Electronic Supplementary Information (ESI)

Tuning the Wavelength of Electrochemiluminescence by Anodic Potential: A Design Using Non-Kekulé-Structured Iridium-Ruthenium Luminophores

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General information and materials

Melting points: The melting points of all solid compounds were measured on a Büchi melting point apparatus (BÜCHI 510) and are uncorrected.

Infrared Spectroscopy: Infrared spectra were measured on a Varian 1000 FT-IR spectrometer.

NMR spectra: ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Advance 400 (400 MHz) or a Varian System 600 (600 MHz). Chemical shifts are reported in ppm.

Luminescence and UV-vis measurements: Using a solution containing the compounds in MeCN (10 µM), the UV-vis measurements were carried out on a Varian Cary 100 Bio UV-Visible Spectrophotometer and the luminescence measurements on a Varian Cary Eclipse Fluorescence Spectrophotometer with excitation and emission slit widths set at 5 nm.

Electroanalytical Investigations: Cyclic voltammetry (CV) and differential pulsed voltammetry (DPV) measurements were done by using a standard three-electrode set-up (1 mm Pt disk working and Pt auxiliary electrode, silver wire as reference electrode) connected to a PARSTAT 2273 Advanced Electrochemical System. The experiments were carried out on a 1 mM solution of the compound in MeCN with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. All potentials are referenced to ferrocene as internal standard at a scan rate = 100 mV s^{-1}.

Mass spectroscopy: ESI-MS measurements were recorded on a LCQ Deca Thermo Quest instrument.

Elemental analysis: Elemental analysis was performed on an elemental analyser Euro EA from EuroVector

ECL Investigations: All ECL measurements were done using solutions (10 µM) of the complexes in MeCN, containing additionally tri-*n*-propylamine (30 mM) as coreactant and tetra-*n*-butylammonium hexafluophosphate (0.1 M) as electrolyte. A standard three-electrode set-up (3.0 mm diameter Pt working electrode, Pt wire auxiliary electrode, and silver wire as reference electrode) connected to a Princeton Applied Research Model 362 potentiostat was used. To generate the ECL reaction, the working electrode was swept between 0.5 to 1.8 V (*vs* silver wire used as quasi-reference electrode) at a scan rate 100 mV/s. The potential dependent ECL measurements were carried out at room temperature in 10 µM solution of **Ir-Ru-Ir** varying the end potential range from 1.3-1.8 V at a scan rate of 100 mV s^{-1}. The resulting emission spectra were obtained with a liquid nitrogen cooled CCD camera at –70 °C (0.500 m Imagining Triple Grating Monochromator / Spectrograph), which was connected to spectrometer Spectrapro 2500i (Acton Research Corporation).

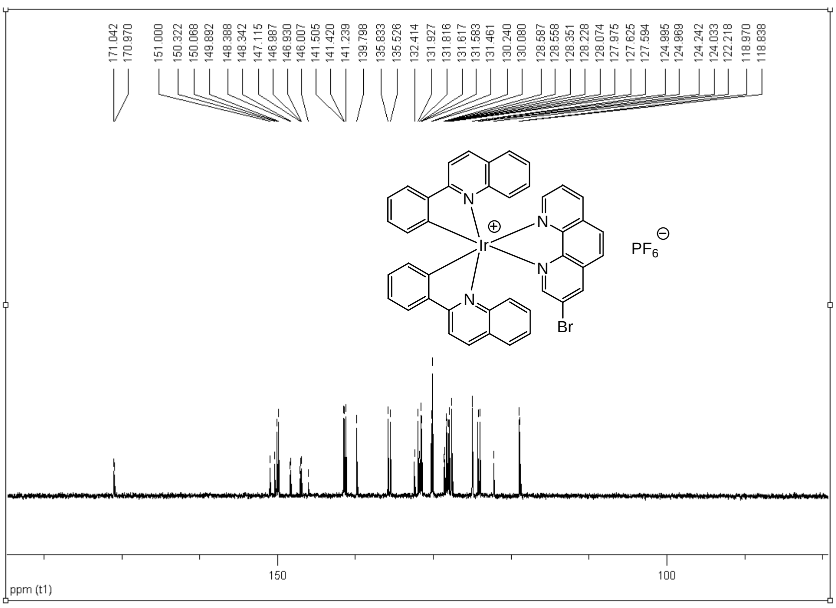
Synthesis and characterisation of the complexes

Synthesis and characterisation of Ir1

$[Ir(pq)_2Cl]_2$ (100 mg, 78.6 μmol) and 3-bromophenanthroline (50.0 mg, 193 μmol) were dissolved in dichloromethane (10 mL) and the solution was refluxed for 6 h. The crude product was purified by chromatography (silica gel/dichloromethane-methanol). To the dichloromethane solution (15 mL) of $[(pq)_2Ir(3\text{-bromophen})]Cl_2$, NH_4PF_6 (100 mg, excess) was added and the resulting solution was stirred for 1 h. The precipitate was filtered off. The filtrate was purified by chromatography on silica gel using dichloromethane and methanol for elution. The solvent was removed to furnish an orange-red powder.
Yield: 125 mg (125 μmol, 80%).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ = 6.67 (dd, 1H, J_1 = 0.7 Hz, J_2 = 7.7 Hz), 6.71 (dd, 1H, J_1 = 0.7 Hz, J_2 = 7.7 Hz), 6.86 (ddd, 1H, J_1 = 1.1 Hz, J_2 = 2.4 Hz, J_3 = 7.1 Hz), 6.90 (dd, 1H, J_1 = 1.3 Hz, J_2 = 2.9 Hz), 6.92 (dd, 1H, J_1 = 1.2 Hz, J_2 = 7.5 Hz), 7.01 (ddd, 1H, J_1 = 1.5 Hz, J_2 = 7.0 Hz, J_3 = 8.7 Hz), 7.22-7.25 (m, 1H), 7.26-7.27 (m, 1H), 7.28 (dd, 2H, J_1 = 1.5 Hz, J_2 = 3.2 Hz), 7.30 (dd, 1H, J_1 = 1.1 Hz, J_2 = 2.4 Hz), 7.34 (dd, 1H, J_1 = 0.7 Hz, J_2 = 9.6 Hz), 7.82 (dd, 2H, J_1 = 1.4 Hz, J_2 = 8.2 Hz), 8.16 (d, 1H, J = 8.9 Hz), 8.11 (dd, 1H, J_1 = 5.3 Hz, J_2 = 8.1 Hz), 8.20 (d, 1H, J = 8.9 Hz), 8.32 (dd, 1H, J_1 = 1.0 Hz, J_2 = 8.0 Hz), 8.36 (dd, 1H, J_1 = 1.0 Hz, J_2 = 8.0 Hz), 8.49 (d, 1H, J = 6.0 Hz), 8.52 (d, 1H, J = 6.0 Hz), 8.57 (d, 1H, J = 8.8 Hz), 8.60 (d, 1H, J = 8.8 Hz), 8.63 (d, 1H, J = 2.0 Hz), 8.76 (dd, 1H, J_1 = 1.3 Hz, J_2 = 2.3 Hz), 8.77 (dd, 1H, J_1 = 1.3 Hz, J_2 = 5.3 Hz), 9.00 (d, 1H, J = 1.9 Hz).

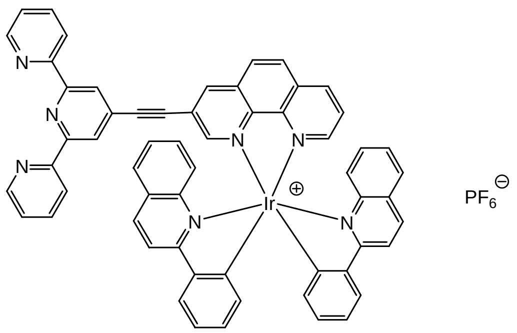
^{13}C-NMR (100 MHz, Acetone-d$_6$): δ = 118.8, 119.0, 122.2, 124.0, 124.2, 125.0 (2x), 127.5, 127.6 (2x), 128.0, 128.1, 128.2, 128.4, 128.6 (2x), 130.1, 130.2, 131.5, 131.6 (2x), 131.8, 131.9, 132.4, 135.5, 135.8, 139.8, 141.2, 141.4, 141.5, 146.0, 147.0 (2x), 147.1, 148.3, 148.4, 149.9, 150.1, 150.3, 151.0, 170.9, 171.0.



ESI-MS: $(C_{42}H_{27}BrIrN_4)^+$ Calcd: m/z = 859.1 Found: m/z = 859.2

Elemental analysis: $(C_{42}H_{27}BrF_6IrN_4P)\cdot 0.5\ H_2O$
Calcd: C, 49.76; H, 2.78; N, 5.53. Found: C, 49.75; H, 2.44; N, 5.43.

Synthesis and characterisation of Ir2

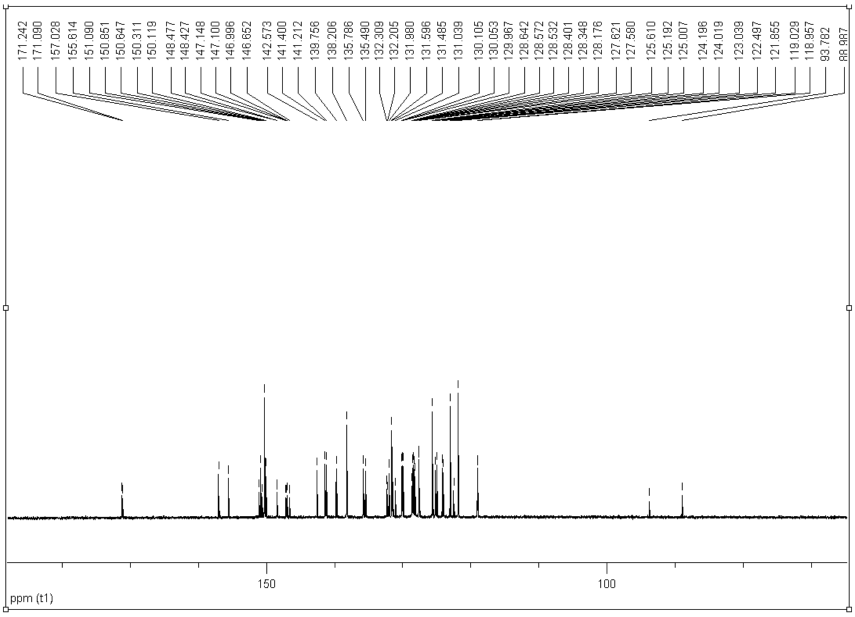


A solution of $[Ir(pq)_2(3\text{-bromophen})]PF_6$ (50.0 mg, 50.0 µmol), 4'-ethynyl-2,2':6',2"-terpyridine (21.0 mg, 85.0 µmol), dry triethylamine (1.00 mL), $Pd(PPh_3)_2Cl_2$ (2.00 mg, 2.91 µmol) and copper(I) iodide (1.71 mg, 8.90 µmol) in dry DMF (3.00 ml) was stirred at room temperature for 1 h. The solvent was distilled in vacuo. Purification was achieved by chromatography on aluminum oxide (neutral) with dichloromethane/methanol (100/1) to afford the product as an orange solid.

