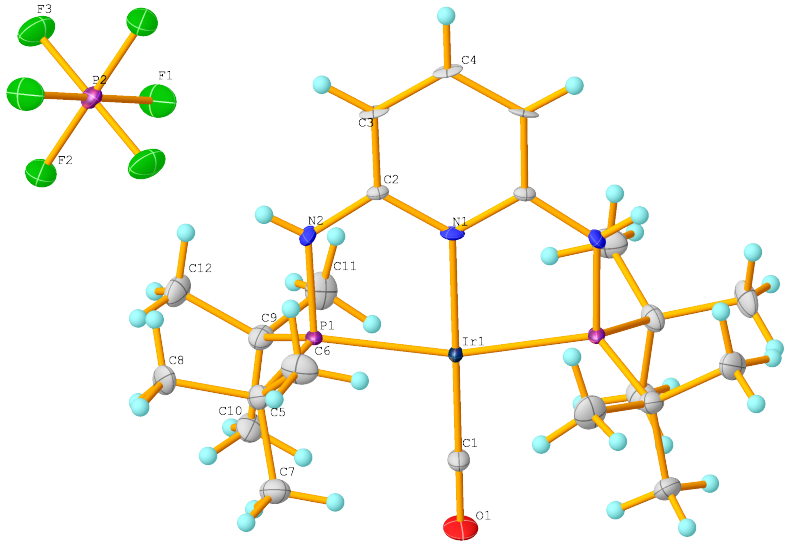


Figure S25. The complete numbering scheme of **3-N** (CCDC number: 007c-18031) with 50% thermal ellipsoid probability levels. Only the asymmetric unit is labeled. The hydrogen atoms are shown as circles for clarity.

Table S7. Crystal data and structure refinement for **3-N.**

Identification code	007c-18031	
Empirical formula	C22 H41 F6 Ir N3 O P3	
Formula weight	762.69	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 11.5628(2) Å	α = 90°.
	b = 11.2503(2) Å	β = 93.550(2)°.
	c = 22.9994(5) Å	γ = 90°.
Volume	2986.14(10) $Å^3$	
Z	4	
Density (calculated)	1.696 Mg/m^3	
Absorption coefficient	4.690 mm^{-1}	
F(000)	1512	
Crystal size	0.100 x 0.100 x 0.050 mm^3	
Crystal color and habit	Yellow Plate	
Diffractometer	Dectris Pilatus 3R	
Theta range for data collection	3.026 to 27.485°.	

Index ranges	-14<=h<=14, -14<=k<=14, -2<=l<=29
Reflections collected	3424
Independent reflections	3424 [R(int) = 0.1175]
Observed reflections (I > 2sigma(I))	3388
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.51643
Solution method	SHELXT-2014/5 (Sheldrick, 2014)
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)
Data / restraints / parameters	3424 / 0 / 174
Goodness-of-fit on F^2	1.082
Final R indices [I>2sigma(I)]	R1 = 0.0488, wR2 = 0.1212
R indices (all data)	R1 = 0.0492, wR2 = 0.1214
Largest diff. peak and hole	3.268 and -9.314 e.$Å^{-3}$

Table S8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3-N**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	5000	3863(1)	7500	9(1)
P(1)	5098(2)	3595(2)	6519(1)	11(1)
P(2)	5000	0	5000	15(1)
F(1)	3974(5)	460(5)	5376(3)	37(1)
F(2)	4919(5)	1196(4)	4624(2)	32(1)
F(3)	4081(5)	-632(5)	4550(2)	34(1)
O(1)	5000	6520(7)	7500	43(3)
N(1)	5000	2018(7)	7500	12(2)
N(2)	4996(6)	2080(5)	6488(3)	14(1)
C(1)	5000	5483(9)	7500	21(2)
C(2)	5008(6)	1403(6)	6986(3)	11(1)
C(3)	5016(6)	169(6)	6978(3)	15(1)
C(4)	5000	-460(8)	7500	15(1)
C(5)	6557(7)	3921(7)	6243(3)	20(2)
C(6)	7420(8)	3132(8)	6607(4)	29(2)
C(7)	6869(8)	5231(7)	6364(4)	25(2)
C(8)	6633(8)	3643(8)	5591(4)	27(2)
C(9)	3847(7)	4109(7)	6044(3)	19(2)
C(10)	3934(8)	5457(7)	5955(4)	23(2)
C(11)	2770(7)	3826(9)	6384(4)	29(2)
C(12)	3699(8)	3470(8)	5455(4)	25(2)

Table S9. Bond lengths [Å] and angles [°] for 3-N.

