Electronic Supporting Information

Syntheses, Crystal and Electronic Structures of Rhodium and Iridium Pyridine Diimine Complexes with O- and S-donor ligands: (Hydroxido, Methoxido and Thiolato)

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Experimental Details

All manipulations of the complexes were performed with standard Schlenk techniques or in a dinitrogen filled glovebox. Pentane, hexane, toluene, dichloromethane (DCM) and diethyl ether (Et_2O) were dried and N_2-saturated with a MBraun solvent purification system. Benzene and tetrahydrofuran (THF) were distilled over sodium benzophenone ketyl prior to use. Sodium methoxide was purchased from ABCR and was used as received. Bis(trifluoromethanesulfonyl)imide ($HNTf_2$) was purchased from TCI and was used as received. Hydrogen 5.0 was purchased from Linde and was used as received. Hydrogen sulfide solution (0.8 M in THF) was purchased from Merck and was used as received.

Synthesis of the Starting Materials

The following syntheses were performed according to literature procedure:

Di-μ-chlorotetrakis(cyclooctene)diiridium(I)[1]

Di-μ-chlorotetraethylene diiridium(I)[1]

Di-μ-chlorotetraethylene dirhodium(I)[2]

2,6-Dibenzoylpyridine[3]

4-*tert*-Butylphenyllithium[4]

3[5]

*N*2,*N*2,*N*6,*N*6-tetramethylpyridine-2,6-dicarboxamide[6]

"^{Me}**L$_3$IrCl**"[7]

sodium thiomethoxide[8]

sodium thiophenolate[9]

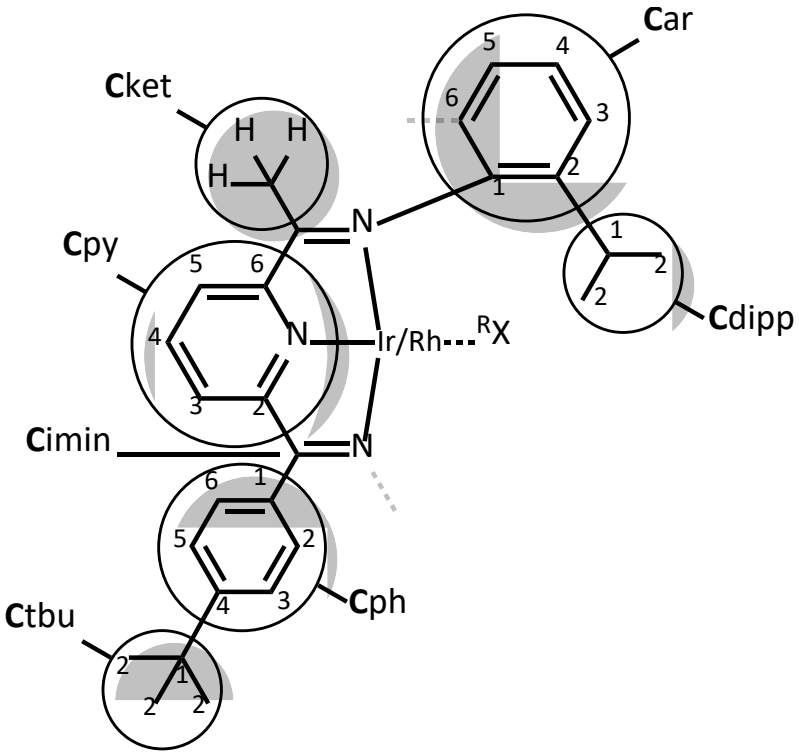


Figure S1: Labeling used for the NMR chemical shifts.

Synthesis of **1**

To a solution of 21.3 g (150 mmol) 4-*tert*-butylphenyllithium and 250 mL THF, 16.6 g (78.9 mmol) N2,N2,N6,N6-tetramethylpyridine-2,6-dicarboxamide was added slowly as a solid at -40 °C. The solution was stirred for 2 hours at RT. Subsequently, the dark solution was added to a 1 M HCl solution and stirred at RT for 15 hours. The organic phase was separated, and the aqueous phase was extracted five times with 30 mL diethyl ether. The combined organic phases were dried over magnesium sulfate, and the solvent was removed. The residue was recrystallized in methanol. 12.9 g (32.2 mmol, 43%) of pale beige crystals were obtained as product.

^{1}H-NMR (500 MHz, $CDCl_3$) δ [ppm] = 8.27-8.25 (d, 7.8 Hz, 2H, Cpy-3,5); 8.16-8.13 (dt, 8.6 Hz, 2.0 Hz, 4H, Cph-2,6); 8.12-8.09 (m, 1H, Cpy-4); 7.46-7.44 (dt, 8.6 Hz, 2.0 Hz, 4H, Cph-3,5); 1.35 (s, 18H, Ctbu).

^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$) δ [ppm] = 192.3 (s, 2C, C=O); 157.0 (s, 2C, Cph-4); 154.4 (s, 2C, Cpy-2,6); 138.4 (s, 1C, Cpy-4); 133.6 (s, 2C, Cph-1); 131.5 (s, 4C, Cph-2,6); 127.0 (s, 2C, Cpy-3,5); 125.3 (s, 4C, Cph-3,5); 35.4 (s, 2C, Ctbu-1); 31.3(s, 6C, Ctbu-2).

CHNO ($C_{27}H_{29}NO_2$; 399.53 g/mol): calc. C, 81.17; H, 7.32; N, 3.51.
meas. C, 81.18; H, 7.28; N, 3.45.

Synthesis of **2**

5.61 g (14.1 mmol) **1**, 33.0 mL (175 mmol) diisopropylaniline and 250 mg para toluene sulphonic acid (PTSA) were dissolved in 170 mL toluene and heated to reflux with a Dean-Stark apparatus for 72 hours. The cooled suspension was filtered at -30 °C and the solvent was removed. The excess diisopropylaniline was removed by ball tube distillation, and the residue was recrystallized in methanol. 7.91 g (1.01 mmol, 78 %) of **2** were obtained as yellow crystals.

^{1}H-NMR (400 MHz, DCM-d_2) δ [ppm] = 8.36 (m); 8.01 (m); 7.83 (m); 7.66 (m); 7.46 (m); 7.36 (m); 7.25 (m); 7.19 (m); 6.96 (m); 2.88 (m); 1.09 (m).

^{13}C{^{1}H}-NMR (101 MHz, DCM-d_2) δ [ppm] = 165.3 (s); 164.1 (s); 163.3 (s); 158.1 (s); 154.7 (s); 154.0 (s); 153.9 (s); 152.8 (s); 152.4 (s); 146.7 (s); 145.9 (s); 136.2 (s); 135.9 (s); 135.5 (s); 135.8 (s); 134.6 (s); 134.4 (s); 131.4 (s); 129.9 (s); 129.8 (s); 129.0 (s); 128.5 (s); 125.4 (s); 125.1 (s); 124.8 (s); 124.3 (s); 124.0 (s); 123.5 (s); 123.0 (s); 122.7 (s); 122.2 (s); 121.7 (s); 34.8 (s); 34.7 (s); 34.6 (s); 34.6 (); 30.9 (s); 28.3 (s); 28.15 (s); 28.1 (s); 23.6 (s); 23.2 (s); 22.4 (s); 21.9 (s); 21.4 (s); 20.9 (s).

CHN ($C_{51}H_{63}N_3$; 718.09 g/mol): calc. C, 85.30; H, 8.84; N, 5.85.
meas. C, 85.25; H, 8.90; N, 5.94.

Synthesis of the Complexes

Synthesis of **4**

To a solution of 522 mg (727 µmol) **2** and 20 mL THF, a solution of 141 mg (363 µmol) di-*µ*-chlorotetraethylene dirhodium(I) and 20 mL THF was added. A color change from pale yellow to dark green was observed. The reaction solution was stirred for 2 hours. Then, the reaction mixture was overlaid with 100 mL pentane. Subsequently, the product was crystallized at -35 °C for 72 hours. The product (446 mg, 521 µmol, 72 % yield) was obtained as dark green crystals, which were washed twice with 10 mL pentane and dried in an oil pump vacuum.

^{1}H-NMR (600 MHz, THF-d_8) δ [ppm] = 8.44 (t, 8.0 Hz, 1H, Cpy-4); 7.58 (d, 8.0 Hz, 2H, Cpy-3,5); 7.42 (m, 8H, Cph-2,3,5,6); 7.06 (m, 2H, Car-4); 6.97 (m, 4H, Car-3,5); 3.25 (sept, 6.8 Hz, 4H, Cdipp-2,3); 1.31 (s, 18H, Ctbu-2); 1.05 (d, 6.9 Hz, 6H, Cdipp-2); 0.96 (d, 6.9 Hz, 6H, Cdipp-2).

^{13}C{^{1}H}-NMR (151 MHz, THF-d_8) δ [ppm] = 169.2 (s, 2C, Cimin); 158.8 (s, 2C, Cpy-2,6); 153.4 (s, 2C, Cph-4); 147.6 (s, 2C, Car-1); 141.6 (s, 4C, Car-2,6); 132.9 (s, 2C, Cph-1); 128.5 (s, 2C, Cpy-3,5); 128.2 (s, 4C, Cph-2,6); 127.0 (s, 2C, Car-4); 126.1 (s, 4C, Cph-3,5); 124.4 (s, 1C, Cpy-4); 123.6 (s, 4C, Car-3,5); 35.8 (s, 2C, Ctbu-1); 31.5 (s, 6C, Ctbu-2); 29.3 (s, 4C, Cdipp-1); 25.2 (s, 4C, Cdipp-2); 23.6 (s, 4C, Cdipp-2).

CHN ($C_{51}H_{63}ClN_3Rh$; 856.44 g/mol): calc. C, 71.52; H, 7.41; N, 4.91.
meas. C, 71.09 H, 7.33; N, 4.93.

Synthesis of **5**

300 mg (495 µmol) **3** were dissolved in 10 mL toluene, giving a yellow solution. 140.5 mg (247.6 µmol) of the di-μ-chlorotetraethylene diiridium(I) were dissolved in 10 mL toluene, cooled to -30 °C, and added to the vigorously stirred yellow solution of the ligand at room temperature. This gave a dark green suspension, with the product partly precipitating from the reaction solution. The solvent was removed under vacuum. The crude product was co-evaporated with pentane three times. The obtained green solid (371 mg, 446 µmol, 90 %) was dried in vacuum.

^{1}H-NMR (300 MHz, THF-d_8): δ [ppm] = 8.62 (t, 6 Hz, 1H, Cpy-4); 7.83 (d, 6 Hz, 2H, Cpy-3,4); 7.69 (dd, 6.3 Hz, 0.78 Hz, 4H, Cph-3,5); 7.57 (tt, 5.6 Hz, 0.96 Hz, 2H, Cph-4); 7.36 (t, 5.9 Hz, 4H, Cph-2,6); 7.05 (m, 6H, Car-3,4,5); 3.15 (sept, 5.2 Hz, 4H, Cdipp-1); 1.01 (d, 5.2 Hz, 12H, Cdipp-2); 0.87 (d, 5.2 Hz, 12H, Cdipp-2).

^{13}C{^{1}H}-NMR (75 MHz, THF-d_8): δ [ppm] = 175.8 (s, 2C, Cimin); 166.4 (s, 2C, Cpy-2,6); 151.4 (s, 2C, Car-1); 141.9 (s, 4C, Car-2,6); 138.6 (s, 2C, Cph-1); 129.4 (s, 4C, Cph-2,6); 129.3 (s, 2C, Cph-4); 127.7 (s, 4C, Car-3,5); 125.5 (s, 4C, Cph-3,5); 125.3 (s, 2C, Cpy-3,5); 125.0 (s, 1C, Cpy-4); 123.6 (s, 2C, Car-4); 29.0 (s, 4C, Cdipp-1); 25.7 (s, 4C, Cdipp-2); 23.7 (s, 4C, Cdipp-2).

Synthesis of **6**

To a solution of 260 mg (305 µmol) **8** and 20 mL THF, 11 mg (0.65 mmol) degassed water was added. The reaction solution was stirred at RT for 15 hours. A color change from turquoise-green to grass-green was observed. The solvent was removed in an oil pump vacuum. The residue was then co-evaporated twice with 2 mL of THF, and the solid was dried in an oil pump vacuum. The product (230 mg, 274 µmol, 90 %) was obtained as a dark grass-green solid. Crystals suitable for X-ray structural analysis were obtained from 1 mL of saturated THF solution layered with 5 mL pentane.

To a solution of 80 mg (93 µmol) **4** and 10 mL THF, 100 mg (0.65 mmol) cesium hydroxide was added. The reaction mixture was stirred at RT for 15 hours. A color change from green to grass-green was observed. The solvent was removed under oil pump vacuum, and the residue was extracted with n-pentane. After removing the solvent under reduced pressure, 49 mg (58 µmol, 62 %) of a dark grass-green solid was obtained as product.

^{1}H-NMR (600 MHz, THF-d_8) δ [ppm] = 8.26 (t, 7.9 Hz, 1H, Cpy-4); 7.67 (d, 7.9 Hz, 2H, Cpy-3,5); 7.51 (d, 8.4 Hz, 4H, Cph-2,6); 7.40 (d, 8.5 Hz, 4H, Cph-3,5); 7.10 (t, 7.7 Hz, 2H, Car-4); 7.00 (d, 7.7 Hz, 4H, Car-3,5); 3.20 (hept, 6.8 Hz, 2H, Cdipp-1); 1.32 (s, 18H, Ctbu-2); 0.99 (d, 6.8 Hz, 12H, Cdipp-2); 0.96 (d, 6.8 Hz, 12H, Cdipp-2).

^{13}C{^{1}H}-NMR (151 MHz, THF-d_8) δ [ppm] = 166.3 (s, 2C, Cimin); 156.9 (s, 2C, Cpy-2,6); 152.7 (s, 2C, Cph-4); 147.1 (s, 2C, Car-1); 142.2 (s, 4C, Car-2,6); 134.3 (s, 2C, Cph-1); 128.1 (s, 2C, Cpy-3,5); 127.7 (s, 4C, Cph-2,6); 126.9 (s, 2C, Car-4); 125.9 (s, 4C, Cph-3,5); 123.6 (s, 4C, Car-3,5); 119.4 (s, 1C, Cpy-4); 35.8 (s, 2C, Ctbu-1); 31.5 (s, 6C, Ctbu-2); 29.1 (s, 4C, Cdipp-1); 25.8 (s, 4C, Cdipp-2); 23.2 (s, 4C, Cdipp-2).

CHNO ($C_{51}H_{64}N_3ORh$; 837.99 g/mol): calc. C, 73.10; H, 7.70; N, 5.01; O, 1.91.
meas. C, 73.51; H, 7.62; N, 5.09; O, 2.09.

IR (ATR-IR) $\tilde{\nu}$ [cm^{-1}] = 3566 (w, O-H).

Synthesis of **6D**

To a solution of 28 mg (33 µmol) **8** in 10 mL THF, 45 mg (2.3 mmol) degassed deuterium oxide was added. The reaction solution was stirred at RT for 15 hours. A color change from turquoise-green to grass-green was observed. The solvent was removed in an oil pump vacuum, the residue was co-evaporated twice with 2 mL THF, and the solid was dried in an oil pump vacuum. 20 mg (24 µmol, 72 %) of a dark, grass-green solid were obtained as product.

IR (ATR-IR) $\tilde{\nu}$ [cm^{-1}] = 2633 (w, O-D).

Synthesis of **7**

100 mg (120 µmol) of **5** together with an excess of cesium hydroxide monohydrate (400 mg, 2.4 mmol) were transferred into a Schlenk tube equipped with a magnetic stirring bar. 10 mL of THF was added, giving a dark green suspension. The reaction mixture was stirred at 65 °C for 65 hours, upon which a color change from dark green to grass-green was observed. The solvent was removed under oil pump vacuum, and the crude product was extracted three times with toluene. The solvent was evaporated in an oil pump vacuum, yielding the product as a grass-green solid (97 mg, 119 µmol, 99 %). Crystallization can be achieved by layering a THF solution of the product with pentane and crystallizing overnight at -35 °C.

^{1}H-NMR (300 MHz, THF-d_8): δ [ppm] = 8.20 (m, 3H, Cpy-3,4,5); 8.05 (s, 1H, Ir-OH); 7.74 (dd, 8.4 Hz, 1.5 Hz, 4H, Cph-3,5); 7.56 (tt, 7.5 Hz, 1.3 Hz, 2H, Cph-4); 7.34 (t, 8.1 Hz, 4H, Cph-2,6); 7.06 (m, 6H, Car-3,4,5); 3.06 (sept, 6.8 Hz, 4H, Cdipp-1); 1.03 (d, 6.9 Hz, 12H, Cdipp-2); 0.86 (d, 6.9 Hz, 12H, Cdipp-2).

^{13}C{^{1}H}-NMR (75 MHz, THF-d_8): δ [ppm] = 169.7 (s, 2C, Cimin); 163.5 (s, 2C, Cpy-2,6); 157.3 (s, 6C, Car-1,2,6); 129.5 (s, 2C, Cph-1); 127.9 (s, 4C, Cph-2,6); 127.6 (s, 2C, Cph-4); 126.5 (s, 2C, Car-4); 123.9 (s, 4C, Cph-3,5); 123.3 (s, 2C, Cpy-3,5); 122.5 (s, 4C, Car-3,5); 118.2 (s, 1C, Cpy-4); 27.5 (s, 4C, Cdipp-1); 25.2 (s, 4C, Cdipp-2); 22.9 (s, 4C, Cdipp-2).

Synthesis of **8**

To a solution of 446 mg (521 µmol) **4** and 20 mL THF, a solution of 259 mg (4.79 mmol) sodium methoxide and 40 mL methanol was added. A color change from dark green to turquoise-green was observed. The reaction solution was stirred at 60 °C for 15 hours. The solvent was removed in an oil pump vacuum, and the residue was extracted with 120 mL of toluene and filtered over diatomaceous earth. The solvent was removed with an oil pump vacuum. 385 mg (452 µmol, 87 %) of a dark, turquoise-green solid was obtained as product.

^{1}H-NMR (600 MHz, THF-d_8) δ [ppm] = 8.19 (t, 7.9 Hz, 1H, Cpy-4); 7.59 (d, 7.9 Hz, 2H, Cpy-3,5); 7.43 (m, 8H, Cph-2,3,5,6); 7.07 (m, 2H, Car-4); 6.98 (m, 4H, Car-3,5); 3.81 (s, 3H, Rh-OC*H*3); 3.17 (sept, 6.8 Hz, 4H, Cdipp-1); 1.31 (s, 18H, Ctbu-2); 1.00 (d, 6.9 Hz, 12H, Cdipp-2); 0.96 (d, 6.7 Hz, 12H, Cdipp-2).

^{13}C{^{1}H}-NMR (151 MHz, THF-d_8) δ [ppm] = 165.5 (s, 1C, Cimin); 156.8 (s, 2C, Cpy-2,6); 152.4 (s, 2C, Cph-4); 148.1 (s, 2C, Car-1); 141.7 (s, 4C, Car-2,6); 134.4 (s, 2C, Cph-1); 128.0 (s, 2C, Cpy-3,5); 127.6 (s, 4C, Cph-2,6); 126.7 (s, 2C, Car-4); 125.6 (s, 4C, Cph-3,5); 123.5 (s, 4C, Car-3,5); 118.7 (s, 1C, Cpy-4); 59.2 (s, 1C, Rh-OCH3); 35.6 (s, 2C, Ctbu-1); 31.4 (s, 6C, Ctbu-2); 29.1 (s, 4C, Cdipp-1); 26.4 (s, 4C, Cdipp-2); 23.0 (s, 4C, Cdipp-2).

CHNO ($C_{52}H_{66}N_3ORh$; 852.03 g/mol): calc. C, 73.30; H, 7.81; N, 4.93; O, 1.88.
meas. C, 73.52; H, 7.84; N, 4.58; O, 1.79.