Yield: 35.0 mg (30.0 µmol, 59%).

^{1}H-NMR (400 MHz, Acetone-d$_6$): δ = 6.69 (dd, 1H, J_1 = 0.4 Hz, J_2 = 7.6 Hz), 6.74 (dd, 1H, J_1 = 0.8 Hz, J_2 = 7.6 Hz), 6.89 (ddd, 1H, J_1 = 1.3 Hz, J_2 = 2.3 Hz, J_3 = 6.8 Hz), 6.91 (dd, 1H, J_1 = 1.0 Hz, J_2 = 2.1 Hz), 6.94 (dd, 1H, J_1 = 1.2 Hz, J_2 = 7.6 Hz), 7.06 (ddd, 1H, J_1 = 1.4 Hz, J_2 = 7.0 Hz, J_3 = 8.6 Hz), 7.24 (dd, 1H, J_1 = 0.8 Hz, J_2 = 7.9 Hz), 7.27-7.28 (m, 1H), 7.30 (d, 1H, J = 3.6 Hz), 7.31 (d, 1H, J = 3.9 Hz), 7.33 (d, 1H, J = 1.7 Hz), 7.46 (d, 1H, J = 8.9 Hz), 7.54 (dd, 1H, J_1 = 1.0 Hz, J_2 = 4.6 Hz), 7.56 (dd, 1H, J_1 = 0.9 Hz, J_2 = 4.7 Hz), 7.83 (td, 2H, J_1 = 1.6 Hz, J_2 = 1.6 Hz, J_3 = 8.5 Hz), 8.06 (dt, 2H, J_1 = 1.8 Hz, J_2 = 7.7 Hz, J_3 = 7.8 Hz), 8.12 (dd, 1H, J_1 = 5.1 Hz, J_2 = 8.2 Hz), 8.16 (d, 1H, J = 8.9 Hz), 8.21 (d, 1H, J = 8.9 Hz), 8.32 (dd, 1H, J_1 = 0.5 Hz, J_2 = 7.9 Hz), 8.39 (dd, 1H, J_1 = 0.4 Hz, J_2 = 7.8 Hz), 8.51 (d, 1H, J = 4.9 Hz), 8.52 (d, 1H, J = 4.9 Hz), 8.57 (d, 1H, J = 8.8 Hz), 8.62 (s, 2H), 8.65 (d, 1H, J = 4.8 Hz), 8.76 (d, 2H, J = 7.9 Hz), 8.78-8.80 (m, 3H), 8.82 (d, 1H, J = 1.3 Hz), 8.89 (d, 1H, J = 1.8 Hz), 9.11 (d, 1H, J = 1.7 Hz).

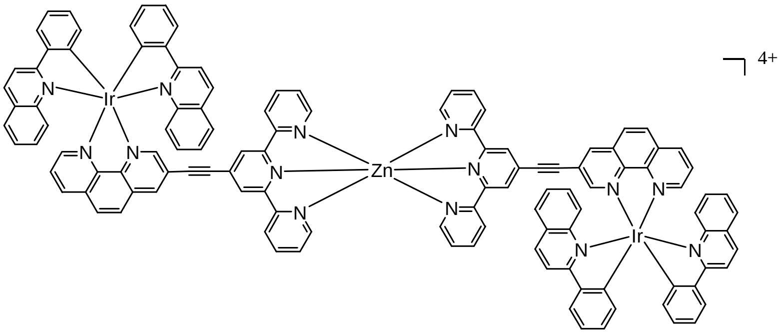
^{13}C-NMR (100 MHz, Acetone-d$_6$): δ =89.0, 93.8, 119.0 (2x), 121.9, 122.5, 123.0, 124.0, 124.1, 125.0, 125.2, 125.6, 127.6 (2x), 128.2, 128.3, 128.4, 128.5, 128.6 (2x), 130.0, 130.1, 131.0, 131.5, 131.6, 132.0, 132.2, 132.3, 135.5, 135.8, 138.2, 139.8, 141.2, 141.4, 142.6, 147.0, 147.1 (2x), 148.4, 148.5, 150.1, 150.3, 150.6, 150.9, 151.1, 155.6, 157.0, 171.1, 171.2.



Elemental analysis: ($C_{59}H_{37}F_6IrN_7P$)
Calcd: C, 59.99; H, 3.16; N, 8.30. Found: C, 59.68; H, 2.92; N, 8.47
ESI-MS: $(C_{59}H_{37}IrN_7)^+$ Calcd: m/z =1036.3 Found: m/z = 1036.4

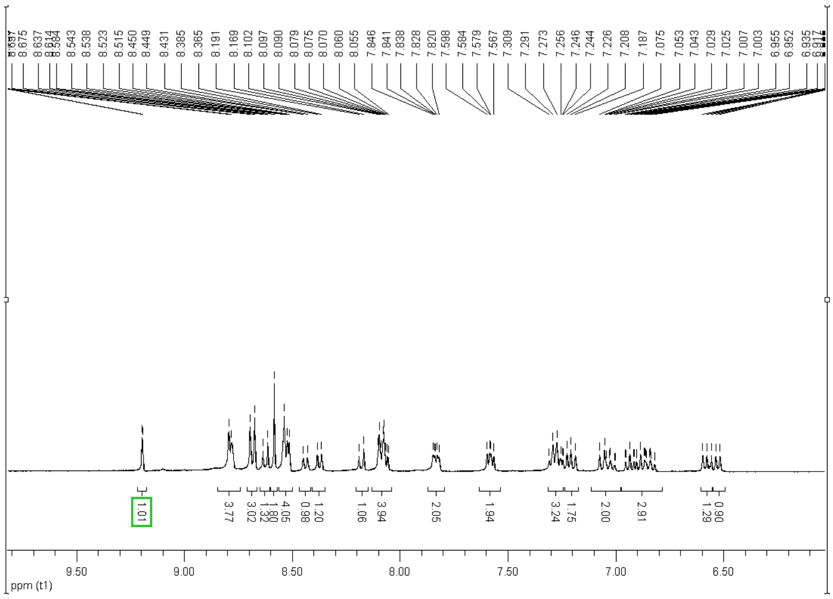
Synthesis and characterisation of Ir-Zn-Ir

A mixture of **Ir2** (2.36 mg, 2.00 μmol) and $Zn(OTf)_2$ (0.360 mg, 1.00 μmol) was dissolved in acetonitrile. The solvent was removed in vacuo to furnish the product as an orange solid.
Yield: Quantitive.



^{1}H-NMR (400 MHz, DMSO-d$_6$): δ = 6.52 (d, 1H, *J* = 7.5 Hz), 6.56 (dd, 1H, J_1 = 0.9 Hz, J_2 = 7.9 Hz), 6.82-6.87 (m, 1H), 6.89 (dd, 1H, J_1 = 0.6 Hz, J_2 = 7.4 Hz), 6.94 (dt, 1H, J_1 = 1.1 Hz, J_2 = 7.6 Hz, J_3 = 7.5 Hz), 7.00-7.03 (m, 1H), 7.06 (d, 1H, *J* = 9.0 Hz), 7.20 (d, 1H, *J* = 8.5 Hz), 7.24 (d, 1H, *J* = 7.9 Hz), 7.28 (dd, 3H, J_1 = 7.2 Hz, J_2 = 14.1 Hz), 7.57 (dd, 1H, J_1 = 0.9 Hz, J_2 = 4.9 Hz), 7.59 (dd, 1H, J_1 = 0.6 Hz, J_2 = 4.9 Hz), 7.83 (ddd, 2H, J_1 = 1.0 Hz, J_2 = 3.5 Hz, J_3 = 8.4 Hz), 8.06-8.10 (m, 4H), 8.17 (d, 1H, *J* = 8.9 Hz), 8.37 (dd, 1H, J_1 = 0.9 Hz, J_2 = 7.9 Hz), 8.44 (d, 1H, J_1 = 0.4 Hz, J_2 = 7.8 Hz), 8.52 (dd, 2H, J_1 = 1.4 Hz, J_2 = 4.8 Hz), 8.54 (dd, 2H, J_1 = 1.4 Hz, J_2 = 2.0 Hz), 8.58 (s, 2H), 8.61 (d, 1H, *J* = 9.0 Hz), 8.67 (d, 3H, *J* = 8.5 Hz), 8.78-8.79 (m, 3H), 9.19 (d, 1H, *J* = 1.7 Hz).

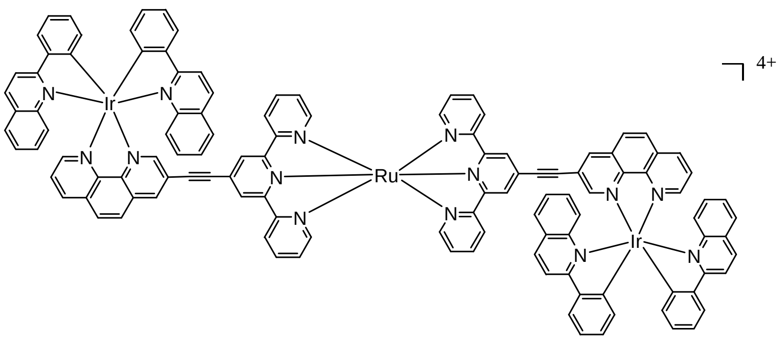
^{13}C-NMR (100 MHz, DMSO-d$_6$): δ = 88.7, 92.7, 118.4, 120.6, 121.1, 122.1, 123.1, 123.3, 123.4, 123.6, 125.1, 126.8, 127.3 (2x), 127.6 (2x), 127.8 (2x), 129.2, 129.3, 129.4, 129.6, 129.7, 130.7, 130.8, 130.9, 131.0, 131.1, 131.3, 134.1, 134.4, 137.8, 139.1, 140.5 (2x), 140.8, 142.2, 145.1, 145.4, 145.9, 146.1, 146.9, 148.7, 148.8, 148.9 (2x), 149.5, 149.6, 154.0, 155.7, 169.7 (2x).



