Electronic Supplementary Material (ESI) for ChemComm.

Calcium-Stabilised Transition Metal *Bis*(Formyl) Complexes: Structure and Bonding

Joseph M. Parr,[a] Andrew J. P. White,[a] and Mark R Crimmin*[a]

Corresponding author. Email: m.crimmin@imperial.ac.uk

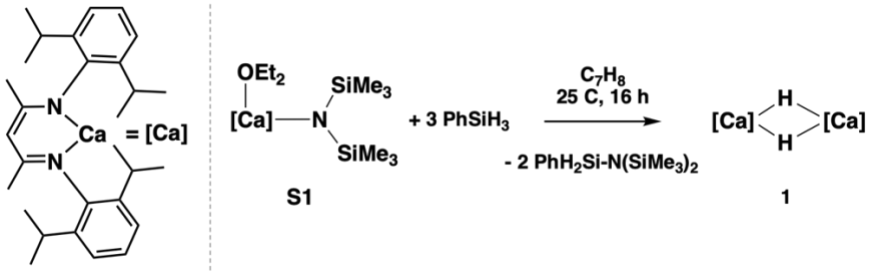
[a] Molecular Sciences Research Hub, Department of Chemistry, Imperial College London, 82 Wood Lane, White City, Shepherds Bush, London, W12 0BZ, UK.

Contents

1. General Experimental

All manipulations were carried out under standard Schlenk-line or glovebox techniques under an inert atmosphere of nitrogen. A MBraun Labmaster glovebox was employed operating at concentrations of H_2O and O_2 below 0.1 ppm. Glassware was dried for 12 hours at 120 °C prior to use. C_6D_6 was freeze-pump thaw degassed three times and stored over molecular sieves for twelve hours before use. All other solvents were dried using a Grubbs type solvent purification system. ^{1}H, ^{13}C, COSY and HSQC NMR experiments were run within J-Young Tap NMR tubes on 400 or 500 MHz BRUKER machines. Spectra were referenced to known residual solvent peaks. NMR analysis was conducted in MestReNova with baseline and phase corrections applied to spectra. Chemical shift values are reported in ppm and coupling constants *J* in Hz. NMR spectra are attached as an .mnova file for reference. Infrared spectra were obtained on a Cary630 spectrometer (placed with in an MBraun glovebox) from crystalline solids or benzene thin-films on an ATR cell. **1** was prepared from the related calcium amide complex[1] as described below. [MCp*$(CO)_2$] (M=Co, Ir) were prepared as described previously.[2-3] All other reagents were purchased from commercial suppliers and used without further purification.

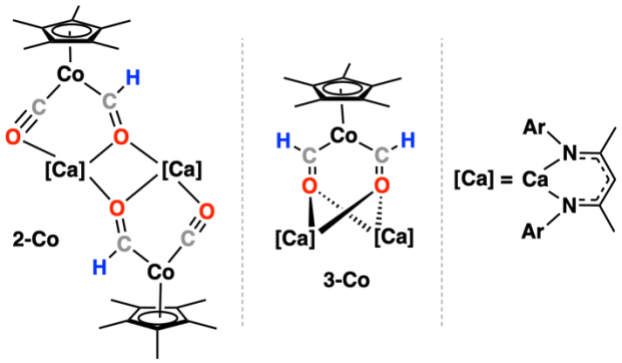
2. Synthetic Procedures



Scheme S1. Synthetic procedure to β-diketiminate calcium hydride **1** (Ar = 2,6-diisopropylphenyl).

In a glovebox, **S1**[1] (0.8 g, 1.16 mmol) was transferred to a small ampoule and dissolved in toluene (5 mL, 0.2 – 0.25 M solution). Phenyl silane (432 μL, 3.5 mmol, 3 equiv.) was added by micropipette. The reaction mixture was agitated to ensure thorough mixing of the reagents and then left to stand at 25 °C for 24 h. Large colourless crystalline blocks formed over this period and were isolated by cannula filtration, then washed with n-hexane (2 x 5 mL) to yield **1** (0.52g, 0.49 mmol, 85 %). Data match that reported in the literature.[4,5]

Synthesis of **2-Co** and **3-Co**



Method A: In a N_2 filled glovebox, **1** (20 mg, 0.02 mmol) was dissolved in C_6D_6 (0.6 mL). THF (0.1 mL) was added by micropipette and the solution transferred to a Youngs Tap NMR tube. An external capillary containing a solution of ferrocene in C_6D_6 was added (0.1 M) and an initial ^{1}H NMR spectra recorded. The tube was returned to the glovebox and [CoCp*$(CO)_2$] (10.5 mg, 0.04 mmol) added. The solution turned immediately from colourless to green-black and the reaction was monitored by ^{1}H NMR spectroscopy. After one day complete consumption of starting materials was observed in the ^{1}H NMR spectra (NMR yield of **2-Co**: 95 %). The tube was returned to the glovebox and the solution decanted into a scintillation vial. The solvent was removed in vacuo to afford a green-black solid (colour derived from trace amounts of unreacted [CoCp*$(CO)_2$]). Subsequent washing with cold *n*-pentane (2 x 0.5 mL) and drying *in vacuo* yielded **2-Co** as an analytically pure orange solid (22.0 mg, 0.015 mmol, 72 %). Single crystals suitable for x-ray diffraction analysis were grown from a saturated *n*-hexane solution at -35 ºC, yielding **2-Co** as orange block crystals.

Method B: In a N_2 filled glovebox, **1** (20 mg, 0.02 mmol) was dissolved in C_6D_6 (0.6 mL) and transferred to a Youngs Tap NMR tube. An external capillary containing a solution of ferrocene in C_6D_6 was added (0.1 M) and an initial ^{1}H NMR spectra recorded. The tube was returned to the glovebox and [CoCp*$(CO)_2$] (10.5 mg, 0.04 mmol) added. The solution turned immediately from colourless to green-black and the reaction was monitored by ^{1}H NMR spectroscopy. **2-Co** and **3-Co** were observed at the first instance in the ^{1}H NMR spectra. After one hour, consumption of **1** was observed. **2-Co** and **3-Co** were formed in 3:2 ratio which did not change upon prolonging reaction time or increasing reaction temperature. Yield based on ^{1}H NMR for **2-Co** and **3-Co** of 25 and 17 %, respectively.

2-Co:

^{1}H NMR (400 MHz, C_6D_6) δ: 0.52 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 12H, CH(C**H**$_3$)$_2$), 1.16 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 12H, CH(C**H**$_3$)$_2$), 1.27 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 12H, CH(C**H**$_3$)$_2$), 1.57 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 12H, CH(C**H**$_3$)$_2$), 1.66 (s, 12H, NC(C**H**$_3$)), 1.90 (s, 30H, C_5(C**H**$_3$)$_5$), 2.83 (sept, $^3J_{H\text{-}H}$ = 6.7 Hz, 4H, C**H**(CH$_3$)$_2$), 3.39 (sept, $^3J_{H\text{-}H}$ = 6.7 Hz, 4H, C**H**(CH$_3$)$_2$), 4.75 (s, 2H, (CH$_3$)C(C**H**)C(CH$_3$)), 7.13-7.22 (12H, Ar–**H**), 13.50 (s, 2H, Co–C**H**O).

^{13}C NMR (101 MHz, C_6D_6) δ: 10.4 (*5x* **C**H_3 in Cp*), 23.0 (*4x* NC(**C**H_3)), 23.9 (*4x* CH(**C**H_3)$_2$), 24.3 (*4x* CH(**C**H_3)$_2$), 25.0 (*4x* CH(**C**H_3)$_2$), 25.3 (*4x* CH(**C**H_3)$_2$), 26.3 (*4x* **C**H(CH_3)$_2$), 28.6 (*4x* **C**H(CH_3)$_2$), 94.3 ((CH_3)C(**C**H)C(CH_3)), 96.0 (*5x* **C**CH_3 in Cp*), 123.6 (Ar-**C**), 124.7 (Ar-**C**), 124.9 (Ar-**C**), 125.7 (*meta*-Ar-**C**), 129.3 (*meta*-Ar-**C**), 142.3 (*ortho*-Ar-**C**), 145.4 (*ipso*-Ar-**C**), 165.7 (N**C**(CH_3)), 298.9 (Co**C**HO). ^{13}C resonances for isocarbonyl ligands were not observed in either the ^{13}C{^{1}H} NMR or HSQC spectra. X-ray diffraction and IR data confirm their presence. The formyl ^{13}C resonance was assigned from the HSQC spectra.

IR (ATR, cm^{-1}), ν_{CO}: 1838 (m, ν*C*O).

Crystal data for **2-Co**: $C_{82}H_{114}Ca_2Co_2N_4O_4 \cdot 2(C_6H_{14})$, M = 1590.13, monoclinic, $P2_1/n$ (no. 14), a = 17.6568(4), b = 13.2884(3), c = 19.2033(4) Å, β = 90.9516(19)°, V = 4505.07(17) Å^3, Z = 2 [C_i symmetry], D_c = 1.172 g cm^{-3}, μ(Cu-Kα) = 4.255 mm^{-1}, T = 173 K, light orange blocks, Agilent Xcalibur PX Ultra A diffractometer; 8902 independent measured reflections (R_{int} = 0.0383), F^2 refinement,[6-8] R_1(obs) = 0.0495, wR_2(all) = 0.1477, 6565 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to θ_{full}(67.7°) = 99.9%], 439 parameters. CCDC 2265688. The structure of **2-Co** was found to sit across a centre of symmetry at the middle of the central Ca_2O_2 ring. The included solvent was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON.[9] This suggested a total of 186 electrons per unit cell, equivalent to 93 electrons per complex. Before the use of SQUEEZE the solvent clearly resembled hexane (C_6H_{14}, 50 electrons) distributed over two sites both adjacent to centre's of symmetry. Two hexane molecules correspond to 100 electrons, so this was used as the solvent present. As a result, the atom list for the asymmetric unit is low by 0.5 x 2(C_6H_{14}) = C_6H_{14} (and that for the unit cell low by $C_{24}H_{56}$) compared to what is presumed to be present.

3-Co.

Select spectroscopic data from mixture: ^{1}H NMR (400 MHz, C_6D_6) δ: 1.90 (s, 15H, C_5(C**H**$_3$)$_5$), 4.82 (s, 2H, (CH_3)C(C**H**)C(CH_3)), 13.54 (s, 2H, Co{C**H**O}$_2$). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6) δ: 10.2 (*5x* **C**H_3 in Cp*), 94.3 ((CH_3)C(**C**H)C(CH_3)), 298.5 (Co**C**HO).

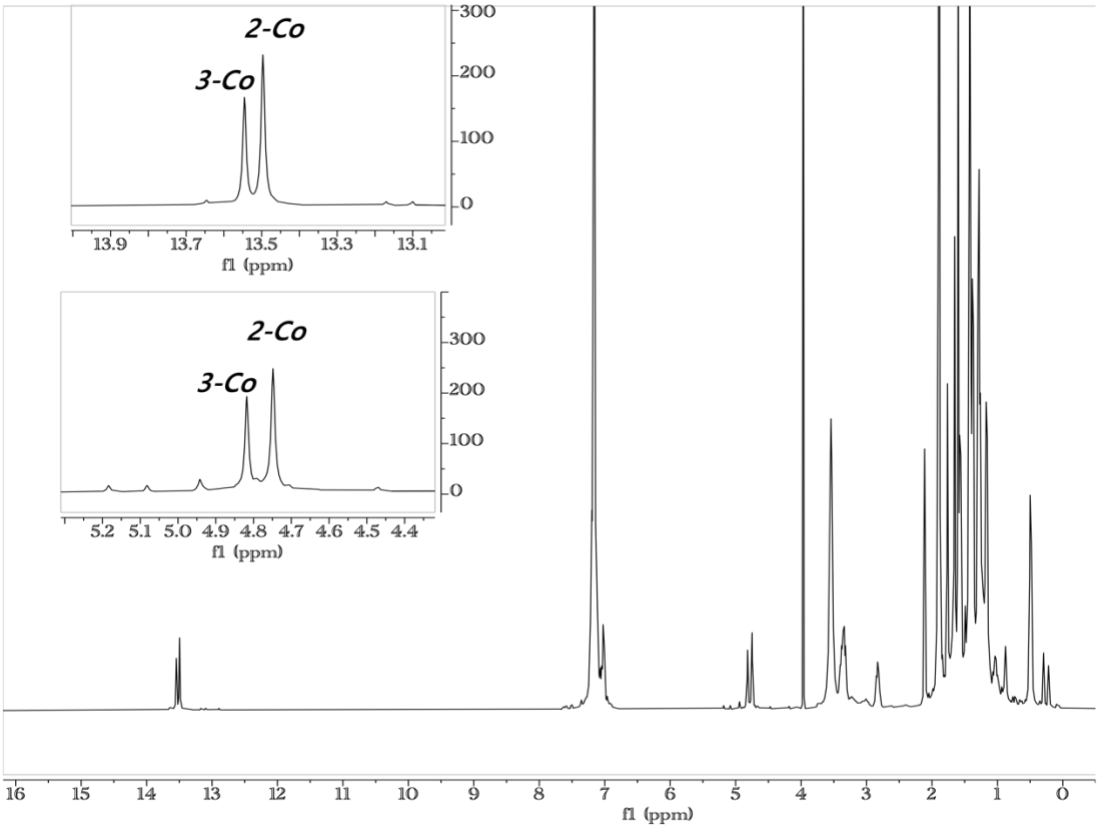


Figure S1. ^{1}H NMR spectra for a **2-Co** and **3-Co** mixture from reaction of **1** and [CoCp*(CO)$_2$] in C_6D_6 solution.

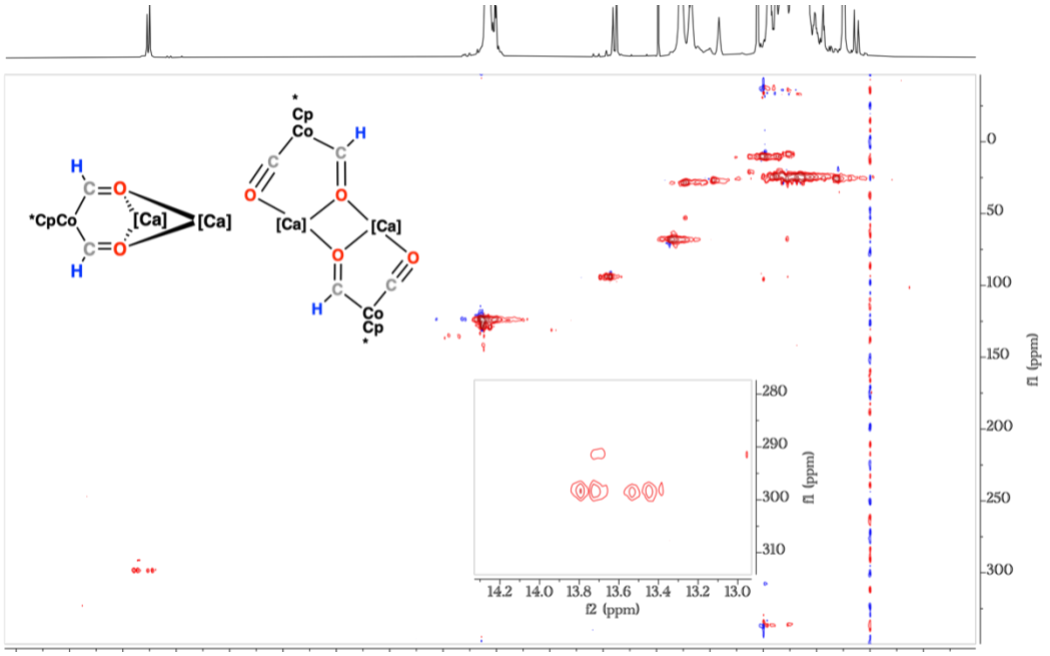
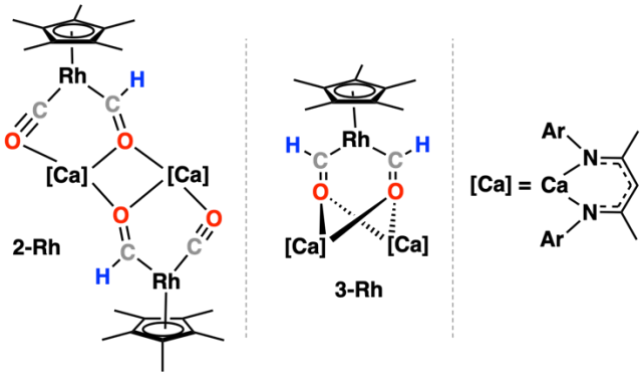


Figure S2. HSQC NMR spectra for a **2-Co** and **3-Co** mixture from reaction of **1** and [CoCp*(CO)$_2$] in C_6D_6 solution.

Synthesis of **2-Rh-THF** and **3-Rh**



Method A: In a N_2 filled glovebox, **1** (20 mg, 0.02 mmol) was dissolved in C_6D_6 (0.6 mL). THF (0.1 mL) was added by micropipette and the solution transferred to a Youngs Tap NMR tube. An external capillary containing a solution of ferrocene in C_6D_6 was added (0.1 M) and an initial ^{1}H NMR spectra recorded. The tube was returned to the glovebox and [RhCp*$(CO)_2$] (12.4 mg, 0.04 mmol) added. The solution turned immediately from colourless to red-orange and the reaction was monitored by ^{1}H NMR spectroscopy. After four hours, complete consumption of starting materials was observed in the ^{1}H NMR spectra (NMR yield of **2-Rh.thf**: 81 %). The tube was returned to the glovebox and the solution decanted into a scintillation vial. The solvent was removed in vacuo to afford an orange solid. Subsequent washing with cold *n*-pentane (2 x 0.5 mL) and drying *in vacuo* yielded **2-Rh.thf** as an orange solid (23.7 mg). Unreacted [RhCp*$(CO)_2$] was present as an impurity and all attempts to purify this compound further were complicated by its instability..

Method B: In a N_2 filled glovebox, **1** (20 mg, 0.02 mmol) was dissolved in C_6D_6 (0.6 mL) and the solution transferred to a Youngs Tap NMR tube. An external capillary containing a solution of ferrocene in C_6D_6 was added (0.1 M) and an initial ^{1}H NMR spectra recorded. The tube was returned to the glovebox and [RhCp*$(CO)_2$] (6.2 mg, 0.02 mmol) added. The solution turned immediately from colourless to red-orange and the reaction was monitored by ^{1}H NMR spectroscopy. After one hour, a mixture of **2-Rh.thf** and **3-Rh** was observed in the ^{1}H NMR spectra in 1:1.8 ratio. Repeat reactions and altering the stoichiometry gave similar results and no interconversion between **2-Rh.thf** and **3-Rh** was observed upon heating. The tube was returned to the glovebox and the solution decanted into a scintillation vial. The solvent was removed in vacuo to afford an orange solid. The crude solid was dissolved in *n*-hexane, filtered through a glass-fibre, and stored at -35 ºC. Orange block single crystals of **3-Rh** deposited from the solution and were picked under a microscope for x-ray diffraction analysis. Repeated attempts to separate **2-Rh.thf** and **3-Rh** were unsuccessful.

2-Rh.thf: ^{1}H NMR (400 MHz, C_6D_6) δ: 0.54 (d, $^3J_{H\text{-}H}$ = 6.7 Hz, 12H, CH(C**H**$_3$)$_2$), 1.14 (d, $^3J_{H\text{-}H}$ = 6.7 Hz, 12H, CH(C**H**$_3$)$_2$), 1.27 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 12H, CH(C**H**$_3$)$_2$), 1.39 (m, 4H, C**H**$_2$ in THF), 1.54 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 12H, CH(C**H**$_3$)$_2$), 1.64 (s, 12H, NC(C**H**$_3$)), 2.00 (s, 30H, C_5(C**H**$_3$)$_5$), 2.80 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 4H,

C**H**$(CH_3)_2$), 3.35 (sept, $^3J_{H\text{-}H}$ = 6.4 Hz, 4H, C**H**$(CH_3)_2$), 3.54 (m, 4H, C**H**$_2$ in THF), 4.75 (s, 2H, $(CH_3)C(CH)C(CH_3)$), 7.12-7.19 (12H , Ar–**H**), 13.55 (d, $^2J_{Rh\text{-}H}$ = 1.7 Hz, 2H, Rh–C**H**O).

^{13}C NMR (101 MHz, C_6D_6) δ: 10.7 (*5x* **C**H_3 in Cp*), 20.5 (*2x* NC(**C**H_3)), 21.4 (*2x* NC(**C**H_3)), 22.7 (*2x* CH(**C**$H_3)_2$), 23.1 (*2x* CH(**C**$H_3)_2$), 23.2 (*2x* CH(**C**$H_3)_2$), 23.8 (*2x* CH(**C**$H_3)_2$), 24.3 (*2x* CH(**C**$H_3)_2$), 24.6 (*2x* CH(**C**$H_3)_2$), 24.8 (*2x* CH(**C**$H_3)_2$), 25.4 (*2x* CH(**C**$H_3)_2$), 25.7 (**C**H_2 in THF), 25.9 (*2x* **C**$H(CH_3)_2$), 26.8 (*2x* **C**$H(CH_3)_2$), 28.4 (*2x* **C**$H(CH_3)_2$), 29.1 (*2x* **C**$H(CH_3)_2$), 68.3 (**C**H_2 in THF), 94.6 ($(CH_3)C(CH)C(CH_3)$), 100.9 (*5x* **C**CH_3 in Cp*), 123.4 (*para*-Ar-**C**), 123.8 (*para*-Ar-**C**), 124.8 (*meta*-Ar-**C**), 124.9 (*meta*-Ar-**C**), 129.3 (*meta*-Ar-**C**), 136.4 (*ortho*-Ar-**C**), 137.9 (*ortho*-Ar-**C**), 142.1 (*ortho*-Ar-**C**), 142.4 (*ipso*-Ar-**C**), 145.2 (*ipso*-Ar-**C**), 165.9 (N**C**(CH_3)), 208.2 (s, $^1J_{Rh\text{-}C}$ = 105.4 Hz, Rh-**C**OCa), 290.2 (s, $^1J_{Rh\text{-}C}$ = 245.6 Hz, Rh-**C**HOCa). Certain ^{13}C resonances for Ar–**C** were not observed in the $^{13}C\{^1H\}$ NMR spectra due to overlap with C_6D_6 solvent residual peaks.

IR (ATR, cm^{-1}), ν_{CO}: 1818 (w, νCO).

3-Rh.

Select spectroscopic data from mixture: ^{1}H NMR (400 MHz, C_6D_6) δ: 1.90 (s, 15H, $C_5(CH_3)_5$), 4.68 (s, 2H, $(CH3)C(CH)C(CH3)$), 13.50 (s, 2H, Rh{C**H**O}$_2$).