Synthesis of **9**

500 mg (600 µmol) of **5** together with an excess of 500 (9.3 mmol) mg sodium methoxide are transferred into a Schlenk tube equipped with a magnetic stirring bar. 10 mL of toluene and 20 mL of methanol were added, giving a dark green suspension. The reaction mixture was stirred at 65 °C for 16 hours. No color change is observed. The solvent mixture was removed in an oil pump vacuum. The crude product was extracted with toluene, and the solvent was subsequently evaporated to dryness. This extraction is performed three times. The obtained green solid (487 mg, 588 µmol, 98 %) was dried in an oil pump vacuum. Crystallization can be achieved by layering a THF solution of the product with pentane and crystallizing overnight at -35 °C.

^{1}H-NMR (600 MHz, THF-d_8): δ [ppm] = 8.11 (m, 3H, Cpy-3,4,5); 7.70 (d, 7.08 Hz, 4H, Cph-3,5); 7.52 (t, 7.5 Hz, 2H, Cph-4); 7.33 (t, 7.74 Hz, 4H, Cph-2,6); 7.08 (m, 2H, Car-4); 7.02 (m, 4H, Car-3,5); 5.01 (s, 3H, Ir-OCH3); 3.05 (sept, 6.8 Hz, 4H, Cdipp-1); 1.02 (d, 6.9 Hz, 12H, Cdipp-2); 0.84 (d, 6.7 Hz, 12H, Cdipp-2).

^{13}C{^{1}H}-NMR (151 MHz, THF-d_8): δ [ppm] = 168.6 (s, 2C, Cimin); 162.3 (s, 2C, Cpy-2,6); 152.2 (s, 2C, Car-1); 141.9 (s, 4C, Car-2,6); 140.3 (s, 2C, Cph-1); 128.8 (s, 4C, Cph-2,6); 128.7 (s, 2C, Cph-4); 127.5 (s, 2C, Car-4); 125.2 (s, 4C, Cph-3,5); 124.6 (s, 4C, Cpy-3,5); 123.7 (s, 4C, Car-3,5); 118.7 (s, 1C, Cpy-4); 66.4 (s, 1C, Ir-OCH3); 29.0 (s, 4C, Cdipp-1); 25.6 (s, 4C, Cdipp-2); 23.3 (s, 4C, Cdipp-2).

Synthesis of **10**

To a solution of 52 mg (61 µmol) **8** and 4 mL THF, a solution of 21 mg (75 µmol) $HNTf_2$ and 14 mL THF was added. A color change from turquoise-green to curry-yellow was observed. The reaction solution was stirred for 10 minutes. The solvent was removed in an oil pump vacuum, and the residue was dissolved in 2 mL of THF, then overlaid with 6 mL of pentane. The product was then crystallized at -35 °C for 72 hours. The dark crystals were washed twice with 2 mL of pentane and dried in an oil pump vacuum. The product was obtained as dark crystals (80 mg, 61 µmol, 100 % yield).

^{1}H-NMR (600 MHz, THF-d_8) δ [ppm] = 8.37 (t, 8.1 Hz, 1H, Cpy-4); 7.72 (d, 8.1 Hz, 2H, Cpy-3,5); 7.47 (m, 8H, Cph-2,6); 7.29 (t, 7.7 Hz, 2H, Car-4); 7.18 (t, 7.8 Hz, 4H, Car-3,5); 3.62 (m, 4H, THF); 3.50 (sept, 6.8 Hz, 4H, Cdipp-1); 1.78 (m, 4H, THF); 1.30 (s, 18H, Ctbu-2); 1.23 (d, 6.8 Hz, 6H, Cdipp-2); 0.92 (d, 6.8 Hz, 6H, Cdipp-2).

^{13}C{^{1}H}-NMR (151 MHz, THF-d_8) δ [ppm] = 171.4 (s, 2C, Cimin); 159.2 (s, 2C, Cpy-2,6); 155.3 (s, 2C, Cph-4); 146.6 (s, 2C, Car-1); 141.6 (s, 4C, Car-2,6); 132.0 (s, 1C, Cpy-4); 130.1 (s, 2C, Cpy-3,5); 130.0 (s, 2C, Cph-1); 129.6 (s, 4C, Cph-2,6); 128.9 (s, 2C, Car-4); 126.7 (s, 4C, Cph-3,5); 125.6 (s, 4C, Car-3,5); 68.3 (s, 2C, THF); 35.9 (s, 2C, Ctbu-1); 31.3 (s, 6C, Ctbu-2); 29.9 (s, 4C, Cdipp-1); 26.5 (s, 2C, THF); 24.6 (s, 4C, Cdipp-2); 23.5 (s, 4C, Cdipp-2).

^{19}F-NMR (565 MHz, THF-d_8) δ [ppm] = -79.8 (s, 6F, NTF_2^-).

CHN ($C_{57}H_{71}F_6N_4O_5RhS_2$; 1173.23 g/mol): calc. C, 58.35; H, 6.10; N, 4.78; S, 5.47.
meas. C, 57.88; H, 6.04; N, 5.13; S, 5.13.

Synthesis of **11**

To 435 mg (524 µmol) of **9** dissolved in 10 mL toluene, a solution of 142 mg (505 µmol) $HNTf_2$ and 5 mL cold toluene were added dropwise under stirring. The reaction mixture is stirred for 10 minutes at room temperature. By adding 10 mL of pentane, precipitation of the product was observed. The liquid was decanted off, and the solid remainder was washed with pentane, then finally dried in an oil pump vacuum. The product was obtained as a glossy solid (550 mg, 495 µmol, 98 %). Crystallization can be achieved by layering a toluene solution of the product with pentane and crystallizing overnight at -35 °C.

^{1}H-NMR (300 MHz,THF-d_8): δ [ppm] = 8.66 (t, 8.1 Hz, 1H, Cpy-4); 7.66 (d, 8.2 Hz, 2H, Cpy-3,5); 7.63-7.58 (m, 6H, Cph-2,4,6); 7.45 (m, 4H, Cph-3,5); 7.34 (m, 1H, CH3-OH); 7.28-7.23 (m, 6H, Car-3,4,5); 3.37 (sept, 6.8 Hz, 4H, Cdipp-1); 2.99 (d, 3.9 Hz, 1H, CH3-OH); 1.08 (d, 6.9 Hz, 12H, Cdipp-2); 1.00 (d, 6.9 Hz, 12H, Cdipp-2).

^{13}C{^{1}H}-NMR (75 MHz, THF-d_8): δ [ppm] = 179.6 (s, 2C, Cimin); 148.5 (s, 2C, Cpy-2,6); 142.1 (s, 2C, Cph-1); 142.0 (s, 6C, Car-1,2,6); 127.0 (s, 4C, Cph-2,6); 130.1 (s, 2C, Cph-4); 129.9 (s, 4C, Cph-3,5); 129.7 (s, 2C, Car-4); 129.6 (s, 1C, Cpy-4); 127.6 (s, 2C, Cpy-3,5); 125.8 (s, 4C, Car-3,5); 58.4 (s, 1C, CH3-OH); 29.5 (s, 4C, Cdipp-1); 25.88 (s, 4C, Cdipp-2); 23.2 (s, 4C, Cdipp-2).

^{1}H-NMR (600 MHz, C_6D_6): δ [ppm] = 7.76 (t, 8.0 Hz, 1H, Cpy-4); 7.29 (m, 4H, Cph-2,6); 7.21 (t, 7.8 Hz, 2H, Car-4); 7.09 (d, 7.8 Hz, 4H, Car-3,5); 7.04 (m, 2H, Cph-4); 7.01 (d, 8.0 Hz, 2H, Cpy-3,5); 6.92 (m, 4H, Cph-3,5); 6.21 (q, 4.3 Hz, 1H, CH3-OH); 3.21 (sept, 6.8 Hz, 4H, Cdipp-1); 3.16 (d, 4.0 Hz, 3H, CH3-OH); 1.03 (d, 6.8 Hz, 12H, Cdipp-2); 0.95 (d, 6.8 Hz, 12H, Cdipp-2).

^{19}F-NMR (594 MHz, C_6D_6): δ [ppm] = -78.4 (s, 6F, NTF_2^-).

$C_{46}H_{51}F_6IrN_3O_5S_2$ (1110.26 g/mol): cald. C, 49.76; H, 4.63; N, 5.05; S, 5.78;
meas. C, 49.65; H, 4.55; N, 5.02; S, 5.75.

Synthesis of **12**

To 179 mg (220 µmol) of **7** dissolved in 15 mL toluene, 61 mg (217 µmol) HNTf2 in 5 mL cold toluene were added dropwise under stirring. The reaction mixture was stirred for 10 minutes at room temperature, then 10 mL of pentane was added, which led to the precipitation of the product. The solvent was removed in an oil pump vacuum, and the residue was washed with pentane and dried in an oil pump vacuum. The product is obtained as a blue-green, glossy solid (220 mg, 201 µmol, 93 %). Crystallization can be achieved by layering a THF solution of the product with pentane and crystallizing overnight at -35 °C.

^{1}H-NMR (300 MHz, THF-d_8): δ [ppm] = 8.68 (t, 8.1 Hz, 1H, Cpy-4); 8.41 (s, 2H, Ir-OH2); 7.68 (d, 8.0 Hz, 2H, Cpy-3,5); 7.62-7.57 (m, 6H, Cph-2,4,6); 7.24 (m, 6H, Car-3,4,5); 7.43 (m, 4H, Cph-3,5); 3.37 (sept, 6.8 Hz, 4H, Cdipp-1); 1.10 (d, 6.7 Hz, 12H, Cdipp-2); 1.00 (d, 6.7 Hz, 12H, Cdipp-2).

^{1}H-NMR (300 MHz, C_6D_6): δ [ppm] = 7.78 (s, 2H, Ir-OH2); 7.71 (t, 8.0 Hz, 1H, Cpy-4); 7.26 (m, 6H, Cph-2,6, Car-4); 7.11 (d, 7.4 Hz, 4H, Car-3,5); 7.05 (tt, 7.5 Hz, 1.8 Hz, 2H, Cph-4); 7.00 (d, 8.0 Hz, 2H, Cpy-3,5); 6.87 (m, 4H, Cph-3,5); 3.19 (sept, 6.8 Hz, 4H, Cdipp-1); 1.11 (d, 6.8 Hz, 12H, Cdipp-2,3); 0.94 (d, 6.8 Hz, 12H, Cdipp-2).

^{13}C{^{1}H}-NMR (75 MHz, C_6D_6): δ [ppm] = 179.9 (s, 2C, Cimin); 156.2 (s, 2C, Cpy-2,6); 137.4 (s, 2C, Cph-1); 130.5 (s, 6C, Car-1,2,6); 128.6 (s, 2C, Cph-4); 128.3 (s, 1C, Cpy-4); 127.3 (s, 4C, Cph-3,5); 125.7 (s, 4C, Cph-2,6); 125.2 (s, 2C, Car-4); 127.6 (s, 4C, Cpy-3,5); 124.7 (s, 4C, Car-3,5); 28.6 (s, 4C, Cdipp-1); 25.64 (s, 4C, Cdipp-2); 22.8 (s, 4C, Cdipp-2).

^{19}F-NMR (594 MHz, C_6D_6): δ [ppm] = -78.4 (s, 6F, NTF_2^-).

$C_{45}H_{49}F_6IrN_4O_5S_2$ (1096.24 g/mol): cald. C, 49.30; H, 4.51; N, 5.11; S, 5.85;
meas. C, 49.31; H, 4.47; N, 4.95; S 6.02.

Synthesis of **13**

306 mg (276 µmol) of **11** were dissolved in 15 mL THF and stirred at room temperature for 5 min. The solvent was removed in an oil pump vacuum, redissolved in 10 mL of THF, and stirred for 4 minutes. This procedure is repeated two more times. The product **13** was obtained as a green, glossy solid (314 mg, 273 µmol, 99 %) after drying in an oil pump vacuum. Crystallization can be achieved by layering a THF solution of the product with pentane and crystallizing overnight at -35 °C.

^{1}H-NMR (300 MHz, THF-d_8): δ [ppm] = 8.61 (t, 8.1 Hz, 1H, Cpy-4); 7.72 (d, 8.1 Hz, 2H, Cpy-3,5); 7.64 (m, 6H, Cph-2,4,6); 7.47 (t, 8.3 Hz, 4H, Cph-3,5); 7.35-7.25 (m, 6 H, Car-3,4,5,); 3.38 (sept, 6.9 Hz, 4H, Cdipp-1); 3.13 (m, 4H, THF); 1.48 (m, 2H, THF); 1.05 (d, 6.8 Hz, 12H, Cdipp-2); 0.99 (d, 6.8 Hz, 12H, Cdipp-2).

^{13}C{^{1}H}-NMR (75 MHz, THF-d_8): δ [ppm] = 180.2 (s, 2C; Cimin); 165.6 (s, 2C, Cpy-2,6); 150.1 (s, 2C, Car-1); 142.1 (s, 4C, Car-2,6); 134.7 (s, 2C, Cph-1); 131.0 (s, 2C, Cph-4); 129.7 (s, 2C, Car-4); 130.1 (s, 4C, Cph-3,5); 127.7 (s, 8C, Cpy-3,5, Cph-2,6); 126.0 (s, 2C, Car-3,5); 132.1 (s, 1C, Cpy-4); 30.0 (s, 4C, Cdipp-1); 25.2 (s, 4C, Cdipp-2); 23.7 (s, 4C, Cdipp-2).

^{19}F-NMR (564 MHz, THF-d_8): δ [ppm] = -79.8 (s, 6F, NTF_2^-).

$C_{49}H_{54}F_6IrN_4O_5S_2$ (1149.32 g/mol): cald. C, 51.21; H, 4.74; N, 4.87; S, 5.58;
meas. C, 51.39; H, 5.10; N, 4.67; S, 5.52.

Synthesis of **14**

To 100 mg (120 µmol) of **5** dissolved in 10 mL THF, 120 mg (1.5 mmol) sodium thiomethoxide was added under vigorous stirring, followed by a rapid color change from dark green to deep violet. The reaction mixture was stirred for 3 hours at room temperature, then the solvent was removed in an oil pump vacuum. The crude product was extracted with toluene. The solvent was evaporated and extracted once more with toluene. This extraction procedure was repeated once. The obtained dark solid (99 mg, 117 µmol, 98 %) was dried in an oil pump vacuum. Crystallization can be achieved by layering a THF solution of the product with pentane and crystallizing overnight at -35 °C.

^{1}H-NMR (600 MHz, THF-d_8) δ [ppm] = 8.30 (t, 7.8 Hz, 1H, Cpy-4); 8.24 (d, 7.7 Hz, 1H, Cpy-3); 8.16 (d, 7.7 Hz, 1H, Cpy-5); 7.66 (m, 4H, Cph-3,5); 7.51 (m, 2H, Cph-4); 7.30 (m, 4H, Cph-2,6); 7.20-7.10 (m, 4H, Car-3,4); 6.97 (m, 2H, Car-5); 3.04 (sept, 6.8 Hz, 2H, Cdipp-1); 2.99 (sept, 6.8 Hz, 2H, Cdipp-1); 2.65 (s, 3H, Ir-SCH3); 1.02 (m, 12H, Cdipp-2); 0.93 (d, 6.8 Hz, 6H, Cdipp-2); 0.91 (d, 6.6 Hz, 6H, Cdipp-2).

^{13}C{^{1}H}-NMR (151 MHz, Tol-d_8): δ [ppm] = 170.5 (s, 2C, Cimin); 155.5 (s, 2C, Cpy-2,6); 139.9 (s, 6C, Car-1,2,6); 136.4 (s, 2C, Cph-1); 128.9 (s, 4C, Cph-2,6); 128.6 (s, 2C, Cph-4); 126.5 (s, 2C, Car-4); 125.8 (s, 4C, Cph-3,5); 125.0 (s, 1C, Cpy-5); 124.7 (s, 1C, Cpy-3); 122.5 (s, 4C, Car-3,5); 120.6 (s, 1C, Cpy-4); 28.7 (s, 2C, Cdipp-1); 28.6 (s, 2C, Cdipp-1); 26.4 (s, 2C, Cdipp-2); 24.5 (s, 2C, Cdipp-2); 24.1 (s, 2C, Cdipp-2); 23.6 (s, 2C, Cdipp-2); 19.7 (s, 1C, Ir-SCH3).

^{1}H-NMR (300 MHz, THF-d_8): δ [ppm] = 8.30-8.20 (m, 2H, Cpy-4,5); 8.15 (d, 7.8 Hz, 1H, Cpy-3); 7.66 (m, 4H, Cph-3,5); 7.51 (m, 2H, Cph-4); 7.30 (m, 4H, Cph-2,6); 7.20-6.96 (m, 6H, Car-3,4,5); 3.01 (sept, 6.8 Hz, 4H, Cdipp-1); 2.65 (s, 3H, Ir-SCH3); 1.02 (m, 12H, Cdipp-2); 0.92 (d, 6.8 Hz, 12H, Cdipp-2).

Synthesis of **15**

Under vigorous stirring, an excess of 150 mg (1.13 mmol) sodium thiophenolate is added to a solution of 150 mg (180 µmol) of **5** in 10 mL THF. The reaction mixture was stirred overnight at room temperature, and a color change from dark green over black to violet was observed. The volatile compounds were removed in an oil pump vacuum. The crude product was extracted with toluene. The solvent was evaporated and extracted once more with toluene. This extraction procedure was repeated once. The product was obtained as a dark solid (147 mg, 162 µmol, 90 %) upon drying in an oil pump vacuum. Crystallization can be achieved by layering a THF solution of the product with pentane and crystallizing overnight at -35 °C.

^{1}H-NMR (300 MHz, THF-d_8): δ [ppm] = 8.41 (t, 8.0 Hz, 1H, Cpy-4); 8.10 (d, 8.0 Hz, 2H, Cpy-3,5); 7.60 (m, 4H, Cph-2,6); 7.50 (m, 2H, Cph-4); 7.28 (m, 4H, Cph-3,5); 7.01 (m, 2H, Car-4); 6.90 (m, 4H, Car-3,5); 6.66 (m, 2H, IrSC-2,6); 6.61 (m, 1H, IrSC-4); 6.56 (m, 2H, IrSC-3,5); 3.13 (sept, 6.8 Hz, 4H, Cdipp-1); 1.03 (d, 6.8 Hz, 12H, Cdipp-2); 0.90 (d, 6.8 Hz, 12H, Cdipp-2).

^{13}C{^{1}H}-NMR (75 MHz, THF-d_8): δ [ppm] = 169.1 (s, 2C, Cimin); 158.0 (s, 2C, Cpy-2,6); 151.9 (s, 1C, Car-1, IrSC-1); 141.3 (s, 4C, Car-2,6); 139.7 (s, 2C, Cph-1); 135.4 (s, 2C, IrSC-3,5); 128.9 (s, 4C, Cph-3,5); 128.7 (s, 2C, IrSC-2,6); 128.6 (s, 2C, Cph-4); 127.9 (s, 2C, Car-4); 126.0 (s, 4C, Cph-2,6); 125.4 (s, 2C, Cpy-3,5); 124.1 (s, 1C, IrSC-4); 123.7 (s, 4C, Car-3,5); 121.7 (s, 1C, Cpy-4); 28.9 (s, 4C, Cdipp-1); 25.6 (s, 4C, Cdipp-2); 24.0 (s, 4C, Cdipp-2).