ESI-MS: $(C_{118}H_{74}Ir_2N_{14}Zn)^{4+}$ Calcd: m/z = 534.1 Found: m/z = 534.4
$(C_{119}H_{74}F_3Ir_2N_{14}O_3SZn)^{3+}$ Calcd: m/z = 761.8 Found: m/z = 761.0
$(C_{119}H_{74}F_9Ir_2N_{14}O_3PSZn)^{2+}$ Calcd: m/z = 1215.2 Found: m/z = 1215.6
$(C_{61}H_{37}F_6IrN_7O_6S_2Zn)^{+}$ Calcd: m/z = 1398.1 Found: m/z = 1398.0

Elemental analysis: $(C_{120}H_{74}F_{18}Ir_2N_{147}O_6P_2S_2Zn)$ + 0.5 CH_2Cl_2
Calcd: C, 52.28; H, 2.73; N, 7.08. Found: C, 52.14; H, 2.39; N, 7.15

Synthesis and characterisation of Ir-Ru-Ir

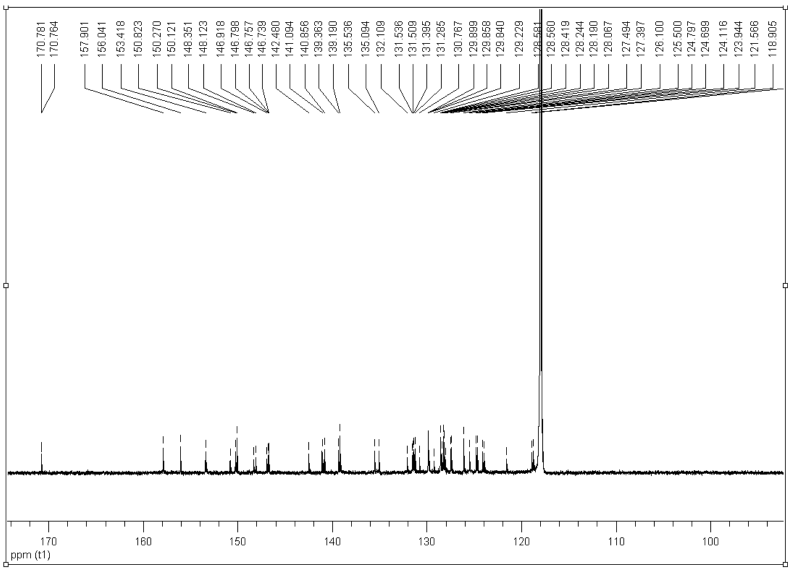


A mixture of **Ir2** (11.8 mg, 10.0 µmol) and $RuCl_3 \cdot nH_2O$ (1.32 mg, 5.10 µmol) was dissolved in ethanol (2 ml) and the resultant solution was refluxed for 72 h. The solvent was removed in vacuo and the residue was dissolved in methanol. NH_4PF_6 (excess) was added to precipitate the product and purification was achieved by chromatography on aluminum oxide (neutral) with dichloromethane/methanol to afford the product as a red solid.

Yield: 12.0 mg (4.30 µmol, 86.0 %).

^{1}H-NMR (600 MHz, CD_3CN): δ = 6.62 (d, 1H, J = 7.2 Hz), 6.67 (d, 1H, J = 7.6 Hz), 6.83 (ddd, 1H, J_1 = 1.4 Hz, J_2 = 6.9 Hz, J_3 = 8.6 Hz), 6.89 (dt, 1H, J_1 = 1.2 Hz, J_2 = 7.5 Hz, J_3 = 7.5 Hz), 6.95-6.99 (m, 2H), 7.21-7.34 (m, 8H), 7.45 (dd, 2H, J_1 = 0.7 Hz, J_2 = 5.7 Hz), 7.77 (dd, 1H, J_1 = 1.3 Hz, J_2 = 8.2 Hz), 7.79 (dd, 1H, J_1 = 1.0 Hz, J_2 = 8.0 Hz), 7.91 (dd, 1H, J_1 = 5.2 Hz, J_2 = 8.3 Hz), 8.02 (dt, 2H, J_1 = 1.4 Hz, J_2 = 8.0 Hz, J_3 = 8.1 Hz), 8.04 (d, 1H, J = 8.8 Hz), 8.07 (d, 1H, J = 8.8 Hz), 8.23 (dd, 1H, J_1 = 0.7 Hz, J_2 = 8.0 Hz), 8.32 (dd, 1H, J_1 = 0.9 Hz, J_2 = 8.0 Hz), 8.36 (d, 1H, J = 8.7 Hz), 8.41 (d, 1H, J = 8.9 Hz), 8.43 (d, 1H, J = 8.9 Hz), 8.48 (d, 1H, J = 8.8 Hz), 8.54 (d, 2H, J = 8.2 Hz), 8.58 (dd, 1H, J_1 = 1.1 Hz, J_2 = 8.3 Hz), 8.63 (dd, 1H, J_1 = 1.2 Hz, J_2 = 5.1 Hz), 8.76 (d, 1H, J = 1.7 Hz), 8.89 (d, 1H, J = 1.5 Hz), 8.91 (s, 2H).

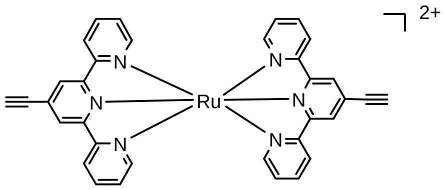
^{13}C-NMR (150 MHz, CD_3CN): δ =118.7, 118.9, 121.6, 123.9, 124.1, 124.7, 124.8, 125.5, 126.1, 127.4, 127.5, 128.1, 128.2 (2x), 128.4, 128.6 (2x), 129.2, 129.8, 129.9 (2x), 130.8, 131.3, 131.4, 131.5 (2x), 132.1, 135.1, 135.5, 139.2, 139.4, 140.9, 141.1, 142.5, 146.7, 146.8 (2x), 146.9, 148.1, 148.4, 150.1, 150.3, 150.8, 153.4, 156.0, 157.9, 170.8 (2x).



ESI-MS: $(C_{118}H_{73}Ir_2N_{14}Ru)^{4+}$ Calcd: m/z = 543.6 Found: m/z = 543.9
$(C_{118}H_{74}F_6Ir_2N_{14}PRu)^{3+}$ Calcd: m/z = 772.8 Found: m/z = 773.5
$(C_{118}H_{74}F_{12}Ir_2N_{14}P_2Ru)^{2+}$ Calcd: m/z = 1232.2 Found: m/z =1233.2

Elemental analysis: $(C_{118}H_{74}F_{24}Ir_2N_{14}P_4Ru)$ + CH_3CN + 3.0 CH_2Cl_2
Calcd: C, 48.45; H, 2.74; N, 6.89. Found: C, 48.26; H, 2.51; N, 6.95

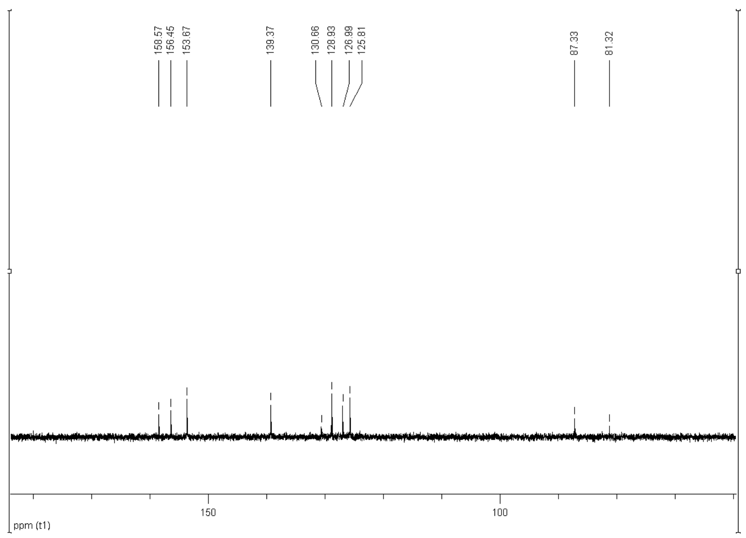
Synthesis and characterisation of Ru



Compound **Ru** was prepared from 4'-ethynyl-2,2':6',2"-terpyridine and $RuCl_3 \cdot nH_2O$ with the same method as used for the synthesis of **Ir-Ru-Ir** from **Ir2**.

^{1}H-NMR (400 MHz, CD_3CN): δ = 4.55 (s, 2H), 7.33-7.37 (ddd, 4H, J_1 = 1.3 Hz, J_2 = 5.6 Hz, J_3 = 7.4 Hz), 7.81 (d, 4H, J = 4.9 Hz), 8.08-8.12 (dt, 4H, J_1 = 1.5 Hz, J_2 = 7.9 Hz, J_3 = 8.0 Hz), 8.91 (d, 4H, J = 8.0 Hz), 9.14 (s, 4H).

^{13}C-NMR (100 MHz, DMSO-d_6): δ = 81.3, 87.3, 125.8, 126.0, 128.9, 130.7, 139.4, 153.7, 156.5, 158.6.

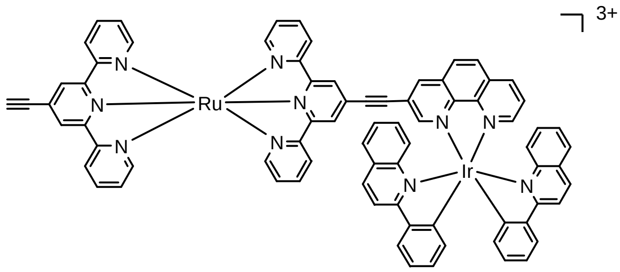


ESI-MS:

$(C_{34}H_{22}F_6N_6PRu)^+$	Calcd: m/z =761.1	Found: m/z = 760.9
$1/2(C_{34}H_{22}F_6N_6PRu)^{2+}$	Calcd: m/z =308.04	Found: m/z = 308.1

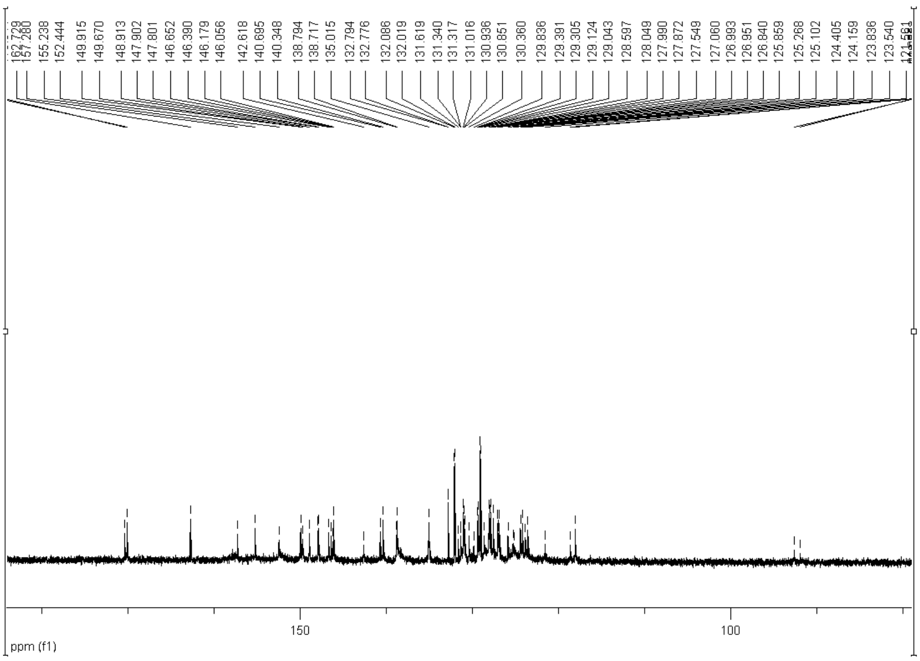
Elemental analysis $(C_{34}H_{22}F_{12}N_6P_2Ru) \cdot 2CH_2Cl_2$:
Calcd: C, 40.21; H, 2.44; N, 7.81. Found: C, 40.20; H, 2.13; N, 8.07

Synthesis and characterisation of Ir-Ru



A solution of **Ir1** (10.1 mg, 10.0 μmol), **Ru** (10.9 mg, 12.0 μmol), dry triethylamine (3 mL), $Pd(PPh_3)_2Cl_2$ (0.351 mg, 0.500 μmol) and copper(I) iodide (0.23 mg, 1.2 μmol) in dry DMF (10 mL) was stirred at 80 °C for 24 h. The solvent was removed in vacuo and the resulting solid was washed with cooled DCM to furnish a solid product.