Ir(1)-C(1)	1.822(10)
Ir(1)-N(1)	2.076(8)
Ir(1)-P(1)	2.2857(17)
Ir(1)-P(1)#1	2.2858(17)
P(1)-N(2)	1.710(6)
P(1)-C(9)	1.850(8)
P(1)-C(5)	1.875(8)
P(2)-F(1)	1.597(5)
P(2)-F(1)#2	1.597(5)
P(2)-F(2)	1.599(5)
P(2)-F(2)#2	1.599(5)
P(2)-F(3)	1.604(5)
P(2)-F(3)#2	1.604(5)
O(1)-C(1)	1.166(14)
N(1)-C(2)#1	1.371(8)
N(1)-C(2)	1.371(8)
N(2)-C(2)	1.374(9)
N(2)-H(2)	0.79(9)
C(2)-C(3)	1.388(9)
C(3)-C(4)	1.395(9)
C(3)-H(3)	0.9500
C(4)-C(3)#1	1.395(9)
C(4)-H(4)	0.9500
C(5)-C(7)	1.539(11)
C(5)-C(8)	1.540(11)
C(5)-C(6)	1.543(12)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800

C(9)-C(12)	1.534(11)
C(9)-C(10)	1.535(11)
C(9)-C(11)	1.545(12)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800

C(1)-Ir(1)-N(1)	180.0
C(1)-Ir(1)-P(1)	97.59(4)
N(1)-Ir(1)-P(1)	82.41(4)
C(1)-Ir(1)-P(1)#1	97.59(4)
N(1)-Ir(1)-P(1)#1	82.41(4)
P(1)-Ir(1)-P(1)#1	164.82(9)
N(2)-P(1)-C(9)	103.7(3)
N(2)-P(1)-C(5)	104.0(3)
C(9)-P(1)-C(5)	115.2(4)
N(2)-P(1)-Ir(1)	99.5(2)
C(9)-P(1)-Ir(1)	117.2(3)
C(5)-P(1)-Ir(1)	114.1(3)
F(1)-P(2)-F(1)#2	180.0
F(1)-P(2)-F(2)	90.0(3)
F(1)#2-P(2)-F(2)	90.0(3)
F(1)-P(2)-F(2)#2	90.0(3)
F(1)#2-P(2)-F(2)#2	90.0(3)
F(2)-P(2)-F(2)#2	180.0
F(1)-P(2)-F(3)	90.5(3)
F(1)#2-P(2)-F(3)	89.5(3)
F(2)-P(2)-F(3)	90.6(3)
F(2)#2-P(2)-F(3)	89.4(3)
F(1)-P(2)-F(3)#2	89.5(3)
F(1)#2-P(2)-F(3)#2	90.5(3)

F(2)-P(2)-F(3)#2	89.4(3)
F(2)#2-P(2)-F(3)#2	90.6(3)
F(3)-P(2)-F(3)#2	180.0
C(2)#1-N(1)-C(2)	119.4(8)
C(2)#1-N(1)-Ir(1)	120.3(4)
C(2)-N(1)-Ir(1)	120.3(4)
C(2)-N(2)-P(1)	121.4(5)
C(2)-N(2)-H(2)	117(6)
P(1)-N(2)-H(2)	121(6)
O(1)-C(1)-Ir(1)	180.0
N(1)-C(2)-N(2)	116.0(6)
N(1)-C(2)-C(3)	121.1(6)
N(2)-C(2)-C(3)	122.9(6)
C(2)-C(3)-C(4)	119.7(7)
C(2)-C(3)-H(3)	120.2
C(4)-C(3)-H(3)	120.2
C(3)-C(4)-C(3)#1	119.1(8)
C(3)-C(4)-H(4)	120.5
C(3)#1-C(4)-H(4)	120.5
C(7)-C(5)-C(8)	110.1(7)
C(7)-C(5)-C(6)	108.4(7)
C(8)-C(5)-C(6)	109.7(7)
C(7)-C(5)-P(1)	109.4(5)
C(8)-C(5)-P(1)	113.4(6)
C(6)-C(5)-P(1)	105.6(5)
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(5)-C(7)-H(7A)	109.5
C(5)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(5)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5

C(5)-C(8)-H(8A)	109.5
C(5)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(5)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(12)-C(9)-C(10)	110.4(7)
C(12)-C(9)-C(11)	107.5(7)
C(10)-C(9)-C(11)	109.4(7)
C(12)-C(9)-P(1)	114.6(5)
C(10)-C(9)-P(1)	109.4(5)
C(11)-C(9)-P(1)	105.2(5)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(9)-C(12)-H(12A)	109.5
C(9)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(9)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2 #2 -x+1,-y,-z+1