Synthesis of **16**

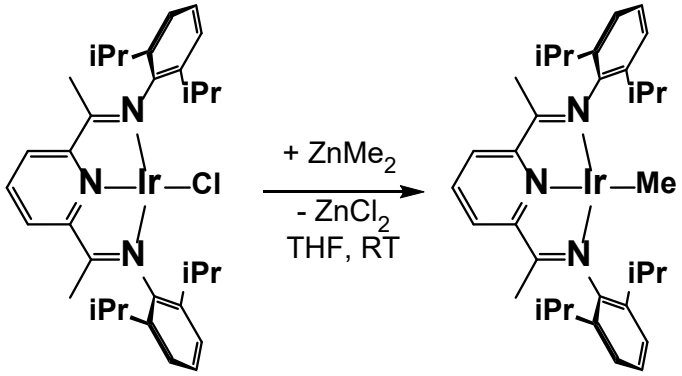
To 250 mg (302 µmol) of **9** dissolved in 10 mL THF, 900 µL (720 µmol) of an 0.8 M hydrogen sulfide solution in THF was added under vigorous stirring, and an immediate color change from dark green to dark violet, almost black, was observed. The reaction mixture was stirred at RT for one hour, and then the solvent was removed in an oil pump vacuum. The obtained dark solid (246 mg, 296 µmol, 98 %) was thoroughly dried in an oil pump vacuum for several hours. Crystallization can be achieved by layering a THF solution of the product with pentane and crystallizing overnight at -35 °C.

^{1}H-NMR (600 MHz, Tol-d_8): δ [ppm] = 7.95 (m, 3H, Cpy-3,4,5); 7.55 (dd, 8.5 Hz, 1.4 Hz, 4H, Cph-2,6); 7.15 (tt, 7.4 Hz, 1.3 Hz, 2H, Cph-4); 6.95 (t, 7.5 Hz, 4H, Cph-3,5); 7.03 (m, 6H, Car-3,4,5); 5.57 (s, 1H, Ir-SH); 3.21 (sept, 6.8 Hz, 4H, Cdipp-1); 1.2 (d, 6.7 Hz, 12H, Cdipp-2); 1.0 (d, 6.7 Hz, 12H, Cdipp-2).

^{13}C{^{1}H}-NMR (151 MHz, Tol-d_8): δ [ppm] = 168.4 (s, 2C, Cimin); 158.3 (s, 2C, Cpy-2,6); 141.0 (s, 6C, Car-1,2,6); 139.2 (s, 2C, Cph-1); 127.9 (s, 2C, Cph-4); 127.4 (s, 2C, Car-4); 128.3 (s, 4C, Cph-3,5); 124.5 (s, 4C, Cph-2,6); 123.9 (s, 2C, Cpy-3,5); 123.0 (s, 4C, Car-3,5); 120.6 (s, 1C, Cpy-4); 28.0 (s, 4C, Cdipp-1); 25.7 (s, 4C, Cdipp-2); 23.6 (s, 4C, Cdipp-2).

^{1}H-NMR (300 MHz, THF-d_8): δ [ppm] = 8.51 (t, 7.9 Hz, 1H, Cpy-4); 8.18 (d, 7.9 Hz, 2H, Cpy-3,5); 7.72 (dd, 8.2 Hz, 1.5 Hz, 4H, Cph-3,5); 7.55 (tt, 7.6 Hz, 1.3 Hz, 2H, Cph-4); 7.32 (t, 7.6 Hz, 4H, Cph-2,6); 7.06 (m, 6 H, Car-3,4,5); 4.87 (s, 1H, Ir-SH); 3.06 (sept, 6.8 Hz, 4H, Cdipp-1); 0.97 (d, 3.6 Hz, 12H, Cdipp-2); 0.94 (d, 3.6 Hz, 12H, Cdipp-2).

Synthesis of **18**



$^{Me}L_3IrCl$ **18**

600 µL (720 µmol) of a 1.2 molar solution of dimethylzinc in toluene was added to a solution of 0.57 g (0.80 mmol) of $^{Me}L_3IrCl$ in 6 mL THF under stirring. After 7 hours, a conversion of 78 % was observed by ^{1}H NMR spectroscopy. The reaction mixture was stirred at room temperature for 24 hours and filtrated. The reaction solution was then concentrated to one half in an oil pump vacuum, and the product was crystallized at -30 °C. The crystalline solid was washed three times with 2 mL of Et_2O and dried in an oil pump vacuum. Single crystals suitable for X-ray structural analysis could be obtained from a saturated solution of **18** in n-hexane at -30 °C.

^{1}H-NMR (300 MHz, THF-d_8): δ [ppm] = 8.97 (t, 7.9 Hz, 1H, Cpy-4); 8.40 (d, 7.9 Hz, 2H, Cpy-3,5); 7.33-7.16 (m, 6H, Car-3,4,5); 7.04 (s, 3H, Ir−CH3); 2.94 (sept, 6.8 Hz, 4H, Cdipp-1); 1.13 (d, 6.8 Hz, 12H, Cdipp-2); 0.69 (d, 6.8 Hz, 12H, Cdipp-2); 0.33 (s, 6H, Cket).

^{13}C{^{1}H}-NMR (75 MHz, THF-d_8): δ [ppm] = 171.5 (s, 2C, Cimin); 164.5 (s, 2C, Cpy-2,6); 153.5 (s, 2C, Car-1); 141.5 (s, 4C, Car-2,6); 127.2 (s, 2C, Car-4); 123.9 (s, 4C, Car-3,5); 124.5 (s, 2C, Cpy-4); 121.1 (s, 4C, Cpy-3,5); 28.5 (s, 4C; Cdipp-1); 24.4(s, 4C, Cdipp-2); 24.3 (s, 4C, Cdipp-2); 22.5 (s, 2C, Cket); 3.9 (s, 1C, Ir−CH3).

NMR Spectroscopy

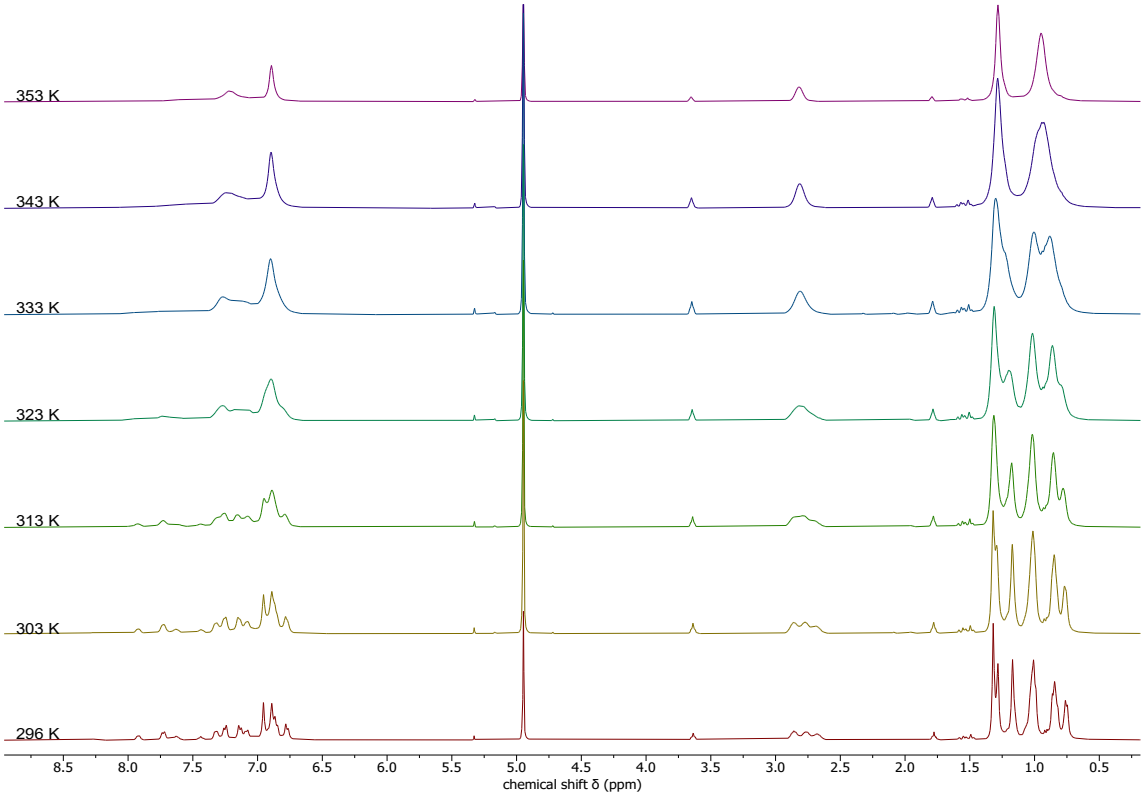


*Figure S2: ^{1}H NMR spectra of **2** in dibromomethane-d_2 between 296 K and 353 K.*

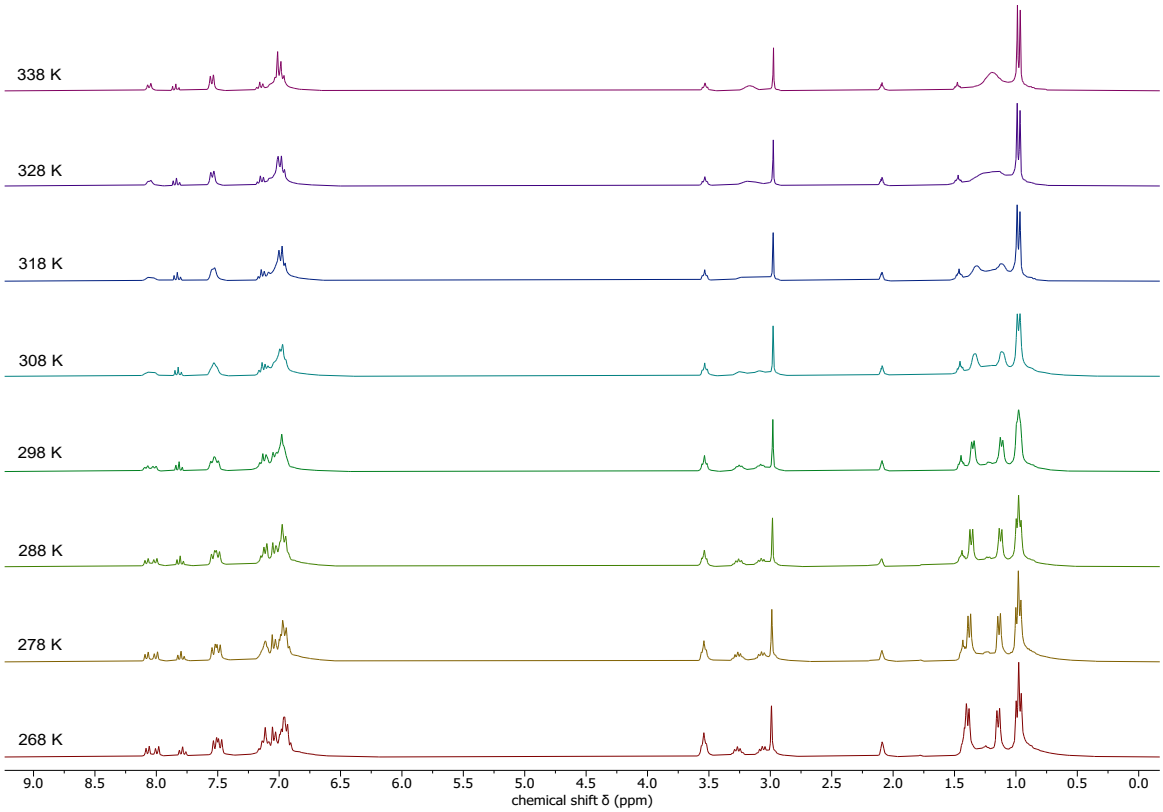


*Figure S3: ^{1}H NMR spectra of **14** in toluene-d_8 between 268 K and 338 K.*

IR Spectroscopy

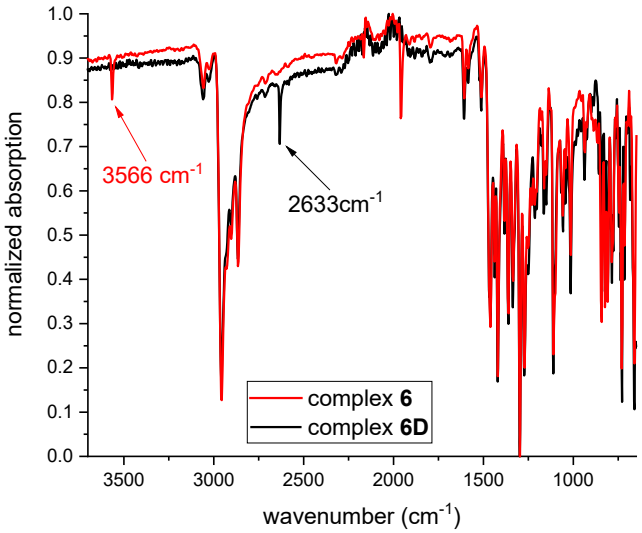


*Figure S4: ATR-IR spectra of **6** (Rh-OH) and the deutero isotopologue **6D** (RH-OD).*

X-ray Crystallographic Studies

Single X-ray crystal measurements were performed using a BRUKER AXS SMART APEX single crystal diffractometer with graphite monochromatic MoKα radiation (λ = 0.71073 Å) or an Oxford Diffractometer Supernova from AGILENT TECHNOLOGIES equipped with CuKα and a MoKα radiation sources at 100 K. The single crystals were mounted in high viscosity polybutene oil on a glass fibre of the goniometer head. Data were analysed using the software packages saint and sadabs (BRUKER) and ChrysAlis Pro (OXFORD DIFFRACTION). The structures were solved and refined with the Shelx[10] and Olex2[11] program packages. All atoms were refined anisotropically except for the hydrogen atoms.

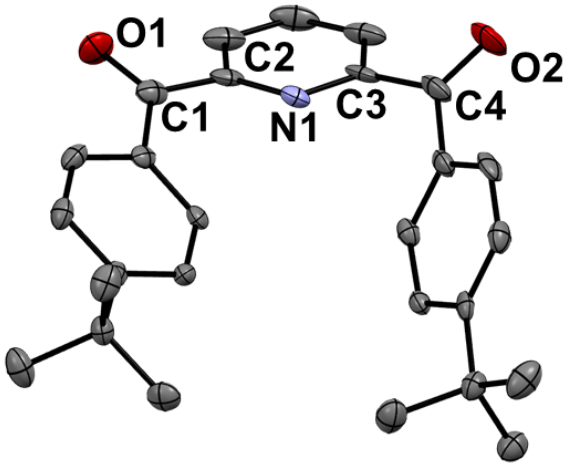


*Figure S5: Ortep diagram of the molecular structure of **1**. Hydrogen atoms are omitted for clarity, ellipsoids are shown at the 50% probability level.*

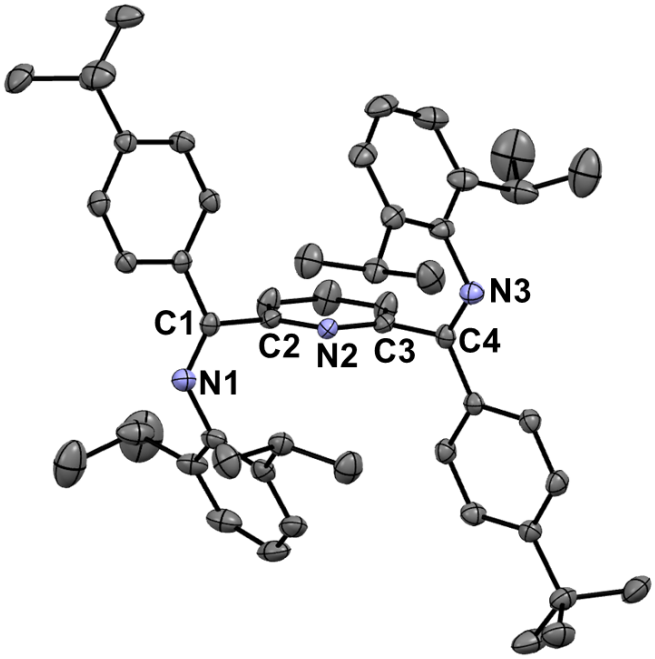


*Figure S6: Ortep diagram of the molecular structure of **2**. Hydrogen atoms and solvent molecules are omitted for clarity, ellipsoids are shown at the 50% probability level.*

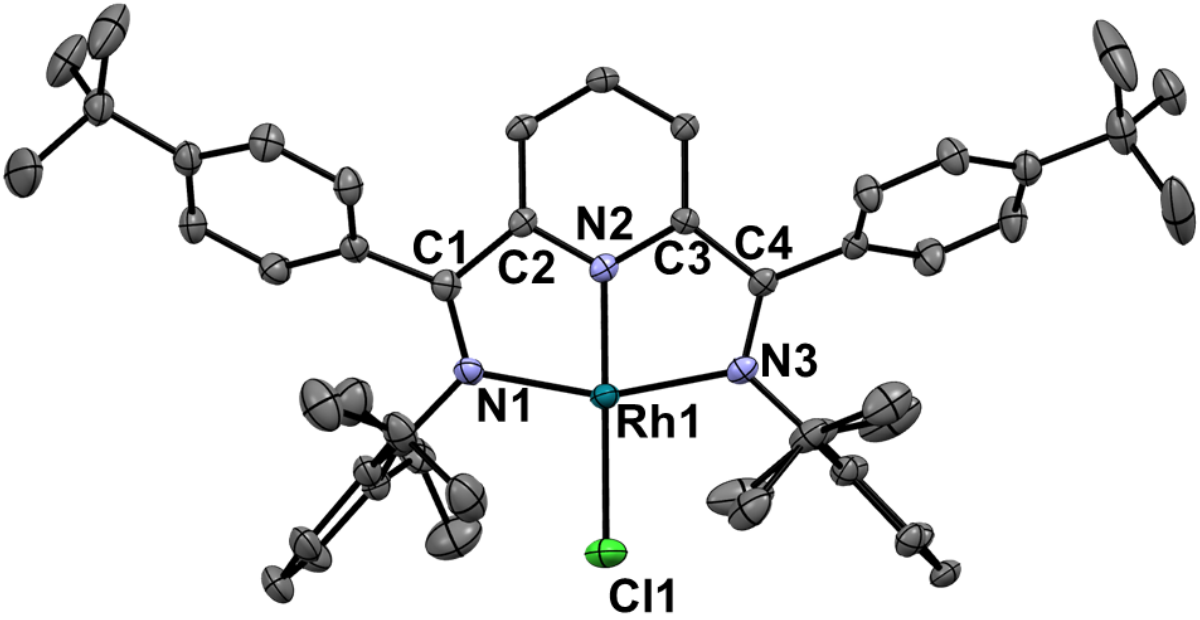


*Figure S7: Ortep diagram of the molecular structure of **4**. Hydrogen atoms and solvent molecules are omitted for clarity, ellipsoids are shown at the 50% probability level.*