Crystal data for **3-Rh**: $C_{70}H_{99}Ca_2N_4O_2Rh{\cdot}1.75(C_6H_{14})$, M = 1362.4, monoclinic, $P2_1/n$ (no. 14), a = 14.1756(5), b = 14.8989(6), c = 36.7539(13) Å, β = 97.759(3)°, V = 7691.4(5) Å^3, Z = 4, D_c = 1.177 g cm^{-3}, μ(Cu-Kα) = 3.303 mm^{-1}, T = 173 K, orange blocks, Agilent Xcalibur PX Ultra A diffractometer; 15187 independent measured reflections (R_{int} = 0.3167), F^2 refinement,[6-8] R_1(obs) = 0.0935, wR_2(all) = 0.2724, 4291 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to θ_{full}(67.7°) = 99.8%], 729 parameters. CCDC 2265689. Reciprocal space analysis of the data set for the structure of **3-Rh** showed the crystal to be slightly twinned, though the best results came from standard, non-twin, data processing. However the main problem with this data set is its intensity, particularly how rapidly the intensity drops off with increasing diffraction angle with the result that data beyond *ca*. 1.10 Å resolution is virtually unobserved (the mean I/σ for the 1.10 Å – 1.02 Å shell is only *ca*. 1.06). It is thus unsurprising that the R_{int} is very poor and that the ratio of observed to unique reflections is only *ca*. 28%. Additionally, the included solvent was found to be highly disordered, and the best approach to handling this diffuse electron density was found to be the SQUEEZE routine of PLATON.[9] This suggested a total of 350 electrons per unit cell, equivalent to 87.5 electrons per complex. Before the use of SQUEEZE the solvent most resembled hexane (C_6H_{14}, 50 electrons), and 1.75 hexane molecules corresponds to 87.5 electrons, so

this was used as the solvent present. As a result, the atom list for the asymmetric unit is low by 1.75(C_6H_{14}) = $C_{10.5}H_{24.5}$ (and that for the unit cell low by $C_{42}H_{98}$) compared to what is actually presumed to be present. However, despite all the issues with this structure the nature of the complex is still clear, and furthermore it is isomorphous with the much better determined iridium analogue **3-Ir** (see below). As such we think it is worthwhile to make this structure available to the wider community.

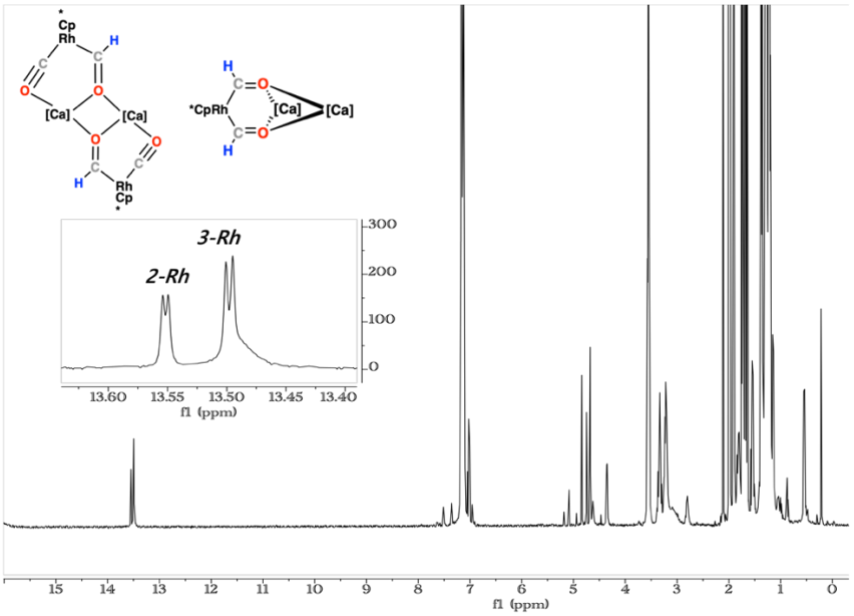


Figure S3. ^{1}H NMR spectra for a **2-Rh.thf** and **3-Rh** mixture from reaction of **1** and [RhCp*$(CO)_2$] in C_6D_6 solution.

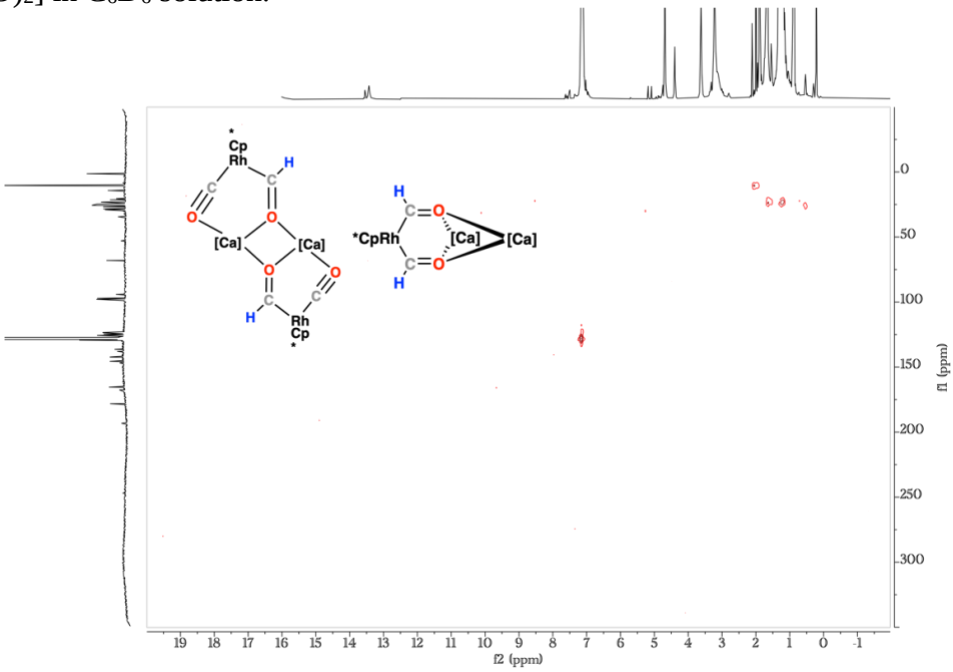
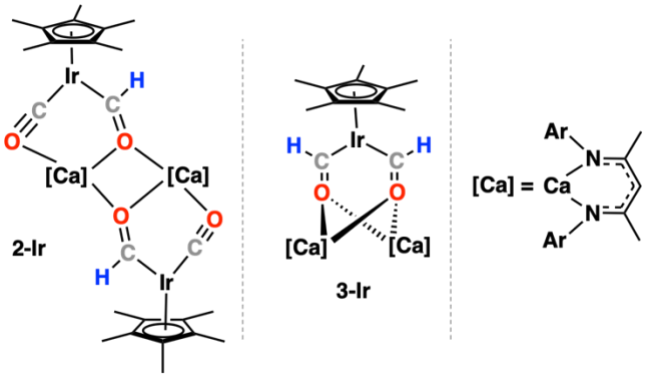


Figure S4. HSQC NMR spectra for a **2-Rh.thf** and **3-Rh** mixture from reaction of **1** and [RhCp*$(CO)_2$] in C_6D_6 solution.

Synthesis of **2-Ir-THF** and **3-Ir**



Method A: In a N_2 filled glovebox, **1** (20 mg, 0.02 mmol) was dissolved in C_6D_6 (0.6 mL). THF (0.1 mL) was added by micropipette and the solution transferred to a Youngs Tap NMR tube. An external capillary containing a solution of ferrocene in C_6D_6 was added (0.1 M) and an initial ^{1}H NMR spectra recorded. The tube was returned to the glovebox and [IrCp*$(CO)_2$] (16.1 mg, 0.04 mmol) added. The solution turned immediately from colourless to yellow and the reaction was monitored by ^{1}H NMR spectroscopy. After four hours, complete consumption of starting materials was observed in the ^{1}H NMR spectra (NMR yield of **2-Ir.thf**: 85 %). The tube was returned to the glovebox and the solution decanted into a scintillation vial. The solvent was removed in vacuo to afford a yellow solid. Subsequent washing with cold *n*-pentane (2 x 0.5 mL) and drying *in vacuo* yielded **2-Ir.thf** as an yellow solid (28.8 mg). Unreacted [IrCp*$(CO)_2$] was present as an impurity and all attempts to purify this compound further were complicated by its instability..

Method B: In a N_2 filled glovebox, **1** (20 mg, 0.02 mmol) was dissolved in C_6D_6 (0.6 mL) and the solution transferred to a Youngs Tap NMR tube. An external capillary containing a solution of ferrocene in C_6D_6 was added (0.1 M) and an initial ^{1}H NMR spectra recorded. The tube was returned to the glovebox and [IrCp*$(CO)_2$] (8.0 mg, 0.02 mmol) added. The solution turned immediately from colourless to yellow and the reaction was monitored by ^{1}H NMR spectroscopy. After one day, a mixture of **2-Ir.thf** and **3-Ir** was observed in the ^{1}H NMR spectra in approximate 1:3 ratio. Repeat reactions and altering the stoichiometry gave similar results and no interconversion between **2-Ir.thf** and **3-Ir** was observed upon heating to 40 ºC. The tube was returned to the glovebox and the solution decanted into a scintillation vial. The solvent was removed in vacuo to afford a yellow solid. The crude solid was dissolved in *n*-hexane, filtered through a glass-fibre and stored at -35 ºC. Yellow block single crystals of **3-Ir** deposited from the solution and were picked under a microscope for x-ray diffraction analysis. All attempts to separate **2-Ir.thf** and **3-Ir** were unsuccessful.

2-Ir.thf: ^{1}H NMR (400 MHz, C_6D_6) δ: 0.61 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 12H, CH(C**H**$_3$)$_2$), 1.18 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, CH(C**H**$_3$)$_2$), 1.28 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 12H, CH(C**H**$_3$)$_2$), 1.40 (m, 4H, C**H**$_2$ in THF), 1.58 (d, $^3J_{H\text{-}H}$ = 6.7 Hz, 12H, CH(C**H**$_3$)$_2$), 1.66 (s, 12H, NC(C**H**$_3$)), 2.01 (s, 30H, C_5(C**H**$_3$)$_5$), 2.87 (sept, $^3J_{H\text{-}H}$ = 6.8 Hz, 4H,

C**H**$(CH_3)_2$), 3.46 (sept, $^3J_{H\text{-}H}$ = 6.7 Hz, 4H, C**H**$(CH_3)_2$), 3.57 (m, 4H, C**H**$_2$ in THF), 4.71 (s, 2H, $(CH_3)C(CH)C(CH_3)$), 7.00- 7.20 (12H, Ar–**H**), 13.96 (s, 2H, Ir–C**H**O).

^{13}C NMR (101 MHz, C_6D_6) δ: 10.4 (*5x* **C**H_3 in Cp*), 21.4 (*4x* NC(**C**H_3)), 22.7 (*2x* CH(**C**$H_3)_2$), 23.2 (*2x* CH(**C**$H_3)_2$), 23.8 (*2x* CH(**C**$H_3)_2$), 24.7 (*2x* CH(**C**$H_3)_2$), 24.4 (*2x* CH(**C**$H_3)_2$), 25.4 (*2x* CH(**C**$H_3)_2$), 25.5 (*2x* CH(**C**$H_3)_2$), 25.7 (**C**H_2 in THF), 26.8 (*2x* CH(**C**$H_3)_2$), 28.4 (*4x* **C**$H(CH_3)_2$), 29.1 (*4x* **C**$H(CH_3)_2$), 68.0 (**C**H_2 in THF), 94.2 (*2x* $(CH_3)C(CH)C(CH_3)$), 98.0 (*5x* **C**CH_3 in Cp*), 123.4 (*para*-Ar-**C**), 123.6 (*para*-Ar-**C**), 123.8 (*para*-Ar-**C**), 124.0 (*para*-Ar-**C**), 124.6 (*ortho*-Ar-**C**), 124.9 (*ortho*-Ar-**C**), 129.3 (*ortho*-Ar-**C**), 125.7 (*ortho*-Ar-**C**), 124.9 (*meta*-Ar-**C**), 124.6 (*meta*-Ar-**C**), 137.8 (*meta*-Ar-**C**), 136.4 (*meta*-Ar-**C**), 145.6 (*ipso*-Ar-**C**), 142.2 (*ipso*-Ar-**C**), 142.3 (*ipso*-Ar-**C**), 146.9 (*ipso*-Ar-**C**), 165.5 (*4x* N**C**(CH_3)), 193.3 (Ir**C**OCa), 247.0 (Ir**C**HOCa). Certain ^{13}C resonances for Ar–**C** were not observed in the $^{13}C\{^1H\}$ NMR spectra due to overlap with C_6D_6 solvent residual peaks. The formyl carbon resonance assignment was confirmed by the HSQC spectra.

IR (ATR, cm^{-1}), ν_{CO}: 1658 (m, *ν*CHO), 1834 (s, νCO).

3-Ir. Select spectroscopic data from mixture: ^{1}H NMR (400 MHz, C_6D_6) δ: 2.00 (s, 15H, $C_5(CH_3)_5$), 4.74 (s, 2H, $(CH_3)C(CH)C(CH_3)$), 14.98 (s, 2H, Ir{C**H**O}$_2$).$^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6) δ: 203.0 (s, 2H, Ir{**C**HO}$_2$).

Crystal data for **3-Ir**: $C_{70}H_{99}Ca_2IrN_4O_2{\cdot}1.5(C_6H_{14})$, M = 1430.14, monoclinic, $P2_1/n$ (no. 14), a = 14.2170(3), b = 14.8985(3), c = 36.7785(5) Å, β = 97.7586(15)°, V = 7718.8(2) Å^3, Z = 4, D_c = 1.231 g cm^{-3}, μ(Cu-Kα) = 4.844 mm^{-1}, T = 173 K, yellow platy needles, Agilent Xcalibur PX Ultra A diffractometer; 14472 independent measured reflections (R_{int} = 0.0784), F^2 refinement,[6-8] R_1(obs) = 0.0656, wR_2(all) = 0.1684, 8974 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to θ_{full}(67.7°) = 96.2%], 728 parameters. CCDC 2265690. The crystal of **3-Ir** that was studied was found to be severely twinned. Although three components could be identified, the best results were obtained by modelling the crystal as a two-component twin and then only using data from the major component. However, signs of the imperfectly resolved twinning are evident in the final ΔF map, with two residual electron density peaks significantly larger than the rest, at *ca*. 2.58 and 2.34 eÅ^{-3} (the next four are 1.55, 1.24, 1.22 and 1.20 eÅ^{-3}). These peaks both sit *ca*. 1 Å away from the iridium centre and are almost diametrically opposite to each other, subtending an angle of *ca*. 179° at the metal atom. Whilst this is a pattern often seen around highly absorbing atoms, the peaks are somewhat larger than typically seen around a third-row transition metal atom, likely a result of a combination of both absorption and the imperfectly resolved twinning. The included solvent was found to be highly disordered, and the best approach to

handling this diffuse electron density was found to be the SQUEEZE routine of PLATON.[9] This suggested a total of 319 electrons per unit cell, equivalent to 79.8 electrons per complex. Before the use of SQUEEZE the solvent most resembled hexane (C_6H_{14}, 50 electrons), and 1.5 hexane molecules corresponds to 75 electrons, so this was used as the solvent present. As a result, the atom list for the asymmetric unit is low by $1.5(C_6H_{14}) = C_9H_{21}$ (and that for the unit cell low by $C_{36}H_{84}$) compared to what is presumed to be present.

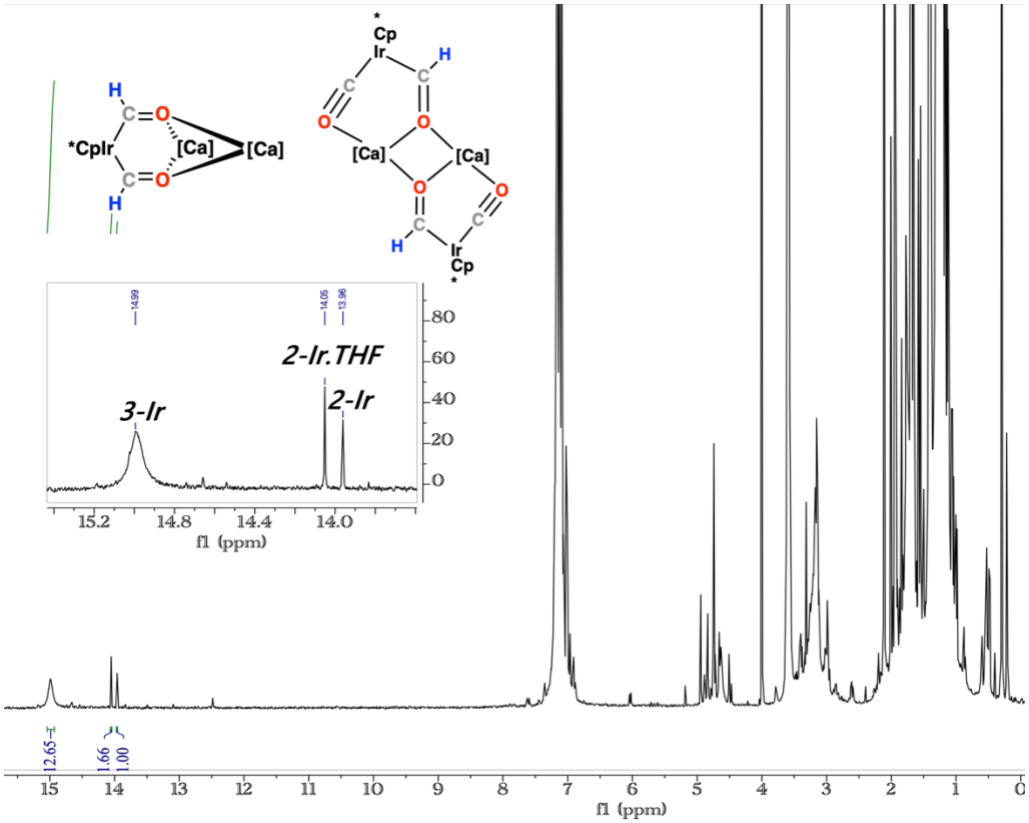


Figure S5. ^{1}H NMR spectra for a **2-Ir.thf** and **3-Ir** mixture from reaction of **1** and [IrCp*$(CO)_2$] in C_6D_6 solution.

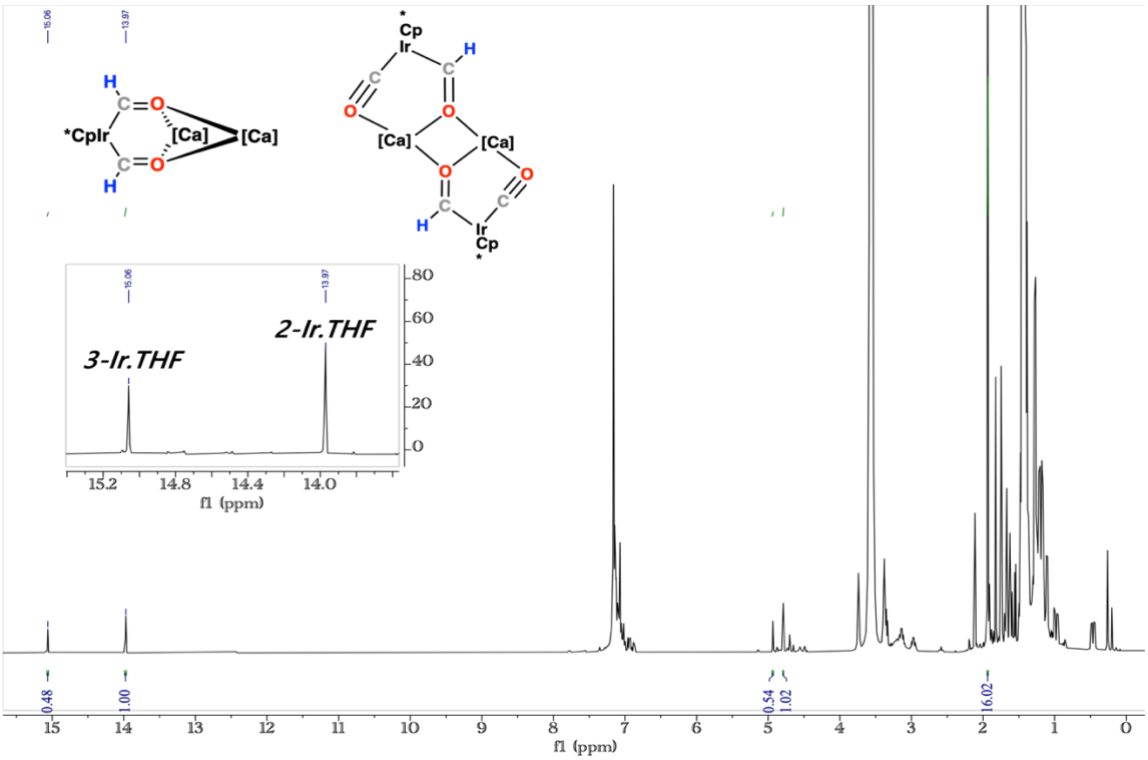


Figure S6. ^{1}H NMR spectra for a **2-Ir.thf** and **3-Ir.thf** mixture from reaction of **1** and [IrCp*(CO)$_2$] in C_6D_6 solution with THF (0.1 mL) added.

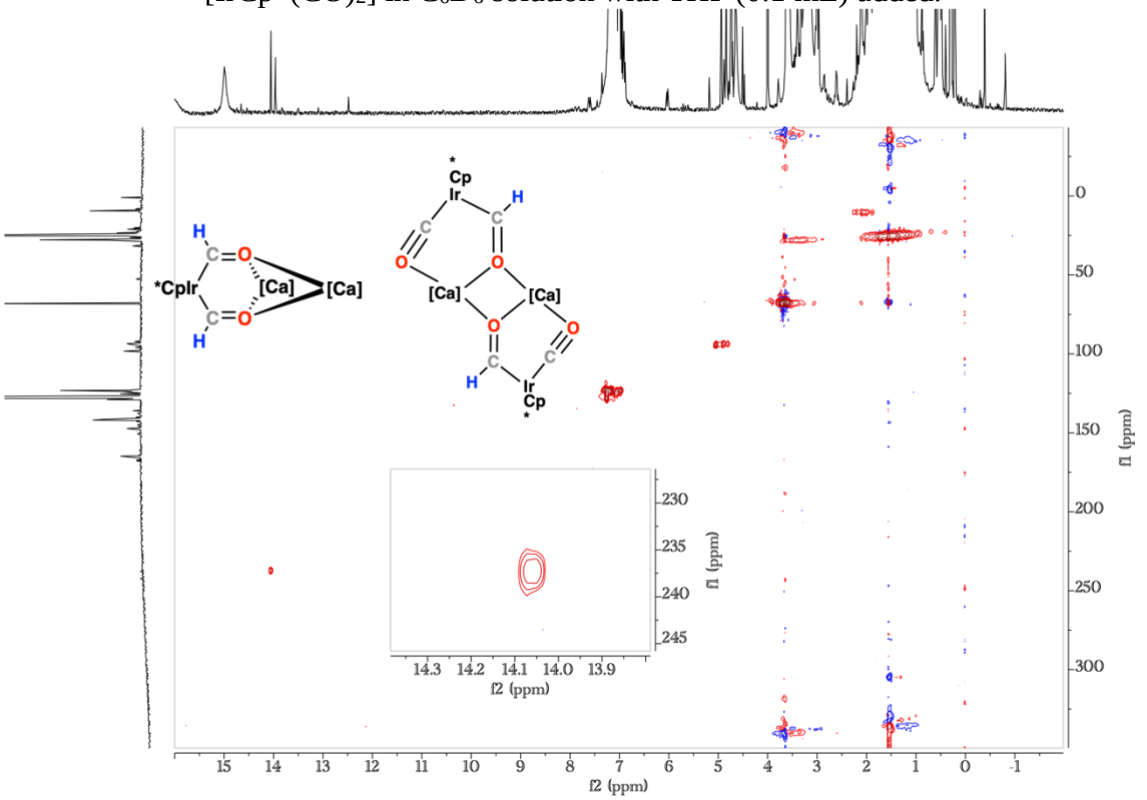


Figure S7. HSQC NMR spectra for a **2-Ir** and **3-Ir** mixture from reaction of **1** and [IrCp*(CO)$_2$] in C_6D_6 solution.