Table S10. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3-N**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	14(1)	7(1)	7(1)	0	1(1)	0
P(1)	19(1)	6(1)	9(1)	0(1)	3(1)	-1(1)
P(2)	19(1)	13(1)	14(1)	-4(1)	4(1)	0(1)
F(1)	36(3)	30(3)	48(3)	-8(2)	27(3)	0(2)
F(2)	48(3)	20(2)	27(3)	3(2)	2(2)	-2(2)
F(3)	37(3)	29(3)	35(3)	-6(2)	-12(2)	-6(2)
O(1)	86(8)	7(4)	37(5)	0	15(6)	0
N(1)	15(4)	4(3)	18(4)	0	3(3)	0
N(2)	23(3)	9(3)	9(3)	-3(2)	3(2)	1(2)
C(1)	36(6)	11(5)	15(5)	0	5(5)	0
C(2)	12(3)	6(3)	14(3)	-1(2)	0(2)	0(2)
C(3)	14(3)	3(2)	26(3)	-5(2)	1(2)	2(2)
C(4)	14(3)	3(2)	26(3)	-5(2)	1(2)	2(2)
C(5)	22(4)	19(4)	18(4)	-3(3)	8(3)	-3(3)
C(6)	20(4)	27(4)	41(5)	1(4)	7(4)	1(3)
C(7)	27(4)	20(4)	29(4)	-3(3)	7(3)	-5(3)
C(8)	30(4)	32(4)	20(4)	-5(3)	15(3)	-10(4)
C(9)	23(4)	15(3)	18(4)	0(3)	-1(3)	3(3)
C(10)	32(4)	18(4)	20(4)	3(3)	-2(3)	7(3)
C(11)	21(4)	39(5)	27(4)	2(4)	-6(3)	6(4)
C(12)	31(4)	26(4)	17(4)	-3(3)	-8(3)	5(3)

Table S11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **3-N**.

	x	y	z	U(eq)
H(2)	5060(70)	1740(80)	6190(40)	10(20)
H(3)	5032	-245	6618	18
H(4)	5000	-1304	7500	18
H(6A)	7378	3320	7021	43
H(6B)	8208	3281	6490	43
H(6C)	7223	2293	6540	43
H(7A)	6285	5745	6166	38
H(7B)	7631	5403	6220	38
H(7C)	6890	5380	6785	38
H(8A)	6379	2824	5514	40
H(8B)	7435	3737	5484	40
H(8C)	6132	4191	5360	40
H(10A)	4072	5848	6334	35
H(10B)	3209	5752	5764	35
H(10C)	4577	5632	5710	35
H(11A)	2785	2987	6500	44
H(11B)	2067	3984	6136	44
H(11C)	2773	4327	6733	44
H(12A)	4378	3622	5231	38
H(12B)	3002	3767	5238	38
H(12C)	3623	2613	5519	38

Table S12. Torsion angles [°] for **3-N**.

C(9)-P(1)-N(2)-C(2)	-127.8(6)
C(5)-P(1)-N(2)-C(2)	111.3(6)
Ir(1)-P(1)-N(2)-C(2)	-6.7(6)
C(2)#1-N(1)-C(2)-N(2)	178.9(7)
Ir(1)-N(1)-C(2)-N(2)	-1.1(7)
C(2)#1-N(1)-C(2)-C(3)	-0.4(5)
Ir(1)-N(1)-C(2)-C(3)	179.6(5)
P(1)-N(2)-C(2)-N(1)	5.8(8)
P(1)-N(2)-C(2)-C(3)	-174.9(6)
N(1)-C(2)-C(3)-C(4)	0.9(10)
N(2)-C(2)-C(3)-C(4)	-178.4(6)
C(2)-C(3)-C(4)-C(3)#1	-0.4(5)
N(2)-P(1)-C(5)-C(7)	-168.5(6)
C(9)-P(1)-C(5)-C(7)	78.7(6)
Ir(1)-P(1)-C(5)-C(7)	-61.1(6)
N(2)-P(1)-C(5)-C(8)	68.2(6)
C(9)-P(1)-C(5)-C(8)	-44.7(7)
Ir(1)-P(1)-C(5)-C(8)	175.5(5)
N(2)-P(1)-C(5)-C(6)	-52.0(6)
C(9)-P(1)-C(5)-C(6)	-164.8(5)
Ir(1)-P(1)-C(5)-C(6)	55.4(6)
N(2)-P(1)-C(9)-C(12)	-46.7(7)
C(5)-P(1)-C(9)-C(12)	66.3(7)
Ir(1)-P(1)-C(9)-C(12)	-155.2(5)
N(2)-P(1)-C(9)-C(10)	-171.3(5)
C(5)-P(1)-C(9)-C(10)	-58.3(6)
Ir(1)-P(1)-C(9)-C(10)	80.2(6)
N(2)-P(1)-C(9)-C(11)	71.2(6)
C(5)-P(1)-C(9)-C(11)	-175.8(5)
Ir(1)-P(1)-C(9)-C(11)	-37.3(6)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+3/2 #2 -x+1,-y,-z+1