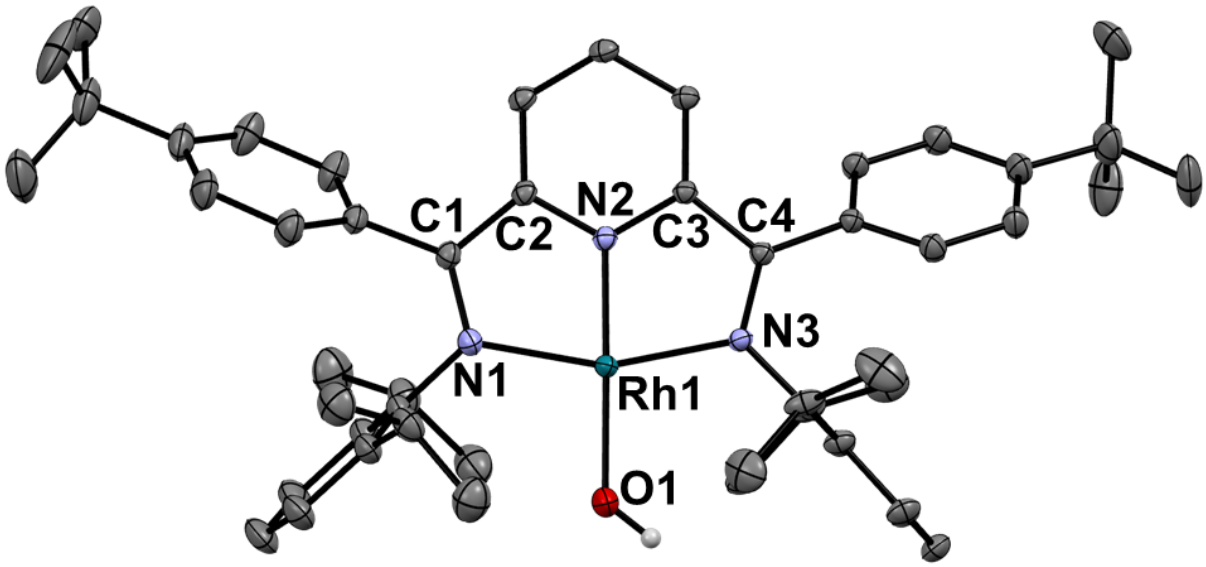


*Figure S8: Ortep diagram of the molecular structure of **6**. Hydrogen atoms with exception of the OH group and solvent molecules are omitted for clarity, ellipsoids are shown at the 50% probability level.*

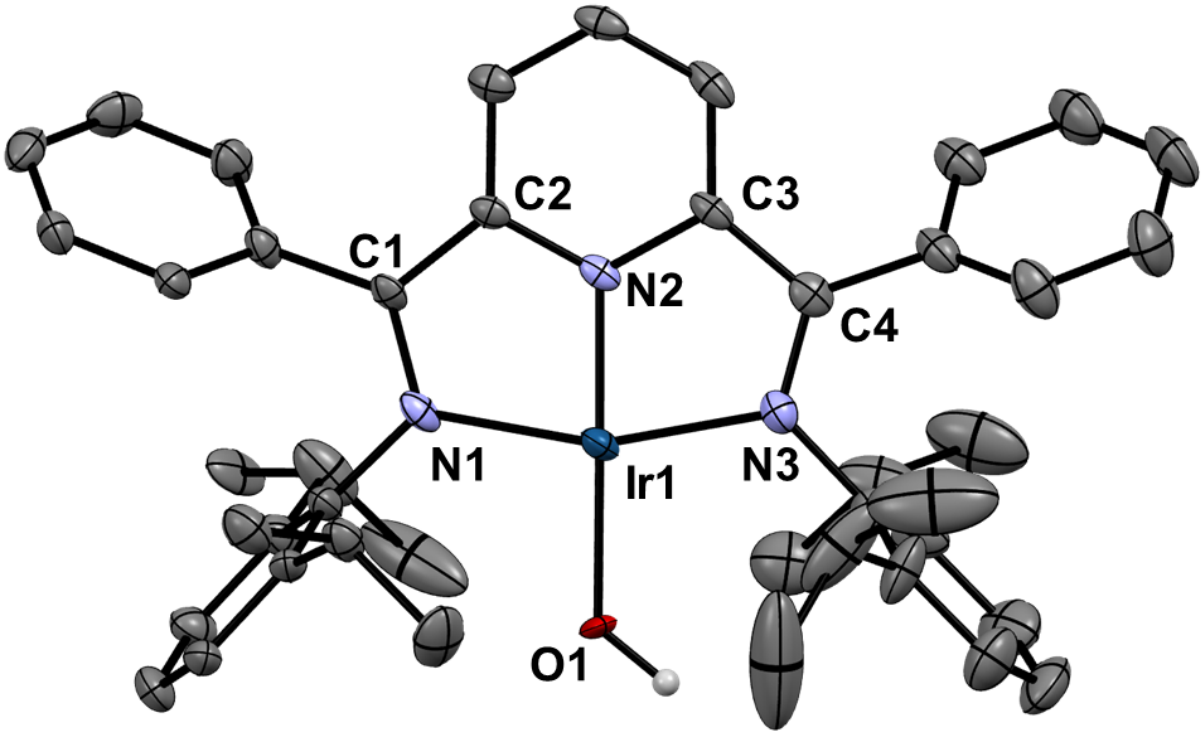


*Figure S9: Ortep diagram of the molecular structure of **7**. Hydrogen atoms with exception of the OH group and solvent molecules are omitted for clarity, ellipsoids are shown at the 50% probability level.*

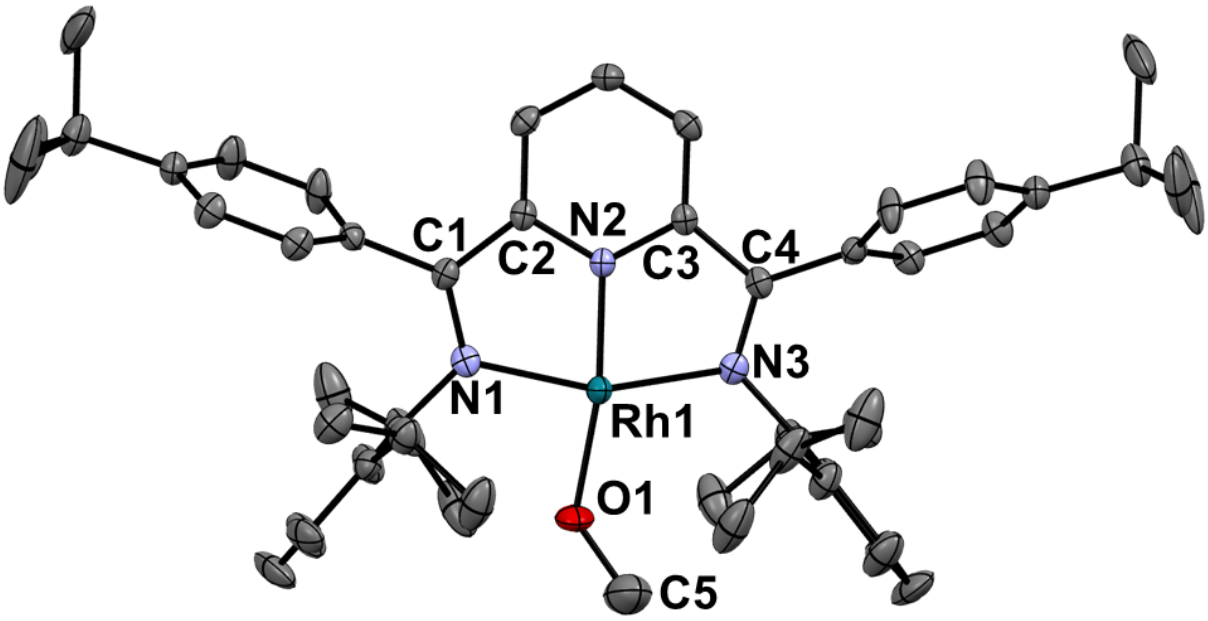


*Figure S10: Ortep diagram of the molecular structure of **8**. Hydrogen atoms and solvent molecules are omitted for clarity, ellipsoids are shown at the 50% probability level.*

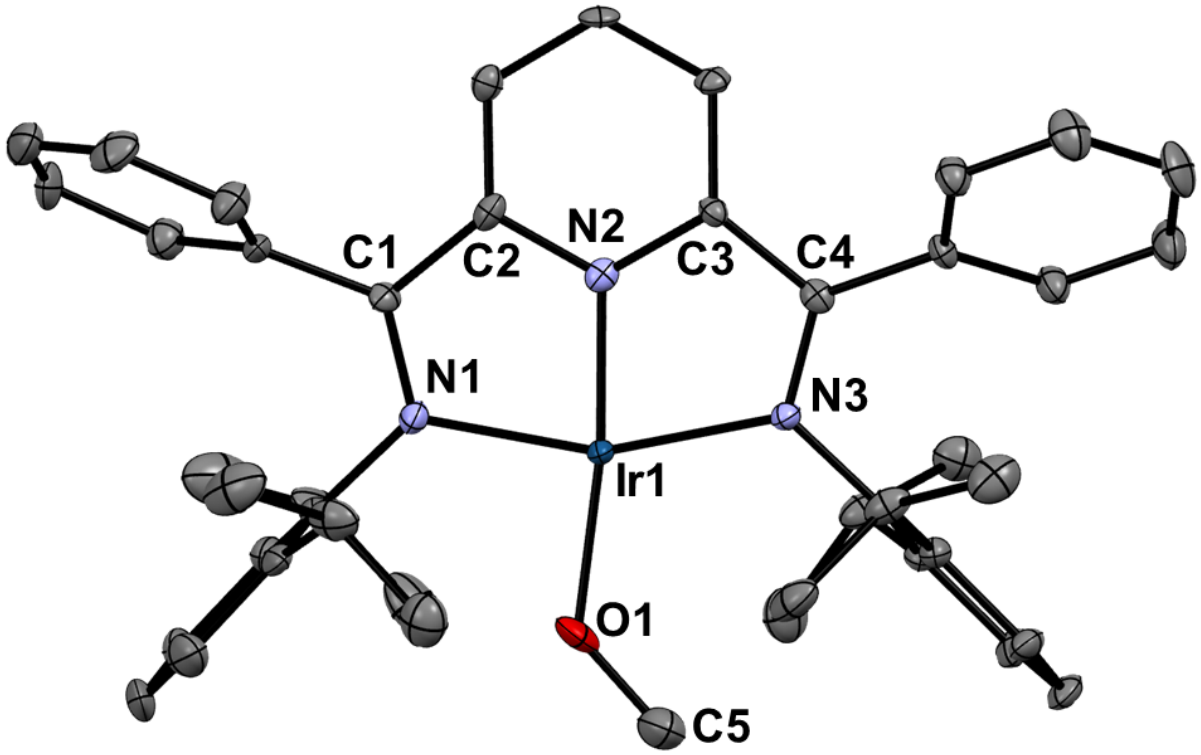


*Figure S11: Ortep diagram of the molecular structure of **9**. Hydrogen atoms and solvent molecules are omitted for clarity, ellipsoids are shown at the 50% probability level.*

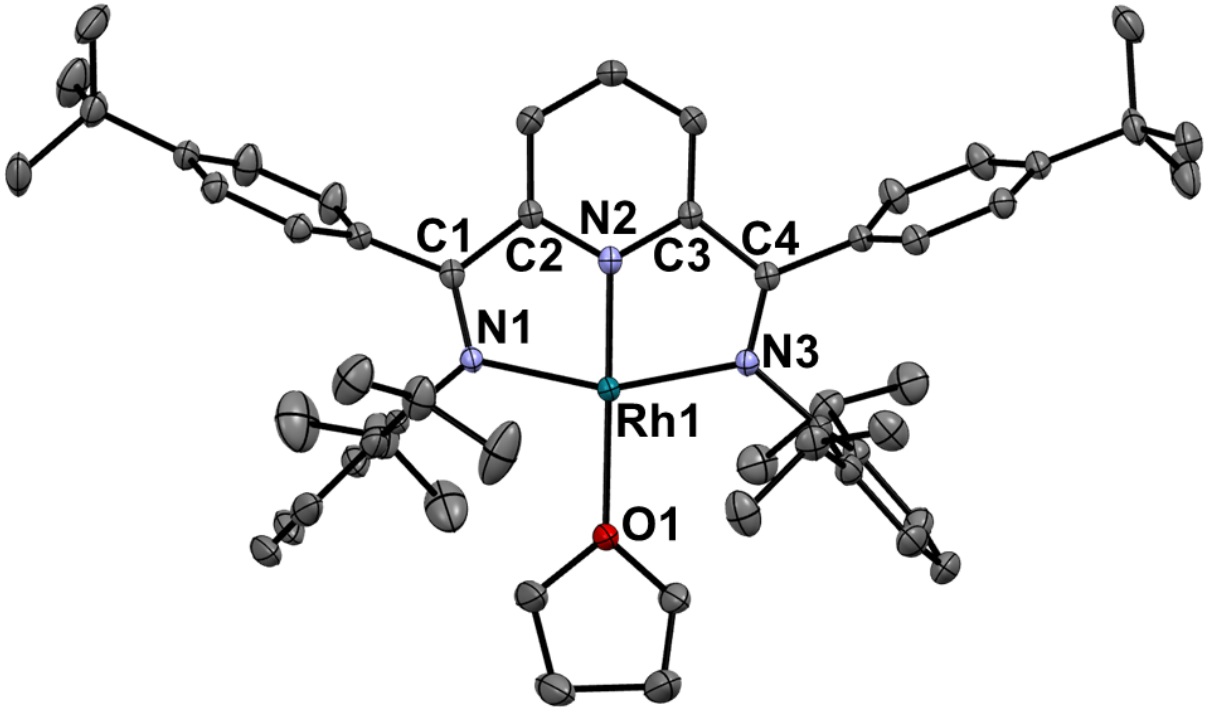


*Figure S12: Ortep diagram of the molecular structure of **10**. Hydrogen atoms, solvent molecules and the counter ion are omitted for clarity, ellipsoids are shown at the 50% probability level.*

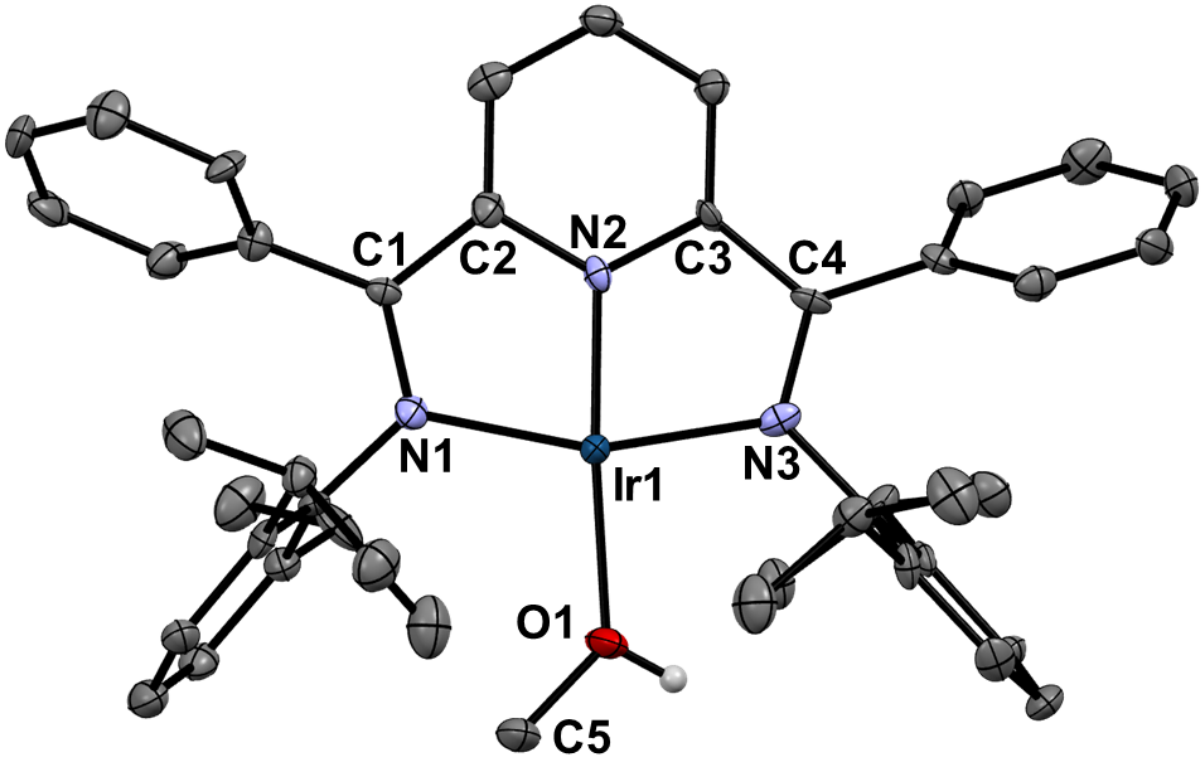


*Figure S13: Ortep diagram of the molecular structure of **11**. Hydrogen atoms except of the OH group, solvent molecules and the counter ion are omitted for clarity, ellipsoids are shown at the 50% probability level.*

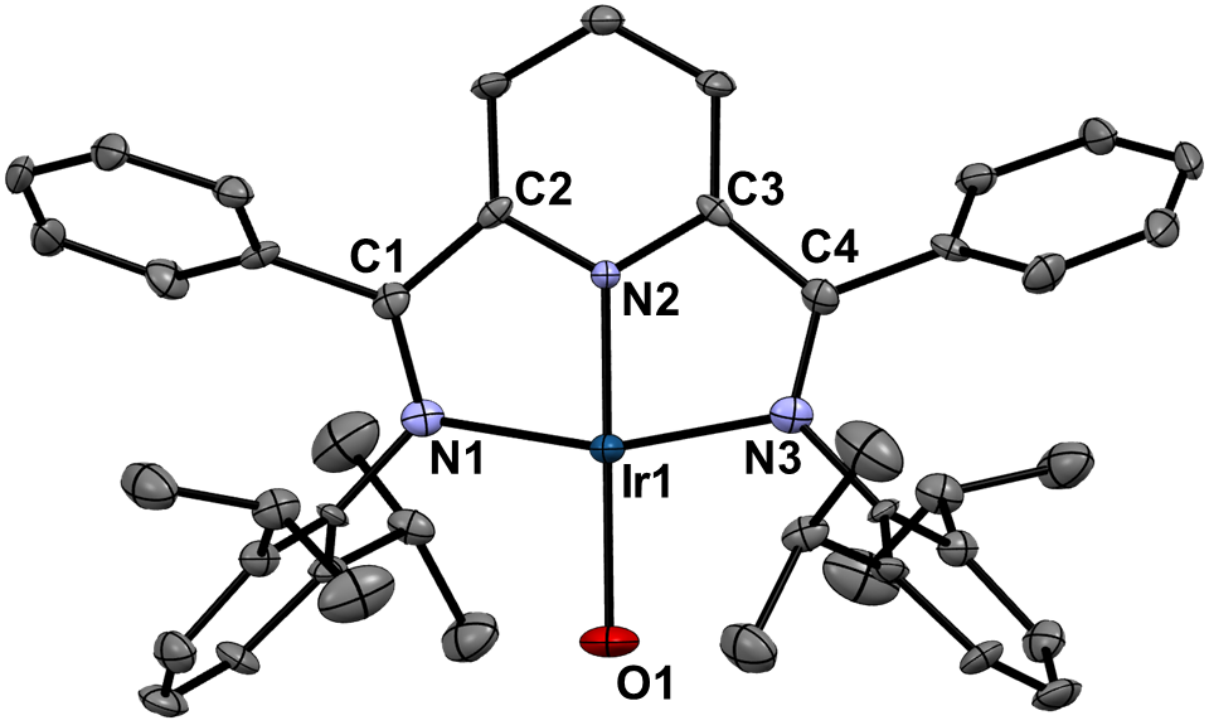


*Figure S14: Ortep diagram of the molecular structure of **12**. Hydrogen atoms, solvent molecules and the counter ion are omitted for clarity, ellipsoids are shown at the 50% probability level.*