Reaction of **2-Co** with carbon monoxide

In a N_2 filled glovebox, **2-Co** (20 mg, 0.01 mmol) was dissolved in C_6D_6 (0.6 mL) and the solution transferred to a Youngs Tap NMR tube. An external capillary containing a solution of ferrocene in C_6D_6 was added (0.1 M) and an initial ^{1}H NMR spectra recorded. The solution of **2-Co** was frozen, the headspace removed *in vacuo*, and the NMR tube refilled with carbon monoxide gas (1 bar). A ^{1}H NMR spectra was recorded immediately, showing decomposition products only. [CH{C(CH_3)N(Dipp)}$_2$] was the only identifiable product from the ^{1}H NMR spectra (Dipp = 2,6-diisopropylphenyl).

3. X-ray Crystallography

	M–C (formyl)	C–O	O–Ca	C–Ca	Ca---Ca
2-Co (xrd)	1.800(3)	1.301(3)	2.307(2), 2.406(2)	-	3.766(3)
2-Co (dft)	1.801, 1.805	1.290, 1.289	2.384, 2.453, 2.315, 2.418	-	3.725
2-Rh (dft)	1.923	1.283	2.331, 2.407	-	3.742
2-Ir (dft)	1.926	1.289	2.320, 2.395	-	3.728
3-Co (dft)	1.792, 1.793	1.297, 1.300	2.309, 2.328, 2.315, 2.349	2.698, 2.714, 2.690, 2.710	3.601
3-Rh (xrd)	1.910(10), 1.931(8)	1.290(10), 1.280(10),	2.337(6), 2.382(6), 2.334(6), 2.349(6)	2.680(10), 2.720(10), 2.702(9), 2.676(9)	3.632(3)
3-Rh (dft)	1.908, 1.908	1.293, 1.293	2.355, 2.338, 2.303, 2.366	2.742, 2.717, 2.761, 2.708	3.589
3-Ir (xrd)	1.915(7), 1.909(7)	1.299(9), 1.314(9)	2.359(5), 2.316(6), 2.358(5), 2.319(6)	2.696(7), 2.718(9), 2.694(7), 2.724(7)	3.623(2)
3-Ir (dft)	1.916, 1.916	1.300, 1.300	2.345, 2.328, 2.354, 2.292	2.744, 2.719, 2.711, 2.765	3.574

Table S1. Bond lengths for **2** and **3** from single crystal x-ray diffraction (xrd) and density functional theory (dft) calculations (Å). Estimated standard deviation shown in parentheses for experimental data.

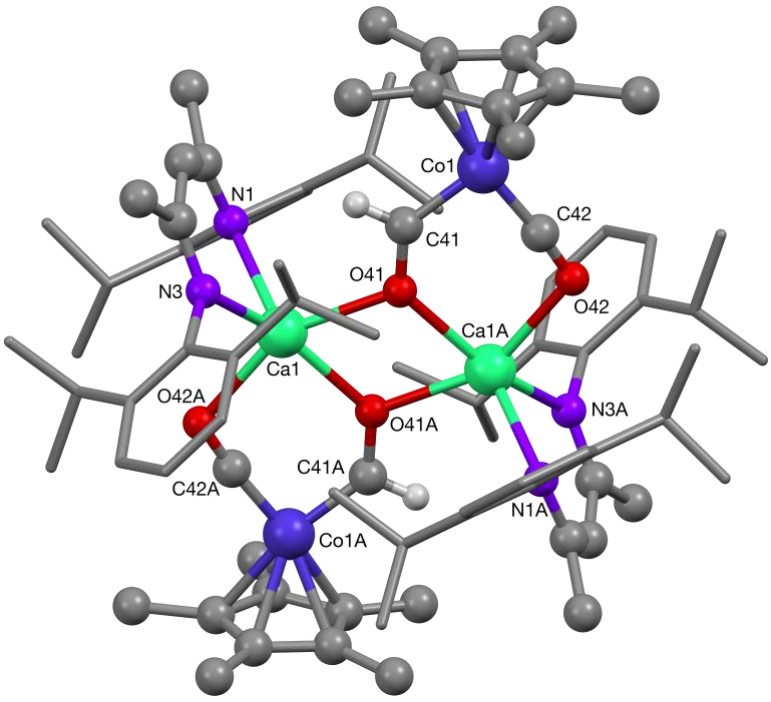


Figure S8. The crystal structure of the C_i-symmetric complex **2-Co**.

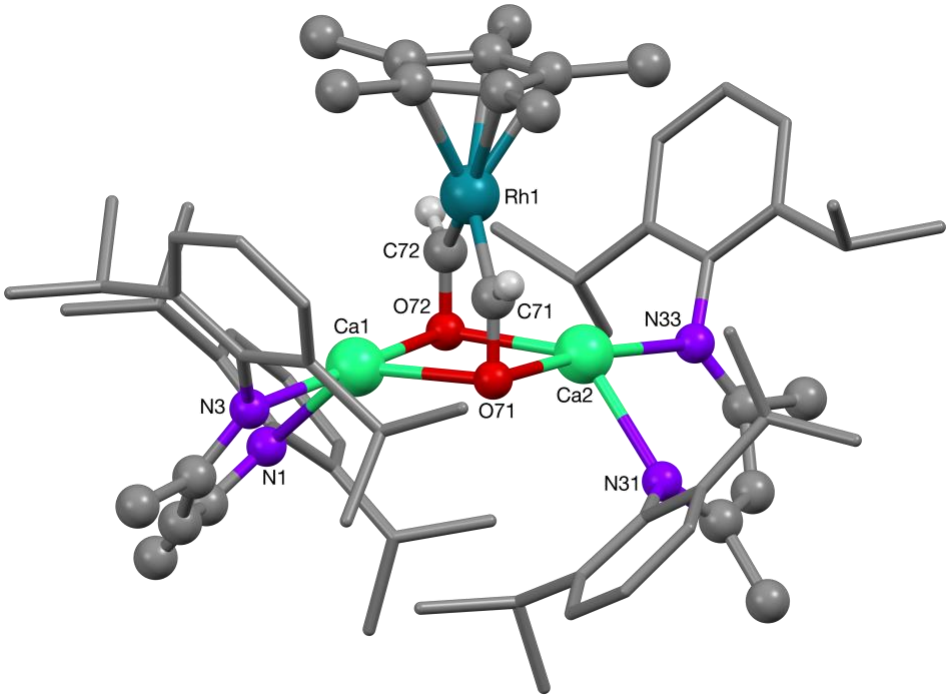


Figure S9. The crystal structure of **3-Rh**.

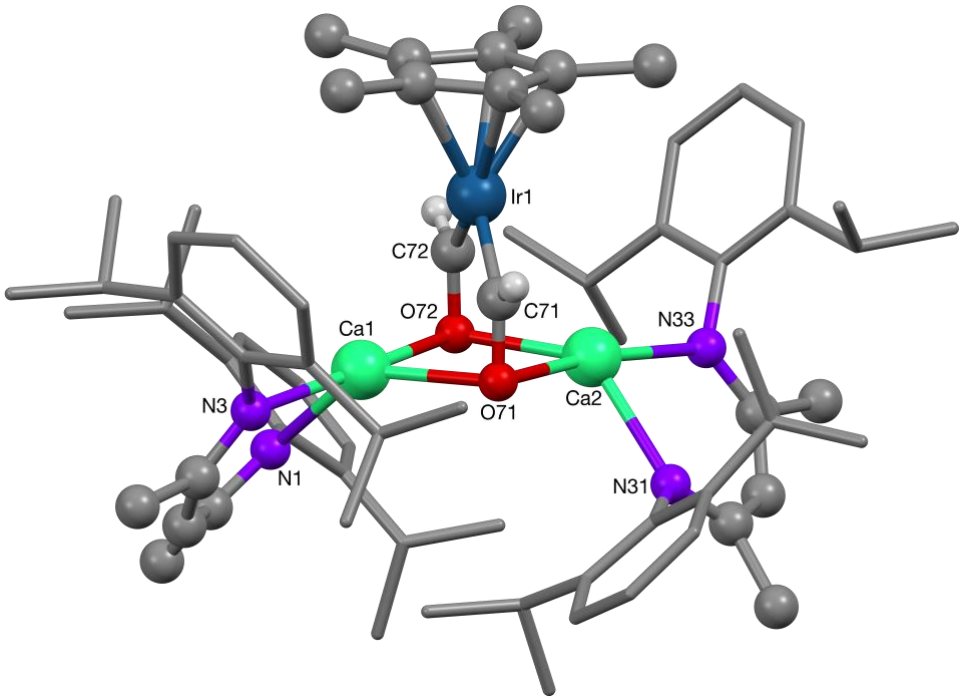


Figure S10. The crystal structure of **3-Ir**.

4. IR spectroscopy

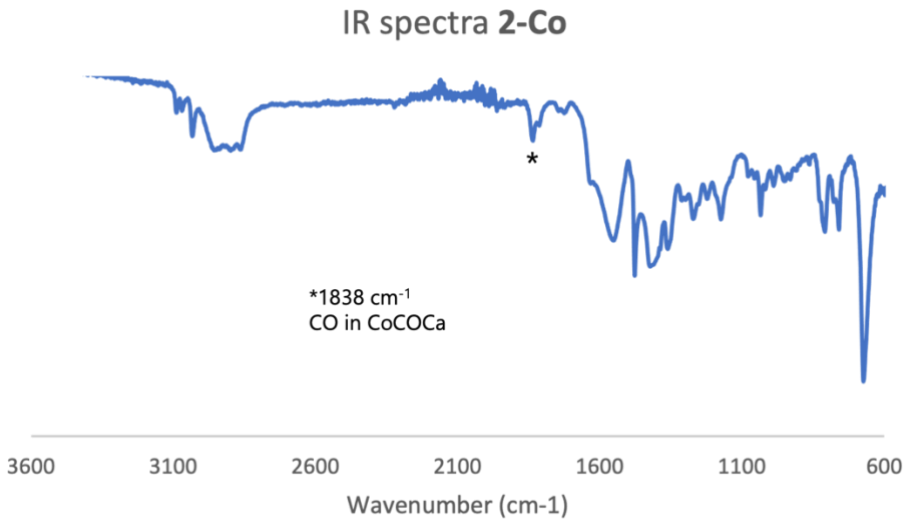


Figure S11. Infrared spectra of **2-Co**.

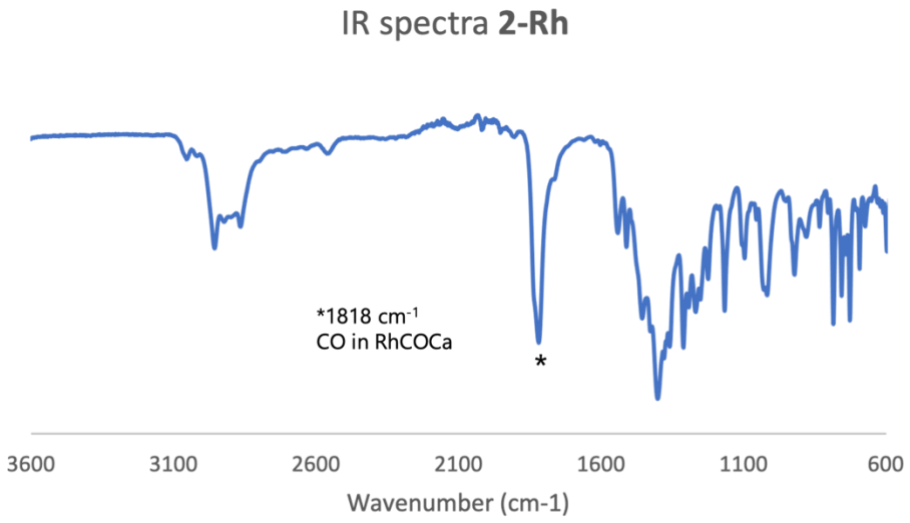


Figure S12. Infrared spectra of **2-Rh**.

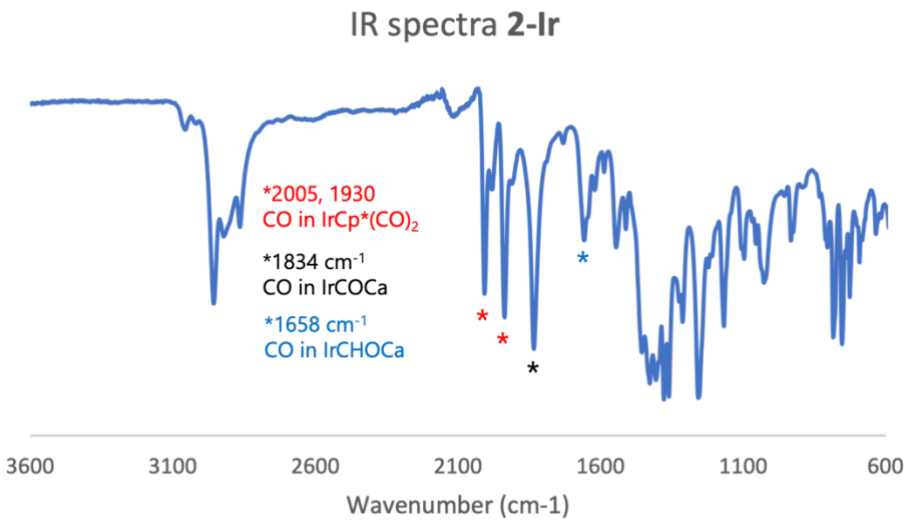


Figure S13. Infrared spectra of **2-Ir**.

5. NMR Spectroscopy

Complete NMR data, including spectra of mixtures, is available as a downloadable .mnova file with this publication.

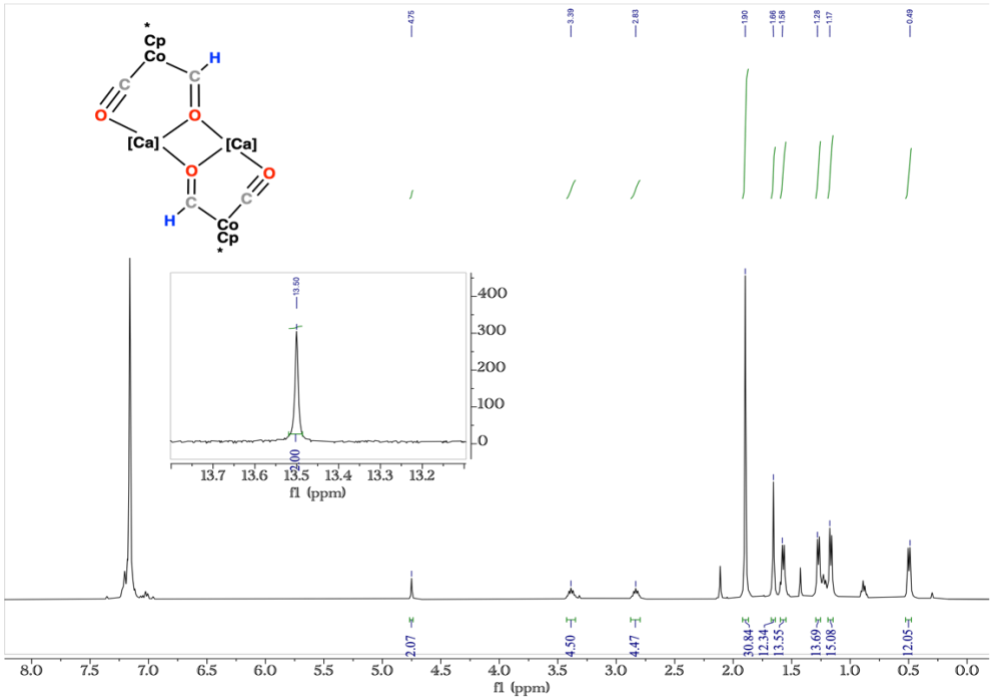


Figure S14. ^{1}H NMR spectra of **2-Co**.

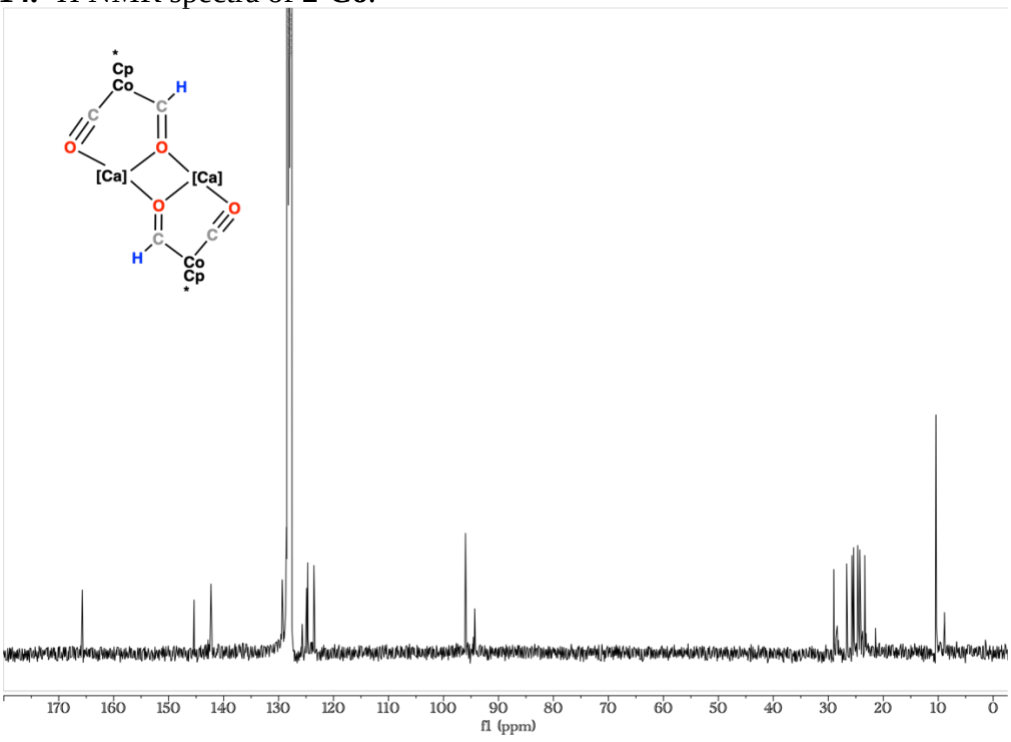


Figure S15. ^{13}C{^{1}H} NMR spectra of **2-Co**.

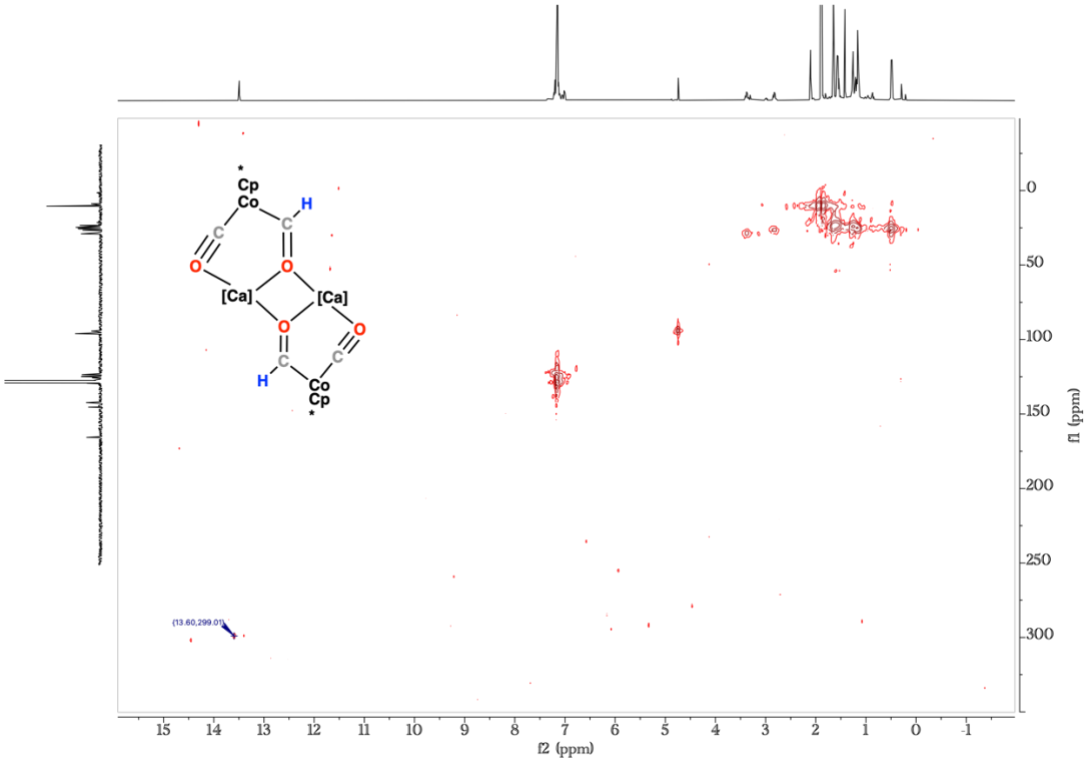


Figure S16. HSQC NMR spectra of **2-Co**.