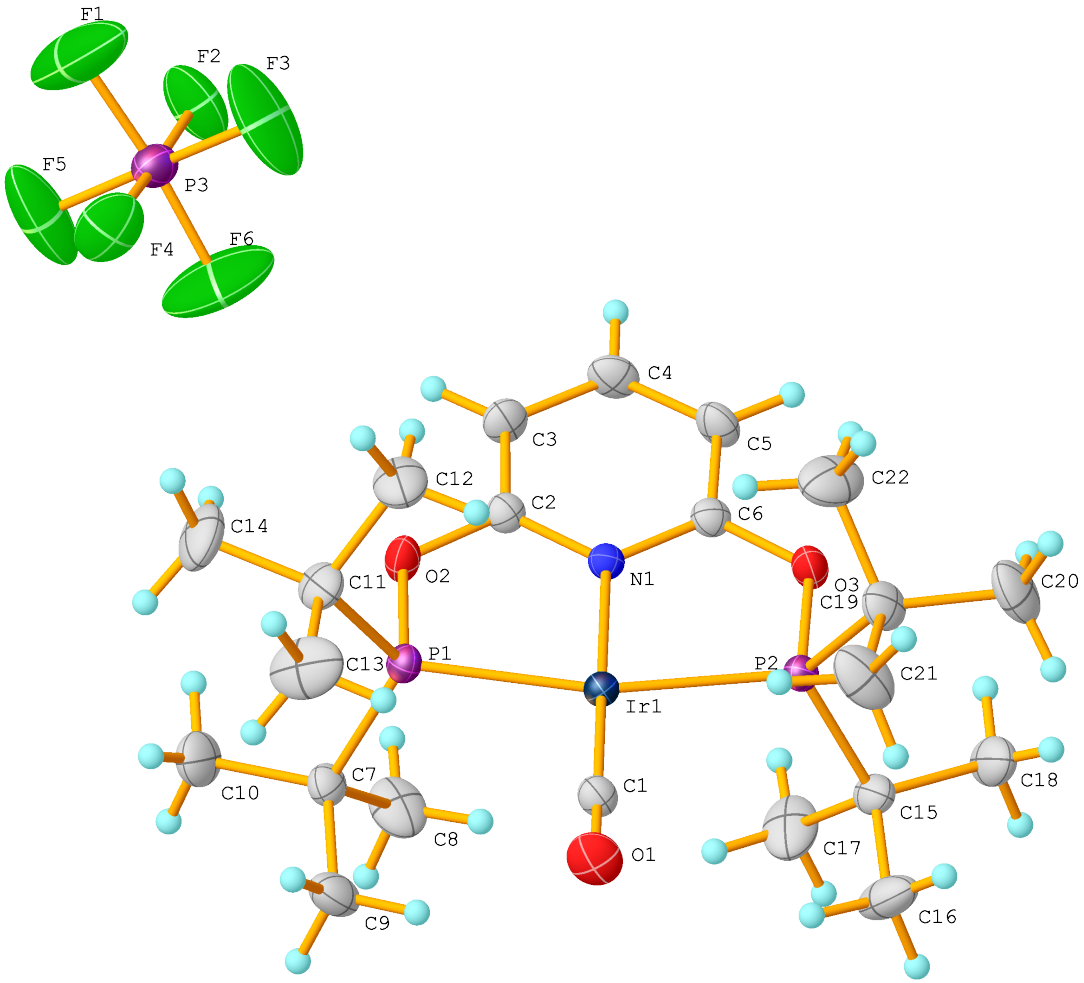


Figure S26. The complete numbering scheme of **3-O** (CCDC number: 007c-18033) with 50% thermal ellipsoid probability levels. The hydrogen atoms are shown as circles for clarity.

Table S13. Crystal data and structure refinement for **3-O**.

Identification code	007c-18033	
Empirical formula	C22 H39 F6 Ir N O3 P3	
Formula weight	764.65	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.4834(2) Å	α = 90°.
	b = 27.8076(7) Å	β = 91.593(2)°.
	c = 12.4613(2) Å	γ = 90°.
Volume	2938.52(11) $Å^3$	