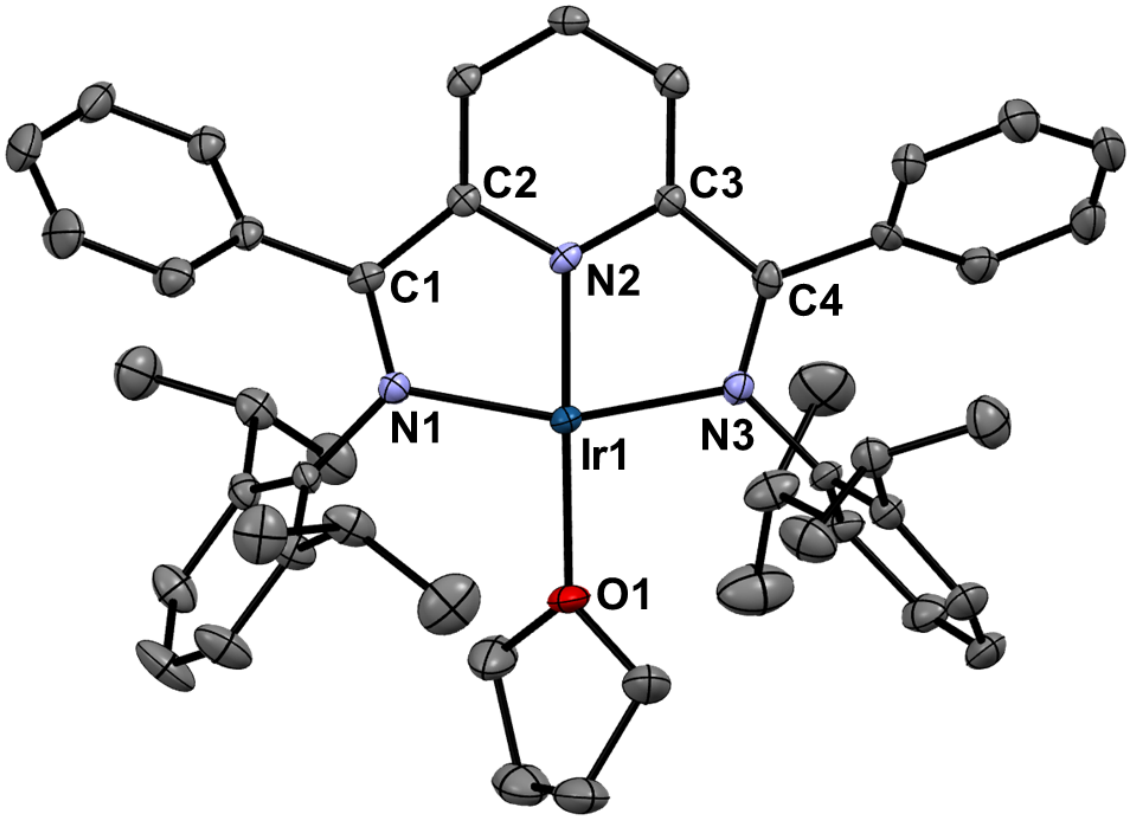


*Figure S15: Ortep diagram of the molecular structure of **13**. Hydrogen atoms, solvent molecules and the counter ion are omitted for clarity, ellipsoids are shown at the 50% probability level.*

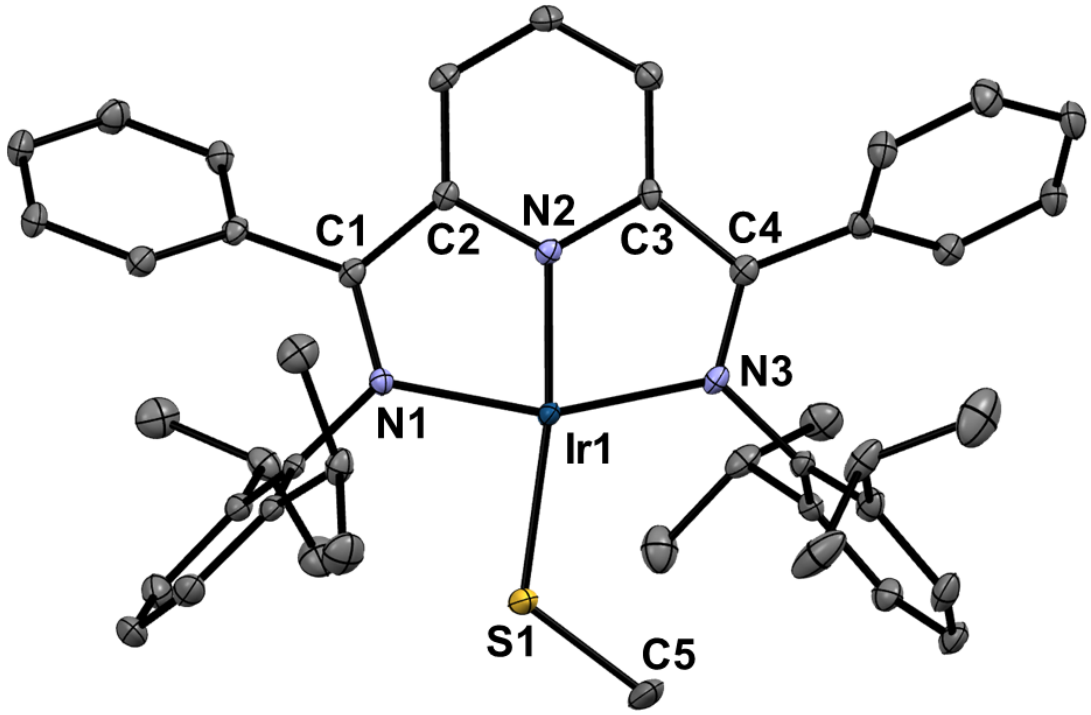


*Figure S16: Ortep diagram of the molecular structure of **14**. Hydrogen atoms and solvent molecules are omitted for clarity, ellipsoids are shown at the 50% probability level.*

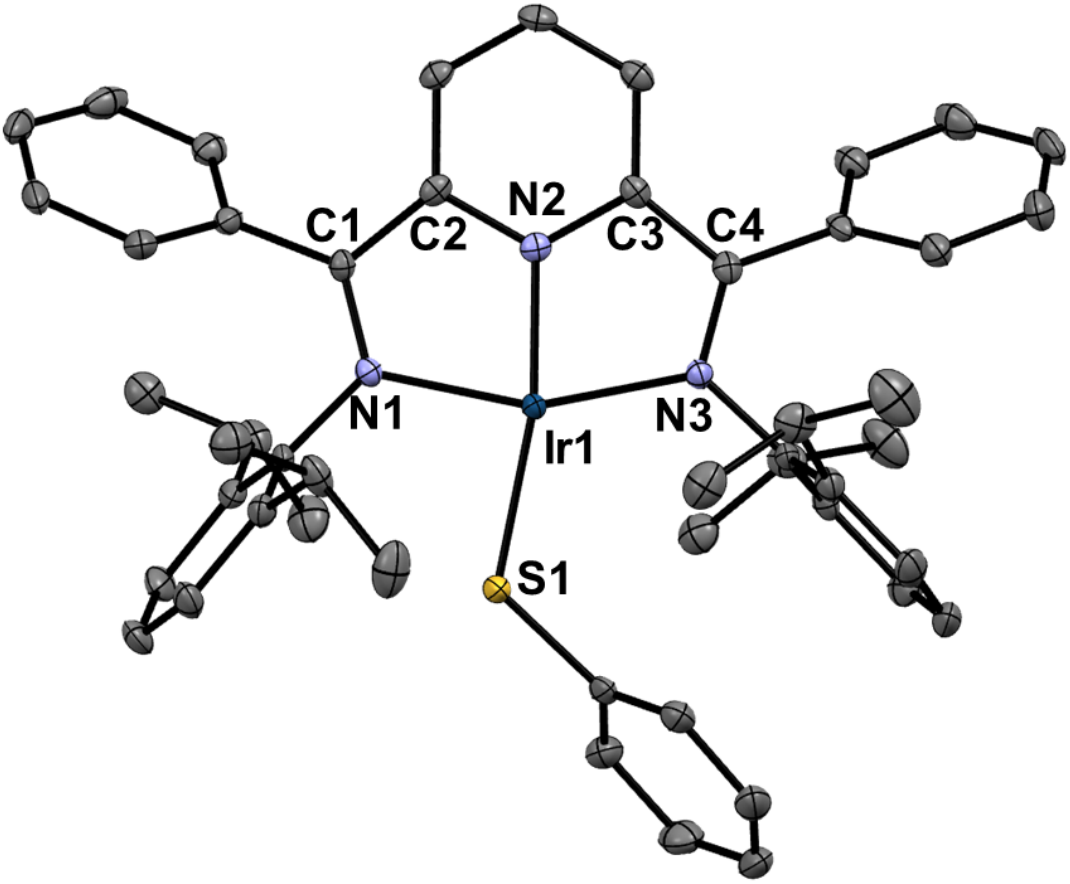


*Figure S17: Ortep diagram of the molecular structure of **15**. Hydrogen atoms and solvent molecules are omitted for clarity, ellipsoids are shown at the 50% probability level.*

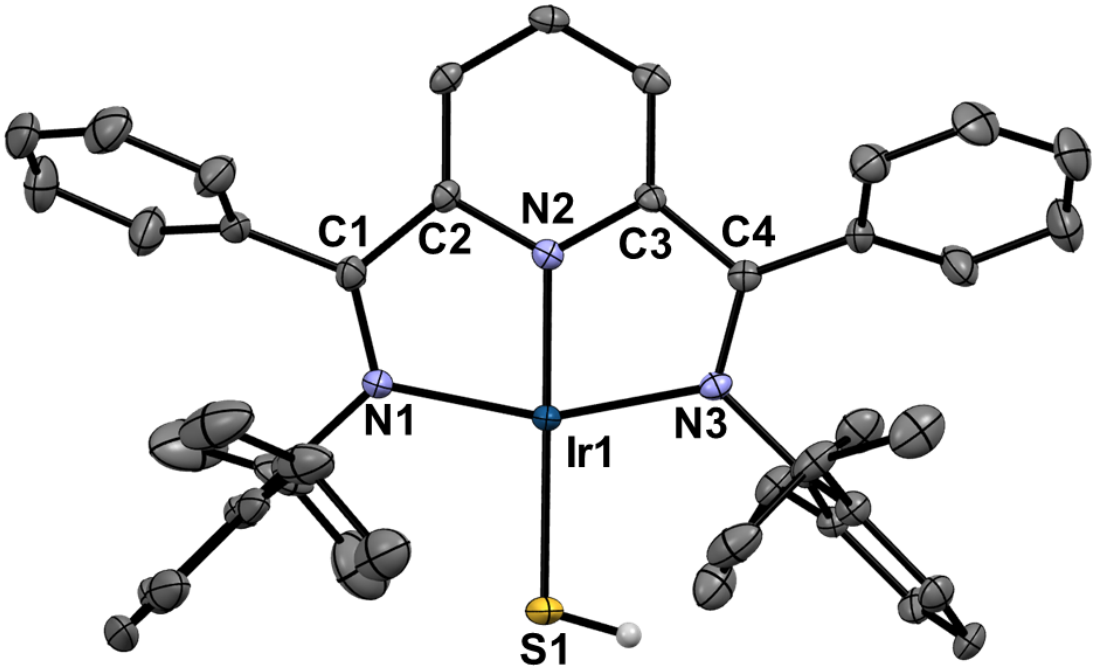


*Figure S18: Ortep diagram of the molecular structure of **16**. Hydrogen atoms with exception of the SH group and solvent molecules are omitted for clarity, ellipsoids are shown at the 50% probability level.*

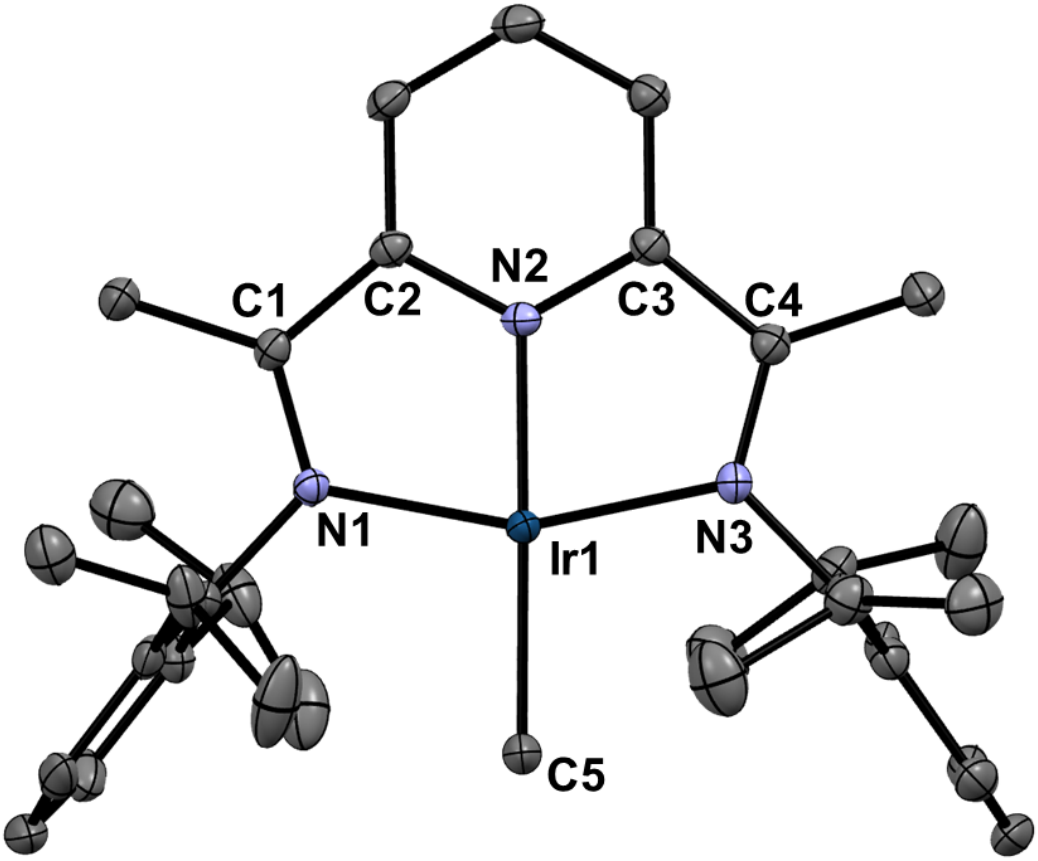


*Figure S19: Ortep diagram of the molecular structure of **18**. Hydrogen atoms and solvent molecules are omitted for clarity, ellipsoids are shown at the 50% probability level.*

Table S1: Summary of the crystal data and structure refinement.

	1	**2**	**4**
Empirical formula	$C_{27}H_{29}NO_2$	$C_{51}H_{63}N_3$	$C_{51}H_{63}ClN_3Rh$
Formula weight	399.51	718.09	856.40
Temperature/K	100	100	100
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	P21/n	F2dd	P21/c
a/Å	9.857(3)	9.7521(8)	17.0626(11)
b/Å	12.624(4)	24.506(2)	13.2415(8)
c/Å	17.963(6)	37.086(3)	20.7408(13)
α/°	90	90	90
β/°	95.104(3)	90	100.030(2)
γ/°	90	90	90
Volume/Å^3	2226.5(12)	8863.1(13)	4614.4(5)
Z	4	1	4
ρ_{calc} mg/cm^3	1.192	1.076	1.233
μ/mm^{-1}	0.074	0.062	0.464
F(000)	856.0	3120.0	1808.0
Crystal size/mm^3	0.3 × 0.1 × 0.1	0.01 × 0.01 × 0.01	0.01 × 0.01 × 0.01
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.948 to 46.168	3.984 to 57.93	3.916 to 58
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -19 ≤ l ≤ 19	-12 ≤ h ≤ 12, -33 ≤ k ≤ 32, -49 ≤ l ≤ 49	-23 ≤ h ≤ 23, -18 ≤ k ≤ 18, -28 ≤ l ≤ 28
Reflections collected	35866	33993	113352
Independent reflections	3129 [R_{int} = 0.1154, R_{sigma} = 0.0541]	5535 [R_{int} = 0.0670, R_{sigma} = 0.0560]	12246 [R_{int} = 0.1917, R_{sigma} = 0.1049]
Data/restraints/parameters	3129/0/277	5535/1/253	12246/9/550
Goodness-of-fit on F^2	1.114	1.029	1.021
Final R indexes [I>=2σ(I)]	R_1 = 0.0560, wR_2 = 0.1034	R_1 = 0.0476, wR_2 = 0.0990	R_1 = 0.0512, wR_2 = 0.0874
Final R indexes [all data]	R_1 = 0.0886, wR_2 = 0.1156	R_1 = 0.0812, wR_2 = 0.1113	R_1 = 0.1129, wR_2 = 0.1097
Largest diff. peak/hole/e Å^{-3}	0.17/-0.20	0.18/-0.18	0.48/-0.83
Flack parameter		-2.4(10)	

Table S2: Summary of the crystal data and structure refinement for the reported complexes.

	6	**7**	**8**
Empirical formula	$C_{51}H_{64}N_3ORh$	$C_{43}H_{48}IrN_3O$	$C_{52}H_{66}N_3ORh$
Formula weight	837.96	815.04	851.98
Temperature/K	100	100	100
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1$	C2/c
a/Å	17.5768(4)	13.806(3)	13.2952(5)
b/Å	13.3760(3)	11.209(2)	18.3006(6)
c/Å	20.9060(4)	14.634(3)	18.2820(6)
α/°	90	90	90
β/°	110.2610(10)	111.464(2)	92.877(3)
γ/°	90	90	90
Volume/Å^3	4611.02(17)	2107.6(7)	4442.6(3)
Z	4	2	4
ρ_{calc} mg/cm^3	1.207	1.284	1.274
μ/mm^{-1}	0.408	3.199	0.425
F(000)	1776.0	824.0	1808.0
Crystal size/mm^3	0.01 × 0.01 × 0.01	0.159 × 0.103 × 0.022	0.01 × 0.01 × 0.01
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.686 to 68.488	2.99 to 52.992	7.352 to 53.99
Index ranges	-27 ≤ h ≤ 27, -20 ≤ k ≤ 20, -33 ≤ l ≤ 32	-17 ≤ h ≤ 17, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18	-16 ≤ h ≤ 16, -23 ≤ k ≤ 23, -23 ≤ l ≤ 23
Reflections collected	128557	27630	34438
Independent reflections	18440 [R_{int} = 0.0223, R_{sigma} = 0.0154]	8668 [R_{int} = 0.0383, R_{sigma} = 0.0511]	4843 [R_{int} = 0.1038, R_{sigma} = 0.0867]
Data/restraints/parameters	18440/0/586	8668/32/454	4843/0/284
Goodness-of-fit on F^2	1.047	1.036	1.034
Final R indexes [I>=2σ(I)]	R_1 = 0.0277, wR_2 = 0.0704	R_1 = 0.0317, wR_2 = 0.0683	R_1 = 0.0517, wR_2 = 0.1066
Final R indexes [all data]	R_1 = 0.0330, wR_2 = 0.0744	R_1 = 0.0369, wR_2 = 0.0699	R_1 = 0.0765, wR_2 = 0.1179
Largest diff. peak/hole/e Å^{-3}	1.20/-0.56	1.95/-1.95	0.80/-0.63
Flack parameter		0.016(5)	

Table S3: Summary of the crystal data and structure refinement for the reported complexes.