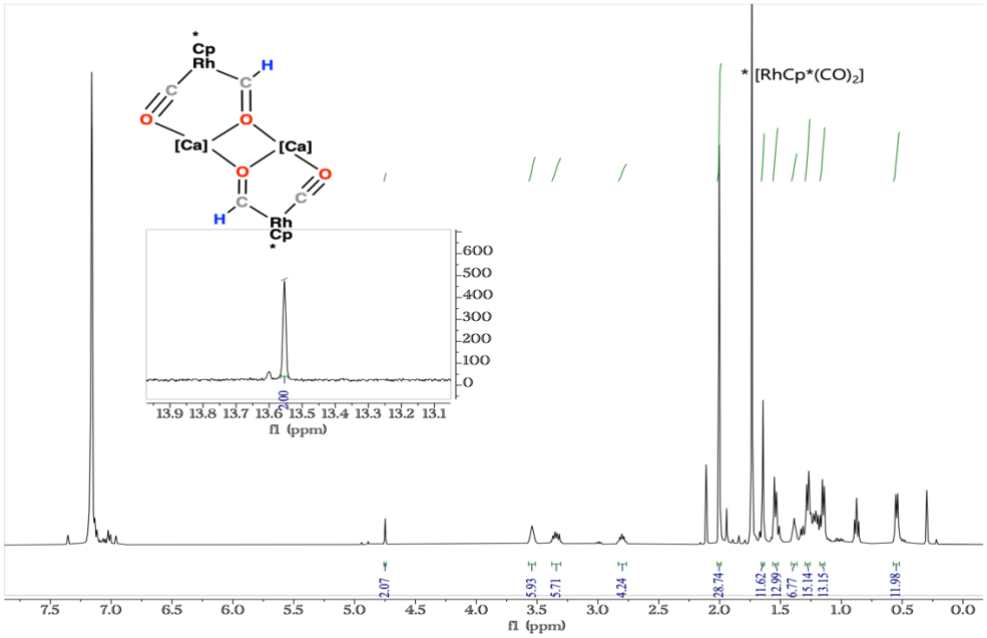


Figure S17. ^{1}H NMR spectra of **2-RhTHF**.

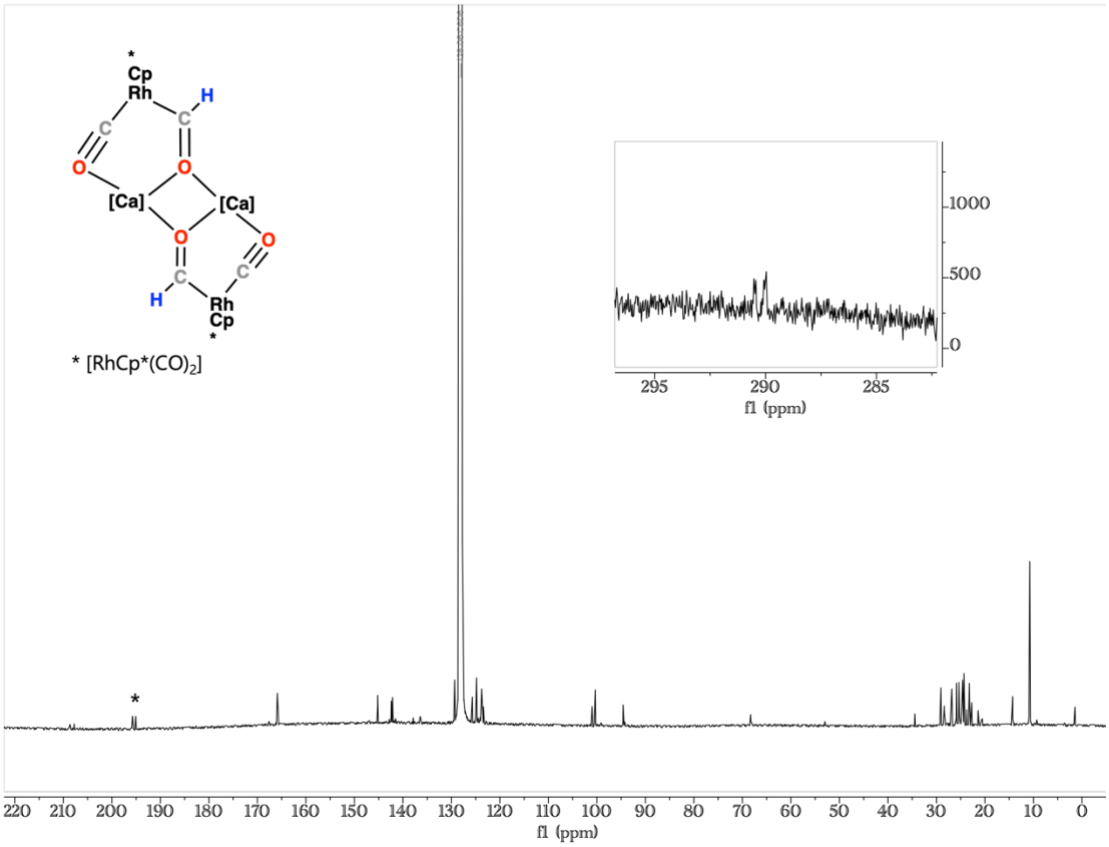


Figure S18. $^{13}C\{^{1}H\}$ NMR spectra of **2-Rh.THF**.

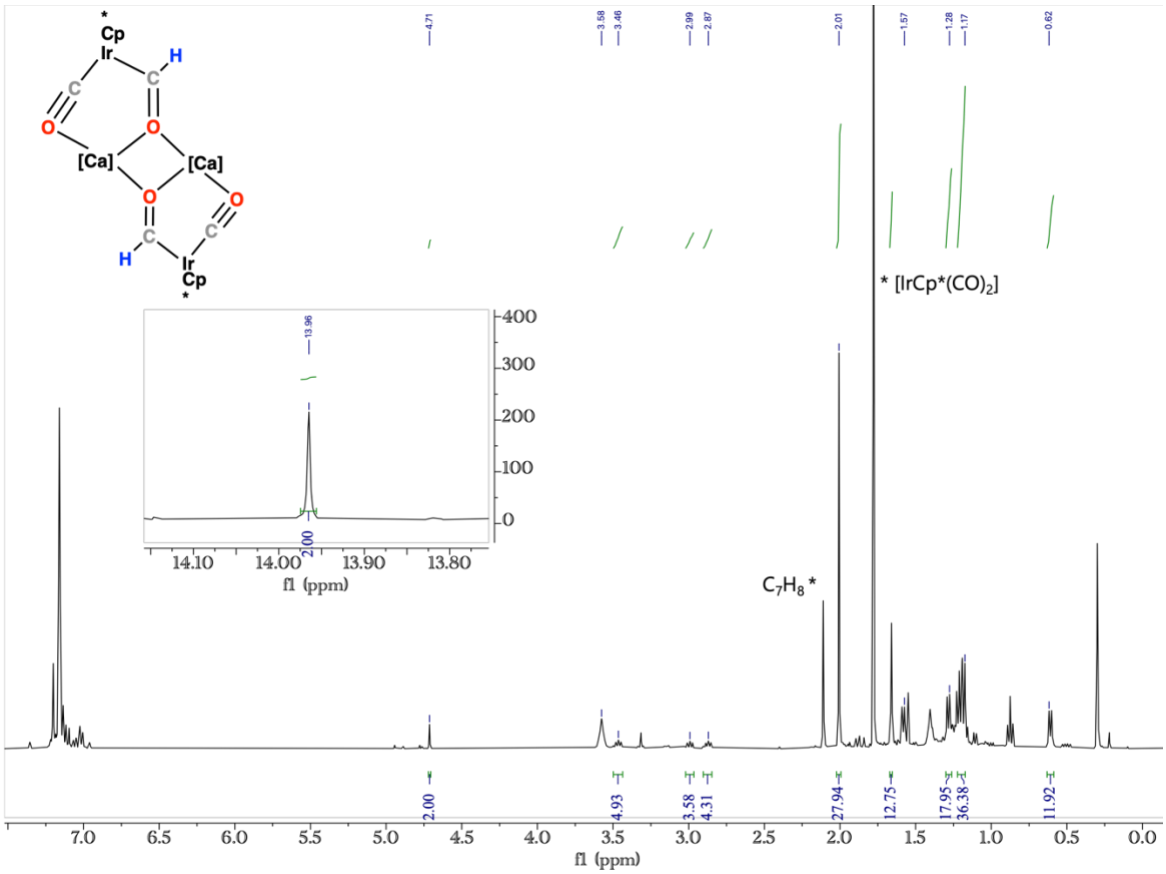


Figure S19. ^{1}H NMR spectra of **2-Ir.THF**.

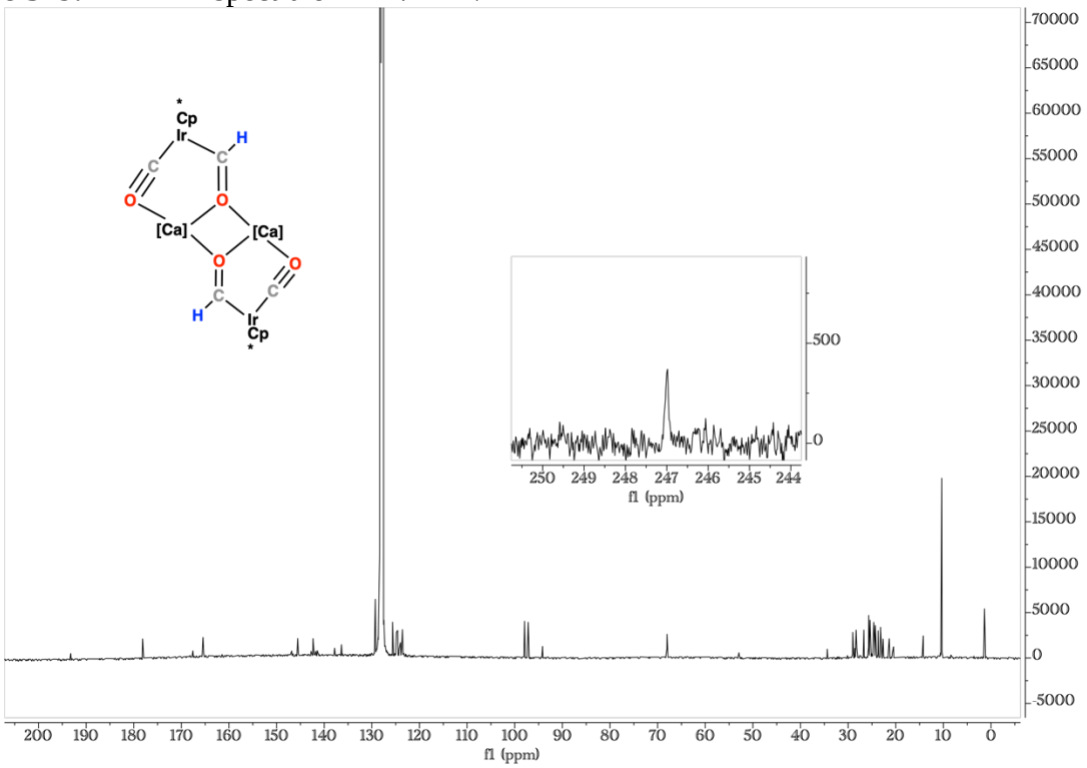


Figure S20. ^{13}C{^{1}H} NMR spectra of **2-Ir.THF**.

6. Computational methods

Density Functional Theory (DFT) calculations were run using Gaussian 09 (Revision D.01)[10] using the ωB97X-D[11] functional and an ultrafine integrations grid (keyword int=ultrafine). Metal atoms (Ca, Co, Rh, Ir) were described with Stuttgart SDDAll RECPs and associated basis sets, while a hybrid basis set was used for the other atoms: 6-31g**(C, H)/ 6-311+g*(N, O).[12-14] The level of theory used has previously been benchmarked in our group and shown to accurately reproduce the experimental results.[15]

Geometry optimisations were performed without symmetry constraints (keyword nosymm). Frequency analyses for all stationary points were performed to confirm their nature of the structures as minima (no imaginary frequency). Single point solvent corrections (benzene, epsilon = 2.2706) were applied using the polarized continuum model (PCM) to free energies.[16] The graphical user interface used to visualise the various properties of compounds **2-3** was GaussView 5.0.9.[17] For comparison, bisanionic analogues of **3** $[MCp^*(CHO)_2]^{2-}$, denoted as **3'**, were calculated.

Natural Bond Orbital analysis was carried out in NBO 6.0.[18-19] NBO analysis for **3** was carried out and the relevant NPA charges and Wiberg Bond Indices tabulated (**Table S2-5**). QTAIM calculations were performed using the AIMAll software (**Table S6-7**).[20-21] Non-covalent interactions were analysed using the NCIPLOT 3.0 program.[22]

ETS-NOCV calculations were performed using DFT as implemented in Orca 4.2.1.[23-24] Optimised geometries of complexes **3** from the Gaussian 09 calculations detailed above were used. Single-point calculations were performed using the ωB97X-D3[25] functional on the relevant fragments. The def2-tzvpp basis set was used for all atoms. Graphical surface representations shown below were plotted using Avogadro 1.2.0.

5.1 Optimised structures.

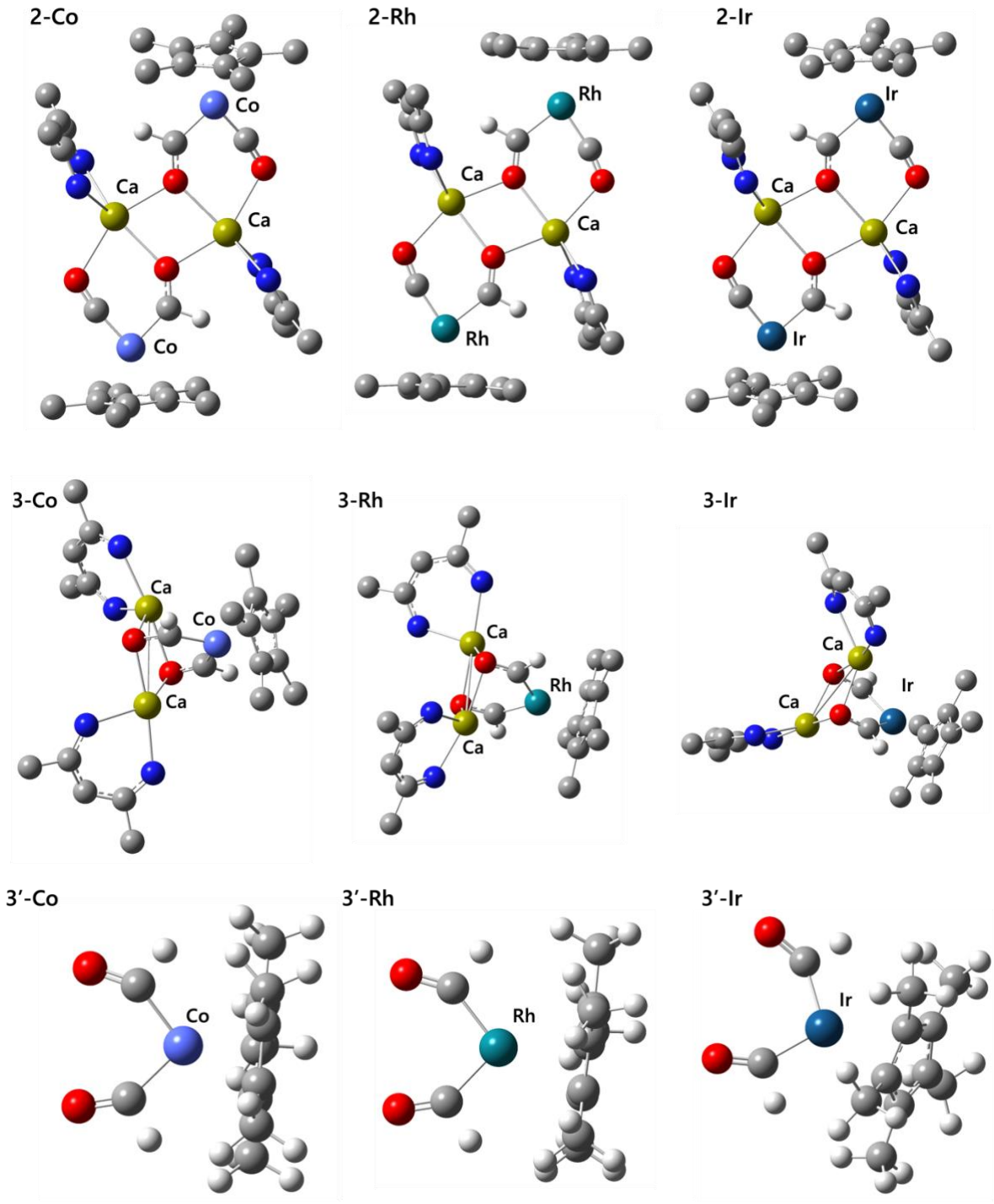
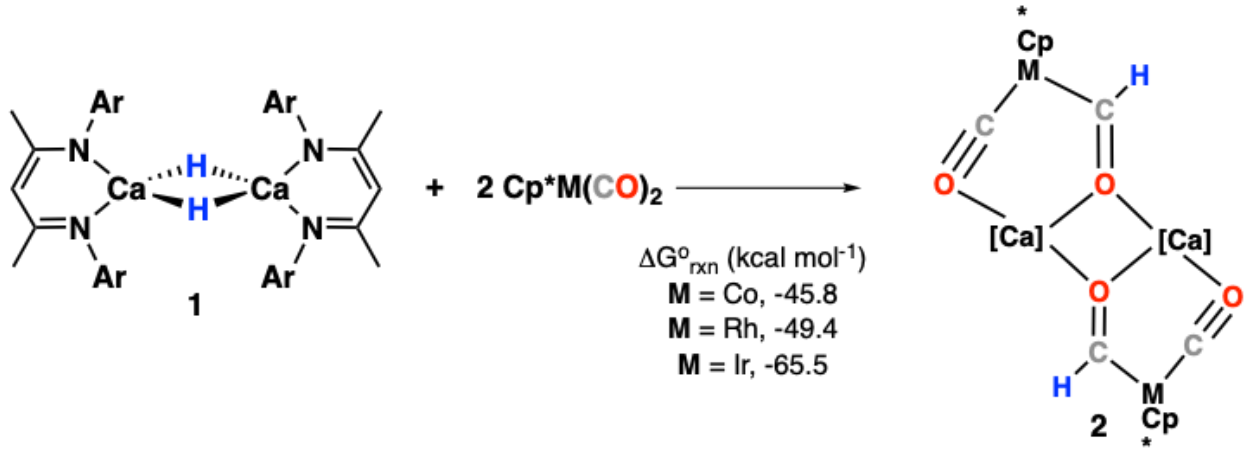
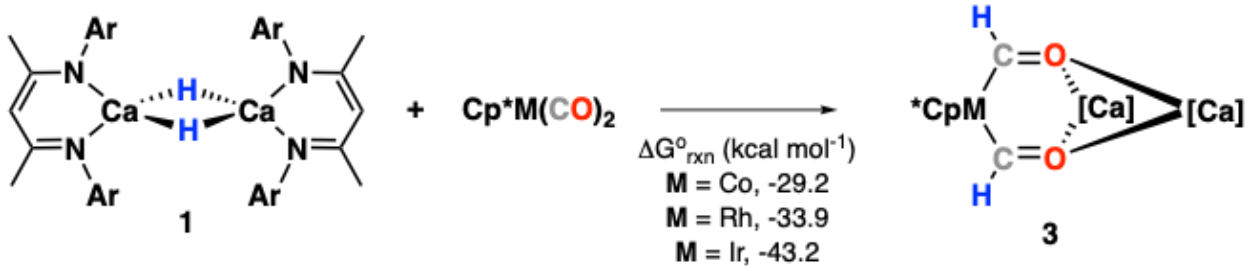


Figure S21. Structures of calculated complexes **2, 3** and **3'**. For clarity, 2,6-diisopropylphenyl units and most hydrogen atoms have been removed.

5.2 Thermodynamics for formation of complexes **2** and **3**.



Scheme S2. Gibbs free energy of reaction for formation of **2** from **1** and two equivalents of [MCp*$(CO)_2$] (M= Co, Rh, Ir; Ar = 2,6-diisopropylphenyl; Cp* = pentamethylcyclopentadienyl). Calculations were performed using the ωB97X-D functional and a hybrid basis set.



Scheme S3. Gibbs free energy of reaction for formation of **3** from **1** and [MCp*$(CO)_2$] (M= Co, Rh, Ir; Ar = 2,6-diisopropylphenyl; Cp* = pentamethylcyclopentadienyl). Calculations were performed using the ωB97X-D functional and a hybrid basis set.

5.3 Frontier molecular orbitals for characterised *bis*(formyl) complexes **3.**

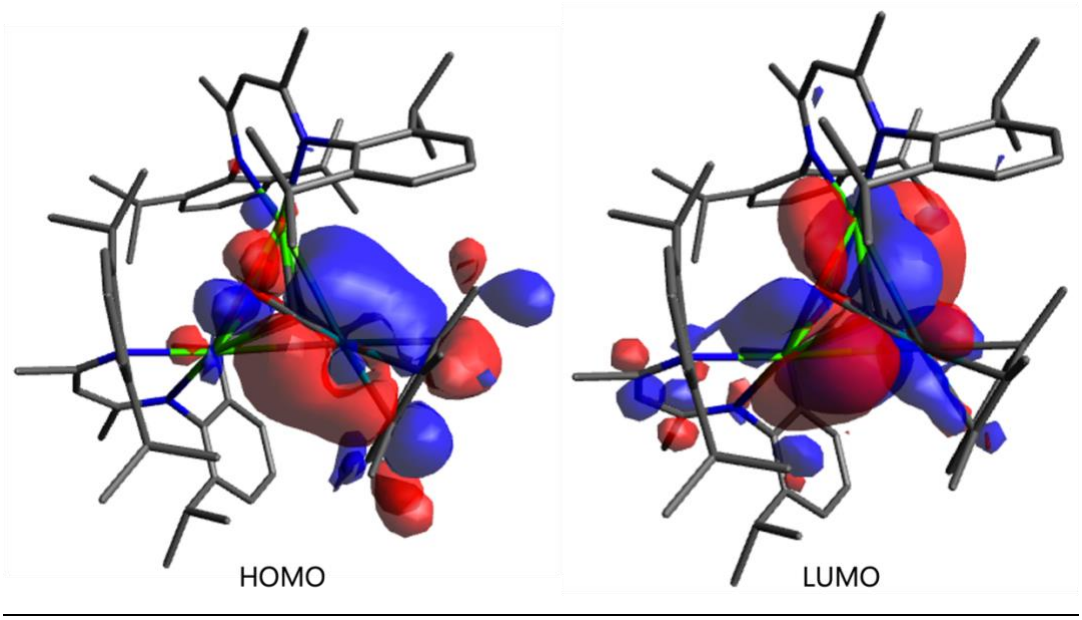


Figure S22. Orbital isosurfaces (isovalue = 0.05) for frontier orbitals on geometry optimized structure of **3-Rh**.