Z	4
Density (calculated)	1.728 Mg/m^3
Absorption coefficient	4.769 mm^{-1}
F(000)	1512
Crystal size	0.320 x 0.150 x 0.060 mm^3
Crystal color and habit	Yellow Plate
Diffractometer	Dectris Pilatus 3R
Theta range for data collection	2.813 to 27.484°.
Index ranges	-11<=h<=11, -36<=k<=36, -16<=l<=16
Reflections collected	76580
Independent reflections	6716 [R(int) = 0.0743]
Observed reflections (I > 2sigma(I))	6332
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.36471
Solution method	SHELXT-2014/5 (Sheldrick, 2014)
Refinement method	SHELXL-2014/7 (Sheldrick, 2014)
Data / restraints / parameters	6716 / 0 / 337
Goodness-of-fit on F^2	1.090
Final R indices [I>2sigma(I)]	R1 = 0.0268, wR2 = 0.0654
R indices (all data)	R1 = 0.0292, wR2 = 0.0666
Largest diff. peak and hole	1.334 and -0.777 $e.Å^{-3}$

Table S14. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3-O**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	3390(1)	6080(1)	4034(1)	17(1)
P(1)	3845(1)	6583(1)	5460(1)	20(1)
P(2)	2279(1)	5751(1)	2509(1)	19(1)
O(1)	5998(3)	5370(1)	4441(2)	37(1)
O(2)	2518(3)	7020(1)	5206(2)	26(1)
O(3)	939(3)	6170(1)	2165(2)	26(1)
N(1)	1736(3)	6600(1)	3677(2)	18(1)
C(1)	4960(4)	5635(1)	4300(3)	24(1)
C(2)	1605(4)	6999(1)	4299(3)	22(1)
C(3)	601(4)	7373(1)	4043(3)	28(1)
C(4)	-305(4)	7334(1)	3100(3)	30(1)
C(5)	-221(4)	6931(1)	2450(3)	29(1)
C(6)	812(4)	6569(1)	2769(3)	22(1)
C(7)	3198(4)	6360(1)	6776(3)	25(1)
C(8)	1463(5)	6210(2)	6597(4)	45(1)
C(9)	4179(6)	5910(2)	7063(3)	38(1)
C(10)	3318(6)	6727(2)	7692(3)	42(1)
C(11)	5676(5)	6947(1)	5466(3)	32(1)
C(12)	5791(6)	7130(2)	4308(4)	44(1)
C(13)	7088(5)	6621(2)	5727(5)	57(1)
C(14)	5648(6)	7383(2)	6226(4)	53(1)
C(15)	967(4)	5229(1)	2699(3)	28(1)
C(16)	2012(6)	4785(2)	2892(4)	49(1)
C(17)	44(6)	5342(2)	3705(4)	53(1)
C(18)	-216(5)	5140(2)	1766(4)	42(1)
C(19)	3503(5)	5744(1)	1300(3)	30(1)
C(20)	2675(6)	5543(2)	290(3)	46(1)
C(21)	5008(5)	5463(2)	1541(4)	48(1)
C(22)	3884(6)	6280(2)	1084(4)	50(1)
P(3)	8225(1)	8663(1)	4421(1)	31(1)
F(1)	8965(6)	9181(1)	4395(5)	124(2)
F(2)	6550(4)	8876(1)	4076(2)	62(1)

F(3)	8611(5)	8563(2)	3229(3)	107(2)
F(4)	9955(3)	8463(1)	4789(3)	60(1)
F(5)	7872(5)	8760(2)	5643(2)	95(2)
F(6)	7594(5)	8149(1)	4552(5)	114(2)

Table S15. Bond lengths [Å] and angles [°] for **3-O**.

Ir(1)-C(1)	1.841(3)
Ir(1)-N(1)	2.054(3)
Ir(1)-P(1)	2.2846(8)
Ir(1)-P(2)	2.2892(8)
P(1)-O(2)	1.680(3)
P(1)-C(7)	1.851(3)
P(1)-C(11)	1.854(4)
P(2)-O(3)	1.676(3)
P(2)-C(15)	1.848(4)
P(2)-C(19)	1.853(4)
O(1)-C(1)	1.158(4)
O(2)-C(2)	1.354(4)
O(3)-C(6)	1.347(4)
N(1)-C(2)	1.359(4)
N(1)-C(6)	1.362(4)
C(2)-C(3)	1.377(5)
C(3)-C(4)	1.391(5)
C(3)-H(3)	0.9500
C(4)-C(5)	1.385(5)
C(4)-H(4)	0.9500
C(5)-C(6)	1.385(5)
C(5)-H(5)	0.9500
C(7)-C(10)	1.534(5)
C(7)-C(9)	1.539(5)
C(7)-C(8)	1.540(6)
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-C(13)	1.529(6)

C(11)-C(12)	1.536(6)
C(11)-C(14)	1.539(6)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-C(17)	1.529(6)
C(15)-C(18)	1.535(5)
C(15)-C(16)	1.535(6)
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-C(21)	1.520(6)
C(19)-C(20)	1.530(6)
C(19)-C(22)	1.549(6)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
P(3)-F(6)	1.537(3)
P(3)-F(3)	1.554(3)