	9	**10**	**11**
Empirical formula	$C_{44}H_{50}IrN_3O$	$C_{57}H_{71}F_6N_4O_5RhS_2$	$C_{46}H_{51}F_6IrN_4O_5S_2$
Formula weight	829.12	1173.23	1110.22
Temperature/K	100	100	100
Crystal system	triclinic	orthorhombic	orthorhombic
Space group	P-1	Pbca	$Pna2_1$
a/Å	14.1834(12)	20.427(19)	23.847(3)
b/Å	16.3279(14)	25.08(2)	10.9865(13)
c/Å	20.8214(17)	25.37(3)	17.654(2)
α/°	111.1830(10)	90	90
β/°	91.6490(10)	90	90
γ/°	114.3510(10)	90	90
Volume/$Å^3$	4005.4(6)	12996(22)	4625.3(9)
Z	2	4	4
ρ_{calc} mg/cm^3	1.435	1.347	1.594
μ/mm^{-1}	3.372	0.398	3.051
F(000)	1760.0	5536.0	2232.0
Crystal size/mm^3	0.01 × 0.01 × 0.01	0.264 × 0.234 × 0.216	0.201 × 0.078 × 0.036
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.146 to 57.848	3.032 to 58.018	3.416 to 54.996
Index ranges	-18 ≤ h ≤ 17, -22 ≤ k ≤ 21, -27 ≤ l ≤ 27	-27 ≤ h ≤ 27, -33 ≤ k ≤ 32, -33 ≤ l ≤ 33	-30 ≤ h ≤ 30, -14 ≤ k ≤ 14, -22 ≤ l ≤ 22
Reflections collected	39576	151038	67592
Independent reflections	12845 [R_{int} = 0.0236, R_{sigma} = 0.0265]	16614 [R_{int} = 0.0240, R_{sigma} = 0.0141]	10603 [R_{int} = 0.1262, R_{sigma} = 0.0917]
Data/restraints/parameters	12845/0/946	16614/194/821	10603/10/589
Goodness-of-fit on F^2	1.025	1.055	1.022
Final R indexes [I>=2σ(I)]	R_1 = 0.0192, wR_2 = 0.0395	R_1 = 0.0398, wR_2 = 0.0981	R_1 = 0.0446, wR_2 = 0.0860
Final R indexes [all data]	R_1 = 0.0262, wR_2 = 0.0416	R_1 = 0.0501, wR_2 = 0.1083	R_1 = 0.0730, wR_2 = 0.0977
Largest diff. peak/hole/e $Å^{-3}$	0.54/-0.28	1.22/-0.65	2.02/-2.07
Flack parameter			-0.005(6)

Table S4: Summary of the crystal data and structure refinement for the reported complexes.

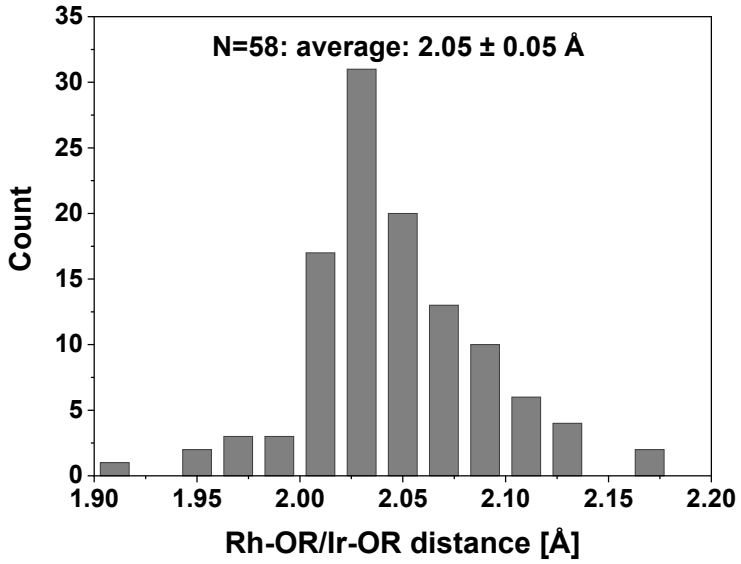
	12	**13**	**14**
Empirical formula	$C_{45}H_{47}F_6IrN_4O_5S_2$	$C_{49}H_{55}F_6IrN_4O_5S_2$	$C_{44}H_{50}IrN_3S$
Formula weight	1094.18	1186.34	845.18
Temperature/K	100	100	100
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	Aea2	$P2_1/c$	$P2_1/n$
a/Å	23.495(5)	14.1152(17)	11.2777(9)
b/Å	11.022(2)	23.586(3)	29.588(2)
c/Å	17.639(4)	15.1227(18)	26.378(2)
α/°	90	90	90
β/°	90	101.4344(15)	94.8920(10)
γ/°	90	90	90
Volume/Å^3	4567.7(17)	4934.7(10)	8769.9(11)
Z	4	4	4
ρ_{calc} mg/cm^3	1.591	1.597	1.428
μ/mm^{-1}	3.088	2.866	3.131
F(000)	2192.0	2400.0	3844.0
Crystal size/mm^3	0.125 × 0.052 × 0.038	0.03 × 0.03 × 0.001	0.137 × 0.075 × 0.049
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.618 to 54.994	2.944 to 57.728	2.072 to 54.996
Index ranges	-30 ≤ h ≤ 30, -14 ≤ k ≤ 13, -22 ≤ l ≤ 22	-18 ≤ h ≤ 18, -30 ≤ k ≤ 30, -20 ≤ l ≤ 20	-14 ≤ h ≤ 14, -38 ≤ k ≤ 38, -34 ≤ l ≤ 34
Reflections collected	28962	73632	133021
Independent reflections	5196 [R_{int} = 0.0721, R_{sigma} = 0.0568]	12199 [R_{int} = 0.0590, R_{sigma} = 0.0437]	20090 [R_{int} = 0.0405, R_{sigma} = 0.0265]
Data/restraints/parameters	5196/1/289	12199/9/767	20090/0/1151
Goodness-of-fit on F^2	1.115	1.041	1.037
Final R indexes [I>=2σ(I)]	R_1 = 0.0436, wR_2 = 0.0715	R_1 = 0.0335, wR_2 = 0.0710	R_1 = 0.0211, wR_2 = 0.0459
Final R indexes [all data]	R_1 = 0.0702, wR_2 = 0.0773	R_1 = 0.0493, wR_2 = 0.0769	R_1 = 0.0280, wR_2 = 0.0491
Largest diff. peak/hole/e Å^{-3}	1.52/-2.37	1.40/-1.09	1.19/-0.51
Flack parameter	0.482(13)	-0.005(6)	-0.005(6)

Table S5: Summary of the crystal data and structure refinement for the reported complexes.

	15	**16**	**18**
Empirical formula	$C_{49}H_{52}IrN_3S$	$C_{43}H_{48}IrN_3S$	$C_{34}H_{46}IrN_3$
Formula weight	907.25	831.16	688.94
Temperature/K	100	100	100
Crystal system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	P-1	$P2_12_12_1$
a/Å	15.0917(15)	14.1777(11)	8.40294(7)
b/Å	10.7852(11)	16.3944(13)	18.04559(14)
c/Å	25.300(3)	20.7684(16)	20.27655(16)
α/°	90	110.9310(10)	90
β/°	100.5470(10)	91.7428(10)	90
γ/°	90	114.2710(9)	90
Volume/Å^3	4048.4(8)	4020.2(5)	3074.66(4)
Z	4	2	4
ρ_{calc} mg/cm^3	1.488	1.433	1.488
μ/mm^{-1}	3.388	3.409	4.368
F(000)	1840.0	1760.0	1392.0
Crystal size/mm^3	0.147 × 0.133 × 0.107	0.087 × 0.057 × 0.045	0.3 × 0.07 × 0.07
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.744 to 54.998	2.146 to 54	5.712 to 65.238
Index ranges	-19 ≤ h ≤ 19, -14 ≤ k ≤ 14, -32 ≤ l ≤ 32	-18 ≤ h ≤ 18, -20 ≤ k ≤ 20, -26 ≤ l ≤ 26	-12 ≤ h ≤ 12, -27 ≤ k ≤ 27, -30 ≤ l ≤ 30
Reflections collected	59248	59972	60851
Independent reflections	9292 [R_{int} = 0.0432, R_{sigma} = 0.0299]	17453 [R_{int} = 0.0387, R_{sigma} = 0.0402]	10693 [R_{int} = 0.0421, R_{sigma} = 0.0316]
Data/restraints/parameters	9292/0/546	17453/18/1031	10693/0/354
Goodness-of-fit on F^2	1.147	1.027	1.034
Final R indexes [I>=2σ(I)]	R_1 = 0.0285, wR_2 = 0.0523	R_1 = 0.0274, wR_2 = 0.0541	R_1 = 0.0221, wR_2 = 0.0435
Final R indexes [all data]	R_1 = 0.0382, wR_2 = 0.0548	R_1 = 0.0400, wR_2 = 0.0585	R_1 = 0.0259, wR_2 = 0.0447
Largest diff. peak/hole/e Å^{-3}	1.59/-1.55	0.95/-0.82	1.21/-0.43
Flack parameter			0.153(3)

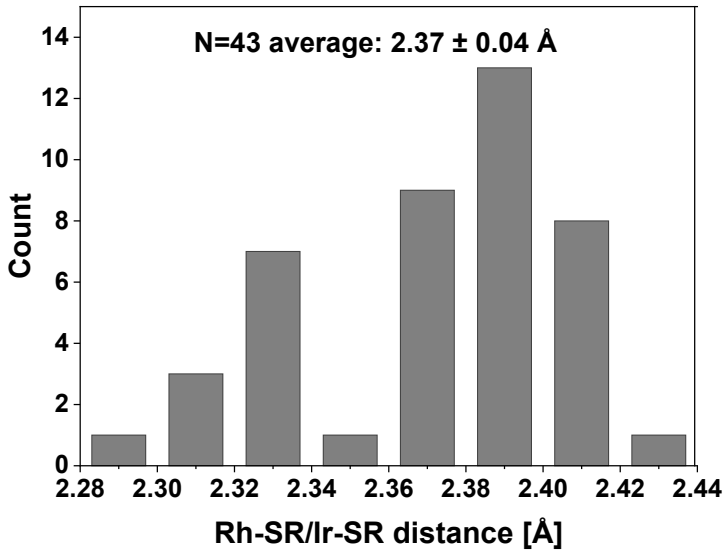
CSD Statistical Analysis of Rh,Ir-O,S Bond Distances

CSD Statistical Analysis of Rh,Ir-O,S Bond Distances in CCSD Database (CSD 5.44 April 2023)



BRNPIR;CAJGUQ;DAKFUR;DOBZEZ;DOBZEZ;BRNPIR;CEZJUP;CEZJUP;FADWUF;IBIWEZ;FADXIU;CTROPR01;FADXAM;HAYQEF;DORWEM;HESDAL;IBIWID;DAVCAE;HAZCIV;CTROPR01;FADXEQ;ERAYAA;HILGAM;FOHDUC;HIMFOY;DENQAO;DENQAO;DIBJUT;GOLPEC;FAFGIC;GETWUY;GAGHOL;DUZJUD;DENQAO;FOHDUC;DACCUG;DENQAO;EXOXIY;HOWRAM;DACCOA;EXOXIY;DAKHED;IYIXUK;ETIQAA;ETIPAZ;GETWUY;DACDER;IBIHUZ;FUJHEX;IBIJAH;IBEWOE;IBEXAR;EXIXIS;FUJHIB;UDIVAI;DUKMAZ;JIMGER

Figure S20, Rh,Ir-O Bond Distances and employed structures by CCSD code.



DOQKUP;JANWOK;JANWOK;SOJBUO;CETMRH;CEHTIW;NUXSAC;UGANEW;GIPYIN;DUKMAZ;YIVQOJ;DOQKUP;ICASEK;JASPEZ;CEHTIW;DAQKAH;WOHKIN;PUFLIL;GOHSEB;ICIVUN;GOHSEB;ICIVOH;ICIVOH;WEQFUT;ICIVUN;XIKDUR;PUFLIL01;GOHSIF;QEFFIQ;WAXTOE;WOHKOT;ICIWAU;ICIWAU;GOHSIF;EGIBIG;WOHKOT;NETVUE;ICIWEY;DEQLOB;WAXTUK;WETJEL;WETJIP;PERCIY

Figure S21: Rh,Ir-S bond distances and employed structures by CCSD code.

Computational Details

The calculations were carried out on our local 32 core and 96 core machines equipped with 512 GB respectively 3 TB RAM and the two 40 core nodes (1 TB RAM) of the "Hummel" computing cluster of the University of Hamburg computing center (RRZ) employing fast SSD/NVME scratch disk space.

DFT calculations were carried out with version 7.7.1 of the parallelized Turbomole program package.[12] def2-TZVP basis sets were employed for all atoms, for the rhodium and iridium atoms the def2-ECP pseudopotentials were used (Ir: ECP-60-MWB, Rh: ECP-28-MWB). The RI-DFT method was used with the corresponding RIJ-auxiliary basis for the PBE functional. For the PW6B95 hybrid functional seminumeric exchange ($senex keyword) was employed. Dispersion was included in the DFT calculations with Grimme's D3 method in combination with Becke-Johnson damping (D3BJ). Solvation effects were included within the COSMO formalism using a dielectric constant of ε = 7.6 for THF. The geometries were fully optimized without geometry or symmetry constraints; minima were confirmed by the absence of imaginary frequencies in the calculations of the analytic second derivatives, for transition states only one imaginary frequency was observed. Transition state optimizations were carried with Kästners DL-FIND optimizer[13] implemented in TCL-Chemshell 3.7[14] starting from transition state geometries obtained from linear transit searches. IRC calculations were carried out to confirm that the transition states connect the starting material and product. The coordinates of the optimized geometries are tabulated below.

Local natural orbital LNO-CCSD(T) calculations were carried out with the freely available MRCC (2022) program package (https://www.mrcc.hu/) using the default thresholds (lcorthr=normal).[15] Geometries optimized at the PBE-D3BJ/def2-TZVP with or without/Cosmo solvation (see text: ε=7.6) level were employed with def2-TZVPP basis sets in combination with complementary def2-QZVPP/C auxiliary correlation basis sets and the aforementioned pseudopotentials. The solvation correction was obtained from the energy differences of two single point calculations at the PBE-D3BJ(COSMO(ε=7.6)/def2-TZVP) and PBE-D3BJ/def2-TZVP (gas phase) level. Back corrections for the LNO-CCSD(T) energies to free enthalpies (ΔG_{298}) were carried out with thermochemical data obtained from the DFT calculations at the PBE-D3BJ/def2-TZVP level. A value of 1.011 was taken as scaling factor from Truhlars database (ver. 5.0). The values for the T1 and D1 diagnostics were typically T1≈0.015 and D1≈0.15 signaling single reference cases.

The QTAIM calculations were performed with the MultiWfn (ver. 3.8) program package (http://sobereva.com/multiwfn/).[16,17] The required wfx file was obtained from a Turbomole generated Molden file and subsequent conversion by Molden2aim (https://github.com/zorkzou/Molden2AIM). Both, basis sets with ECPs (def2-TZVP) and the x2c-TZVPall all-electron basis sets in combination with the X2C relativistic all-electron approach were tested and gave essentially identical results.

For the oxidation states analyses Head-Gordon´s WB97X-D functional was employed using either Qchem 6.0[18] or Gausssian 16 rev. C01[19] with tight DFT grids (def2-TZVP basis and def2-ECP pseudopotentials for rhodium and iridium). Oxidation states based on the LOBA and OSLO method were calculated with a prelease version of Q-Chem 6.1 with either Loewdin or Mulliken charges.[18] The APOST-3D program of Pedro Salvador Sedano[20] was used to perform the calculations of the oxidation states by the EOS method using a Gaussian 16 formatted checkpoint file. QTAIM and TFVC charges were employed.

ALMO-EDA calculations were performed with Qchem 6.0 for converged WB97X-D Kohn-Sham wavefunctions (def2-TZVP basis and def2-ECP pseudopotentials for rhodium and iridium).[18]

The NBO 7.0 calculations[21] were performed with a FILE47 input file generated by a Orca 5.04[22] DFT PBE-D3BJ/def2-TZVP single point calculation using geometries optimized by Turbomole.

The AOMIX program package ver. 6.92 was utilized to decompose the Wiberg/Mayer bond orders into their symmetry components.[23,24] The required Molden input file was prepared by Turbomole with the tm2aomix program for a PBE-D3BJ/def2-TZVP(def2-ECP) calculation of an optimized geometry at that level.

PNO-UCCSD(T1) calculations were carried out with Molpro version 2022.3 with the domopt=tight setting.[25] The SO-SCI SCF optimization scheme was employed to converge to the ground state of the Hartree-Fock reference wave function. Enthalpy corrections to the thermochemical data were provided by the “freeh” program of the Turbomole package from the analytical second derivatives obtained at the UPBE-D3BJ/def2-TZVP level. A value of 1.011 was taken as scaling factor from Truhlars database (ver. 5.0). For the hydrogen atom a value of 5/2 RT was employed. The default def2-TZVP pseudopotentials were employed for rhodium (ECP-28MWB) and iridium (ECP-60MWB). For all atoms the corresponding RIJK auxiliary density fitting basis was used. The values for the T1 and D1 diagnostics were typically T1≈0.015 and D1≈0.15 signaling single reference cases, which was further corroborated by neglible spin contamination (<S**2> ≈ 0.75) of the Hartree-Fock reference wave functions of the S=1/2 radicals.

Local vibrational force constants were derived employing the local mode vibrational theory developed by Cremer and Kraka et al..[27,28] The calculations were performed with the LMODEA(F90) program kindly provided by Elfi Kraka.[29] The required hessians (and dipole gradients) were obtained from Turbomole (aoforce) calculations of the analytical second derivatives.

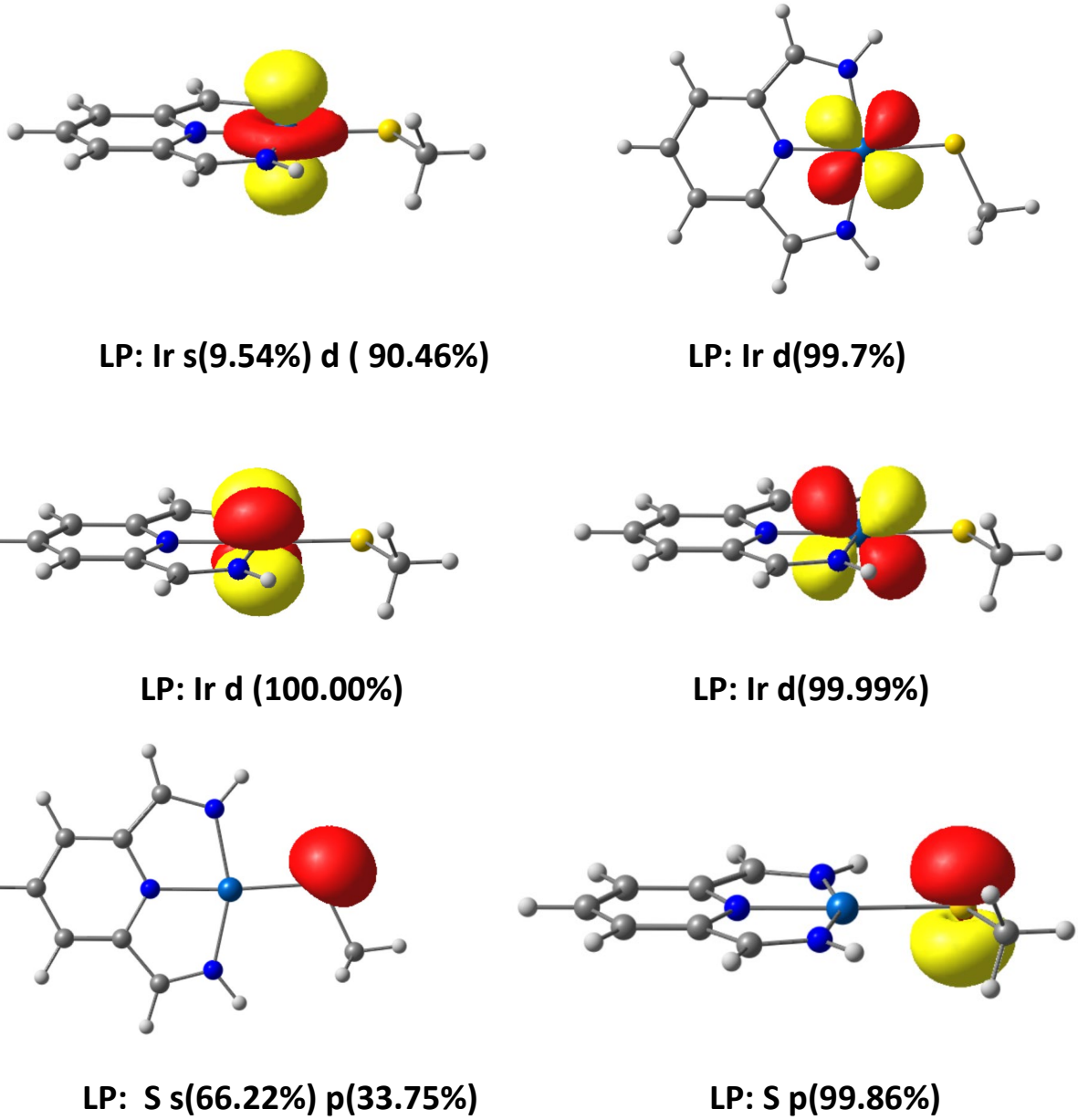
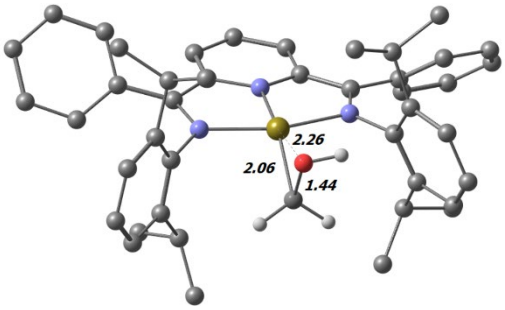


Figure S22: NBOs of (PDI)Ir-SMe model complex: LPs of the Ir and S atoms.