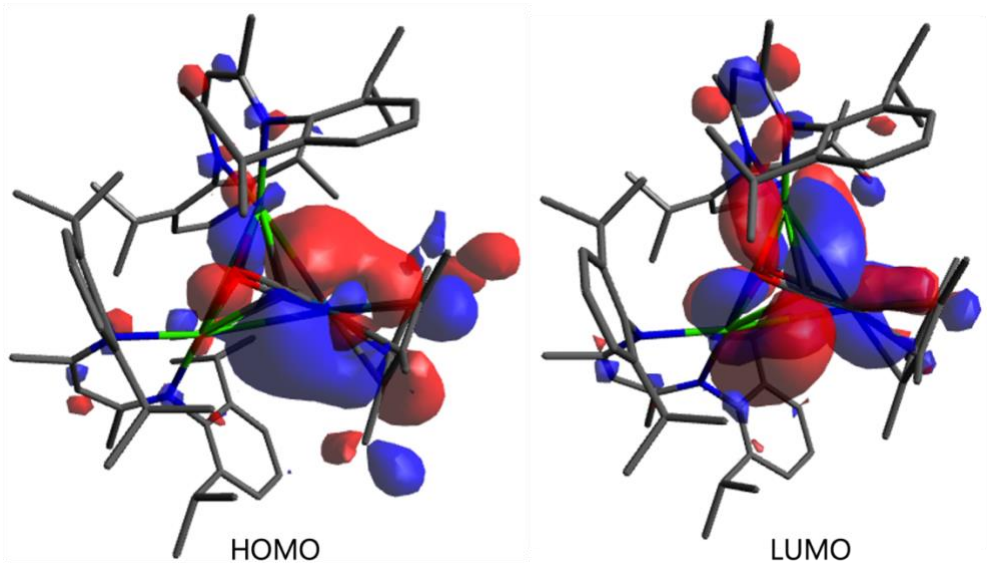


Figure S23. Orbital isosurfaces (isovalue = 0.05) for frontier orbitals on geometry optimized structure of **3-Ir**.

5.4 NBO analysis for complexes **3** and **3'.**

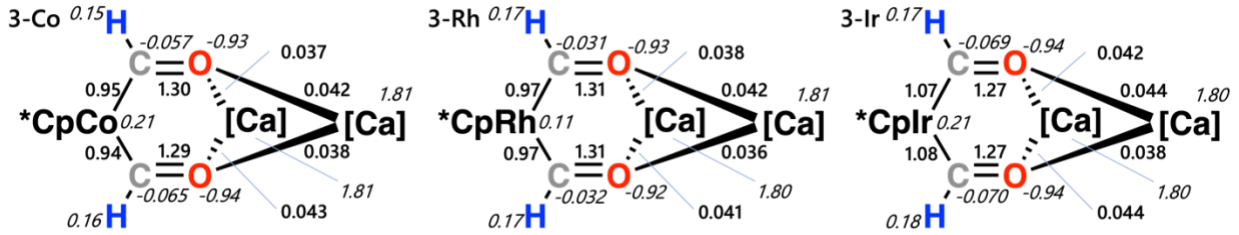


Figure S24. Select *Natural Population Analysis (NPA) charges* and **Wiberg Bond Indices (WBI)** for complexes **3.**

	M	**C**HO	CH**O**	CHO**Ca**
3-Co	0.21	-0.065, -0.057	-0.94, -0.94	1.81, 1.81
3-Rh	0.11	-0.032, -0.031	-0.93, -0.93	1.80, 1.81
3-Ir	0.21	-0.070, -0.070	-0.94, -0.94	1.80, 1.80

Table S2. Natural Population Analysis (NPA) Charges from NBO analysis for complexes **3**.

	M–C	C–O	O–Ca	Ca–Ca
3-Co	0.95, 0.94	1.29, 1.30	0.043, 0.037, 0.038, 0.042	0.00
3-Rh	0.97, 0.97	1.31, 1.31	0.041, 0.038, 0.037, 0.042	0.00
3-Ir	1.08, 1.07	1.27, 1.27	0.042, 0.038, 0.039, 0.044	0.00

Table S3. Wiberg Bond Index (WBI) from NBO analysis for complexes **3**.

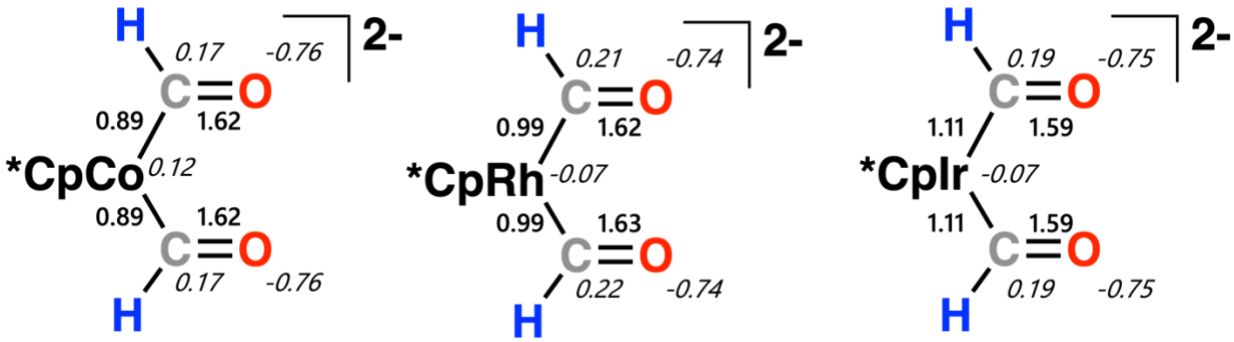


Figure S25. Select *Natural Population Analysis (NPA) charges* and **Wiberg Bond Indices (WBI)** for anionic free bis(formyl) complexes **3'**.

	NPA Charge			**Wiberg Bond Index**	
	M	**C**HO	CH**O**	M–C	C–O
3'-Co	0.12	0.17	-0.76	0.89	1.62
3'-Rh	-0.07	0.21, 0.22	-0.74	0.99	1.62, 1.63
3'-Ir	-0.07	0.19	-0.75	1.11	1.59

Table S4. Natural Population Analysis (NPA) Charges and Wiberg Bond Index (WBI) from NBO analysis for anionic free bis(formyl) complexes **3'**.

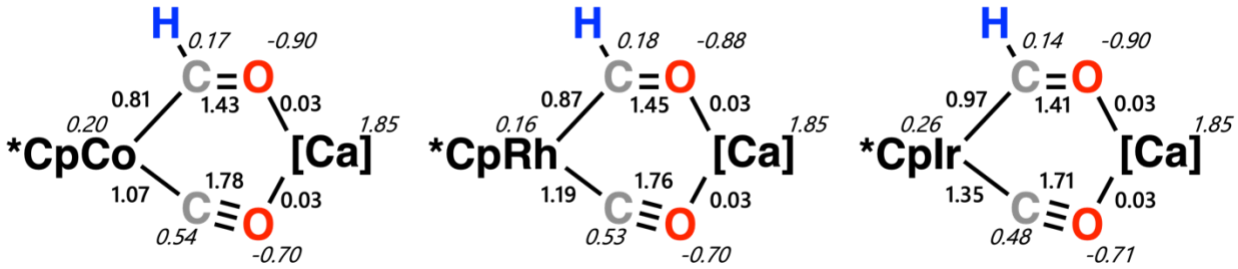


Figure S26. Select *Natural Population Analysis (NPA) charges* and **Wiberg Bond Indices (WBI)** for monomeric monoformyl complexes **2'**.

	NPA Charge						**Wiberg Bond Index**				
	M	**C**HO	CH**O**	**C**O	C**O**	Ca	M–CHO	MCH–O	M–CO	MC–O	O–Ca
2'-Co	0.20	0.17	-0.90	0.54	-0.70	1.85	0.81	1.43	1.07	1.78	0.03
2'-Rh	0.16	0.18	-0.88	0.53	-0.70	1.85	0.87	1.45	1.19	1.76	0.03
2'-Ir	0.26	0.14	-0.90	0.48	-0.71	1.85	0.97	1.41	1.35	1.71	0.03

Table S5. Natural Population Analysis (NPA) Charges and Wiberg Bond Index (WBI) from NBO analysis for monomeric mono(formyl) complexes **2'**.

5.5 QTAIM analysis for complexes **3.**

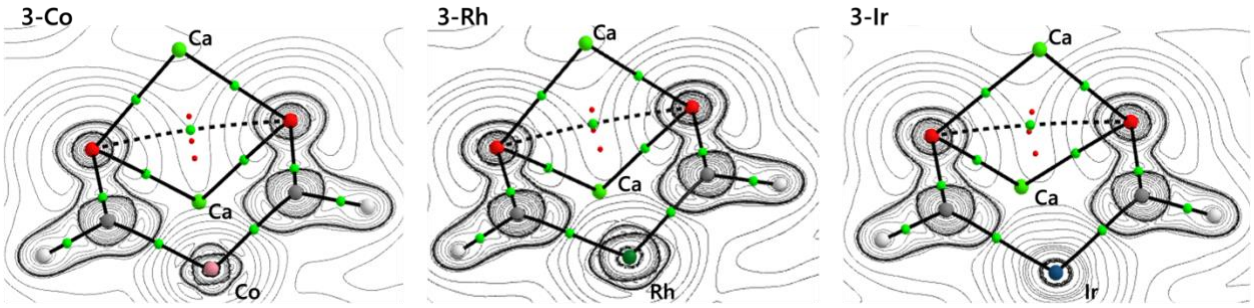


Figure S27. QTAIM contour plots of ρ for **3**. Bond critical points (ρ) are shown as green dots, ring critical points as red dots. Carbon, oxygen, and hydrogen atoms are in grey, red, and white respectively. QTAIM charges are tabulated below.

	M	**C**HO	CH**O**	CHO**Ca**
3-Co	0.52	0.38, 0.41	-1.30, -1.31	1.61, 1.62
3-Rh	0.28	0.47. 0.48	-1.30, -1.30	1.60, 1.61
3-Ir	0.31	0.45, 0.44	-1.30, -1.30	1.66, 1.61

Table S6. QTAIM charges for complexes **3**.

	Bond ρ (del ρ squared)		
	M–C	C–O	O–Ca
3-Co	0.159 (0.350)	0.331 (-0.172)	0.0401 (0.211)
3-Rh	0.163 (0.311)	0.336 (-0.171)	0.0367 (0.188)
3-Ir	0.177 (0.285)	0.333 (-0.244)	0.0428 (0.222)

Table S7. QTAIM data for bond critical points for complexes **3**. All values in units of e bohr^{-3} (ρ) and e bohr^{-5} (del ρ squared).

5.6 ETS-NOCV analysis for complexes **3.**

ETS-NOCV calculations were performed on complexes **2'** and **3** to give insight into bonding. Two sets of calculations with different fragment splitting were conducted: (i) fragmentation between the M–C bonds; (ii) fragmentation between the anionic metal bis-formyl and cationic $[Ca]_2$ unit.

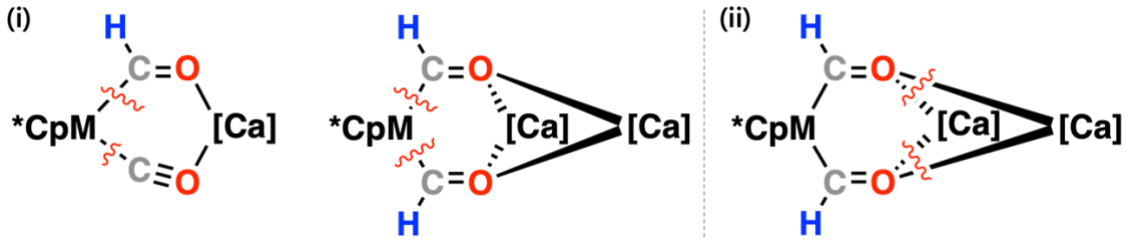


Figure S28. Splitting of fragments for ETS-NOCV calculations for complexes **2'** and **3**.

Splitting	ΔE_{ORB}	$\Delta\rho 1$	$\Delta\rho 2$	$\Delta\rho 3$	$\Delta\rho 4$
2'-Co (i)	-198.3	-68.1(34)	-63.9 (32)	-27.6 (14)	-21.4 (11)
2'-Rh (i)	-270.5	-82.2 (30)	-60.5 (22)	-42.4 (16)	-31.9 (12)
2'-Ir (i)	-442.7	-132.7 (30)	-105.9 (24)	-73.6 (17)	-55.4 (13)
3-Co (i)	-347.5	-258.9 (75)	-40.1 (12)	-24.8 (7)	-12.0 (3)
3-Co (ii)	-189.0	-24.5 (13)	-19.0 (10)	-13.4 (7)	-13.3 (7)
3-Rh (i)	-412.0	-270.8 (66)	-35.5 (9)	-31.8 (8)	-14.9 (4)
3-Rh (ii)	-184.1	-23.6 (13)	-18.8 (10)	-13.2 (7)	-13.1 (7)
3-Ir (i)	-1057.7	-739.9 (70)	-108.8 (10)	-67.6 (6)	-62.5 (6)
3-Ir (ii)	-192.1	-23.8 (12)	-18.9 (10)	-14.2 (7)	-13.7 (7)

Table S8. Summary of ETS-NOCV data for complexes **2'** and **3**. All values in kcal mol^{-1}. Percentage contribution of $\Delta\rho_X$ to ΔE_{ORB} shown in brackets.

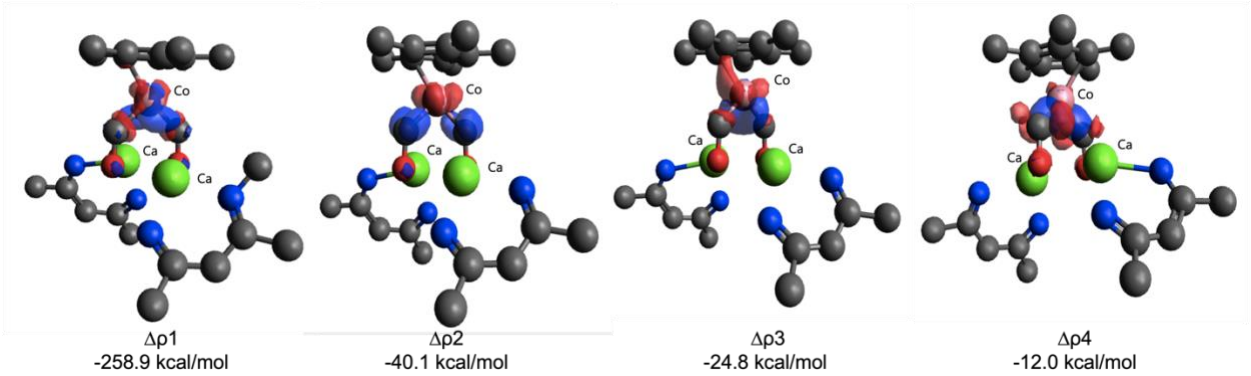


Figure S29. Selected deformation density data for complex **3-Co** with splitting (i). Charge flow is from red to blue. Diisopropylphenyl groups omitted for clarity.

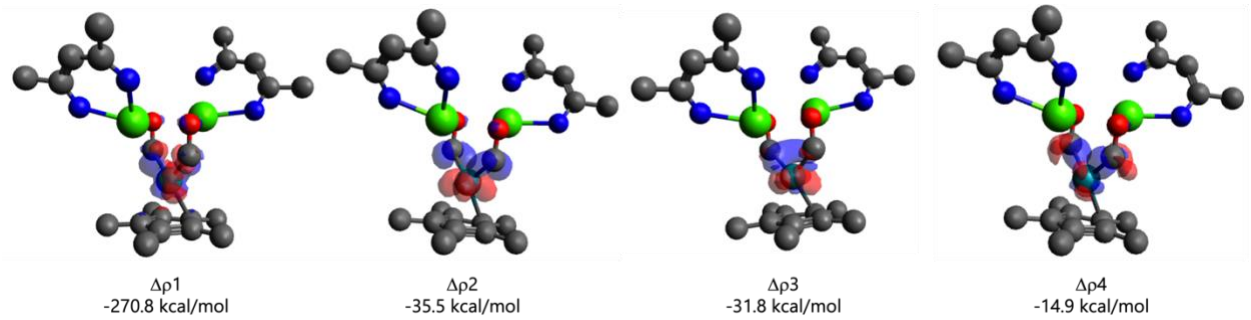


Figure S30. Selected deformation density data for complex **3-Rh** with splitting (i). Charge flow is from red to blue. Diisopropylphenyl groups omitted for clarity.

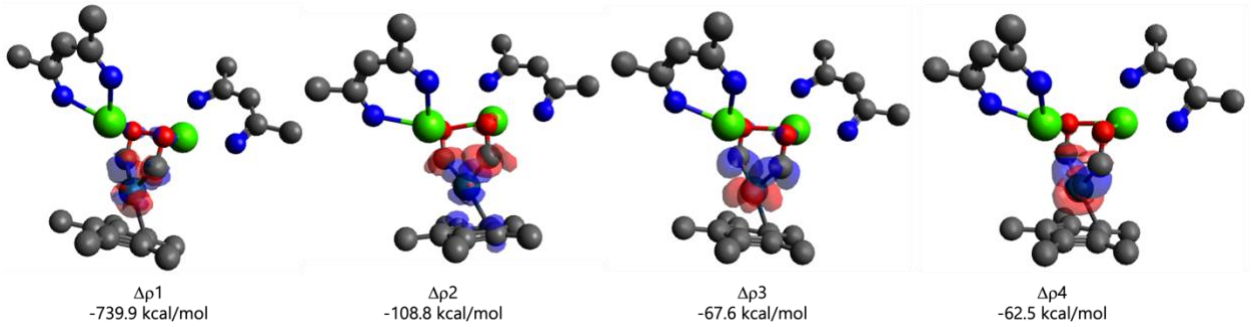


Figure S31. Selected deformation density data for complex **3-Ir** with splitting (i). Charge flow is from red to blue. Diisopropylphenyl groups omitted for clarity. Δρ2 for **3-Ir**, further splitting of the metal-based d-orbitals (due to overlap with ligand SALCs of CO) results in both ρ1 and ρ2 interactions being s-donation from the HOMO of $\{CHO\}^-$ to empty orbitals on the Ir fragment. ρ3 is π-backdonation.

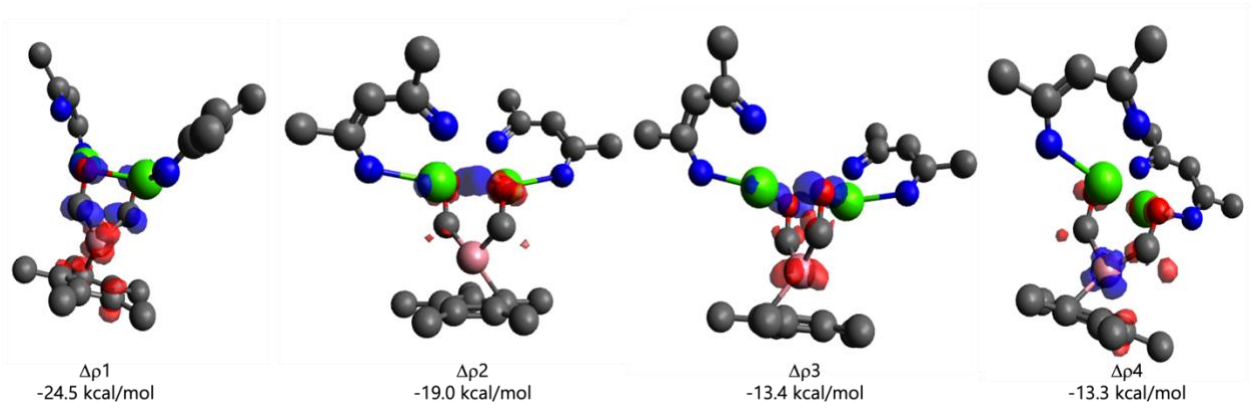


Figure S32. Selected deformation density data for complex **3-Co** with splitting (ii). Charge flow is from red to blue. Diisopropylphenyl groups omitted for clarity.

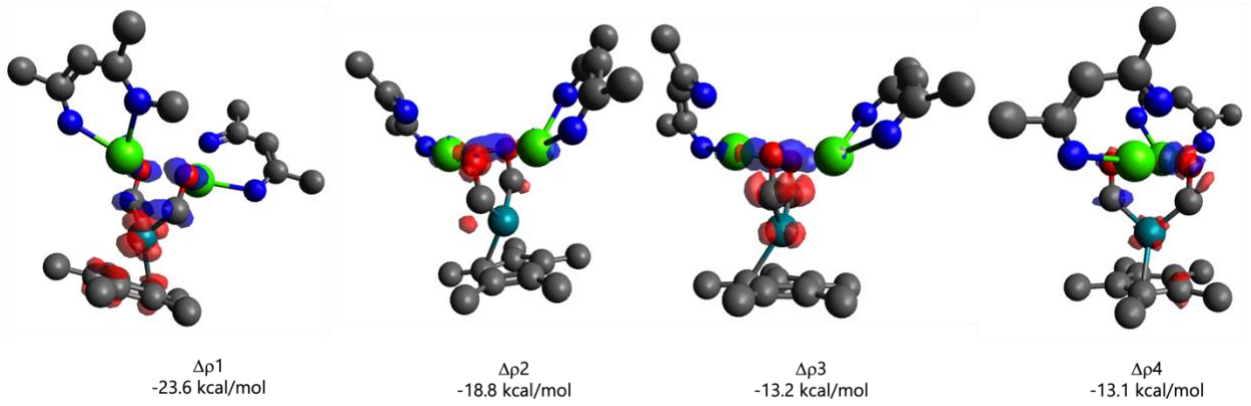


Figure S33. Selected deformation density data for complex **3-Rh** with splitting (ii). Charge flow is from red to blue. Diisopropylphenyl groups omitted for clarity.

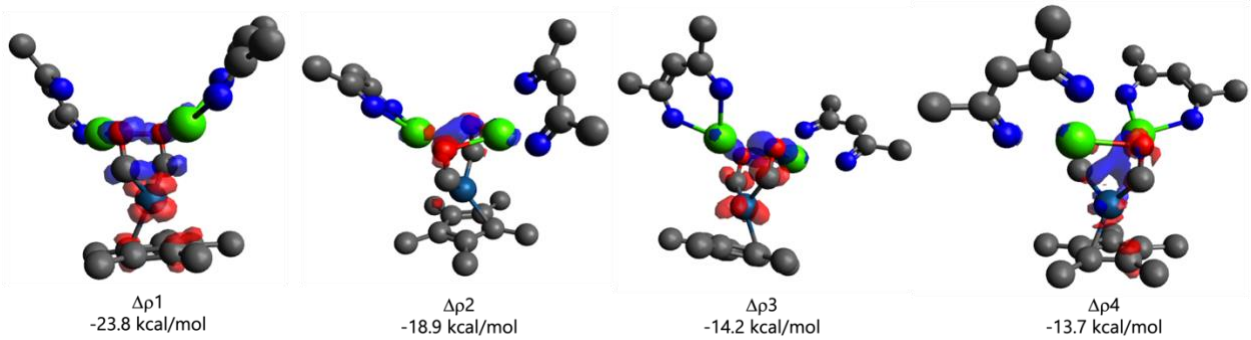


Figure S34. Selected deformation density data for complex **3-Ir** with splitting (ii). Charge flow is from red to blue. Diisopropylphenyl groups omitted for clarity.