Yield: 12.8 mg (6.99 μmol, 69.9 %).
^{1}H-NMR (600 MHz, CD_2Cl_2): δ = 3.38 (s, 1H), 6.71 (dd, 2H, J_1 = 5.0 Hz, J_2 = 7.3 Hz), 6.76-6.79 (m, 1H), 6.88 (ddd, 1H, J_1 = 1.0 Hz, J_2 = 7.4 Hz, J_3 = 7.4 Hz), 6.91-6.93 (m, 1H), 6.97-6.99 (m, 1H), 7.16 (d, 1H, J = 9.0 Hz), 7.18-7.29 (m, 7H), 7.31-7.37 (m, 3H), 7.40 (d, 1H, J = 4.8 Hz), 7.50-7.53 (m, 2H), 7.60-7.64 (m, 2H), 7.66-7.68 (m, 2H), 7.84-7.86 (m, 2H), 7.93-7.98 (m, 5H), 8.17 (d, 1H, J = 7.8 Hz), 8.26-8.36 (m, 5H), 8.47-8.52 (m, 3H), 8.57-8.61 (m, 3H), 8.81 (d, 1H, J = 1.8 Hz), 8.91 (s, 1H), 9.01 (d, 1H, J = 1.2 Hz).
^{13}C-NMR (150 MHz, CD_2Cl_2): 91.9 , 92.6, 118.1, 118.6, 121.6, 122.5, 123.5, 124.0, 123.8, 124.2, 124.4, 125.1, 125.3, 125.9, 126.8, 127.0 (2x), 127.1, 127.5, 127.9, 128.0 (2x), 128.6, 129.0, 129.1, 129.3, 129.4, 129.8, 130.4, 130.9 (2x), 131.0, 131.3 (2x), 131.6, 132.0, 132.1, 132.8 (2x), 135.0, 138.7, 138.8, 140.3, 140.7, 142.6, 146.1, 146.2, 146.4, 146.7, 147.8, 147.9, 148.9, 149.7, 149.9, 152.4, 155.2, 157.3, 162.7, 170.0, 170.3



Elemental analysis: $C_{76}H_{48}F_{18}IrN_{10}P_3Ru\cdot 2.5CH_2Cl_2$
Calcd: C, 45.77; H, 2.74; N, 6.67. Found: C, 46.08; H, 2.53; N, 6.39

Photophysical studies and ECL measurements

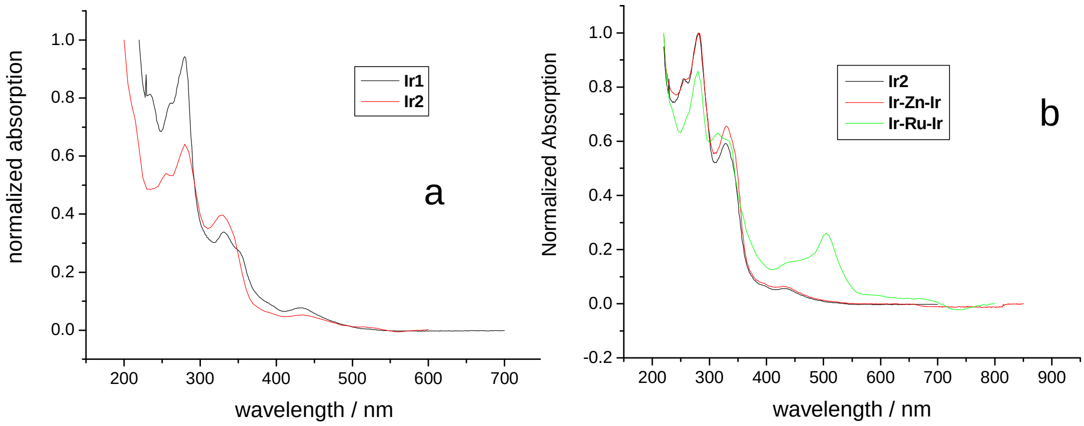


Figure S1. Normalised absorption spectra of (a) **Ir1, Ir2** and (b) **Ir2, Ir-M-Ir** in MeCN (10 μM).

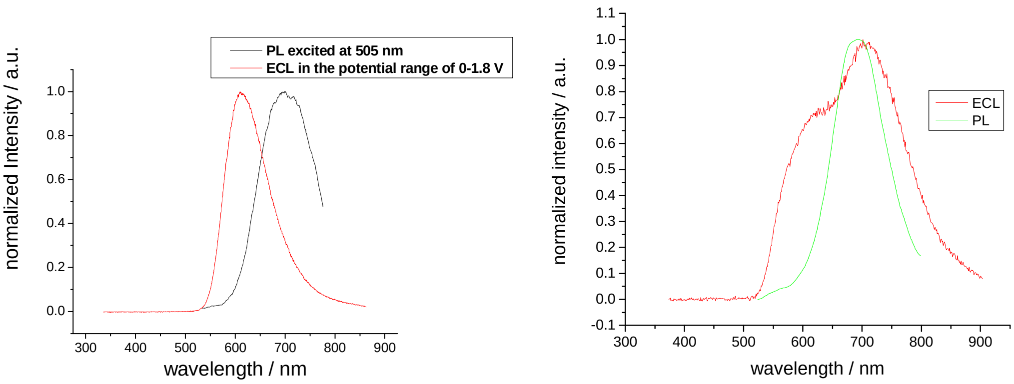


Figure S2. Normalised **PL** and **ECL** spectra of **Ir-Ru-Ir** (left) and **Ir-Ru** (right)

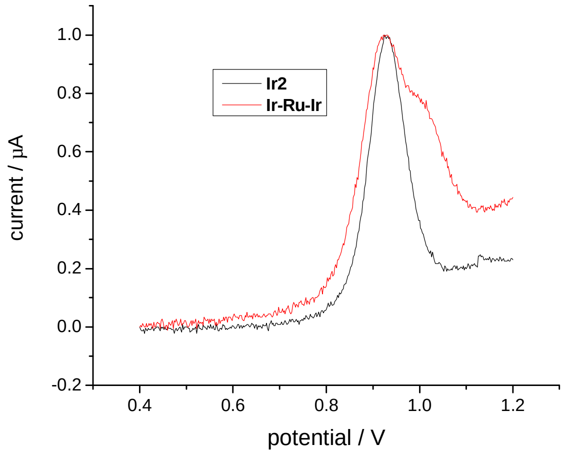


Figure S3. Normalised DPV of **Ir2** and **Ir-Ru-Ir** *vs*. Fc/Fc^+.

Deconvolution of DPV

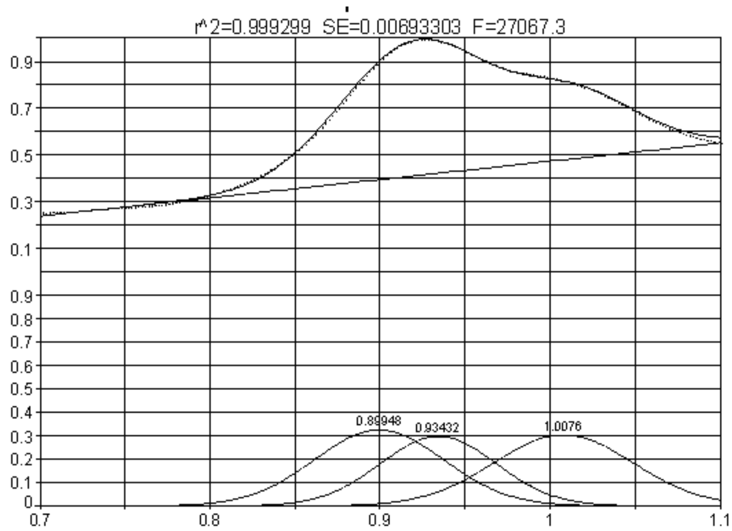


Figure S4. Deconvolution of the DPV of Ir-Ru-Ir achieved using Peak-Fitting software.

Digital CV simulation

Using Digisim 3.03b (by Bioanalytical Systems Inc., Feb. 2004) the concentration of all species in the mixture at a distance of 0.027021 cm from the working electrode was evaluated by analyzing the CV-movie during the potential scan (starting at 0 V); the results are listed in following table, in which the concentration percentage of each species was calculated from integration of the curves using different end potential from 1.3 V to 1.8 V.

Input (for Digisim3):

Ir4+Ru3+Ir4+ + e = Ir4+Ru2+Ir4+ 1.01 V
Ir4+Ru2+Ir4+ + e = Ir4+Ru2+Ir3+ 0.93 V
Ir4+Ru2+Ir3+ + e = Ir3+Ru2+Ir3+ 0.90 V

Table S1. Digital simulation of the oxidation of **Ir-Ru-Ir** applying different end potentials. The occurrence of the different oxidised species was determined at a distance of 0.027021 cm from the working electrode (determined as intensity in a.u.).