Cpd. (PDI)Ir-CH_2OH: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/ def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e); selected hydrogen atoms with H-H interatomic distances in Å are shown.

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99
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C     -0.0079310    2.2850709   -1.2318594
C      0.0795693    4.3758601   -0.0120213
C      0.0065474    3.6948881    1.2066185
N     -0.1122578    1.6209530   -0.0005988
H      0.1461641    5.4636595   -0.0181762
H     -0.0091265    4.2431330    2.1474028
C      0.0404388    1.3785735   -2.3343893
C     -0.1313370    1.4112838    2.3398170
N     -0.2173083    0.0975394    1.9811487
N      0.1209163    0.0696478   -1.9572898
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C      0.9030443   -2.9424258   -4.7958772
C      1.7160057   -1.3609626   -3.1305458
C     -0.7004313   -1.5561151   -3.6037289
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H      2.9734746   -2.6877853   -4.2711343
H      1.1120867   -3.7150506   -5.5378019
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C     -0.3109511   -3.4562739    4.2255121
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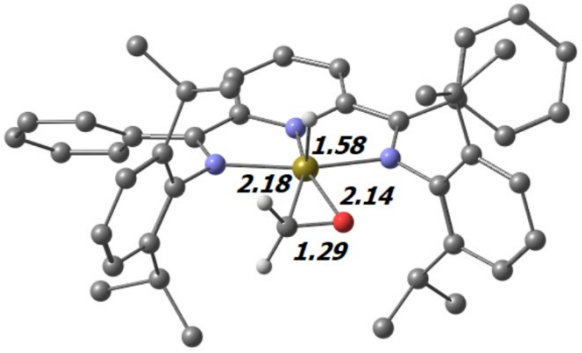
Cpd. TS-rota (PDI)Ir(H)(η^2-CH_2O): Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e); selected hydrogen atoms with H-H interatomic distances in Å are shown.



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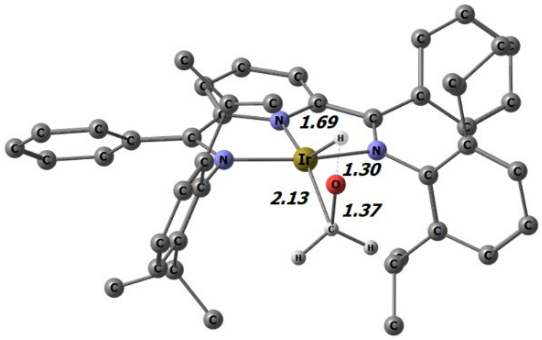
Cpd. TS ß-O-H (PDI)IrCH$_2$O-H: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e); selected hydrogen atoms with H-H interatomic distances in Å are shown.



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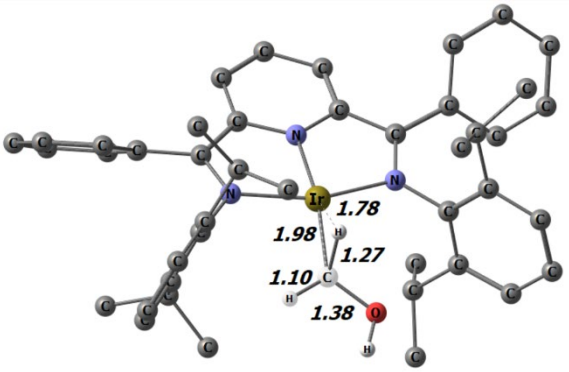
Cpd. (PDI)IrCH$_2$OH: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e); selected hydrogen atoms with H-H interatomic distances in Å are shown

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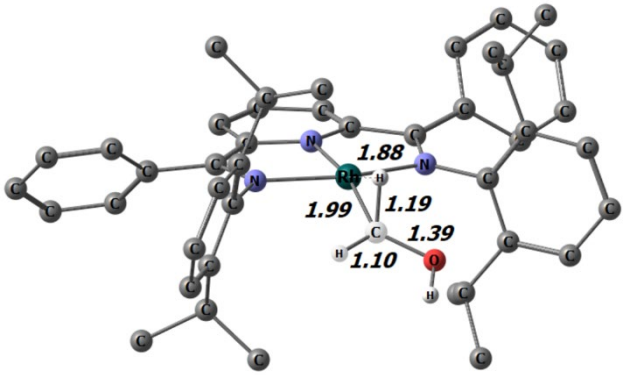
Cpd. (PDI)RhCH$_2$OH: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e); selected hydrogen atoms with H-H interatomic distances in Å are shown.

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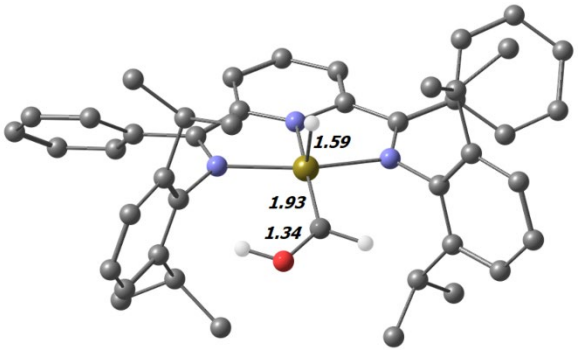
Cpd. (PDI)(H)Ir=C(H)(OH): (hydroxycarbene) Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e); selected hydrogen atoms with H-H interatomic distances in Å are shown

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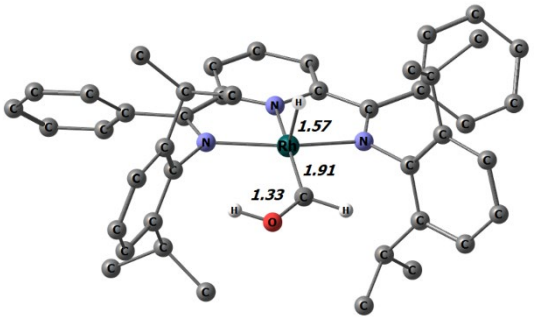
Cpd. (PDI)(H)Rh=C(H)(OH): (hydroxycarbene) Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e); selected hydrogen atoms with H-H interatomic distances in Å are shown

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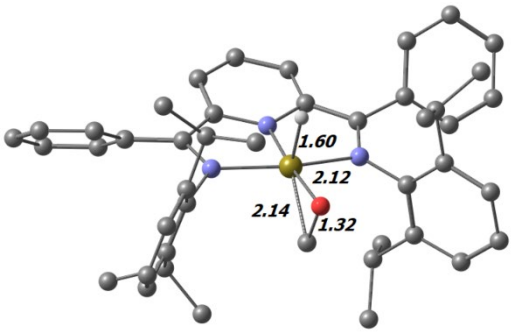
Cpd. Ir(H)(η²CH₂O): Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e); selected hydrogen atoms with H-H interatomic distances in Å are shown.

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Cpd. TS ß-elim. Ir(OMe): Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e); selected hydrogen atoms with H-H interatomic distances in Å are shown.

99

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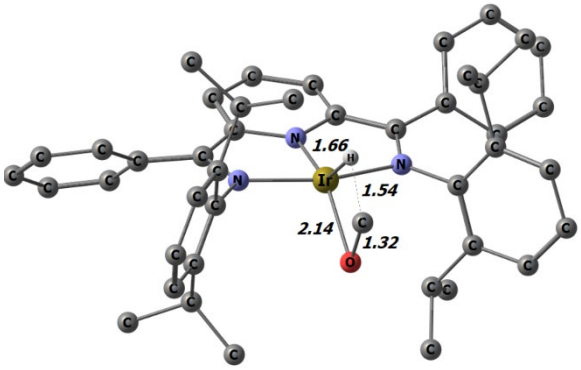

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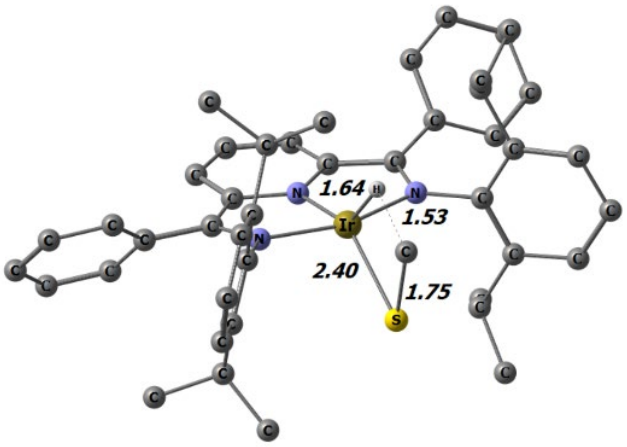
Cpd. TS: ß-elim. Ir(SMe): Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e); selected hydrogen atoms with H-H interatomic distances in Å are shown.



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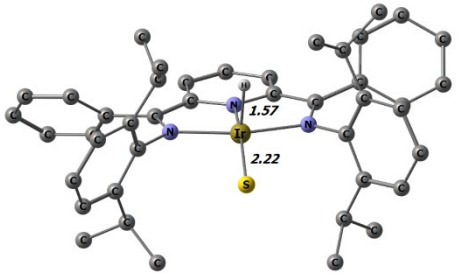
Cpd. Ir(S)(H): Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e); selected hydrogen atoms with H-H interatomic distances in Å are shown.

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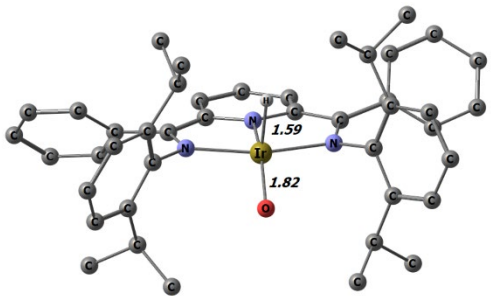
Cpd. Ir(O)(H): Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e); selected hydrogen atoms with H-H interatomic distances in Å are shown.

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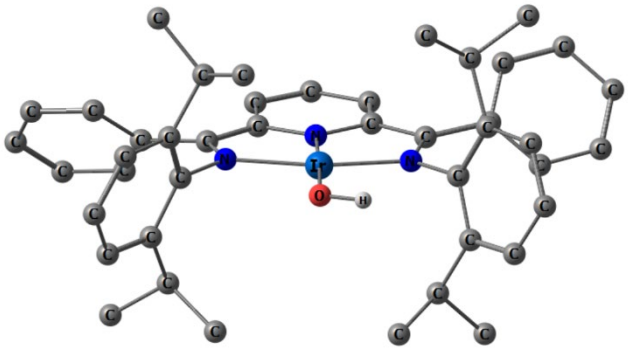
Cpd. 7: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e; the hydroxide hydrogen atom is shown.



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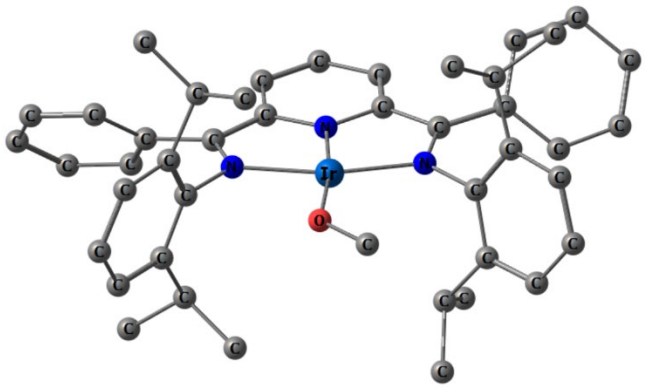
Cpd. 9: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e).



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C     -0.7928197   -4.0087126    3.4155428
H     -0.4870940   -4.8887133    2.8306134
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H      0.2256153    3.9489590    4.1904002
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H     -2.4681773    4.3494183   -2.7209030
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H	0.0268589	3.9290187	-3.4167080
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H	0.3331233	4.2446622	-1.6927358
C	1.9307664	0.0822024	-3.7323824
C	2.8672435	-0.1233418	-6.3869023
C	2.8506436	-0.9187339	-4.1036362
C	1.4876414	0.9752545	-4.7244901
C	1.9530690	0.8719146	-6.0341016
C	3.3134953	-1.0202215	-5.4141922
H	3.1762266	-1.6442122	-3.3571573
H	0.7728606	1.7548622	-4.4720287
H	1.5954716	1.5777253	-6.7854138
H	4.0151744	-1.8131222	-5.6782075
H	3.2248751	-0.2030181	-7.4145330
C	1.9351489	-0.1481611	3.7009980
C	2.8522642	0.0865397	6.3523433
C	2.7883446	0.9054713	4.0776264
C	1.5542216	-1.0830401	4.6768452
C	2.0095271	-0.9663483	5.9885401
C	3.2403589	1.0223524	5.3912819
H	3.0710324	1.6537515	3.3358520
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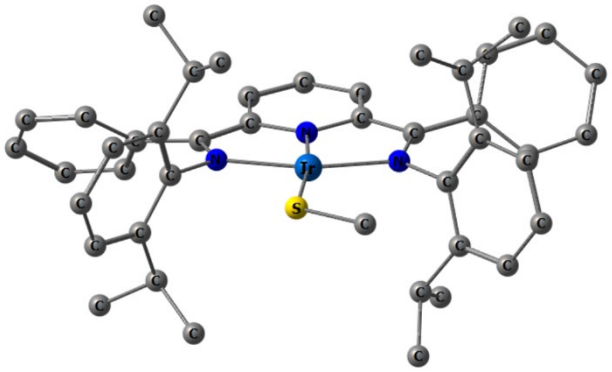
H	3.8892072	1.8553353	5.6666539
H	3.2029243	0.1788431	7.3813489

Cpd. 14: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e).



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C      2.3407269    0.0235512   -1.1994380
C      4.4268902   -0.0670102    0.0165669
C      3.7258643   -0.1287928    1.2257408
N      1.6621503   -0.0181634    0.0064978
H      5.5165865   -0.0868269    0.0213784
H      4.2538960   -0.2163351    2.1737614
C      1.4351544    0.1215059   -2.3116274
C      1.4141443   -0.1487254    2.3302045
N      0.1145399   -0.1994865    1.9800342
N      0.1311199    0.2075835   -1.9605624
Ir    -0.2688488    0.0114851    0.0063509
S     -2.4921548    0.0164858    0.3027409
C     -3.5745087    0.0893253   -1.1637822
H     -3.2071387   -0.5417532   -1.9800277
H     -4.5665527   -0.2563625   -0.8452137
H     -3.6583589    1.1203889   -1.5287030
C     -0.8568065    0.3823511   -2.9789363
C     -2.7820577    0.7532595   -4.9458741
C     -1.2448807   -0.7191104   -3.7683266
C     -1.4488132    1.6596711   -3.1213524
C     -2.4026821    1.8200331   -4.1311232
C     -2.2189097   -0.5046661   -4.7514397
H     -2.8720301    2.7940001   -4.2725287
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C     -0.8962483   -0.3483778    2.9886834
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C     -1.5076245   -1.6129597    3.1379855
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C     -2.3770929   -3.4649350    1.6522035
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H     -0.0752415   -4.7018669    2.3764383
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H	0.4397194	4.3195492	-1.8709164
C	1.9204144	0.0270698	-3.7052649
C	2.8732407	-0.3060310	-6.3419917
C	2.8047437	-1.0203822	-4.0330710
C	1.5215260	0.9010390	-4.7325899
C	1.9944315	0.7344166	-6.0329315
C	3.2758788	-1.1846640	-5.3343130
H	3.0962089	-1.7316679	-3.2592051
H	0.8346856	1.7153688	-4.5160556
H	1.6703999	1.4266838	-6.8116026
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C	2.8291193	0.9451092	4.0465717
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H	0.7367628	-1.6959379	4.5399271
H	1.5877740	-1.4398936	6.8342126
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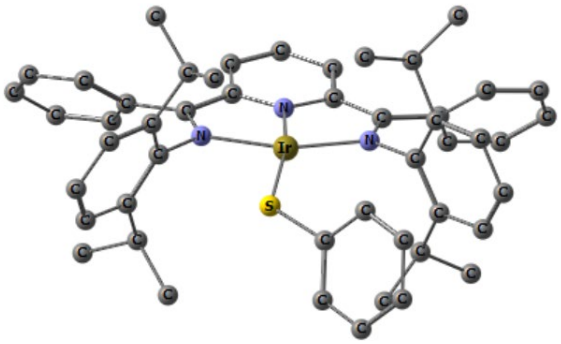
H	3.2349001	0.3533147	7.3781713

Cpd. 15: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e).



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H	-4.2107342	-1.7037985	-1.8807422
C	-1.2362378	1.8368476	3.9072849
H	-0.4916105	2.6133807	3.7238559
C	-0.5248703	-0.2523289	-4.1658698
H	-1.3985872	-0.2668419	-4.8158155
C	-4.7231182	0.8909402	1.3041594
H	-5.2418282	1.8056848	1.5952810
C	-5.5118984	-0.6389317	-3.2201980
H	-6.3422283	-1.3294856	-3.0644450
C	-2.2615989	2.0470872	4.8274945
H	-2.3204369	2.9976486	5.3612745
C	0.7669248	-0.3355891	-4.6892338
H	0.9128914	-0.4250588	-5.7655265
C	-5.1933662	-0.3373331	1.7563750
H	-6.0692202	-0.3812296	2.4057308
C	-5.6556727	0.4457157	-4.0881422
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C	-3.2047360	1.0448674	5.0719649
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H	-4.9425029	-2.4732066	1.7097341
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C	4.0917958	-1.2676850	2.8212217
H	4.2295918	-2.1664901	3.4246724
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H	4.5996624	3.9272989	-0.4866973
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H	1.6481208	-2.3229117	0.7065481
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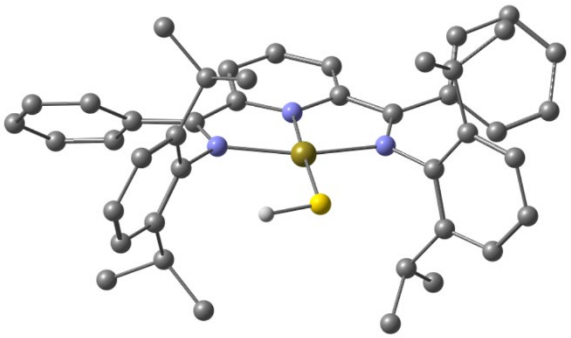
Cpd. 16: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e).