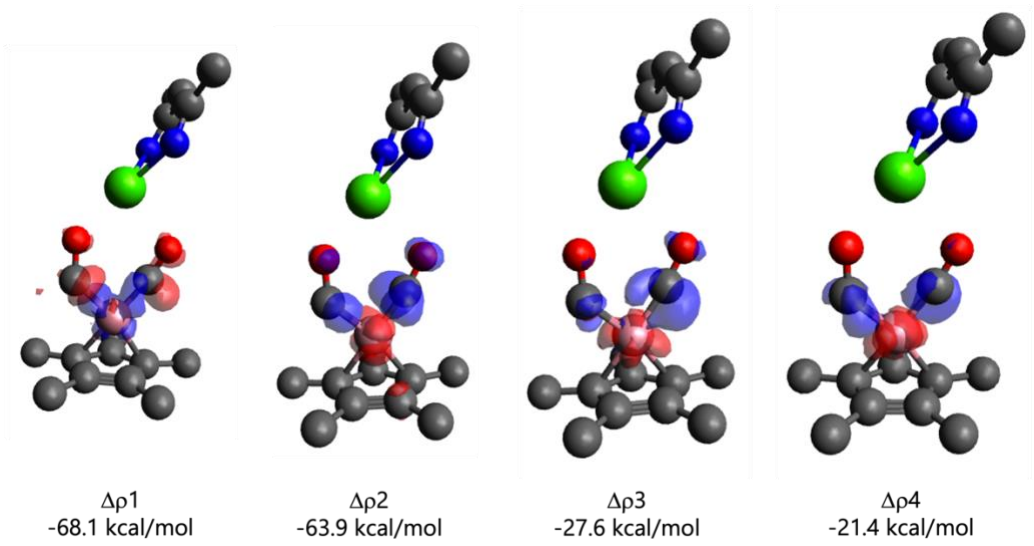


Figure S35. Selected deformation density data for complex **2'-Co** with splitting (i). Charge flow is from red to blue. Diisopropylphenyl groups omitted for clarity.

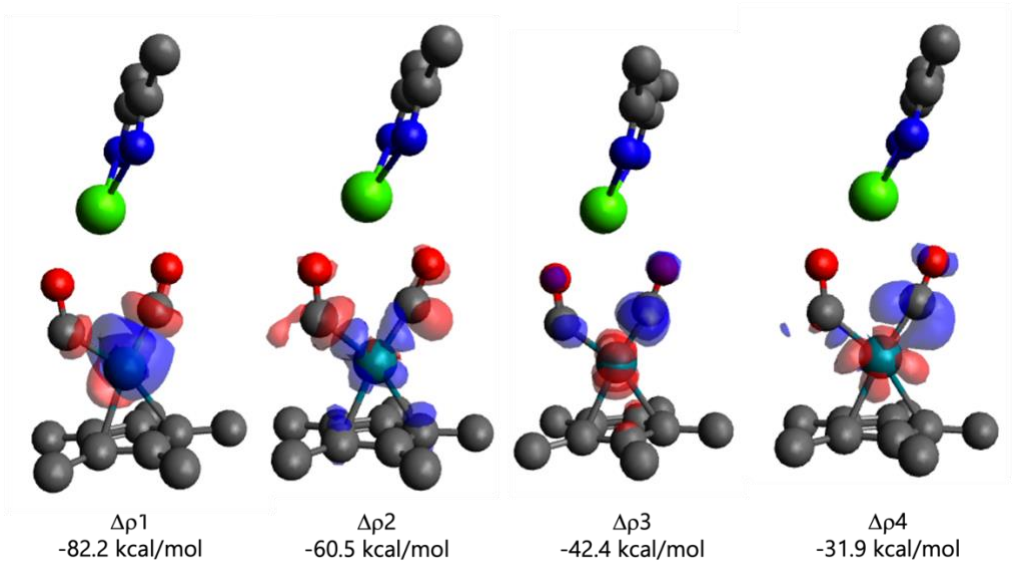


Figure S36. Selected deformation density data for complex **2'-Rh** with splitting (i). Charge flow is from red to blue. Diisopropylphenyl groups omitted for clarity.

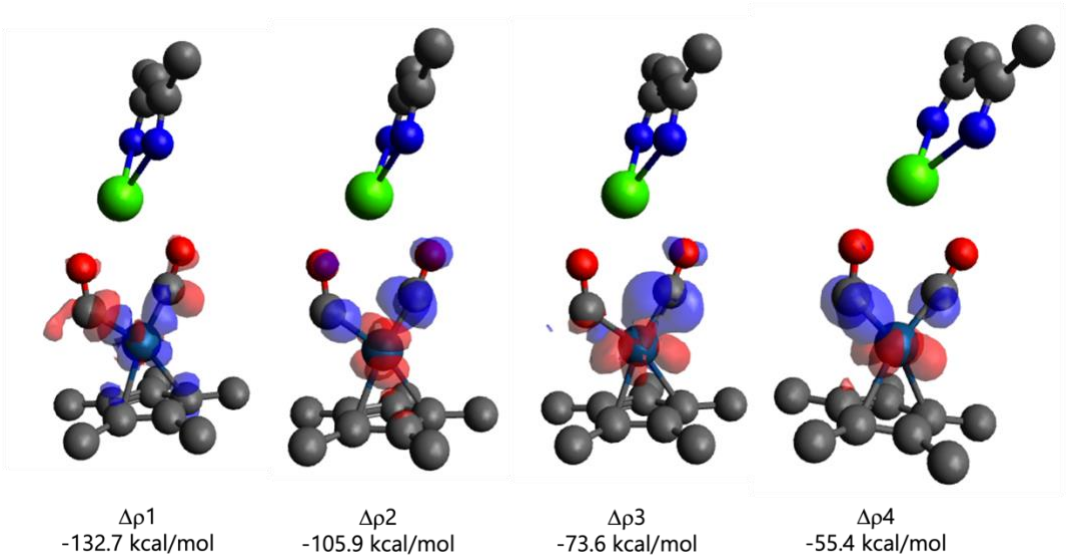


Figure S37. Selected deformation density data for complex **2'-Ir** with splitting (i). Charge flow is from red to blue. Diisopropylphenyl groups omitted for clarity.

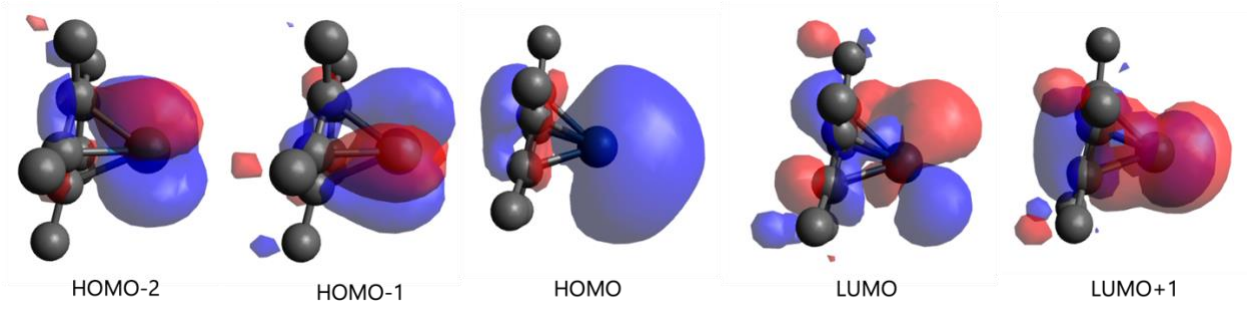


Figure S38. Orbital isosurfaces (isovalue = 0.02) for frontier orbitals on neutral singlet complex [IrCp*].

5.7 NCI plots for complexes **3'.**

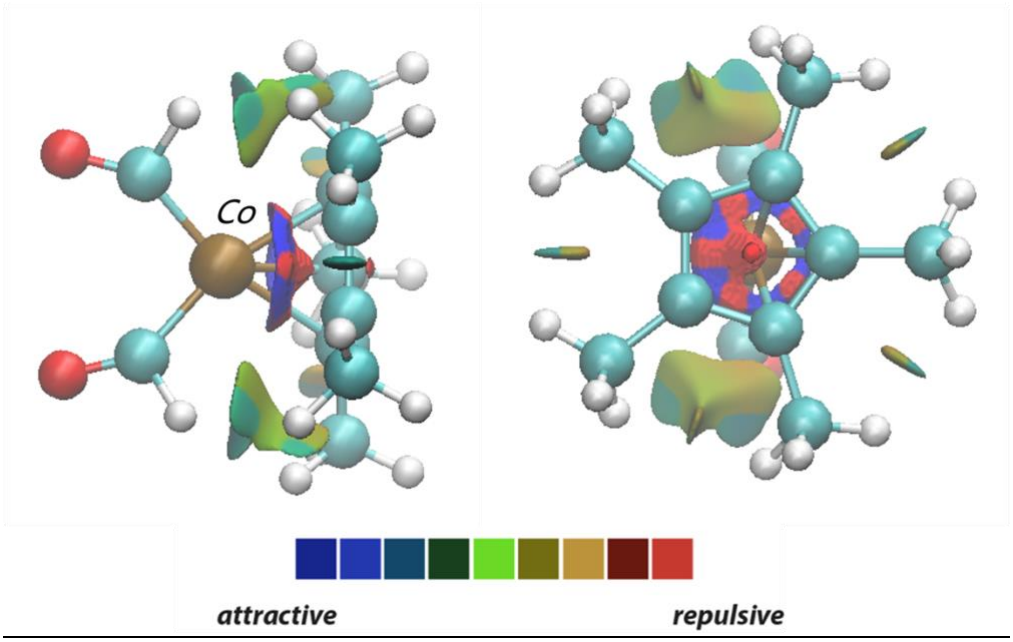


Figure S39. NCI plot for **3'-Co**.

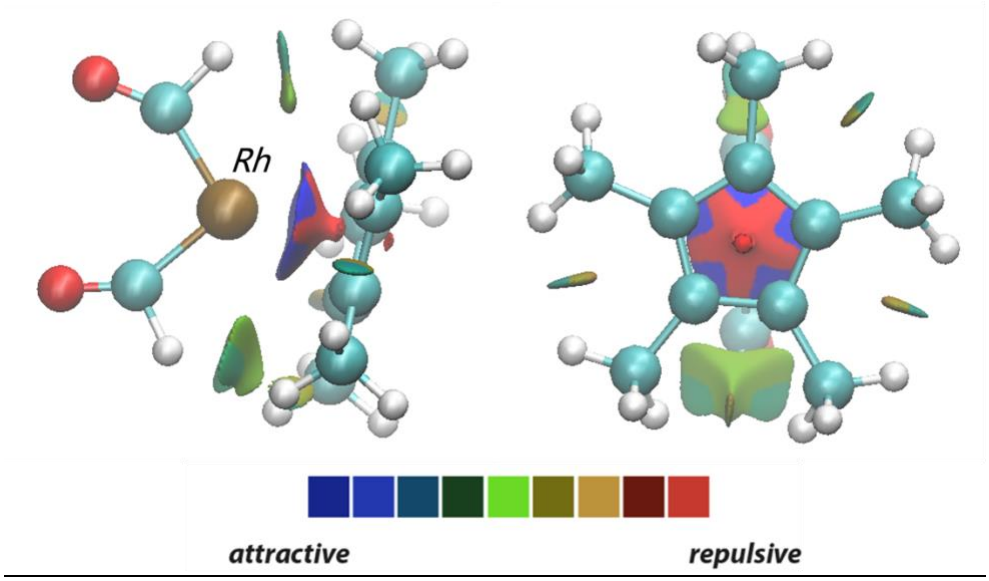


Figure S40. NCI plot for **3'-Rh**.

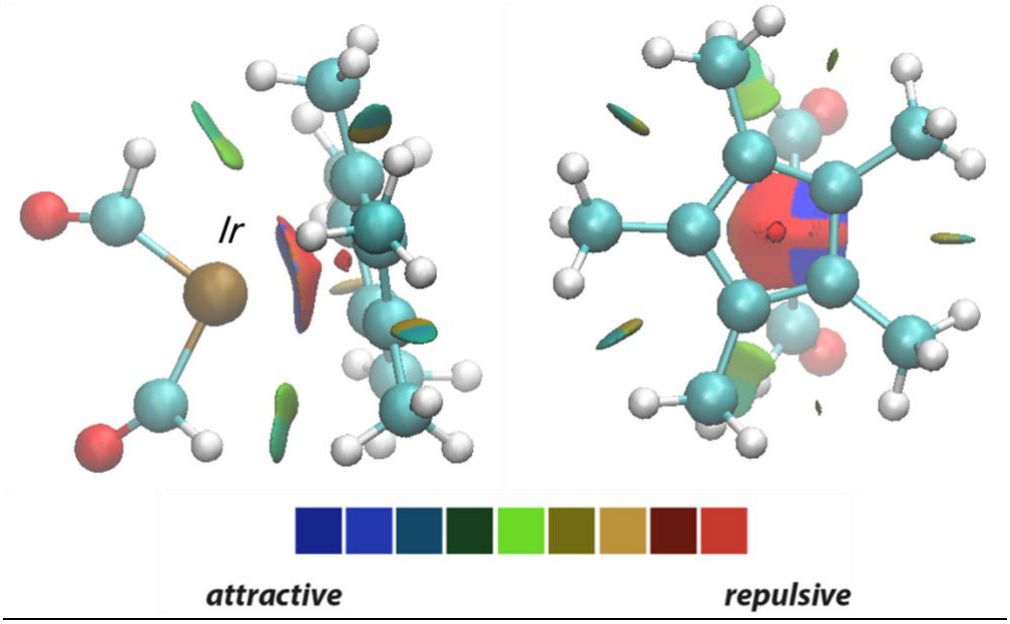


Figure S41. NCI plot for **3'-Ir**.

5.8 Computational coordinates.

2-Co.log

SCF (wB97x) = -4078.31481297
E(SCF)+ZPE(0 K)= -4076.512474
H(298 K)= -4076.403955
G(298 K)= -4076.652490
Lowest Frequency = 10.9614cm-1

Ca	8.420022	5.929853	7.842387
Co	11.172451	9.898383	8.859625
N	7.531505	7.219310	6.132682
C	8.127594	7.799584	5.104918
C	9.430423	7.490250	4.671653
H	9.771257	8.040495	3.801836
C	10.301049	6.463517	5.106737
N	10.110750	5.730904	6.186534
C	7.399447	8.878355	4.325243
H	6.347944	8.623749	4.175222
H	7.866346	9.054186	3.355178
H	7.423681	9.817454	4.888868
C	11.527447	6.251183	4.238264
H	12.339427	6.897429	4.588635
H	11.319258	6.511439	3.199152
H	11.883933	5.220470	4.283572
C	6.159046	7.455047	6.412490
C	5.215784	6.490104	5.984203
C	3.879269	6.658780	6.343656
H	3.142483	5.929457	6.022760
C	3.471289	7.743536	7.110899
H	2.427113	7.854202	7.386544
C	4.405354	8.679217	7.528819
H	4.083195	9.516704	8.141315
C	5.755312	8.556024	7.195923
C	5.650164	5.313038	5.120456
H	6.672307	5.057427	5.414833
C	4.785948	4.062715	5.310206
H	4.660812	3.815339	6.367379
H	5.260570	3.209323	4.815145
H	3.792753	4.182259	4.862875
C	5.701470	5.694528	3.633187
H	4.723988	6.052238	3.290787
H	5.976478	4.824043	3.027904
H	6.440230	6.475692	3.442179
C	6.752845	9.587398	7.703998
H	7.707648	9.411788	7.201221
C	6.306516	11.019733	7.388074
H	6.175856	11.173816	6.312528
H	7.044458	11.740657	7.752613

H	5.358502	11.261499	7.878436
C	6.993842	9.432785	9.210730
H	7.177801	8.381593	9.455953
H	6.123058	9.751748	9.786981
H	7.860743	10.025390	9.525960
C	10.964205	4.634336	6.487121
C	12.208337	4.809047	7.129038
C	12.941190	3.672467	7.480739
H	13.895306	3.794760	7.985893
C	12.474719	2.393897	7.211542
H	13.063807	1.526106	7.491811
C	11.244491	2.231596	6.585466
H	10.879708	1.230245	6.380606
C	10.470610	3.333498	6.224505
C	12.783535	6.179468	7.458172
H	12.111329	6.941733	7.053154
C	14.163772	6.363350	6.810225
H	14.553109	7.365970	7.012536
H	14.129309	6.219197	5.726574
H	14.889164	5.650852	7.216174
C	12.884171	6.411983	8.971084
H	11.916148	6.293086	9.463983
H	13.230451	7.430473	9.172440
H	13.578597	5.707881	9.438838
C	9.133628	3.146415	5.521430
H	8.500813	3.999055	5.783670
C	8.386764	1.879241	5.945840
H	8.860531	0.973509	5.551724
H	7.363209	1.908346	5.559830
H	8.331759	1.793472	7.035177
C	9.299175	3.197387	3.995965
H	9.728374	4.149987	3.674801
H	8.327553	3.083289	3.503204
H	9.956341	2.391265	3.651493
C	12.135411	10.459907	7.071160
C	12.951279	10.798687	8.182833
C	12.198987	11.694865	9.016523
C	10.929339	11.933787	8.400900
C	10.883896	11.153319	7.209819
C	12.494491	9.603616	5.896026
H	13.336517	8.945707	6.119077
H	12.772597	10.221477	5.033708
H	11.648797	8.979065	5.589747
C	14.352610	10.332079	8.437475
H	14.552201	10.234294	9.507676
H	15.086544	11.033810	8.023782
H	14.532093	9.355030	7.982584
C	12.693199	12.327679	10.284571
H	11.869214	12.546994	10.968501
H	13.214916	13.268697	10.076135
H	13.390157	11.671100	10.812146

C	9.860498	12.857942	8.901351
H	8.864295	12.475996	8.665465
H	9.953060	13.854711	8.453567
H	9.913117	12.976051	9.986731
C	9.798143	11.127592	6.179576
H	9.633246	10.113779	5.800645
H	10.068201	11.754247	5.321246
H	8.853753	11.500117	6.578985
C	10.175865	8.486567	8.351672
H	10.029464	8.378585	7.253619
O	9.582373	7.544839	9.002600
C	11.135288	9.235522	10.382931
O	10.986647	8.632661	11.379317
Ca	8.972271	7.236348	11.286737
Co	5.946867	3.467084	10.378238
N	9.795873	5.814288	12.934157
C	9.155244	5.315557	13.980341
C	7.954339	5.833893	14.498438
H	7.578099	5.332000	15.383094
C	7.253726	7.011389	14.146431
N	7.478694	7.714036	13.053421
C	9.729983	4.107169	14.696959
H	10.782200	4.257261	14.949942
H	9.174291	3.878766	15.607253
H	9.686984	3.233114	14.039154
C	6.176398	7.422038	15.134076
H	5.287054	6.798846	14.987671
H	6.521323	7.267260	16.158416
H	5.879999	8.464721	15.011778
C	11.113934	5.362366	12.647762
C	12.202980	6.109618	13.153279
C	13.496491	5.691817	12.843085
H	14.344929	6.247638	13.229940
C	13.722709	4.579568	12.040268
H	14.738318	4.274266	11.807149
C	12.646462	3.873799	11.523170
H	12.827118	3.026540	10.867405
C	11.333327	4.246859	11.815593
C	11.967222	7.328849	14.036169
H	10.992245	7.739086	13.758481
C	13.011392	8.431961	13.832273
H	13.156124	8.652778	12.771981
H	12.680542	9.349168	14.331037
H	13.981015	8.162428	14.265831
C	11.885310	6.952163	15.523148
H	12.795620	6.433529	15.844526
H	11.773863	7.853233	16.135992
H	11.029225	6.306299	15.730125
C	10.175201	3.482791	11.194215
H	9.248929	3.804764	11.679306
C	10.289129	1.965835	11.369972

H	10.364202	1.684843	12.425121
H	9.407206	1.480250	10.941041
H	11.166518	1.564205	10.852957
C	10.067153	3.815148	9.702128
H	10.121977	4.900664	9.555031
H	10.899990	3.383305	9.144174
H	9.128604	3.422779	9.293776
C	6.774841	8.918019	12.781096
C	5.438459	8.911364	12.326262
C	4.839688	10.129250	11.997472
H	3.811643	10.135166	11.645585
C	5.533615	11.327336	12.086789
H	5.049834	12.261258	11.818367
C	6.853674	11.323128	12.518888
H	7.393120	12.262112	12.589447
C	7.491776	10.134674	12.873282
C	4.641078	7.626692	12.159253
H	5.234506	6.805986	12.566270
C	3.313087	7.683165	12.926502
H	2.779076	6.730592	12.845224
H	3.466013	7.901018	13.987309
H	2.651109	8.454559	12.519804
C	4.389376	7.307492	10.681040
H	5.320021	7.256667	10.112666
H	3.893848	6.337972	10.574031
H	3.755995	8.069322	10.215464
C	8.909940	10.151014	13.425174
H	9.381284	9.195762	13.177818
C	9.791399	11.255601	12.835978
H	9.496903	12.248731	13.192671
H	10.832276	11.095256	13.134059
H	9.752497	11.257030	11.741345
C	8.890696	10.217190	14.959090
H	8.338554	9.373022	15.381651
H	9.911155	10.186605	15.356020
H	8.414760	11.143060	15.300283
C	4.882889	3.217847	12.177142
C	4.013066	2.971908	11.077978
C	4.582997	1.902414	10.318757
C	5.777273	1.456138	10.977776
C	5.972327	2.280712	12.117918
C	4.674194	4.181176	13.302965
H	3.929506	4.937231	13.051214
H	4.325483	3.652948	14.198147
H	5.603340	4.694759	13.573468
C	2.712995	3.656494	10.781468
H	2.604557	3.864456	9.713628
H	1.862831	3.036389	11.090401
H	2.634216	4.609878	11.309554
C	3.985345	1.289026	9.086623
H	4.757439	0.870825	8.435165

H	3.295114	0.478263	9.347543
H	3.426801	2.028216	8.506250
C	6.616112	0.289266	10.549806
H	7.587941	0.294157	11.048016
H	6.122951	-0.657665	10.799859
H	6.795874	0.294276	9.471251
C	7.047305	2.178618	13.155762
H	7.341856	3.171311	13.508783
H	6.700665	1.609395	14.026961
H	7.939340	1.683714	12.766783
C	6.927477	4.920561	10.807087
H	6.968341	5.156480	11.895855
O	7.624809	5.759415	10.118985
C	6.413796	3.741655	8.807916
O	6.877251	4.051099	7.772848