P(3)-F(1)	1.571(4)
P(3)-F(5)	1.584(3)
P(3)-F(2)	1.587(3)
P(3)-F(4)	1.624(3)

C(1)-Ir(1)-N(1)	176.37(13)
C(1)-Ir(1)-P(1)	99.55(11)
N(1)-Ir(1)-P(1)	80.66(8)
C(1)-Ir(1)-P(2)	99.15(11)
N(1)-Ir(1)-P(2)	80.72(8)
P(1)-Ir(1)-P(2)	161.28(3)
O(2)-P(1)-C(7)	101.27(15)
O(2)-P(1)-C(11)	99.41(16)
C(7)-P(1)-C(11)	116.63(17)
O(2)-P(1)-Ir(1)	101.45(9)
C(7)-P(1)-Ir(1)	115.83(12)
C(11)-P(1)-Ir(1)	117.43(13)
O(3)-P(2)-C(15)	99.90(16)
O(3)-P(2)-C(19)	100.99(16)
C(15)-P(2)-C(19)	116.71(18)
O(3)-P(2)-Ir(1)	101.22(9)
C(15)-P(2)-Ir(1)	116.30(12)
C(19)-P(2)-Ir(1)	116.88(13)
C(2)-O(2)-P(1)	119.4(2)
C(6)-O(3)-P(2)	119.7(2)
C(2)-N(1)-C(6)	118.0(3)
C(2)-N(1)-Ir(1)	121.1(2)
C(6)-N(1)-Ir(1)	120.7(2)
O(1)-C(1)-Ir(1)	176.6(3)
O(2)-C(2)-N(1)	117.2(3)
O(2)-C(2)-C(3)	119.7(3)
N(1)-C(2)-C(3)	123.1(3)
C(2)-C(3)-C(4)	117.4(3)
C(2)-C(3)-H(3)	121.3
C(4)-C(3)-H(3)	121.3
C(5)-C(4)-C(3)	121.4(3)
C(5)-C(4)-H(4)	119.3

C(3)-C(4)-H(4)	119.3
C(6)-C(5)-C(4)	117.5(3)
C(6)-C(5)-H(5)	121.2
C(4)-C(5)-H(5)	121.2
O(3)-C(6)-N(1)	117.5(3)
O(3)-C(6)-C(5)	119.9(3)
N(1)-C(6)-C(5)	122.6(3)
C(10)-C(7)-C(9)	110.2(3)
C(10)-C(7)-C(8)	109.4(3)
C(9)-C(7)-C(8)	108.8(3)
C(10)-C(7)-P(1)	114.9(3)
C(9)-C(7)-P(1)	107.9(2)
C(8)-C(7)-P(1)	105.5(3)
C(7)-C(8)-H(8A)	109.5
C(7)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(7)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(13)-C(11)-C(12)	109.1(4)
C(13)-C(11)-C(14)	111.1(4)
C(12)-C(11)-C(14)	108.6(4)
C(13)-C(11)-P(1)	109.3(3)
C(12)-C(11)-P(1)	104.6(3)
C(14)-C(11)-P(1)	113.9(3)

C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(11)-C(14)-H(14A)	109.5
C(11)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(11)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(17)-C(15)-C(18)	108.4(4)
C(17)-C(15)-C(16)	110.1(4)
C(18)-C(15)-C(16)	110.6(3)
C(17)-C(15)-P(2)	105.5(3)
C(18)-C(15)-P(2)	114.3(3)
C(16)-C(15)-P(2)	107.7(3)
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(15)-C(18)-H(18A)	109.5

C(15)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(15)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(21)-C(19)-C(20)	109.8(3)
C(21)-C(19)-C(22)	110.6(4)
C(20)-C(19)-C(22)	107.5(4)
C(21)-C(19)-P(2)	109.3(3)
C(20)-C(19)-P(2)	114.7(3)
C(22)-C(19)-P(2)	104.8(3)
C(19)-C(20)-H(20A)	109.5
C(19)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(19)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(19)-C(21)-H(21A)	109.5
C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(19)-C(22)-H(22A)	109.5
C(19)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(19)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
F(6)-P(3)-F(3)	91.0(3)
F(6)-P(3)-F(1)	174.3(3)
F(3)-P(3)-F(1)	92.9(3)
F(6)-P(3)-F(5)	88.8(3)
F(3)-P(3)-F(5)	178.6(2)
F(1)-P(3)-F(5)	87.2(3)
F(6)-P(3)-F(2)	93.7(2)
F(3)-P(3)-F(2)	91.1(2)

F(1)-P(3)-F(2)	90.5(2)
F(5)-P(3)-F(2)	90.32(17)
F(6)-P(3)-F(4)	88.0(2)
F(3)-P(3)-F(4)	89.7(2)
F(1)-P(3)-F(4)	87.8(2)
F(5)-P(3)-F(4)	88.86(18)
F(2)-P(3)-F(4)	178.14(18)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2 #2 -x+1,-y,-z+1