End Potential /V	**Ir^+-Ru-Ir**		**Ir^+-Ru-Ir^+**		**Ir^+-Ru^+-Ir^+**	
	int. /a.u.	conc%	int. /a.u.	conc%	int. /a.u.	conc%
1.3	50.19235	41.2	43.22618	35.5	28.46011	23.3
1.4	59.81405	40.3	57.46028	38.7	31.14117	21.0
1.5	69.90545	42.3	61.86212	37.5	33.40672	20.2
1.6	80.33465	44.3	65.65329	36.2	35.39329	19.5
1.7	91.00545	46.1	69.04057	35.0	37.19134	18.9
1.8	101.84335	47.8	72.16497	33.9	38.86442	18.3

Computational studies

Geometry optimisation of symmetric **Ir-Ru-Ir**, **Ir-Ru-Ir^{2+}** and **Ir-Ru-Ir^{3+}** complexes was performed within C_2 symmetry constraints, whereas C_1 symmetry was used for **Ir-Ru-Ir^+** complex. All calculations were performed using the Gaussian 03 program.[1] The hybrid DFT method B3LYP[2] with a conventional all-electron basis set 3-21G* on H, C, N atoms, and double-ζ quality basis set (LANL2DZ)[3], containing Hay and Wadt's effective core potential (ECP), on Ir and Ru atoms was applied. While restricted-DFT was used for the closed shell geometry of **Ir-Ru-Ir**, the unrestricted-DFT method was applied on **Ir-Ru-Ir^+**, **Ir-Ru-Ir^{2+}** and **Ir-Ru-Ir^{3+}**. Single point calculations at (U)B3LYP/6-31G(d)/LANL2DZ+ECP level were carried out on gas phase optimised geometries to obtain MOs and spin densities. Solvent effects were included by using self-consistent reaction field (SCRF) with a UAHF (united atom Hartree-Fock) parametrisation[4] of the polarisable continuum model (PCM)[5] as implemented in the Gaussian 03 package. Acetonitrile ($\varepsilon = 36.64$) was employed as solvent to mimic measurement conditions. Single point calculations with PCM model indicate a more stable state for triplet **Ir-Ru-Ir**$^{2+}$ by 61.9 cal/mol and almost degenerate for quartet **Ir-Ru-Ir**$^{3+}$ with respect to their low spin states. Therefore, high spin states were considered. Visualisation of MOs and spin densities were done with GaussView 3.07 using an isocontour value of 0.02 and 0.0004 ebohr^{-3}, respectively.

Spin densities

Spin densities on Ir atoms in **Ir-Ru-Ir**$^{+\bullet}$ are 0.22, which can emerge from the occupancy of the two degenerate orbitals. The rest of spin (~0.5) are mainly located on the phenyl groups of phenyl quinoline. The interesting observation is that 0.5 spin in fragment I or III are almost equally spread out on Ir and phenyl quinoline ligand with a ratio of 1.26:1, respectively. Triplet **Ir-Ru-Ir**$^{2+}$ diradical possess 0.44 spin up electrons on each Ir atom. Spin density for quartet **Ir-Ru-Ir**$^{3+\bullet}$ is localised on all three fragments with spin-up electrons. While Ir atoms hold 0.42 electrons, Ru keeps 0.83.

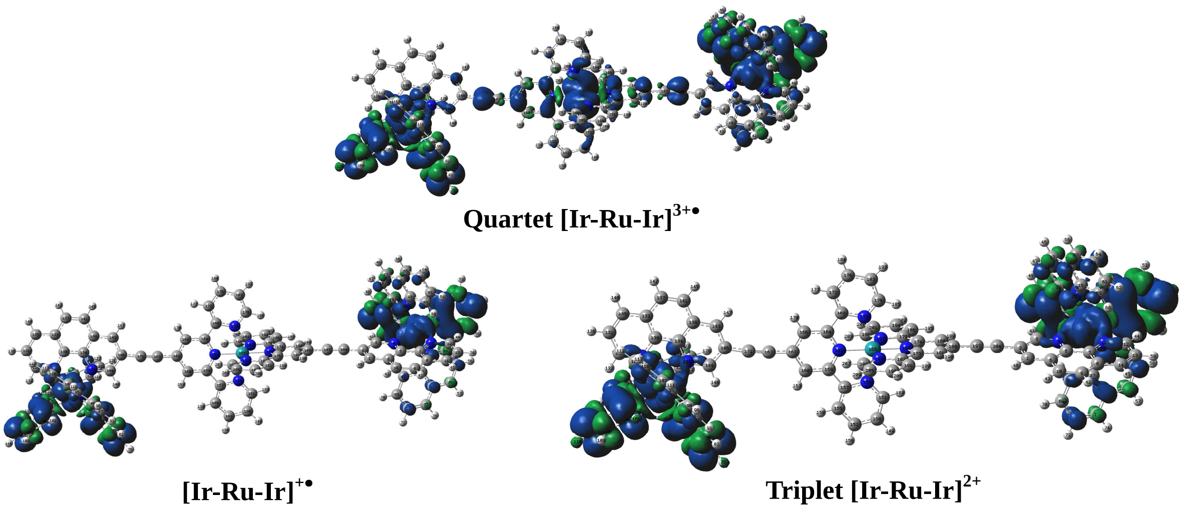


Figure S5. Spin density distributions obtained from SP-PCM calculations. Blue: spin-up, green: spin-down.

Cartesian coordinates after optimisation

Ir-Ru-Ir

C	2.56014	9.23712	1.71885
C	1.44534	8.71823	1.05184
C	0.60099	9.61027	0.33849
N	0.83954	10.92732	0.28593
C	1.91469	11.44398	0.96655
C	2.81724	10.62033	1.68599
C	2.11516	12.85681	0.92524
C	3.25342	13.42421	1.54742
C	4.16554	12.56663	2.25435
C	3.95097	11.22350	2.33324
N	1.17828	13.61741	0.27444
C	1.37898	14.94529	0.17742
C	2.49842	15.57467	0.74904
C	3.42973	14.82306	1.44373
C	-1.80093	12.57219	2.19268
C	-2.67411	12.05253	3.20416
C	-3.52189	10.96548	2.87089
C	-3.51084	10.45797	1.60149
C	-2.62880	10.98271	0.62141
N	-1.75853	11.98682	0.92479
C	-2.61401	10.52084	-0.76263
C	-3.49941	9.55285	-1.27668
C	-3.47505	9.24056	-2.62995
C	-2.57248	9.89827	-3.47787
C	-1.68973	10.85467	-2.97476
C	-1.68417	11.18156	-1.60802
C	-2.73847	14.49695	-0.70179
C	-3.35178	15.65970	-1.17374
C	-2.79412	16.38497	-2.23504
C	-1.62497	15.93551	-2.83409
C	-1.00256	14.76054	-2.36620
C	-1.54723	14.03098	-1.27764
C	0.18478	14.17624	-2.97181
C	0.87682	14.78156	-4.05448
C	1.97547	14.18098	-4.60047
C	2.40189	12.91600	-4.11607
C	1.67549	12.31809	-3.03582
N	0.60530	12.99067	-2.44360
Ir	-0.43990	12.45753	-0.67237
H	3.22863	8.57730	2.25767
H	-0.26400	9.25018	-0.20280
H	5.02850	13.01506	2.73199
H	4.63713	10.58651	2.87807
H	0.62188	15.50751	-0.35319
H	4.29011	15.29279	1.90519
H	-4.19415	10.56940	3.62360
H	-4.18349	9.66091	1.32176
H	-4.22545	9.06766	-0.63424
H	-4.17246	8.51665	-3.03423
H	-2.57309	9.67534	-4.53922
H	-1.01533	11.35997	-3.65392
H	-3.19803	13.95659	0.11512
H	-4.27315	16.00286	-0.71679
H	-3.27825	17.28423	-2.59458
H	-1.21224	16.49088	-3.66777
H	0.52241	15.72852	-4.43295
H	2.51723	14.64774	-5.41507
H	2.61042	16.64583	0.64661
C	-1.03256	13.71628	2.50712
H	-0.42445	14.15522	1.73857
C	-1.09556	14.29103	3.75996
H	-0.51210	15.17959	3.96951
C	-1.92559	13.75246	4.76842
H	-1.96148	14.21805	5.74504
C	-2.70554	12.65359	4.48783
H	-3.37326	12.24241	5.23638
C	2.05286	11.01901	-2.62450
H	1.47330	10.53420	-1.86024
C	3.11646	10.36861	-3.21650
H	3.37966	9.36902	-2.89035
C	3.86096	10.97903	-4.24935
H	4.69771	10.45814	-4.69708
C	3.49941	12.23106	-4.69425
H	4.04000	12.70954	-5.50289
H	4.17246	-8.51665	-3.03423
C	3.47505	-9.24056	-2.62995
C	2.57248	-9.89827	-3.47787
C	3.49941	-9.55285	-1.27668
C	1.68973	-10.85467	-2.97476
H	2.57309	-9.67534	-4.53922
C	2.61401	-10.52084	-0.76263
H	4.22545	-9.06766	-0.63424
C	1.68417	-11.18156	-1.60802
H	1.01533	-11.35997	-3.65392
C	2.62880	-10.98271	0.62141
Ir	0.43990	-12.45753	-0.67237
C	3.51084	-10.45797	1.60149
N	1.75853	-11.98682	0.92479
C	1.54723	-14.03098	-1.27764
C	3.52189	-10.96548	2.87089
H	4.18349	-9.66091	1.32176
C	1.80093	-12.57219	2.19268
C	1.00256	-14.76054	-2.36620
C	2.73847	-14.49695	-0.70179
C	2.67411	-12.05253	3.20416
H	4.19415	-10.56940	3.62360
C	1.03256	-13.71628	2.50712
C	-0.18478	-14.17624	-2.97181
C	1.62497	-15.93551	-2.83409
C	3.35178	-15.65970	-1.17374
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C	2.70554	-12.65359	4.48783
H	0.42445	-14.15522	1.73857
C	1.09556	-14.29103	3.75996
C	-0.87682	-14.78156	-4.05448
N	-0.60530	-12.99067	-2.44360
C	2.79412	-16.38497	-2.23504
H	1.21224	-16.49088	-3.66777
H	4.27315	-16.00286	-0.71679
C	1.92559	-13.75246	4.76842
H	3.37326	-12.24241	5.23638
H	0.51210	-15.17959	3.96951
C	-1.97547	-14.18098	-4.60047
H	-0.52241	-15.72852	-4.43295
C	-1.67549	-12.31809	-3.03582
H	3.27825	-17.28423	-2.59458
H	1.96148	-14.21805	5.74504
C	-2.40189	-12.91600	-4.11607
H	-2.51723	-14.64774	-5.41507
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C	-3.49941	-12.23106	-4.69425
H	-1.47330	-10.53420	-1.86024
C	-3.11646	-10.36861	-3.21650
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H	-4.04000	-12.70954	-5.50289
H	-3.37966	-9.36902	-2.89035
H	-4.69771	-10.45814	-4.69708
N	-1.17828	-13.61741	0.27444
C	-1.37898	-14.94529	0.17742
C	-2.11516	-12.85681	0.92524
C	-2.49842	-15.57467	0.74904
H	-0.62188	-15.50751	-0.35319
C	-3.25342	-13.42421	1.54742
C	-1.91469	-11.44398	0.96655
C	-3.42973	-14.82306	1.44373
H	-2.61042	-16.64583	0.64661
C	-4.16554	-12.56663	2.25435
C	-2.81724	-10.62033	1.68599
N	-0.83954	-10.92732	0.28593
H	-4.29011	-15.29279	1.90519
C	-3.95097	-11.22350	2.33324
H	-5.02850	-13.01506	2.73199
C	-2.56014	-9.23712	1.71885
C	-0.60099	-9.61027	0.33849
H	-4.63713	-10.58651	2.87807
C	-1.44534	-8.71823	1.05184
H	-3.22863	-8.57730	2.25767
H	0.26400	-9.25018	-0.20280
H	3.75367	0.25941	-2.62506
C	3.09571	-0.39624	-2.07061
C	2.22603	0.13644	-1.12404
C	3.10015	-1.77539	-2.28660
H	2.19104	1.19859	-0.92712
N	1.37952	-0.63757	-0.40061
C	2.23361	-2.58047	-1.54746
H	3.76551	-2.21668	-3.01747
C	1.37898	-2.00361	-0.60848
H	2.22276	-3.65066	-1.70242
C	0.42766	-2.76988	0.21872
C	0.23143	-4.14732	0.20341
N	-0.30596	-1.98460	1.06198
C	-0.73180	-4.72894	1.06135
H	0.80181	-4.78343	-0.45821
C	-1.24221	-2.51058	1.90601
Ru	0.00000	0.00000	1.06152
C	-1.47192	-3.88238	1.92073
C	-0.95860	-6.12728	1.05823
C	-1.91803	-1.49274	2.73285
N	0.30596	1.98460	1.06198
H	-2.20910	-4.31515	2.58156
C	-1.17155	-7.32371	1.05729
C	-2.90673	-1.78452	3.67204
N	-1.50673	-0.19031	2.52424
C	-0.42766	2.76988	0.21872
C	1.24221	2.51058	1.90601
C	-3.48976	-0.75552	4.41136
H	-3.21984	-2.80785	3.82713
C	-2.07982	0.80315	3.24788
C	-1.37898	2.00361	-0.60848
C	-0.23143	4.14732	0.20341
C	1.47192	3.88238	1.92073
C	1.91803	1.49274	2.73285
C	-3.06910	0.55787	4.19512
H	-4.25719	-0.97549	5.14232
H	-1.72612	1.80523	3.05067
C	-2.23361	2.58047	-1.54746
N	-1.37952	0.63757	-0.40061
C	0.73180	4.72894	1.06135
H	-0.80181	4.78343	-0.45821
H	2.20910	4.31515	2.58156
C	2.90673	1.78452	3.67204
N	1.50673	0.19031	2.52424
H	-3.49790	1.38149	4.75008
C	-3.10015	1.77539	-2.28660
H	-2.22276	3.65066	-1.70242
C	-2.22603	-0.13644	-1.12404
C	0.95860	6.12728	1.05823
C	3.48976	0.75552	4.41136
H	3.21984	2.80785	3.82713
C	2.07982	-0.80315	3.24788
C	-3.09571	0.39624	-2.07061
H	-3.76551	2.21668	-3.01747
H	-2.19104	-1.19859	-0.92712
C	1.17155	7.32371	1.05729
C	3.06910	-0.55787	4.19512
H	4.25719	0.97549	5.14232
H	1.72612	-1.80523	3.05067
H	-3.75367	-0.25941	-2.62506
H	3.49790	-1.38149	4.75008