2-Ir.log

SCF (wB97x) = -3995.59387113
E(SCF)+ZPE(0 K)= -3993.791879
H(298 K)= -3993.683012
G(298 K)= -3993.933300
Lowest Frequency = 9.9098cm-1

Ca	8.428414	5.954188	7.885729
Ir	11.278381	9.989499	8.824049
N	7.590924	7.410534	6.271470
C	8.207711	7.943256	5.228503
C	9.455715	7.519113	4.731018
H	9.799965	8.048146	3.849376
C	10.265566	6.421867	5.110582
N	10.072485	5.685321	6.186391
C	7.555797	9.099116	4.490830
H	6.517777	8.872516	4.235638
H	8.099423	9.349754	3.579110
H	7.534137	9.985218	5.133329
C	11.439889	6.147729	4.188276
H	12.290327	6.771900	4.483345
H	11.188516	6.395746	3.155519
H	11.763210	5.106706	4.237555
C	6.260174	7.819420	6.571092
C	5.190998	7.018701	6.109041
C	3.885913	7.410262	6.409799
H	3.053207	6.813461	6.051097
C	3.630355	8.549957	7.161574
H	2.607313	8.837179	7.384827
C	4.688744	9.304301	7.647109
H	4.486728	10.170013	8.271782
C	6.010619	8.955728	7.368943
C	5.452451	5.774556	5.270683
H	6.448333	5.409487	5.535133

C	4.457978	4.642900	5.552433
H	4.347853	4.466596	6.625828
H	4.812867	3.716106	5.090470
H	3.467723	4.855369	5.134031
C	5.482438	6.098969	3.769884
H	4.541822	6.563109	3.452424
H	5.623659	5.183055	3.186019
H	6.302150	6.777967	3.522734
C	7.144631	9.758826	7.983967
H	8.081365	9.455268	7.508927
C	7.001151	11.271327	7.795754
H	6.907927	11.543458	6.739515
H	7.882187	11.770273	8.211702
H	6.124197	11.663395	8.321073
C	7.248105	9.443651	9.480433
H	7.202399	8.359487	9.635145
H	6.408024	9.874082	10.028474
H	8.180766	9.852666	9.885999
C	10.894118	4.555997	6.458933
C	12.162220	4.688965	7.064277
C	12.862051	3.529323	7.406793
H	13.833137	3.620401	7.885489
C	12.341108	2.266906	7.163463
H	12.903081	1.380046	7.439633
C	11.094308	2.146104	6.562418
H	10.691090	1.157466	6.368484
C	10.353705	3.272603	6.206268
C	12.801045	6.038525	7.361060
H	12.151298	6.820701	6.959701
C	14.170036	6.154833	6.674464
H	14.615184	7.136918	6.863095
H	14.098091	6.011059	5.592429
H	14.871460	5.409038	7.061794
C	12.948961	6.290791	8.866829
H	11.994339	6.199560	9.389974
H	13.319130	7.305040	9.047179
H	13.643463	5.578412	9.321876
C	9.012607	3.122989	5.502308
H	8.408948	4.002301	5.742585
C	8.221351	1.889191	5.946615
H	8.662096	0.962136	5.563498
H	7.198655	1.949066	5.562220
H	8.166434	1.819285	7.037141
C	9.195980	3.130666	3.977442
H	9.657254	4.061579	3.637334
H	8.227513	3.032250	3.475613
H	9.833337	2.297714	3.660455
C	12.374417	10.391542	6.843034
C	13.264943	10.745070	7.905345
C	12.657245	11.824964	8.630782
C	11.417081	12.165513	7.990246

C	11.235506	11.270353	6.892897
C	12.618733	9.399936	5.748156
H	13.393192	8.683282	6.023308
H	12.942576	9.911932	4.834438
H	11.707998	8.842998	5.506646
C	14.622776	10.164068	8.157059
H	14.885662	10.218149	9.215867
H	15.391568	10.701757	7.589445
H	14.661646	9.112104	7.866134
C	13.274013	12.566895	9.780385
H	12.507927	12.987614	10.436263
H	13.898889	13.392799	9.421512
H	13.901958	11.909618	10.386618
C	10.540182	13.325993	8.352282
H	9.533433	13.203244	7.948035
H	10.950117	14.259711	7.949161
H	10.451187	13.439149	9.435300
C	10.141417	11.289325	5.870061
H	9.899711	10.275010	5.541109
H	10.446855	11.862402	4.986339
H	9.229861	11.739618	6.265969
C	10.310351	8.393775	8.350191
H	10.263128	8.172997	7.263741
O	9.683667	7.516139	9.055746
C	10.881596	9.568539	10.519153
O	10.506478	9.143729	11.556613
Ca	8.909475	7.334195	11.314913
Ir	6.059482	3.298904	10.376604
N	9.746954	5.877844	12.929174
C	9.130158	5.345130	13.972140
C	7.882164	5.769295	14.469630
H	7.537908	5.240269	15.351274
C	7.072329	6.866555	14.090070
N	7.265413	7.603094	13.014256
C	9.782052	4.189256	14.709809
H	10.820076	4.415837	14.965004
H	9.238420	3.938621	15.621527
H	9.803699	3.303157	14.067306
C	5.898022	7.140716	15.012389
H	5.047576	6.516546	14.717343
H	6.149409	6.892714	16.045146
H	5.574707	8.181741	14.963098
C	11.077698	5.468936	12.629556
C	12.146887	6.269632	13.091620
C	13.451966	5.878047	12.790866
H	14.284681	6.474829	13.149578
C	13.707507	4.738354	12.039084
H	14.730545	4.451113	11.815835
C	12.649107	3.984033	11.553537
H	12.851109	3.118321	10.928860
C	11.327237	4.332629	11.831698

C	11.885453	7.513775	13.929987
H	10.889579	7.878864	13.665535
C	12.879948	8.645414	13.648250
H	12.990080	8.821724	12.574857
H	12.525074	9.572211	14.110219
H	13.870197	8.432924	14.066655
C	11.855454	7.189351	15.430783
H	12.796058	6.725186	15.748243
H	11.714253	8.105264	16.014654
H	11.035725	6.510371	15.677926
C	10.193213	3.529555	11.216666
H	9.256482	3.833134	11.691699
C	10.336657	2.017051	11.404880
H	10.429874	1.744919	12.461119
H	9.455607	1.518127	10.988934
H	11.213601	1.624962	10.879562
C	10.089758	3.844732	9.720200
H	10.135481	4.928896	9.565489
H	10.929837	3.414290	9.172165
H	9.157095	3.435730	9.314625
C	6.443792	8.732427	12.741715
C	5.175676	8.599471	12.136396
C	4.475856	9.759120	11.793882
H	3.504759	9.668051	11.315206
C	4.996822	11.021532	12.037188
H	4.434858	11.908397	11.761018
C	6.243636	11.142322	12.638206
H	6.646873	12.130956	12.832121
C	6.984228	10.015816	12.994355
C	4.536829	7.249917	11.839635
H	5.186569	6.467737	12.240998
C	3.167842	7.133635	12.526243
H	2.722678	6.151554	12.337628
H	3.239798	7.277420	13.608276
H	2.466425	7.879435	12.138911
C	4.388900	6.997636	10.333870
H	5.343519	7.088853	9.810717
H	4.018721	5.983389	10.153532
H	3.694401	7.710017	9.878821
C	8.325341	10.165418	13.698291
H	8.928978	9.286088	13.458023
C	9.116614	11.399191	13.253947
H	8.675892	12.326262	13.637049
H	10.139314	11.339305	13.638328
H	9.171517	11.469073	12.163418
C	8.141989	10.157773	15.223159
H	7.680695	9.226877	15.563289
H	9.110465	10.256173	15.724973
H	7.504657	10.990746	15.540140
C	4.963430	2.896899	12.357615
C	4.072898	2.543385	11.295304

C	4.680574	1.463472	10.569877
C	5.920729	1.122900	11.210420
C	6.102320	2.018061	12.307764
C	4.719132	3.888515	13.452489
H	3.944676	4.605174	13.177338
H	4.395292	3.376528	14.366212
H	5.629873	4.445448	13.693989
C	2.715079	3.124414	11.043582
H	2.452197	3.070336	9.984773
H	1.946273	2.586744	11.611194
H	2.676229	4.176380	11.334504
C	4.063793	0.721549	9.420276
H	4.829871	0.300798	8.764410
H	3.438888	-0.104331	9.779151
H	3.435875	1.378840	8.814030
C	6.797605	-0.037601	10.848395
H	7.804360	0.085137	11.252633
H	6.387657	-0.971306	11.251533
H	6.886590	-0.150775	9.765379
C	7.196403	1.999069	13.330606
H	7.438121	3.013379	13.659564
H	6.890953	1.425992	14.214324
H	8.107955	1.548765	12.934701
C	7.027502	4.894638	10.850450
H	7.074700	5.115438	11.936896
O	7.654204	5.772258	10.144892
C	6.456325	3.719814	8.681500
O	6.831482	4.144589	7.644039

2-Rh.log

SCF (wB97x) = -4007.87701507
E(SCF)+ZPE(0 K)= -4006.075919
H(298 K)= -4005.967209
G(298 K)= -4006.216117
Lowest Frequency = 7.5209cm-1

Ca	8.438121	5.963763	7.872793
Rh	11.296585	10.001185	8.832980
N	7.594578	7.408828	6.260144
C	8.207971	7.939587	5.213120
C	9.453990	7.513973	4.714225
H	9.800083	8.043881	3.833976
C	10.263885	6.418527	5.096797
N	10.070229	5.685503	6.175637
C	7.553522	9.093819	4.475731
H	6.513297	8.869214	4.228190
H	8.091988	9.340181	3.559891
H	7.539162	9.982218	5.115288
C	11.437346	6.140452	4.175117
H	12.284776	6.772394	4.462391

H	11.182596	6.377416	3.140595
H	11.765800	5.101543	4.233670
C	6.261796	7.811169	6.559530
C	5.196799	7.006268	6.094274
C	3.889910	7.388669	6.398677
H	3.059990	6.789043	6.038387
C	3.628798	8.523110	7.156715
H	2.604390	8.802861	7.382957
C	4.683066	9.282592	7.643061
H	4.476356	10.145222	8.270441
C	6.006732	8.943884	7.360721
C	5.465214	5.767452	5.249616
H	6.460273	5.402287	5.518171
C	4.469909	4.632722	5.515786
H	4.349771	4.448327	6.586719
H	4.829329	3.709652	5.049847
H	3.483095	4.846921	5.090427
C	5.505337	6.099739	3.750639
H	4.568035	6.568428	3.430271
H	5.646598	5.186109	3.163282
H	6.328787	6.776648	3.511118
C	7.136801	9.757002	7.970938
H	8.073791	9.459365	7.491875
C	6.979897	11.267786	7.776734
H	6.883049	11.533374	6.719327
H	7.856363	11.778601	8.187854
H	6.099638	11.653527	8.301152
C	7.248632	9.447415	9.468559
H	7.209998	8.363177	9.627054
H	6.408433	9.873976	10.019651
H	8.180898	9.861283	9.870473
C	10.885825	4.552020	6.450054
C	12.155470	4.679424	7.053174
C	12.848825	3.516677	7.398306
H	13.821709	3.603321	7.874168
C	12.319373	2.256782	7.159903
H	12.876193	1.367319	7.437990
C	11.071040	2.141404	6.560729
H	10.661960	1.154507	6.370423
C	10.337106	3.271282	6.201289
C	12.801573	6.026902	7.343086
H	12.155544	6.810253	6.938165
C	14.170191	6.135429	6.654747
H	14.618655	7.116476	6.840491
H	14.095653	5.989616	5.573233
H	14.868773	5.387349	7.042922
C	12.951925	6.285068	8.847838
H	11.999659	6.190177	9.374897
H	13.320464	7.300975	9.023657
H	13.650441	5.576966	9.303647
C	8.995334	3.128815	5.496616

H	8.394025	4.009036	5.740983
C	8.200473	1.894400	5.932580
H	8.638598	0.969048	5.542678
H	7.178074	1.959346	5.548119
H	8.145370	1.815191	7.022479
C	9.177874	3.144499	3.971627
H	9.641341	4.075687	3.635715
H	8.208763	3.051199	3.470114
H	9.812618	2.311336	3.650216
C	12.380005	10.387735	6.852579
C	13.272173	10.755941	7.899481
C	12.652717	11.823949	8.629136
C	11.413631	12.162511	7.984740
C	11.233208	11.261344	6.901423
C	12.618351	9.391983	5.760290
H	13.418419	8.696416	6.017310
H	12.901955	9.900654	4.830972
H	11.714771	8.811086	5.547401
C	14.632949	10.182235	8.156451
H	14.886456	10.221547	9.218736
H	15.405757	10.733310	7.606876
H	14.686321	9.134947	7.848982
C	13.266712	12.577235	9.773273
H	12.499524	12.990368	10.433217
H	13.878122	13.411528	9.409355
H	13.909039	11.931650	10.377528
C	10.533039	13.319801	8.350771
H	9.536552	13.214428	7.916001
H	10.956393	14.262397	7.983012
H	10.414081	13.409660	9.433710
C	10.138313	11.258667	5.878959
H	9.879861	10.236323	5.588098
H	10.450124	11.789612	4.971007
H	9.233600	11.740048	6.254550
C	10.318999	8.409691	8.375177
H	10.277193	8.200014	7.283394
O	9.688100	7.529992	9.062926
C	10.909123	9.578319	10.526039
O	10.516759	9.124849	11.538153
Ca	8.899755	7.324636	11.327858
Rh	6.041289	3.287215	10.367672
N	9.743298	5.879570	12.940507
C	9.129904	5.348811	13.987530
C	7.883886	5.774427	14.486425
H	7.537792	5.244520	15.366675
C	7.073992	6.869875	14.103854
N	7.267649	7.602899	13.025015
C	9.784351	4.194578	14.724919
H	10.824576	4.419181	14.972460
H	9.245885	3.948217	15.640759
H	9.798710	3.306179	14.085362

C	5.900533	7.147952	15.025535
H	5.053103	6.516010	14.738264
H	6.155284	6.910989	16.060058
H	5.572080	8.186861	14.966982
C	11.076079	5.477227	12.641121
C	12.141077	6.282125	13.106378
C	13.447966	5.899722	12.801975
H	14.277887	6.499346	13.162266
C	13.709076	4.765281	12.043936
H	14.733484	4.485528	11.817695
C	12.654807	4.005802	11.557590
H	12.861516	3.143171	10.930209
C	11.331142	4.344512	11.839929
C	11.872664	7.520941	13.951036
H	10.877606	7.886108	13.682482
C	12.867972	8.655670	13.684868
H	12.988110	8.840065	12.613935
H	12.508553	9.578740	14.150807
H	13.854785	8.441469	14.110226
C	11.832541	7.188653	15.450013
H	12.769842	6.719962	15.770381
H	11.691282	8.102283	16.037371
H	11.009090	6.511746	15.689535
C	10.201071	3.531397	11.229712
H	9.264082	3.829035	11.708774
C	10.357972	2.020611	11.423915
H	10.454819	1.755023	12.481322
H	9.481505	1.509799	11.012795
H	11.238230	1.634869	10.899497
C	10.089242	3.840984	9.732090
H	10.127878	4.925222	9.573596
H	10.929441	3.414422	9.180999
H	9.156976	3.427117	9.330175
C	6.452054	8.736383	12.750597
C	5.182408	8.608980	12.147480
C	4.489054	9.771728	11.802348
H	3.516169	9.685085	11.326488
C	5.018509	11.031623	12.040749
H	4.461689	11.921085	11.762662
C	6.266842	11.146999	12.639920
H	6.675924	12.133896	12.830225
C	7.000776	10.017120	12.999361
C	4.536302	7.261503	11.857569
H	5.182331	6.478152	12.262491
C	3.167685	7.152978	12.545910
H	2.719220	6.171932	12.360168
H	3.242224	7.298793	13.627424
H	2.469104	7.901059	12.157735
C	4.385950	7.003336	10.352818
H	5.338215	7.098225	9.825758
H	4.017408	5.987429	10.177000

H	3.687434	7.711438	9.897009
C	8.342549	10.159585	13.704031
H	8.943856	9.279363	13.459665
C	9.137412	11.393998	13.268065
H	8.699289	12.319352	13.657966
H	10.159811	11.329051	13.652525
H	9.192513	11.473206	12.178165
C	8.160011	10.143903	15.229020
H	7.696543	9.212716	15.564934
H	9.129123	10.237201	15.730532
H	7.525269	10.977068	15.550432
C	4.957868	2.900669	12.348073
C	4.065699	2.532465	11.301171
C	4.685152	1.464455	10.571517
C	5.924237	1.125890	11.215913
C	6.104663	2.027057	12.299230
C	4.719524	3.896422	13.440361
H	3.919457	4.591990	13.183342
H	4.435920	3.387752	14.369680
H	5.623105	4.477318	13.653249
C	2.704924	3.106174	11.044201
H	2.451418	3.066863	9.981915
H	1.932115	2.555100	11.593774
H	2.651554	4.153461	11.351670
C	4.071156	0.711170	9.427380
H	4.838342	0.298033	8.767437
H	3.459743	-0.123121	9.791298
H	3.428831	1.356756	8.823124
C	6.804828	-0.031402	10.849883
H	7.801315	0.073970	11.284652
H	6.381471	-0.973997	11.217643
H	6.923784	-0.121262	9.766944
C	7.199557	2.029732	13.321694
H	7.458011	3.052075	13.612556
H	6.887745	1.498786	14.229645
H	8.104270	1.548350	12.946103
C	7.018874	4.878710	10.825474
H	7.060677	5.088390	11.917256
O	7.649775	5.758408	10.137724
C	6.428757	3.710076	8.674612
O	6.821125	4.163543	7.662499

3-Co_bisanion.log

SCF (wB97x) = -763.543606950

Co	3.456231	3.818318	21.077685
C	3.291926	4.416281	18.997253
C	3.263955	2.990567	19.059778
C	4.508587	2.531859	19.586819
C	5.316033	3.673145	19.851154

C	4.566698	4.831860	19.486452
C	4.846304	1.091977	19.827998
H	5.740317	0.993642	20.454347
H	5.030626	0.527907	18.897229
H	4.023356	0.593414	20.358626
C	2.144715	2.097942	18.614841
H	1.953947	1.317226	19.362811
H	2.352791	1.600086	17.652371
H	1.212884	2.662480	18.500841
C	2.251511	5.297269	18.372706
H	1.249416	4.878753	18.510187
H	2.404010	5.444148	17.285405
H	2.243863	6.287093	18.840042
C	5.075566	6.239246	19.574703
H	4.254345	6.960225	19.498573
H	5.804932	6.479744	18.782416
H	5.562170	6.412531	20.543536
C	6.696517	3.706827	20.433005
H	6.974311	2.733016	20.852307
H	6.745078	4.437713	21.252074
H	7.470799	3.982787	19.696253
C	2.296069	2.727372	21.965627
H	2.355164	1.665848	21.451418
O	1.481817	2.721339	22.900293
C	3.851773	4.922622	22.473642
H	4.948195	5.324894	22.298399
O	3.371314	5.388262	23.517187

3-Co.log

SCF (wB97x) = -3315.73199551
E(SCF)+ZPE(0 K)= -3314.176492
H(298 K)= -3314.086059
G(298 K)= -3314.298616
Lowest Frequency = 15.4794cm-1

Co	3.508588	3.783415	21.030389
Ca	3.712392	2.613520	23.936654
Ca	1.401190	5.193357	22.950368
N	4.393073	2.930320	26.152088
C	4.448340	2.024260	27.115671
C	4.097172	0.664065	26.974572
H	4.142909	0.089908	27.892834
C	3.918145	-0.110935	25.812624
N	3.827172	0.372258	24.582164
C	5.008532	2.401883	28.476858
H	6.103240	2.384955	28.428362
H	4.695083	1.690671	29.242580
H	4.721986	3.409308	28.781742
C	3.939578	-1.613641	26.035518
H	3.356016	-2.150349	25.286167

H	3.563139	-1.862174	27.029515
H	4.970425	-1.979842	25.968970
C	4.898135	4.234541	26.423150
C	6.257622	4.516952	26.195178
C	6.750242	5.780606	26.525630
H	7.801659	6.003473	26.364550
C	5.917839	6.759157	27.049057
H	6.316710	7.732031	27.319306
C	4.559069	6.498864	27.181164
H	3.901761	7.283083	27.543831
C	4.023675	5.256262	26.846763
C	7.169661	3.512986	25.506919
H	6.631055	2.561591	25.435142
C	7.462523	4.003794	24.079927
H	6.537232	4.125678	23.504388
H	8.111062	3.307572	23.539648
H	7.955249	4.981712	24.099299
C	8.467010	3.242886	26.275506
H	9.096186	4.137141	26.336192
H	9.051440	2.463248	25.775421
H	8.259205	2.910234	27.296717
C	2.524482	5.020043	26.926966
H	2.300041	4.192137	26.244341
C	2.079373	4.584691	28.328934
H	2.386693	5.325456	29.075469
H	2.508258	3.619404	28.610070
H	0.989471	4.495209	28.371570
C	1.710679	6.236095	26.472416
H	0.651227	5.982826	26.375998
H	2.055827	6.619717	25.508359
H	1.774698	7.062808	27.187872
C	3.941065	-0.515094	23.476348
C	2.801107	-0.868361	22.718797
C	2.972483	-1.711722	21.618227
H	2.106709	-2.005551	21.034163
C	4.226254	-2.182617	21.250735
H	4.332821	-2.834621	20.389339
C	5.342369	-1.804303	21.983493
H	6.323559	-2.159057	21.681808
C	5.222657	-0.974216	23.097575
C	1.411276	-0.380146	23.104465
H	1.503626	0.645872	23.467732
C	0.809079	-1.207701	24.248648
H	-0.212510	-0.869428	24.449576
H	1.383546	-1.097456	25.171066
H	0.773641	-2.271037	23.984869
C	0.430030	-0.336679	21.928339
H	0.083635	-1.338351	21.647159
H	0.875863	0.125900	21.042264
H	-0.446275	0.252418	22.210181
C	6.469204	-0.538015	23.855973