Table S16. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3-O**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	15(1)	17(1)	18(1)	0(1)	1(1)	1(1)
P(1)	18(1)	20(1)	21(1)	-2(1)	-1(1)	-1(1)
P(2)	22(1)	18(1)	17(1)	-1(1)	1(1)	2(1)
O(1)	30(1)	39(2)	41(2)	1(1)	-2(1)	15(1)
O(2)	29(1)	24(1)	26(1)	-7(1)	-5(1)	5(1)
O(3)	33(1)	25(1)	21(1)	-3(1)	-5(1)	6(1)
N(1)	19(1)	19(1)	18(1)	0(1)	2(1)	1(1)
C(1)	24(2)	25(2)	21(2)	0(1)	0(1)	2(1)
C(2)	22(2)	23(2)	22(2)	-1(1)	1(1)	1(1)
C(3)	29(2)	24(2)	29(2)	-3(1)	2(1)	7(1)
C(4)	29(2)	29(2)	33(2)	4(2)	0(2)	12(2)
C(5)	30(2)	33(2)	24(2)	2(1)	-6(1)	8(2)
C(6)	24(2)	23(2)	21(2)	1(1)	3(1)	2(1)
C(7)	29(2)	27(2)	20(2)	-2(1)	3(1)	-2(1)
C(8)	34(2)	65(3)	36(2)	5(2)	11(2)	-11(2)
C(9)	54(3)	35(2)	25(2)	5(2)	4(2)	9(2)
C(10)	60(3)	40(2)	27(2)	-9(2)	9(2)	1(2)
C(11)	26(2)	32(2)	36(2)	0(2)	-3(2)	-13(2)
C(12)	47(3)	45(2)	41(2)	6(2)	5(2)	-24(2)
C(13)	25(2)	58(3)	89(4)	11(3)	-11(2)	-9(2)
C(14)	58(3)	49(3)	53(3)	-16(2)	-3(2)	-28(2)
C(15)	29(2)	26(2)	29(2)	3(1)	-7(1)	-7(1)
C(16)	49(3)	25(2)	71(3)	10(2)	-23(2)	-8(2)
C(17)	52(3)	61(3)	46(3)	-4(2)	14(2)	-34(2)
C(18)	45(2)	36(2)	44(2)	3(2)	-19(2)	-12(2)
C(19)	34(2)	35(2)	22(2)	-4(1)	8(2)	4(2)
C(20)	54(3)	62(3)	21(2)	-7(2)	2(2)	17(2)
C(21)	41(2)	69(3)	33(2)	1(2)	11(2)	18(2)
C(22)	63(3)	44(3)	43(3)	7(2)	24(2)	-2(2)
P(3)	38(1)	25(1)	30(1)	0(1)	5(1)	1(1)
F(1)	111(3)	44(2)	211(5)	24(3)	-92(4)	-18(2)
F(2)	48(2)	98(3)	41(2)	3(2)	-8(1)	19(2)

F(3)	86(3)	206(5)	31(2)	-14(2)	18(2)	19(3)
F(4)	47(2)	49(2)	84(2)	-10(2)	1(2)	12(1)
F(5)	95(3)	155(4)	36(2)	-16(2)	-9(2)	81(3)
F(6)	90(3)	52(2)	203(5)	20(3)	25(3)	-33(2)

Table S17. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **3-O**.

	x	y	z	U(eq)
H(3)	530	7648	4494	33
H(4)	-996	7589	2897	36
H(5)	-848	6904	1809	35
H(8A)	824	6495	6430	67
H(8B)	1082	6057	7249	67
H(8C)	1380	5982	5997	67
H(9A)	4050	5671	6489	57
H(9B)	3818	5774	7738	57
H(9C)	5294	5998	7143	57
H(10A)	4430	6788	7878	63
H(10B)	2786	6601	8321	63
H(10C)	2813	7029	7462	63
H(12A)	5821	6855	3816	66
H(12B)	6754	7321	4242	66
H(12C)	4871	7330	4127	66
H(13A)	7048	6515	6476	86
H(13B)	8068	6800	5622	86
H(13C)	7055	6340	5252	86
H(14A)	4634	7549	6140	80
H(14B)	6503	7604	6051	80
H(14C)	5789	7273	6970	80
H(16A)	2566	4708	2234	73
H(16B)	1354	4511	3092	73
H(16C)	2784	4852	3473	73
H(17A)	782	5391	4315	79
H(17B)	-660	5073	3860	79
H(17C)	-581	5634	3586	79
H(18A)	-767	5441	1587	63
H(18B)	-984	4897	1977	63

H(18C)	347	5026	1139	63
H(20A)	2518	5196	373	68
H(20B)	3326	5603	-333	68
H(20C)	1650	5701	183	68
H(21A)	5565	5604	2164	71
H(21B)	5686	5475	918	71
H(21C)	4743	5127	1698	71
H(22A)	2914	6449	866	75
H(22B)	4646	6302	510	75
H(22C)	4331	6426	1739	75

Table S18. Torsion angles [°] for **3-O**.