Ir-Ru-Ir+

C	2.15299	9.24026	1.55635
C	1.01537	8.78186	0.88443
C	0.17364	9.73664	0.25219
N	0.43784	11.05094	0.28096
C	1.53885	11.50389	0.96366
C	2.43908	10.61683	1.60736
C	1.77621	12.91241	1.00843
C	2.94132	13.40893	1.64289
C	3.84690	12.48723	2.27239
C	3.60078	11.14759	2.26705
N	0.85191	13.74119	0.42859
C	1.08600	15.06739	0.41869
C	2.23103	15.62889	1.00876
C	3.15400	14.80696	1.63015
C	-2.13317	12.65399	2.33509
C	-3.01719	12.09907	3.32088
C	-3.90240	11.06413	2.92995
C	-3.91808	10.63341	1.63077
C	-3.03074	11.19223	0.67864
N	-2.12895	12.15118	1.03222
C	-3.04266	10.81728	-0.73367
C	-3.96096	9.91648	-1.29905
C	-3.95714	9.69183	-2.67303
C	-3.03949	10.36681	-3.49111
C	-2.12194	11.25986	-2.93900
C	-2.10217	11.50154	-1.55319
C	-3.05326	14.78883	-0.36243
C	-3.64543	15.99417	-0.73169
C	-3.09444	16.77593	-1.75985
C	-1.95101	16.34238	-2.42871
C	-1.34829	15.12804	-2.06751
C	-1.88846	14.33305	-1.01226
C	-0.19177	14.55729	-2.74685
C	0.48983	15.22172	-3.79644
C	1.56190	14.63155	-4.40818
C	1.96406	13.32741	-4.02206
C	1.24382	12.66975	-2.96984
N	0.20231	13.32517	-2.31418
Ir	-0.83645	12.69867	-0.56542
H	2.82060	8.53561	2.03629
H	-0.70971	9.42728	-0.29033
H	4.72997	12.88350	2.75916
H	4.28195	10.45984	2.75303
H	0.33669	15.68735	-0.05461
H	4.03567	15.22146	2.10433
H	-4.58208	10.64442	3.66275
H	-4.61841	9.87623	1.31145
H	-4.69870	9.41445	-0.68466

H	-4.68155	9.01742	-3.11303
H	-3.05714	10.20791	-4.56320
H	-1.43467	11.78290	-3.59064
H	-3.50037	14.20305	0.42855
H	-4.54253	16.33146	-0.22603
H	-3.56299	17.71064	-2.04119
H	-1.55237	16.94782	-3.23313
H	0.15462	16.20168	-4.10138
H	2.09831	15.14116	-5.20021
H	2.36911	16.70148	0.97806
C	-1.32062	13.74647	2.71586
H	-0.69666	14.21200	1.97616
C	-1.35610	14.24105	4.00355
H	-0.73909	15.09200	4.26605
C	-2.20057	13.66999	4.98250
H	-2.21478	14.07487	5.98624
C	-3.02007	12.61860	4.64035
H	-3.69696	12.18471	5.36725
C	1.59801	11.33704	-2.65618
H	1.02467	10.81096	-1.91443
C	2.63415	10.70765	-3.31468
H	2.88107	9.68234	-3.06558
C	3.37245	11.37235	-4.31952
H	4.18672	10.86451	-4.82020
C	3.03366	12.65974	-4.66988
H	3.56997	13.18019	-5.45484
H	4.68161	-9.01742	-3.11293
C	3.95720	-9.69182	-2.67295
C	3.03956	-10.36681	-3.49105
C	3.96098	-9.91647	-1.29896
C	2.12200	-11.25986	-2.93896
H	3.05723	-10.20790	-4.56314
C	3.04267	-10.81728	-0.73360
H	4.69870	-9.41444	-0.68456
C	2.10220	-11.50154	-1.55315
H	1.43475	-11.78290	-3.59061
C	3.03072	-11.19222	0.67870
Ir	0.83646	-12.69867	-0.56540
C	3.91804	-10.63340	1.63085
N	2.12893	-12.15118	1.03226
C	1.88848	-14.33305	-1.01223
C	3.90234	-11.06413	2.93004
H	4.61837	-9.87622	1.31155
C	2.13312	-12.65399	2.33514
C	1.34833	-15.12804	-2.06748
C	3.05326	-14.78883	-0.36237
C	3.01712	-12.09907	3.32094
H	4.58200	-10.64441	3.66284
C	1.32057	-13.74647	2.71589
C	0.19183	-14.55729	-2.74685
C	1.95106	-16.34238	-2.42867
C	3.64544	-15.99417	-0.73162
H	3.50036	-14.20305	0.42862
C	3.01997	-12.61860	4.64041
H	0.69663	-14.21201	1.97617
C	1.35602	-14.24105	4.00357
C	-0.48975	-15.22172	-3.79646
N	-0.20227	-13.32517	-2.31419
C	3.09449	-16.77593	-1.75979
H	1.55244	-16.94782	-3.23310
H	4.54253	-16.33146	-0.22594
C	2.20046	-13.66999	4.98254
H	3.69684	-12.18470	5.36733
H	0.73901	-15.09201	4.26606
C	-1.56180	-14.63155	-4.40822
H	-0.15452	-16.20168	-4.10139
C	-1.24376	-12.66975	-2.96987
H	3.56304	-17.71064	-2.04112
H	2.21465	-14.07488	5.98629
C	-1.96397	-13.32741	-4.02211
H	-2.09820	-15.14116	-5.20026
C	-1.59796	-11.33704	-2.65621
C	-3.03356	-12.65974	-4.66994
H	-1.02464	-10.81096	-1.91445
C	-2.63409	-10.70766	-3.31473
C	-3.37236	-11.37235	-4.31959
H	-3.56985	-13.18019	-5.45492
H	-2.88101	-9.68234	-3.06564
H	-4.18663	-10.86451	-4.82029
N	-0.85192	-13.74119	0.42857
C	-1.08601	-15.06739	0.41867
C	-1.77623	-12.91241	1.00839
C	-2.23105	-15.62889	1.00871
H	-0.33669	-15.68735	-0.05463
C	-2.94136	-13.40893	1.64283
C	-1.53887	-11.50389	0.96363
C	-3.15403	-14.80696	1.63008
H	-2.36913	-16.70148	0.97801
C	-3.84694	-12.48723	2.27231
C	-2.43911	-10.61683	1.60731
N	-0.43785	-11.05094	0.28095
H	-4.03572	-15.22146	2.10425
C	-3.60082	-11.14759	2.26698
H	-4.73003	-12.88351	2.75906
C	-2.15302	-9.24026	1.55631
C	-0.17365	-9.73664	0.25218
H	-4.28200	-10.45984	2.75294
C	-1.01538	-8.78186	0.88440
H	-2.82064	-8.53562	2.03624
H	0.70972	-9.42728	-0.29031
H	3.73215	0.50256	-2.89100
C	3.11780	-0.19468	-2.33721
C	2.21400	0.27960	-1.39133
C	3.21303	-1.57042	-2.55339
H	2.10972	1.33721	-1.19469
N	1.41927	-0.54795	-0.66849
C	2.40032	-2.43046	-1.81477
H	3.90679	-1.96671	-3.28367
C	1.50886	-1.91128	-0.87645
H	2.46043	-3.49895	-1.96996
C	0.60983	-2.73843	-0.04925
C	0.50386	-4.12734	-0.06464
N	-0.17316	-2.00217	0.79423
C	-0.41813	-4.77044	0.79323
H	1.11488	-4.72245	-0.72802
C	-1.07192	-2.58901	1.63951
Ru	-0.00001	0.00000	0.79370
C	-1.21048	-3.97366	1.65364
C	-0.56493	-6.18367	0.79589
C	-1.81284	-1.61881	2.46785
N	0.17315	2.00217	0.79423
H	-1.91728	-4.45257	2.31580
C	-0.73528	-7.38685	0.82130
C	-2.77727	-1.97633	3.40947
N	-1.49009	-0.29169	2.25827
C	-0.60984	2.73843	-0.04925
C	1.07190	2.58901	1.63952
C	-3.42630	-0.98892	4.15086
H	-3.02093	-3.01818	3.56595
C	-2.12683	0.66071	2.98378
C	-1.50887	1.91128	-0.87645
C	-0.50387	4.12734	-0.06463
C	1.21046	3.97366	1.65365
C	1.81282	1.61881	2.46786
C	-3.09510	0.34958	3.93369
H	-4.17519	-1.25978	4.88402
H	-1.84195	1.68442	2.78649
C	-2.40034	2.43047	-1.81476
N	-1.41929	0.54795	-0.66849
C	0.41811	4.77044	0.79323
H	-1.11489	4.72246	-0.72802
H	1.91726	4.45257	2.31581
C	2.77725	1.97632	3.40948
N	1.49007	0.29168	2.25827
H	-3.57673	1.14232	4.49032
C	-3.21304	1.57043	-2.55339
H	-2.46044	3.49895	-1.96996
C	-2.21401	-0.27960	-1.39133
C	0.56492	6.18367	0.79590
C	3.42628	0.98892	4.15087
H	3.02091	3.01817	3.56596
C	2.12681	-0.66071	2.98378
C	-3.11782	0.19469	-2.33721
H	-3.90680	1.96671	-3.28368
H	-2.10973	-1.33720	-1.19469
C	0.73527	7.38685	0.82132
C	3.09508	-0.34958	3.93369
H	4.17517	1.25977	4.88402
H	1.84193	-1.68442	2.78649
H	-3.73217	-0.50255	-2.89101
H	3.57671	-1.14233	4.49032