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C      3.6326542   -2.0604693    0.7225722
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N      1.3210458   -0.6898444    0.0960599
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H      2.9650159   -3.5305238   -0.7245005
C      1.7118582    1.1219948    1.5232343
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Ir    -0.2829769    0.2705111   -0.3491262
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H      0.1346233    5.2825121   -1.4667296
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H      1.9628885    6.0745229    0.2611794
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H      0.1568976   -0.5819315   -5.9598031
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H	2.4879650	3.8967984	5.2144916
H	5.7394130	3.2082251	2.4694452
H	4.8562279	4.2919938	4.5368576
C	0.4782968	-3.5713874	-2.1087725
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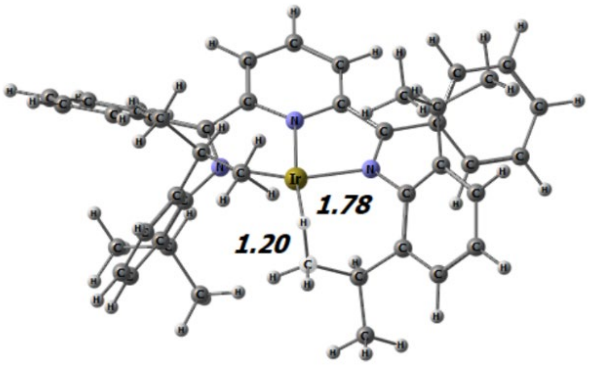
C	0.6884416	-4.7185282	-1.3177601
C	0.2003956	-3.7504269	-3.4755895
C	0.1463037	-5.0281629	-4.0290087
C	0.6311861	-5.9950951	-1.8736238
H	0.8621239	-4.6033438	-0.2472884
H	0.0192846	-2.8863569	-4.1100524
H	-0.0694011	-5.1407420	-5.0925666
H	0.7827800	-6.8676390	-1.2362031
H	0.3130983	-7.1545650	-3.6709989

Cpd. Ir…H-CH$_2$-*i*Pr: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e). The values of the Ir-H and C-H bond distances are given in Å.

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C      2.2448986     0.0831948     1.3348949
C      2.1888014     0.2514615    -1.1021025
C      4.2900353     0.3839425     0.0774156
C      3.6431729     0.1792367     1.2990569
N      1.5723506     0.1293185     0.1250358
H      5.3748101     0.4931077     0.0592696
H      4.2149208     0.0884452     2.2201460
C      1.2474901     0.1716404    -2.1967307
C      1.3604876    -0.0938724     2.4597366
N      0.0366023    -0.1877290     2.1176260
N     -0.0442489     0.0111614    -1.7997529
Ir    -0.3145567    -0.1768686     0.1704799
C     -1.1231109    -0.1504832    -2.7237633
C     -3.3826076    -0.5329611    -4.3182243
C     -1.3031561    -1.3886147    -3.3803607
C     -2.0559880     0.9039350    -2.8684184
C     -3.1789524     0.6850714    -3.6727683
C     -2.4477254    -1.5538439    -4.1700575
H     -3.9079573     1.4885979    -3.7970692
H     -2.6070787    -2.5065235    -4.6791284
H     -4.2674830    -0.6848163    -4.9384773
C     -1.0250790    -0.0850045     3.0554851
C     -3.1589417     0.0106758     4.8649153
C     -2.0859654    -1.0256748     2.9476263
C     -1.1103376     0.9901736     3.9744322
C     -2.1781989     0.9970004     4.8803053
C     -3.1264932    -0.9732871     3.8759747
H     -2.2504718     1.8114058     5.6026221
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H     -3.9707669     0.0297724     5.5935646
C     -0.3194032    -2.5387787    -3.2382334
H      0.5479213    -2.1756683    -2.6706659
C     -0.9267002    -3.6999920    -2.4363108
H     -0.2085643    -4.5299951    -2.3583826
H     -1.8390076    -4.0841196    -2.9168971
H     -1.1830348    -3.3824884    -1.4156293
C      0.1871657    -3.0178875    -4.6062738
H      0.9655340    -3.7844816    -4.4768023
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H     -4.1431174    -2.8134675     1.9547198
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H      0.6936139     1.9432586     3.3270669
C     -0.9291470     3.2995134     3.0709065
H     -0.2838640     4.1833328     2.9535943
H     -1.8577753     3.6151348     3.5701982
H     -1.1878518     2.9258941     2.0693014
C      0.2397807     2.7392125     5.2550127
H      0.7195587     1.9495950     5.8490789
H     -0.6031726     3.1435431     5.8351081
H      0.9643811     3.5561026     5.1236567
C     -1.8644901     2.2528043    -2.1894720
H     -0.9003351     2.2238277    -1.6605780
C     -2.9512921     2.5135719    -1.1364402
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H     -2.7916652     3.4892338    -0.6537340
H     -2.9317320     1.7459087    -0.3512505
C     -1.8255509     3.4062910    -3.2041778
H     -2.7827778     3.5054292    -3.7374706
H     -1.0380030     3.2662785    -3.9578738
H     -1.6312809     4.3581778    -2.6883558
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C	2.5043337	0.1816767	-6.3040665
C	2.7754426	-0.5763570	-4.0215925
C	1.0021382	0.9659102	-4.5736327
C	1.4092181	0.9528104	-5.9054821
C	3.1854116	-0.5822891	-5.3533126
H	3.2837643	-1.2142826	-3.2979385
H	0.1527558	1.5772312	-4.2772617
H	0.8683498	1.5551860	-6.6372962
H	4.0311422	-1.2034861	-5.6532135
H	2.8208564	0.1721650	-7.3480093
C	1.8423164	-0.2493639	3.8371656
C	2.7575207	-0.5772955	6.4904692
C	2.8621643	0.5700308	4.3617413
C	1.2856750	-1.2314388	4.6818353
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H	0.4960894	-1.8782863	4.2988181
H	1.2895611	-2.1592842	6.6215087
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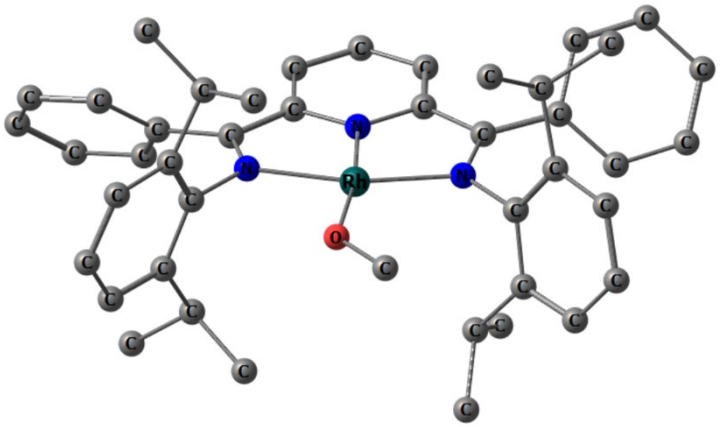
H	3.1090338	-0.7035005	7.5154422

Cpd. 8: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Rh: def2-ECP (28e).



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C      2.3629894   -0.0128165   -1.2169516
C      4.4543153   -0.0643955   -0.0061178
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H      5.5440566   -0.0528476   -0.0016475
H      4.2775351   -0.2300934    2.1522692
C      1.4534151    0.0987047   -2.3328851
C      1.4468134   -0.2261273    2.3116794
N      0.1575983   -0.2980546    1.9800192
N      0.1602005    0.1609245   -1.9791707
Rh    -0.2144441   -0.0927245   -0.0077102
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C     -3.1980191   -0.0547276   -0.6361341
H     -2.9466568   -0.4356341   -1.6417330
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H     -3.5407432    0.9919834   -0.7576501
C     -0.8531936    0.3474255   -2.9618046
C     -2.8754975    0.7419213   -4.8282885
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C     -2.5138752    1.7746577   -3.9629860
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H     -3.0339608    2.7307925   -4.0250509
H     -2.5617620   -1.3111396   -5.3869237
H     -3.6619776    0.9004743   -5.5680433
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C     -2.9275097   -0.4248008    4.8448211
C     -1.5012729   -1.5750963    3.2444720
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C     -2.3085255    0.7845662    4.5384926
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H     -2.6407429    1.6993791    5.0324335
H     -3.0302714   -2.5322996    4.4205643
H     -3.7305936   -0.4572865    5.5830693
C     -0.6215795   -2.1078604   -3.6447642
H      0.3178415   -2.0046722   -3.0854019
C     -1.5469857   -2.9992416   -2.7994304
H     -1.1047696   -3.9983929   -2.6685805
H     -2.5272670   -3.1192350   -3.2851008
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H      0.2454212   -3.7110320   -4.8244623
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H     -1.1842737   -2.9843698   -5.5760342
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H     -0.9697878    2.1807940   -1.0453152
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C	2.8495859	-0.9293198	-4.1098647
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H	0.8045756	1.7741660	-4.4456718
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H	4.0048428	-1.8177159	-5.6950637
H	3.2403417	-0.1731478	-7.4096401
C	1.9422937	-0.1492180	3.7026100
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C	2.7849640	0.9144955	4.0724574
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H	3.0577000	1.6640282	3.3280655
H	0.9217821	-1.9143399	4.4097778
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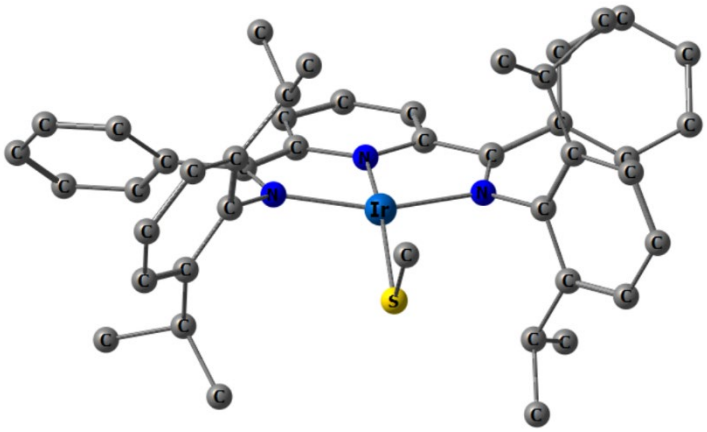
Cpd. TS IrSMe: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e).



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C      2.1889004    0.3800653   -1.4004841
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H      4.2137501    0.8802696    1.8763951
C      1.2378731    0.1400678   -2.4745113
C      1.3791413    0.4926617    2.1550899
N      0.0844561    0.2874273    1.8571509
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C     -3.2420461   -0.6306493   -4.6999549
C     -1.3757783   -1.4430620   -3.3685346
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C     -0.8731899    0.0007166    2.8874640
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H      1.3028344   -2.1225818    2.3125643
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C	1.6076523	-0.2351318	4.5744124
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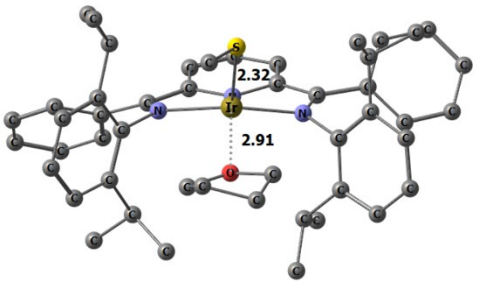
Cpd. TS IrSMe_THF: Xmol xyz coordinates (Å) and total energy in Hartree DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e).



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H	-5.082128700	-0.389834500	0.898726000
H	-4.483152400	1.490652700	-0.640257400
C	-0.510098200	-1.193606700	1.630420900
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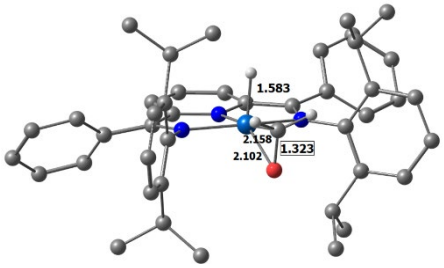
Cpd. IrH(CH_2O)3 C_{2v}: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e); selected hydrogen atoms and distances in Å are shown.

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Cpd. TS ß-H-elim. Ir(OCH$_3$)3 C$_{2v}$: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e);selected hydrogen atoms and distances in Å are shown.

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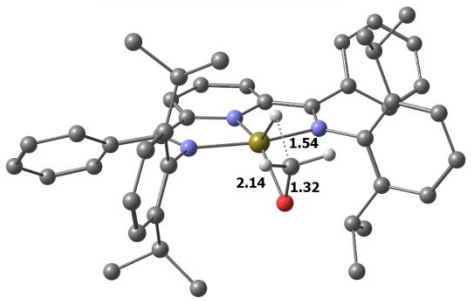

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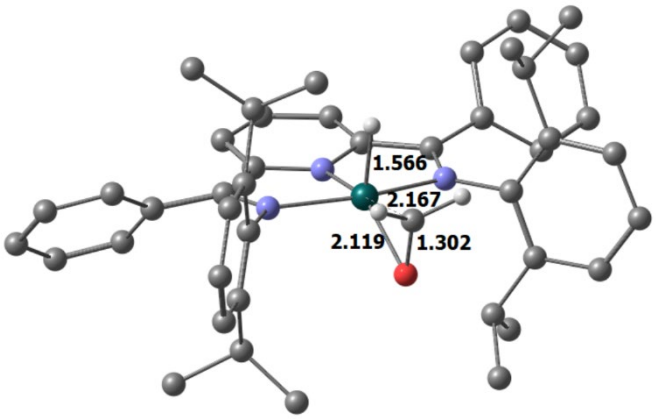
Cpd. Rh(H)(CH$_2$O)3 C$_{2v}$: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e);selected hydrogen atoms and distances in Å are shown.

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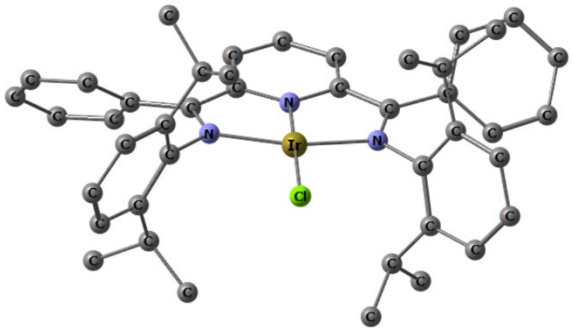
Cpd. 5: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e).



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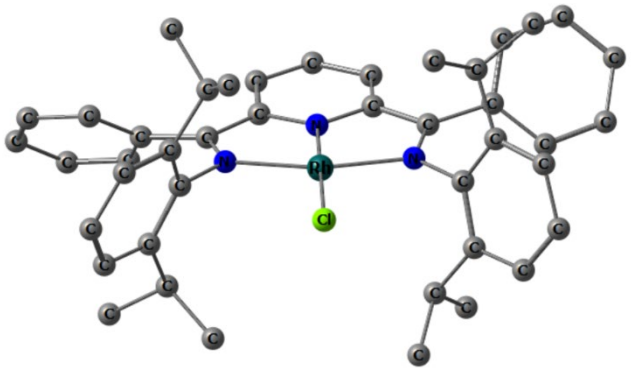
Cpd. RhCl: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e).



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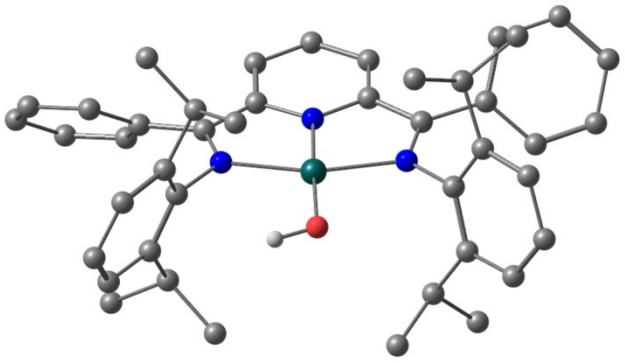
Cpd. RhOH: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e).



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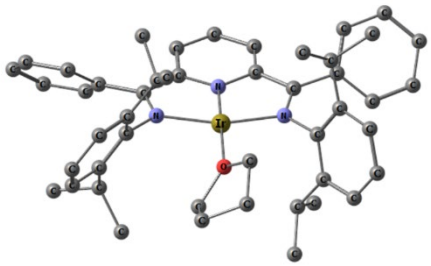
Cpd. 13: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e).



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C      5.0179913    1.2773496   -0.6527777
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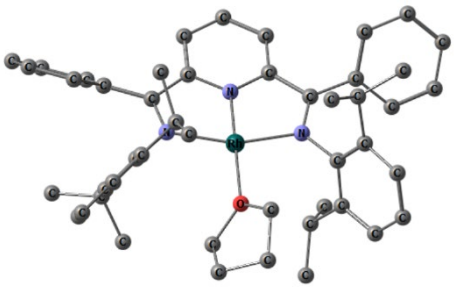
Cpd. Rh(THF)$^+$: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e).



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H      3.3615254    3.2417419    0.8751362
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H      4.6233229    3.0072993   -1.9074351
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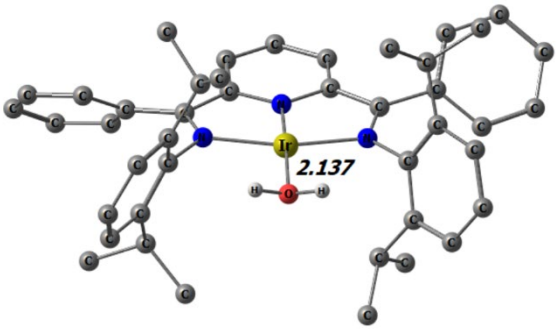
Cpd. Ir(OH$_2$)$^+$: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e). The Ir-O distance (in Å) is shown.

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H      4.3223038    2.8195450    2.4376002
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H	4.3722742	2.3892989	4.1584237
H	3.1818833	3.5624870	3.5798346
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C	-3.7134356	5.7544332	-2.7683395
C	-3.1400934	4.3103820	-0.9173038
C	-1.9061607	4.1596038	-2.9952934
C	-2.7026722	5.1673608	-3.5331632
C	-3.9252925	5.3266137	-1.4560673
H	-3.2905225	4.0078152	0.1196839
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H	-2.5311570	5.4966860	-4.5584974
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C	0.0135931	-2.0785113	2.5262804
C	-0.0510076	-4.5127499	3.9352959
C	0.8305326	-2.2754072	3.6546405
C	-0.8304184	-3.1289177	2.1127702
C	-0.8565319	-4.3355085	2.8081771
C	0.7901259	-3.4789688	4.3543015
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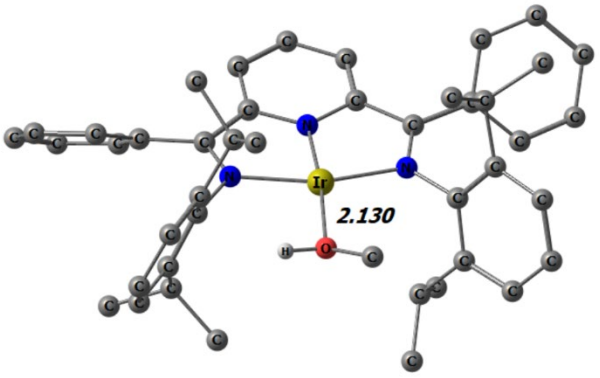
H	-1.4369777	-3.0134151	1.2139140
H	-1.5026354	-5.1432927	2.4627796
H	1.4215245	-3.6097544	5.2336423
H	-0.0752194	-5.4554695	4.4829765

Cpd. Ir(MeOH)$^+$: Xmol xyz coordinates (Å) and total energy in Hartree of DFT PBE-D3BJ/def2-TZVP optimized geometry (gas phase); Ir: def2-ECP (60e). The Ir-O distance (in Å) is shown.

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H	1.1034011	-3.3673522	5.3262441
H	-0.3052951	-5.2622191	4.5291416

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