C(7)-P(1)-O(2)-C(2)	-122.0(3)
C(11)-P(1)-O(2)-C(2)	118.2(3)
Ir(1)-P(1)-O(2)-C(2)	-2.4(3)
C(15)-P(2)-O(3)-C(6)	120.4(3)
C(19)-P(2)-O(3)-C(6)	-119.7(3)
Ir(1)-P(2)-O(3)-C(6)	0.8(3)
P(1)-O(2)-C(2)-N(1)	5.0(4)
P(1)-O(2)-C(2)-C(3)	-175.0(3)
C(6)-N(1)-C(2)-O(2)	179.1(3)
Ir(1)-N(1)-C(2)-O(2)	-5.3(4)
C(6)-N(1)-C(2)-C(3)	-0.9(5)
Ir(1)-N(1)-C(2)-C(3)	174.7(3)
O(2)-C(2)-C(3)-C(4)	179.7(3)
N(1)-C(2)-C(3)-C(4)	-0.2(5)
C(2)-C(3)-C(4)-C(5)	1.0(6)
C(3)-C(4)-C(5)-C(6)	-0.6(6)
P(2)-O(3)-C(6)-N(1)	-3.7(4)
P(2)-O(3)-C(6)-C(5)	175.8(3)
C(2)-N(1)-C(6)-O(3)	-179.3(3)
Ir(1)-N(1)-C(6)-O(3)	5.1(4)
C(2)-N(1)-C(6)-C(5)	1.3(5)
Ir(1)-N(1)-C(6)-C(5)	-174.3(3)
C(4)-C(5)-C(6)-O(3)	180.0(3)
C(4)-C(5)-C(6)-N(1)	-0.6(5)
O(2)-P(1)-C(7)-C(10)	-63.7(3)
C(11)-P(1)-C(7)-C(10)	43.0(4)
Ir(1)-P(1)-C(7)-C(10)	-172.4(3)
O(2)-P(1)-C(7)-C(9)	173.0(3)
C(11)-P(1)-C(7)-C(9)	-80.3(3)
Ir(1)-P(1)-C(7)-C(9)	64.3(3)
O(2)-P(1)-C(7)-C(8)	56.8(3)
C(11)-P(1)-C(7)-C(8)	163.5(3)
Ir(1)-P(1)-C(7)-C(8)	-51.9(3)
O(2)-P(1)-C(11)-C(13)	178.0(3)
C(7)-P(1)-C(11)-C(13)	70.2(4)

Ir(1)-P(1)-C(11)-C(13)	-73.8(3)
O(2)-P(1)-C(11)-C(12)	-65.4(3)
C(7)-P(1)-C(11)-C(12)	-173.1(3)
Ir(1)-P(1)-C(11)-C(12)	42.8(3)
O(2)-P(1)-C(11)-C(14)	53.0(3)
C(7)-P(1)-C(11)-C(14)	-54.7(4)
Ir(1)-P(1)-C(11)-C(14)	161.3(3)
O(3)-P(2)-C(15)-C(17)	-69.1(3)
C(19)-P(2)-C(15)-C(17)	-176.8(3)
Ir(1)-P(2)-C(15)-C(17)	38.8(3)
O(3)-P(2)-C(15)-C(18)	49.9(3)
C(19)-P(2)-C(15)-C(18)	-57.8(4)
Ir(1)-P(2)-C(15)-C(18)	157.8(3)
O(3)-P(2)-C(15)-C(16)	173.3(3)
C(19)-P(2)-C(15)-C(16)	65.6(3)
Ir(1)-P(2)-C(15)-C(16)	-78.8(3)
O(3)-P(2)-C(19)-C(21)	167.8(3)
C(15)-P(2)-C(19)-C(21)	-85.1(3)
Ir(1)-P(2)-C(19)-C(21)	59.1(3)
O(3)-P(2)-C(19)-C(20)	-68.4(3)
C(15)-P(2)-C(19)-C(20)	38.7(4)
Ir(1)-P(2)-C(19)-C(20)	-177.1(3)
O(3)-P(2)-C(19)-C(22)	49.3(3)
C(15)-P(2)-C(19)-C(22)	156.4(3)
Ir(1)-P(2)-C(19)-C(22)	-59.4(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+3/2 #2 -x+1,-y,-z+1

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