Ir-Ru-Ir++

C	3.48001	8.73827	1.47277
C	2.28574	8.53985	0.77262
C	1.65645	9.67280	0.18672
N	2.17082	10.90974	0.28584
C	3.32966	11.10504	0.99456
C	4.02881	10.02747	1.59635
C	3.84243	12.43391	1.11269
C	5.07271	12.65632	1.77998
C	5.76826	11.54412	2.36674
C	5.26166	10.28233	2.28959
N	3.11508	13.46030	0.57019
C	3.60979	14.71267	0.63322
C	4.83207	15.00360	1.26044
C	5.56105	13.98225	1.84271
C	-0.06273	12.90366	2.40565
C	-1.06715	12.49360	3.34956
C	-2.13483	11.68352	2.89445
C	-2.20847	11.32559	1.57315
C	-1.20684	11.73869	0.66548
N	-0.13845	12.47849	1.07815
C	-1.26088	11.44179	-0.76643
C	-2.33274	10.79195	-1.39324
C	-2.33716	10.63594	-2.78018
C	-1.27254	11.12533	-3.55158
C	-0.20014	11.77196	-2.94026
C	-0.17686	11.94721	-1.54282
C	-0.47846	15.31654	-0.11636
C	-0.83061	16.62618	-0.41968
C	-0.14600	17.33233	-1.42519
C	0.89283	16.72203	-2.13667
C	1.25693	15.40525	-1.84402
C	0.57291	14.67548	-0.81551
C	2.28574	14.65928	-2.56235
C	3.08585	15.23678	-3.57423
C	4.03350	14.48394	-4.21755
C	4.18082	13.11239	-3.89624
C	3.33974	12.54701	-2.87682
N	2.43070	13.35326	-2.19534
Ir	1.25399	12.85034	-0.48856
H	3.99111	7.89498	1.92013
H	0.73904	9.56665	-0.37609
H	6.70426	11.73281	2.87868
H	5.78517	9.44953	2.74280
H	3.01072	15.49654	0.19131
H	6.49967	14.18719	2.34401
H	-2.90341	11.37757	3.59494
H	-3.04072	10.74237	1.20863
H	-3.18098	10.43604	-0.82190
H	-3.17844	10.15556	-3.26452
H	-1.29529	11.01825	-4.62956
H	0.60442	12.15827	-3.55105
H	-1.01859	14.79000	0.65699
H	-1.63980	17.10817	0.11547
H	-0.42815	18.35208	-1.65675
H	1.38896	17.28185	-2.91913
H	2.94630	16.27656	-3.82973
H	4.66203	14.92282	-4.98380
H	5.18147	16.02721	1.28871
C	0.94893	13.78278	2.85618
H	1.67867	14.14396	2.15571
C	0.98284	14.20926	4.16822
H	1.75569	14.89862	4.48626
C	0.01302	13.77938	5.10317
H	0.05701	14.13018	6.12621
C	-0.99635	12.93783	4.69479
H	-1.76564	12.61872	5.38829
C	3.44124	11.15878	-2.62618
H	2.77818	10.71012	-1.90834
C	4.35113	10.38338	-3.31426
H	4.40566	9.31981	-3.11496
C	5.20786	10.94818	-4.28715
H	5.91896	10.32303	-4.81154
C	5.11580	12.29059	-4.57569
H	5.74648	12.73949	-5.33410
H	3.17844	-10.15556	-3.26452
C	2.33716	-10.63594	-2.78018
C	1.27254	-11.12533	-3.55158
C	2.33274	-10.79195	-1.39324
C	0.20014	-11.77196	-2.94026
H	1.29529	-11.01825	-4.62956
C	1.26088	-11.44179	-0.76643
H	3.18098	-10.43604	-0.82190
C	0.17686	-11.94721	-1.54282
H	-0.60442	-12.15827	-3.55105
C	1.20684	-11.73869	0.66548
Ir	-1.25399	-12.85034	-0.48856
C	2.20847	-11.32559	1.57315
N	0.13845	-12.47849	1.07815
C	-0.57291	-14.67548	-0.81551
C	2.13483	-11.68352	2.89445
H	3.04072	-10.74237	1.20863
C	0.06273	-12.90366	2.40565
C	-1.25693	-15.40525	-1.84402
C	0.47846	-15.31654	-0.11636
C	1.06715	-12.49360	3.34956
H	2.90341	-11.37757	3.59494
C	-0.94893	-13.78278	2.85618
C	-2.28574	-14.65928	-2.56235
C	-0.89283	-16.72203	-2.13667
C	0.83061	-16.62618	-0.41968
H	1.01859	-14.79000	0.65699
C	0.99635	-12.93783	4.69479
H	-1.67867	-14.14396	2.15571
C	-0.98284	-14.20926	4.16822
C	-3.08585	-15.23678	-3.57423
N	-2.43070	-13.35326	-2.19534
C	0.14600	-17.33233	-1.42519
H	-1.38896	-17.28185	-2.91913
H	1.63980	-17.10817	0.11547
C	-0.01302	-13.77938	5.10317
H	1.76564	-12.61872	5.38829
H	-1.75569	-14.89862	4.48626
C	-4.03350	-14.48394	-4.21755
H	-2.94630	-16.27656	-3.82973
C	-3.33974	-12.54701	-2.87682
H	0.42815	-18.35208	-1.65675
H	-0.05701	-14.13018	6.12621
C	-4.18082	-13.11239	-3.89624
H	-4.66203	-14.92282	-4.98380
C	-3.44124	-11.15878	-2.62618
C	-5.11580	-12.29059	-4.57569
H	-2.77818	-10.71012	-1.90834
C	-4.35113	-10.38338	-3.31426

C	-5.20786	-10.94818	-4.28715
H	-5.74648	-12.73949	-5.33410
H	-4.40566	-9.31981	-3.11496
H	-5.91896	-10.32303	-4.81154
N	-3.11508	-13.46030	0.57019
C	-3.60979	-14.71267	0.63322
C	-3.84243	-12.43391	1.11269
C	-4.83207	-15.00360	1.26044
H	-3.01072	-15.49654	0.19131
C	-5.07271	-12.65632	1.77998
C	-3.32966	-11.10504	0.99456
C	-5.56105	-13.98225	1.84271
H	-5.18147	-16.02721	1.28871
C	-5.76826	-11.54412	2.36674
C	-4.02881	-10.02747	1.59635
N	-2.17082	-10.90974	0.28584
H	-6.49967	-14.18719	2.34401
C	-5.26166	-10.28233	2.28959
H	-6.70426	-11.73281	2.87868
C	-3.48001	-8.73827	1.47277
C	-1.65645	-9.67280	0.18672
H	-5.78517	-9.44953	2.74280
C	-2.28574	-8.53985	0.77262
H	-3.99111	-7.89498	1.92013
H	-0.73904	-9.56665	-0.37609
H	3.76308	-0.01743	-3.10604
C	3.05965	-0.62369	-2.55110
C	2.22998	-0.02994	-1.60448
C	2.96587	-1.99955	-2.76666
H	2.27181	1.03210	-1.40875
N	1.33030	-0.74036	-0.88012
C	2.04396	-2.73991	-2.02636
H	3.59829	-2.48700	-3.49754
C	1.23282	-2.10356	-1.08738
H	1.95775	-3.80661	-2.18139
C	0.23058	-2.79988	-0.25812
C	-0.06273	-4.16313	-0.27039
N	-0.44400	-1.96196	0.58479
C	-1.06086	-4.67438	0.59019
H	0.46236	-4.83469	-0.93435
C	-1.41238	-2.42119	1.43283
Ru	0.00000	0.00000	0.58285
C	-1.73609	-3.77539	1.44993
C	-1.40444	-6.05725	0.60217
C	-2.01464	-1.35902	2.26079
N	0.44400	1.96196	0.58479
H	-2.49979	-4.15147	2.11525
C	-1.75518	-7.22056	0.65018
C	-3.01710	-1.58223	3.20406
N	-1.51602	-0.08768	2.04890
C	-0.23058	2.79988	-0.25812
C	1.41238	2.42119	1.43283
C	-3.52638	-0.51568	3.94528
H	-3.39915	-2.58130	3.36271
C	-2.01790	0.94231	2.77416
C	-1.23282	2.10356	-1.08738
C	0.06273	4.16313	-0.27039
C	1.73609	3.77539	1.44993
C	2.01464	1.35902	2.26079
C	-3.01805	0.76558	3.72580
H	-4.30388	-0.68217	4.67985
H	-1.59831	1.91828	2.57570
C	-2.04396	2.73991	-2.02636
N	-1.33030	0.74036	-0.88012
C	1.06086	4.67438	0.59019
H	-0.46236	4.83469	-0.93435
H	2.49979	4.15147	2.11525
C	3.01710	1.58223	3.20406
N	1.51602	0.08768	2.04890
H	-3.38786	1.61643	4.28223
C	-2.96587	1.99955	-2.76666
H	-1.95775	3.80661	-2.18139
C	-2.22998	0.02994	-1.60448
C	1.40444	6.05725	0.60217
C	3.52638	0.51568	3.94528
H	3.39915	2.58130	3.36271
C	2.01790	-0.94231	2.77416
C	-3.05965	0.62369	-2.55110
H	-3.59829	2.48700	-3.49754
H	-2.27181	-1.03210	-1.40875
C	1.75518	7.22056	0.65018
C	3.01805	-0.76558	3.72580
H	4.30388	0.68217	4.67985
H	1.59831	-1.91828	2.57570
H	-3.76308	0.01743	-3.10604
H	3.38786	-1.61643	4.28223

Ir-Ru-Ir+++

C	1.43668	9.25700	1.00432
C	0.20237	8.84126	0.49432
C	-0.72231	9.84510	0.09009
N	-0.44807	11.15986	0.18611
C	0.75635	11.56149	0.71197
C	1.74104	10.62523	1.12071
C	1.02096	12.96130	0.83808
C	2.28249	13.39911	1.31507
C	3.26765	12.42781	1.70309
C	3.00357	11.09433	1.62170
N	0.03065	13.84559	0.49431
C	0.28294	15.16885	0.57359
C	1.51609	15.67192	1.01697
C	2.51466	14.79233	1.39601
C	-2.67859	12.63063	2.73418
C	-3.47931	12.04570	3.78249
C	-4.47258	11.09854	3.43188
C	-4.67598	10.77829	2.11529
C	-3.88539	11.37143	1.10461
N	-2.87442	12.25186	1.41175
C	-4.11358	11.13833	-0.31207
C	-5.16796	10.36011	-0.81961
C	-5.35965	10.26784	-2.19432
C	-4.49642	10.94577	-3.08174
C	-3.44482	11.71522	-2.59451
C	-3.23543	11.83935	-1.20681
C	-3.89270	15.00760	0.47087
C	-4.52567	16.23308	0.29777
C	-4.16007	17.08940	-0.76741
C	-3.16117	16.71090	-1.66170
C	-2.51466	15.47613	-1.50269
C	-2.87537	14.59510	-0.41726
C	-1.49382	14.97316	-2.40270
C	-0.99012	15.72824	-3.48639
C	-0.03726	15.19654	-4.31520
C	0.41216	13.86862	-4.10813
C	-0.12946	13.11507	-3.00354
N	-1.04336	13.70039	-2.14020
Ir	-1.81963	12.91985	-0.31284
H	2.17004	8.52056	1.30821
H	-1.68218	9.57222	-0.32675
H	4.22453	12.78026	2.06931
H	3.74530	10.36630	1.92634
H	-0.51994	15.83735	0.29635
H	3.46949	15.15948	1.75407
H	-5.08452	10.65790	4.21052
H	-5.45843	10.08919	1.83554
H	-5.85916	9.85444	-0.15778
H	-6.18803	9.69115	-2.58696
H	-4.67124	10.88138	-4.14929
H	-2.80677	12.23974	-3.29215
H	-4.19534	14.37363	1.29102
H	-5.31197	16.53881	0.97787
H	-4.66502	18.03974	-0.89104
H	-2.91136	17.37533	-2.47851
H	-1.36021	16.72886	-3.65224
H	0.36430	15.77463	-5.13954
H	1.66457	16.74268	1.06680
C	-1.74104	13.63193	3.09989
H	-1.16721	14.11389	2.33093
C	-1.58921	14.01543	4.41563
H	-0.88220	14.79601	4.66878
C	-2.35829	13.42037	5.44295
H	-2.22851	13.73944	6.46933
C	-3.28985	12.45040	5.12390
H	-3.90301	12.00140	5.89654
C	0.27473	11.76216	-2.86092
H	-0.16267	11.16960	-2.07721
C	1.18635	11.20369	-3.73017
H	1.47366	10.16609	-3.61208
C	1.74783	11.95878	-4.78738
H	2.46735	11.50398	-5.45606
C	1.35789	13.27013	-4.97272
H	1.76223	13.85622	-5.78974
H	6.18803	-9.69115	-2.58696
C	5.35965	-10.26784	-2.19432
C	4.49642	-10.94577	-3.08174
C	5.16796	-10.36011	-0.81961
C	3.44482	-11.71522	-2.59451
H	4.67124	-10.88138	-4.14929
C	4.11358	-11.13833	-0.31207
H	5.85916	-9.85444	-0.15778
C	3.23543	-11.83935	-1.20681
H	2.80677	-12.23974	-3.29215
C	3.88539	-11.37143	1.10461
Ir	1.81963	-12.91985	-0.31284
C	4.67598	-10.77829	2.11529
N	2.87442	-12.25186	1.41175
C	2.87537	-14.59510	-0.41726
C	4.47258	-11.09854	3.43188
H	5.45843	-10.08919	1.83554
C	2.67859	-12.63063	2.73418
C	2.51466	-15.47613	-1.50269
C	3.89270	-15.00760	0.47087
C	3.47931	-12.04570	3.78249
H	5.08452	-10.65790	4.21052
C	1.74104	-13.63193	3.09989
C	1.49382	-14.97316	-2.40270
C	3.16117	-16.71090	-1.66170
C	4.52567	-16.23308	0.29777
H	4.19534	-14.37363	1.29102
C	3.28985	-12.45040	5.12390
H	1.16721	-14.11389	2.33093
C	1.58921	-14.01543	4.41563
C	0.99012	-15.72824	-3.48639
N	1.04336	-13.70039	-2.14020
C	4.16007	-17.08940	-0.76741
H	2.91136	-17.37533	-2.47851
H	5.31197	-16.53881	0.97787
C	2.35829	-13.42037	5.44295
H	3.90301	-12.00140	5.89654
H	0.88220	-14.79601	4.66878
C	0.03726	-15.19654	-4.31520
H	1.36021	-16.72886	-3.65224
C	0.12946	-13.11507	-3.00354
H	4.66502	-18.03974	-0.89104
H	2.22851	-13.73944	6.46933
C	-0.41216	-13.86862	-4.10813
H	-0.36430	-15.77463	-5.13954
C	-0.27473	-11.76216	-2.86092
C	-1.35789	-13.27013	-4.97272
H	0.16267	-11.16960	-2.07721
C	-1.18635	-11.20369	-3.73017
C	-1.74783	-11.95878	-4.78738
H	-1.76223	-13.85622	-5.78974
H	-1.47366	-10.16609	-3.61208
H	-2.46735	-11.50398	-5.45606
N	-0.03065	-13.84559	0.49431
C	-0.28294	-15.16885	0.57359
C	-1.02096	-12.96130	0.83808
C	-1.51609	-15.67192	1.01697
H	0.51994	-15.83735	0.29635
C	-2.28249	-13.39911	1.31507
C	-0.75635	-11.56149	0.71197
C	-2.51466	-14.79233	1.39601
H	-1.66457	-16.74268	1.06680
C	-3.26765	-12.42781	1.70309
C	-1.74104	-10.62523	1.12071
N	0.44807	-11.15986	0.18611
H	-3.46949	-15.15948	1.75407
C	-3.00357	-11.09433	1.62170
H	-4.22453	-12.78026	2.06931
C	-1.43668	-9.25700	1.00432
C	0.72231	-9.84510	0.09009
H	-3.74530	-10.36630	1.92634
C	-0.20237	-8.84126	0.49432
H	-2.17004	-8.52056	1.30821
H	1.68218	-9.57222	-0.32675
H	3.65183	0.91948	-3.34595
C	3.12188	0.15699	-2.79083
C	2.16891	0.52477	-1.84528
C	3.37584	-1.19855	-3.00535
H	1.94376	1.56372	-1.65087
N	1.47466	-0.38727	-1.12077
C	2.66754	-2.14542	-2.26491
H	4.11094	-1.51257	-3.73531
C	1.72188	-1.73187	-1.32722
H	2.85185	-3.19969	-2.41953
C	0.92460	-2.65656	-0.49873
C	0.97925	-4.05124	-0.51312
N	0.06175	-2.01295	0.34390
C	0.13736	-4.79665	0.34320
H	1.65543	-4.56808	-1.17889
C	-0.76239	-2.70102	1.19024
Ru	0.00000	0.00000	0.34227
C	-0.73993	-4.09427	1.20365
C	0.13621	-6.22587	0.34659
C	-1.61062	-1.82408	2.01967
N	-0.06175	2.01295	0.34390
H	-1.38808	-4.64789	1.86757
C	0.06214	-7.43969	0.38528
C	-2.52449	-2.29183	2.96339
N	-1.44598	-0.46799	1.80879
C	-0.92460	2.65656	-0.49873
C	0.76239	2.70102	1.19024
C	-3.28419	-1.38753	3.70617
H	-2.64429	-3.35473	3.12209
C	-2.18938	0.40255	2.53552
C	-1.72188	1.73187	-1.32722
C	-0.97925	4.05124	-0.51312
C	0.73993	4.09427	1.20365
C	1.61062	1.82408	2.01967
C	-3.11292	-0.01973	3.48753
H	-3.99466	-1.74385	4.44114
H	-2.02777	1.45269	2.33809
C	-2.66754	2.14542	-2.26491
N	-1.47466	0.38727	-1.12077
C	-0.13736	4.79665	0.34320
H	-1.65543	4.56808	-1.17889
H	1.38808	4.64789	1.86757
C	2.52449	2.29183	2.96339
N	1.44598	0.46799	1.80879
H	-3.68377	0.71074	4.04511
C	-3.37584	1.19855	-3.00535
H	-2.85185	3.19969	-2.41953
C	-2.16891	-0.52477	-1.84528
C	-0.13621	6.22587	0.34659
C	3.28419	1.38753	3.70617

H	2.64429	3.35473	3.12209	H	-1.94376	-1.56372	-1.65087	H	2.02777	-1.45269	2.33809
C	2.18938	-0.40255	2.53552	C	-0.06214	7.43969	0.38528	H	-3.65183	-0.91948	-3.34595
C	-3.12188	-0.15699	-2.79083	C	3.11292	0.01973	3.48753	H	3.68377	-0.71074	4.04511
H	-4.11094	1.51257	-3.73531	H	3.99466	1.74385	4.44114				

References

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Rob, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03; Gaussian, Inc., Wallingford, CT, 2003.

[2] a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372-1377; b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652; c) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.

[3] a) P. J. Hay and R. W. Wadt, *J. Chem. Phys.*, 1985, **82**, 270-283; b) W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284-298; (c) P. J. Hay and R. W. Wadt, *J. Chem. Phys.*, 1985, **82**, 299-310.

[4] V. Barone, M. Cossi and J. Tomasi, *J. Chem. Phys.*, 1997, **107**, 3210-3221.

[5] a) S. Miertus, E. Scrocco and J. Tomasi, *Chem. Phys.*, 1981, **55**, 117-129; b) R. Cammi and J. Tomasi, *J. Comput. Chem.*, 1995, **16**, 1449-1458; c) V. Barone; M. Cossi and J. Tomasi, *J. Comput. Chem.*, 1998, **19**, 404-417.