H	6.161592	-0.156660	24.832593
C	7.159130	0.620027	23.125326
H	8.028869	0.974669	23.688386
H	6.478973	1.470173	22.992628
H	7.497809	0.311585	22.129665
C	7.455638	-1.683953	24.106681
H	7.916998	-2.039830	23.179552
H	6.959914	-2.535973	24.581365
H	8.263813	-1.348422	24.764189
N	-0.740857	5.019634	23.895550
C	-1.456458	5.999837	24.427901
C	-1.065548	7.354908	24.485790
H	-1.746054	7.998242	25.032059
C	-0.070313	8.046999	23.766171
N	0.877624	7.475732	23.040865
C	-2.841421	5.702680	24.973582
H	-3.523352	5.496481	24.141403
H	-3.237071	6.546806	25.539138
H	-2.847497	4.812731	25.604846
C	-0.203926	9.560118	23.797271
H	0.722085	10.064512	23.518970
H	-0.507298	9.892360	24.792779
H	-0.982070	9.876725	23.094564
C	-1.347699	3.735197	23.755201
C	-1.996914	3.416206	22.544733
C	-2.618763	2.173765	22.412525
H	-3.131691	1.929915	21.485870
C	-2.592254	1.243052	23.440571
H	-3.089767	0.284786	23.328211
C	-1.893550	1.539533	24.602426
H	-1.841611	0.798162	25.395475
C	-1.251132	2.765319	24.775507
C	-2.004675	4.370530	21.358912
H	-1.512972	5.299148	21.668432
C	-1.202943	3.768950	20.193142
H	-0.149719	3.628164	20.465162
H	-1.244267	4.415410	19.311036
H	-1.596057	2.787317	19.909220
C	-3.425684	4.741044	20.918032
H	-3.975755	3.866560	20.554694
H	-3.396855	5.474967	20.105804
H	-3.994423	5.173428	21.746481
C	-0.445342	2.991814	26.045378
H	0.020089	3.977720	25.966845
C	-1.323954	2.982972	27.304063
H	-1.868522	2.037345	27.396962
H	-2.058826	3.792766	27.295008
H	-0.709207	3.096888	28.202484
C	0.671573	1.945433	26.172871
H	1.345067	2.178232	27.002470
H	1.257152	1.886557	25.252094

H	0.262234	0.945581	26.350918
C	1.625484	8.241530	22.104377
C	2.989338	8.533055	22.345701
C	3.712349	9.198086	21.353990
H	4.757231	9.433077	21.525043
C	3.130010	9.557742	20.145316
H	3.717339	10.065045	19.386271
C	1.793988	9.263241	19.916567
H	1.339233	9.543042	18.970192
C	1.021755	8.616919	20.882839
C	3.652470	8.177849	23.669826
H	3.293775	7.191736	23.973510
C	3.265361	9.166624	24.778535
H	3.800248	8.917855	25.700459
H	2.195121	9.132490	24.994429
H	3.528826	10.191467	24.493589
C	5.177558	8.061873	23.588840
H	5.658806	9.043500	23.505586
H	5.493026	7.456654	22.733553
H	5.551248	7.581177	24.496589
C	-0.438428	8.309050	20.579665
H	-0.916309	7.957179	21.496855
C	-0.545484	7.171574	19.560386
H	-0.092744	7.450448	18.602412
H	-1.592438	6.905330	19.379317
H	-0.026053	6.279783	19.921632
C	-1.211760	9.545250	20.104122
H	-0.864627	9.889074	19.124080
H	-1.101933	10.377763	20.805256
H	-2.277429	9.312684	20.011275
C	3.292226	4.382814	19.024428
C	3.275896	2.957019	19.099785
C	4.503017	2.522227	19.681927
C	5.300981	3.687961	19.934175
C	4.554621	4.831092	19.524941
C	4.911452	1.097645	19.905464
H	5.662568	1.014639	20.693346
H	5.337732	0.660763	18.994171
H	4.066224	0.475383	20.209013
C	2.172368	2.064625	18.622807
H	2.170459	1.111080	19.159386
H	2.286755	1.839697	17.556705
H	1.189943	2.526164	18.761430
C	2.236201	5.252429	18.414464
H	1.243210	4.807468	18.519338
H	2.422027	5.398275	17.343143
H	2.212111	6.239290	18.884612
C	5.027096	6.251808	19.564667
H	4.194809	6.952446	19.666217
H	5.576139	6.506206	18.650496
H	5.703619	6.428889	20.406661

C	6.703508	3.708729	20.462883
H	6.922496	2.818111	21.057364
H	6.880076	4.581589	21.098490
H	7.430222	3.748359	19.642970
C	2.148455	2.874579	21.763442
H	1.637276	2.137362	21.113839
O	1.637026	2.877589	22.959113
C	4.031915	4.810118	22.402217
H	4.903131	5.470018	22.208438
O	3.603050	4.938581	23.619627

3-Ir_bisanion.log

SCF (wB97x) = -722.183436974

Ir	3.494188	3.646317	21.648497
C	3.449731	4.390137	18.624548
C	3.324786	3.000924	18.854322
C	4.433442	2.570066	19.632339
C	5.246266	3.722153	19.896691
C	4.620779	4.837249	19.276284
C	4.839695	1.138574	19.849652
H	5.462808	1.041843	20.743656
H	5.406044	0.724838	18.994522
H	3.963965	0.499503	20.006205
C	2.175347	2.125887	18.449362
H	2.509872	1.158128	18.048594
H	1.558040	2.601572	17.677148
H	1.517498	1.908027	19.307349
C	2.393739	5.270753	18.020762
H	1.649328	5.588100	18.765356
H	1.847632	4.761213	17.214889
H	2.823464	6.182581	17.584479
C	5.094003	6.254787	19.406475
H	4.561796	6.923695	18.719147
H	6.168649	6.358494	19.195839
H	4.928789	6.635327	20.428233
C	6.645662	3.706999	20.446520
H	6.770650	2.898485	21.172938
H	6.871916	4.640655	20.973092
H	7.410028	3.575947	19.658036
C	2.158664	2.572571	22.472287
H	1.494048	2.208513	21.580639
O	1.823202	2.093974	23.561709
C	3.892841	4.885786	23.034226
H	4.205523	5.860916	22.469675
O	4.002825	4.972376	24.262504

3-Ir.log

SCF (wB97x) = -3274.37918280

E(SCF)+ZPE(0 K)= -3272.823483
H(298 K)= -3272.732740
G(298 K)= -3272.945910
Lowest Frequency = 14.9611cm-1

Ir	3.704599	3.870949	21.047483
Ca	3.627965	2.610503	23.972931
Ca	1.283840	5.098898	22.929771
N	4.362247	2.918303	26.173484
C	4.437703	2.019003	27.142105
C	4.076994	0.659229	27.019424
H	4.160172	0.083719	27.934529
C	3.847571	-0.111231	25.862468
N	3.691103	0.386613	24.647712
C	5.033624	2.405096	28.485634
H	6.126667	2.378001	28.413409
H	4.731018	1.705334	29.266265
H	4.762250	3.418421	28.785125
C	3.890809	-1.615002	26.067147
H	3.331752	-2.152532	25.299833
H	3.499586	-1.882034	27.051060
H	4.929880	-1.959904	26.020023
C	4.886664	4.221457	26.409790
C	6.238576	4.489682	26.126331
C	6.751061	5.757378	26.411303
H	7.798462	5.967704	26.210870
C	5.944758	6.753143	26.941320
H	6.359740	7.728363	27.177111
C	4.589032	6.506033	27.125435
H	3.949544	7.304494	27.488891
C	4.033890	5.261070	26.838374
C	7.128515	3.464471	25.439139
H	6.566063	2.527208	25.361322
C	7.453378	3.944418	24.015217
H	6.543078	4.056076	23.413791
H	8.113644	3.241402	23.498737
H	7.949926	4.920417	24.036322
C	8.409890	3.160454	26.222843
H	9.056679	4.041270	26.295534
H	8.983024	2.369690	25.727056
H	8.181955	2.828876	27.240024
C	2.534656	5.043246	26.962385
H	2.285114	4.209392	26.298190
C	2.121685	4.634769	28.382052
H	2.450547	5.385403	29.109339
H	2.551841	3.671455	28.668777
H	1.032302	4.552247	28.452886
C	1.720809	6.256986	26.502675
H	0.655929	6.012440	26.453537
H	2.033584	6.597311	25.512384
H	1.820134	7.104566	27.189241

C	3.753265	-0.452718	23.503474
C	2.578640	-0.757088	22.777524
C	2.699648	-1.500707	21.601516
H	1.807234	-1.749268	21.036809
C	3.935805	-1.930910	21.136227
H	4.002987	-2.507882	20.218949
C	5.083783	-1.612528	21.847679
H	6.051471	-1.935474	21.473374
C	5.015558	-0.874889	23.029231
C	1.209486	-0.314055	23.272947
H	1.326714	0.671031	23.726732
C	0.662613	-1.249928	24.359574
H	-0.341577	-0.925958	24.653775
H	1.292101	-1.241131	25.252710
H	0.596273	-2.280865	23.993268
C	0.176918	-0.154160	22.154296
H	-0.167813	-1.122608	21.772346
H	0.576663	0.420229	21.313511
H	-0.693501	0.381404	22.538303
C	6.299591	-0.491594	23.750486
H	6.035842	-0.085806	24.730277
C	7.025205	0.621754	22.986272
H	7.913325	0.956016	23.532621
H	6.374951	1.491799	22.832159
H	7.345897	0.273616	21.997421
C	7.230987	-1.686409	23.984981
H	7.627358	-2.084766	23.045055
H	6.709271	-2.500308	24.496909
H	8.085451	-1.386541	24.600055
N	-0.791963	4.964031	24.006818
C	-1.468117	5.972292	24.544359
C	-1.089369	7.329834	24.499487
H	-1.751955	7.997775	25.037219
C	-0.124666	7.990094	23.709260
N	0.824008	7.391006	23.009915
C	-2.784984	5.691223	25.246135
H	-3.483143	5.197885	24.563057
H	-3.244754	6.607883	25.615568
H	-2.638072	5.008993	26.087584
C	-0.296941	9.496686	23.624034
H	0.636132	10.009220	23.386966
H	-0.695215	9.891988	24.560654
H	-1.015768	9.735036	22.832442
C	-1.433780	3.690058	23.943042
C	-2.106481	3.336951	22.754181
C	-2.818520	2.138377	22.703835
H	-3.361769	1.878017	21.799317
C	-2.834176	1.266162	23.782436
H	-3.394393	0.337883	23.731263
C	-2.088124	1.574701	24.910922
H	-2.056771	0.868087	25.735735

C	-1.377555	2.771504	25.012102
C	-2.046176	4.206489	21.506938
H	-1.423184	5.079291	21.733422
C	-1.388021	3.428576	20.356465
H	-0.385283	3.088249	20.637507
H	-1.305931	4.046673	19.457744
H	-1.970193	2.538740	20.096668
C	-3.424079	4.748281	21.110398
H	-4.116281	3.936064	20.863824
H	-3.347200	5.399161	20.232774
H	-3.863373	5.329242	21.926907
C	-0.518920	3.008275	26.244627
H	-0.140768	4.033407	26.197120
C	-1.293560	2.850816	27.558936
H	-1.656151	1.826247	27.690988
H	-2.159743	3.517476	27.604450
H	-0.645656	3.076673	28.411408
C	0.684297	2.054947	26.215600
H	1.373534	2.235369	27.044855
H	1.228821	2.166244	25.274150
H	0.360344	1.010149	26.266078
C	1.564181	8.128323	22.044335
C	2.899679	8.517670	22.304297
C	3.599733	9.186767	21.298493
H	4.620396	9.504480	21.481425
C	3.025838	9.452619	20.060946
H	3.595148	9.972155	19.296358
C	1.724676	9.044103	19.809521
H	1.281189	9.237241	18.836494
C	0.977784	8.383261	20.785506
C	3.562080	8.238090	23.647985
H	3.278337	7.226783	23.952130
C	3.078792	9.195754	24.746784
H	3.626123	8.997415	25.673950
H	2.015346	9.069531	24.958492
H	3.256215	10.238689	24.460265
C	5.093752	8.264135	23.594623
H	5.481396	9.287342	23.521983
H	5.484501	7.696303	22.744522
H	5.493780	7.818757	24.509325
C	-0.429879	7.910909	20.451336
H	-0.903304	7.558750	21.371634
C	-0.373211	6.722384	19.484898
H	0.085022	7.013091	18.533463
H	-1.378854	6.343227	19.276814
H	0.224799	5.900147	19.895674
C	-1.311198	9.028326	19.880046
H	-0.960530	9.358762	18.896576
H	-1.323834	9.901975	20.538015
H	-2.340335	8.674908	19.760216
C	3.796329	4.698901	18.924611

C	3.658766	3.268452	18.833804
C	4.813724	2.672882	19.428296
C	5.685773	3.736269	19.864623
C	5.059717	4.980369	19.551302
C	5.115787	1.205541	19.491037
H	5.747579	0.967056	20.348644
H	5.633092	0.873538	18.582683
H	4.204879	0.612412	19.598580
C	2.522877	2.525454	18.198032
H	2.336217	1.576796	18.711020
H	2.735350	2.296604	17.147981
H	1.597630	3.106649	18.237637
C	2.887333	5.719005	18.310352
H	1.877904	5.322225	18.186124
H	3.256684	6.012562	17.319991
H	2.816404	6.618412	18.926998
C	5.636745	6.343018	19.788242
H	4.848411	7.091741	19.901131
H	6.284564	6.648946	18.958796
H	6.240330	6.362721	20.701393
C	7.070032	3.566524	20.412936
H	7.165906	2.636098	20.975958
H	7.338526	4.387901	21.081451
H	7.804001	3.544355	19.598564
C	2.222129	2.826102	21.664561
H	1.796319	2.099621	20.941326
O	1.601580	2.796236	22.806746
C	4.005001	4.934789	22.612487
H	4.821112	5.681858	22.559538
O	3.411045	4.945170	23.769292

3-Rh_bisanion.log

SCF (wB97x) = -728.343052923

Rh	3.389942	3.803311	21.407784
C	3.359380	4.321683	18.837309
C	3.358192	2.905662	18.951251
C	4.581220	2.502478	19.553514
C	5.337005	3.677883	19.818904
C	4.581222	4.800113	19.376353
C	5.031931	1.087471	19.778776
H	5.711584	1.023299	20.634803
H	5.557119	0.655873	18.906807
H	4.183621	0.433419	20.006632
C	2.227048	2.011951	18.534375
H	2.544169	0.963578	18.481107
H	1.831368	2.282075	17.544361
H	1.388390	2.060883	19.249818
C	2.250132	5.135230	18.235935
H	1.270965	4.725596	18.509906

H	2.289596	5.174377	17.132212
H	2.272753	6.168488	18.599176
C	5.039476	6.224803	19.476874
H	4.209874	6.921286	19.310607
H	5.831492	6.476453	18.750783
H	5.436940	6.433383	20.479877
C	6.714330	3.755603	20.408302
H	6.985236	2.817041	20.904457
H	6.767206	4.545018	21.170426
H	7.494349	3.969108	19.657076
C	1.765907	3.166490	22.179077
H	1.185016	2.683316	21.275151
O	1.138202	3.080131	23.237411
C	4.085495	4.729414	22.920864
H	5.030253	5.303289	22.521469
O	3.895809	4.917689	24.124579

3-Rh.log

SCF (wB97x) = -3280.51728822
E(SCF)+ZPE(0 K)= -3278.962468
H(298 K)= -3278.871588
G(298 K)= -3279.084924
Lowest Frequency = 11.5814cm-1

Rh	3.690738	3.865611	21.043041
Ca	3.654008	2.610191	23.956316
Ca	1.297583	5.114965	22.937600
N	4.362166	2.923614	26.164893
C	4.432118	2.025314	27.135424
C	4.071700	0.665976	27.013010
H	4.147934	0.092251	27.929794
C	3.850795	-0.106594	25.856096
N	3.707421	0.388192	24.638118
C	5.021948	2.412057	28.481460
H	6.115219	2.378844	28.415263
H	4.711530	1.715285	29.261699
H	4.754367	3.427229	28.777726
C	3.889306	-1.609796	26.065938
H	3.335317	-2.149229	25.296414
H	3.490224	-1.872579	27.047807
H	4.928107	-1.956667	26.027744
C	4.886191	4.226358	26.406217
C	6.240437	4.493139	26.132718
C	6.751976	5.760097	26.422305
H	7.800763	5.969938	26.228989
C	5.942894	6.755839	26.948303
H	6.357136	7.730502	27.187587
C	4.586023	6.509535	27.124751
H	3.945307	7.307835	27.486382
C	4.031723	5.265203	26.832960

C	7.133825	3.466777	25.451575
H	6.573246	2.528199	25.375449
C	7.461590	3.942586	24.027001
H	6.552089	4.060414	23.425207
H	8.116875	3.234995	23.510548
H	7.963676	4.915734	24.046711
C	8.413751	3.167025	26.239228
H	9.059758	4.048529	26.309958
H	8.988541	2.375021	25.747466
H	8.183972	2.838983	27.257143
C	2.532144	5.046387	26.952471
H	2.284256	4.214822	26.284328
C	2.115707	4.632123	28.369569
H	2.443550	5.379795	29.100334
H	2.544336	3.667501	28.653735
H	1.026117	4.550219	28.437591
C	1.718404	6.262230	26.498129
H	0.654125	6.016686	26.442338
H	2.034610	6.612820	25.512420
H	1.813564	7.104483	27.191759
C	3.774299	-0.460696	23.500345
C	2.602320	-0.772540	22.773534
C	2.727307	-1.531634	21.607814
H	1.837018	-1.787012	21.042757
C	3.965026	-1.968717	21.153464
H	4.035552	-2.556890	20.243657
C	5.110448	-1.642767	21.865662
H	6.079081	-1.972054	21.499680
C	5.038259	-0.890976	23.038006
C	1.231089	-0.324103	23.258723
H	1.347208	0.662005	23.710952
C	0.674888	-1.254566	24.345426
H	-0.331407	-0.928682	24.630000
H	1.297030	-1.242166	25.243635
H	0.610958	-2.287053	23.983178
C	0.205795	-0.167513	22.132547
H	-0.142328	-1.137377	21.757508
H	0.614148	0.395455	21.288040
H	-0.663825	0.376654	22.506430
C	6.319099	-0.506277	23.764691
H	6.050423	-0.097268	24.741861
C	7.051679	0.603521	23.001823
H	7.940054	0.933873	23.550289
H	6.406647	1.477190	22.847130
H	7.371954	0.255336	22.013024
C	7.247248	-1.701832	24.008567
H	7.650209	-2.102701	23.072569
H	6.720770	-2.513954	24.518484
H	8.097494	-1.401555	24.629216
N	-0.782032	4.968348	24.000878
C	-1.464532	5.972664	24.538555

C	-1.089355	7.331189	24.501208
H	-1.755759	7.995361	25.038930
C	-0.123870	7.996878	23.716473
N	0.827962	7.402150	23.017600
C	-2.783902	5.684622	25.232455
H	-3.476793	5.190807	24.544424
H	-3.248918	6.598448	25.602302
H	-2.638794	5.000306	26.072455
C	-0.299366	9.503272	23.637278
H	0.629963	10.018097	23.390931
H	-0.687295	9.894711	24.579921
H	-1.028320	9.742668	22.855411
C	-1.419654	3.692325	23.928680
C	-2.088825	3.343533	22.736492
C	-2.795233	2.141945	22.677845
H	-3.337218	1.885245	21.771583
C	-2.808513	1.263153	23.751106
H	-3.364407	0.332672	23.693376
C	-2.066902	1.568873	24.883229
H	-2.034936	0.858194	25.704538
C	-1.362083	2.768308	24.992946
C	-2.037528	4.224814	21.497045
H	-1.401389	5.088378	21.722542
C	-1.407896	3.455156	20.325537
H	-0.405173	3.097835	20.585024
H	-1.330885	4.086131	19.435461
H	-2.005639	2.577561	20.059898
C	-3.416192	4.786290	21.131093
H	-4.122102	3.983502	20.892515
H	-3.348629	5.442982	20.257076
H	-3.832718	5.366157	21.960246
C	-0.510816	3.002637	26.231049
H	-0.131303	4.027467	26.187173
C	-1.295074	2.845015	27.539807
H	-1.661042	1.821052	27.667156
H	-2.160027	3.513480	27.580748
H	-0.652592	3.067790	28.397215
C	0.691244	2.047599	26.211583
H	1.373294	2.227511	27.046792
H	1.245677	2.157128	25.275784
H	0.365355	1.003317	26.260220
C	1.567506	8.142921	22.053275
C	2.903376	8.530798	22.313762
C	3.604748	9.199163	21.308468
H	4.626177	9.514333	21.491163
C	3.031179	9.466386	20.071244
H	3.601621	9.984478	19.306577
C	1.728971	9.061348	19.819977
H	1.285581	9.256893	18.847421
C	0.980404	8.401639	20.795492
C	3.564503	8.252045	23.658311

H	3.278279	7.242239	23.964781
C	3.082196	9.213240	24.754390
H	3.627498	9.015933	25.682997
H	2.017910	9.090435	24.964293
H	3.262674	10.254949	24.465577
C	5.096196	8.272512	23.605918
H	5.487376	9.293983	23.528797
H	5.485068	7.699255	22.758612
H	5.494198	7.830002	24.522819
C	-0.430083	7.937303	20.461592
H	-0.903369	7.581451	21.380592
C	-0.381924	6.754985	19.487301
H	0.078227	7.047663	18.537498
H	-1.390362	6.384238	19.277488
H	0.210453	5.926062	19.892554
C	-1.306823	9.063172	19.899599
H	-0.956973	9.397283	18.917119
H	-1.312564	9.933134	20.562533
H	-2.338269	8.716279	19.780580
C	3.758970	4.667104	18.910490
C	3.626833	3.238653	18.850035
C	4.789437	2.656925	19.441376
C	5.654104	3.728338	19.857842
C	5.016309	4.963262	19.532590
C	5.095104	1.190582	19.521106
H	5.757238	0.966223	20.360002
H	5.581868	0.838751	18.602899
H	4.189404	0.597292	19.669433
C	2.491021	2.476744	18.236681
H	2.300660	1.544824	18.779552
H	2.704591	2.210271	17.195455
H	1.565562	3.059371	18.252023
C	2.837104	5.674068	18.292256
H	1.829037	5.269581	18.177815
H	3.194343	5.963414	17.295848
H	2.763097	6.580354	18.899329
C	5.586951	6.331460	19.753933
H	4.797301	7.082982	19.836890
H	6.252087	6.623721	18.932843
H	6.173849	6.371307	20.678007
C	7.042241	3.580265	20.404705
H	7.156544	2.649545	20.964947
H	7.298778	4.404128	21.075820
H	7.779072	3.573355	19.592163
C	2.212637	2.837076	21.674755
H	1.781447	2.119109	20.944506
O	1.603397	2.800463	22.814654
C	4.012071	4.932194	22.592182
H	4.828803	5.678265	22.507193
O	3.444958	4.957736	23.754027

7. References

1- M. H. Chisholm, J. C. Gallucci and K. Phomphrai, *Inorg. Chem*., 2004, **43**, 6717-6725.

2- S. Kirschner, *Inorganic Syntheses*, Volume **23**, 1985.

3- R. G. Ball, W. A. G. Graham, D. M. Heinekey, J. K. Hoyano, A. D. McMaster, B. M. Mattson and S. T. Michel, *Inorg. Chem*. 1990, **29**, 2023-2025

4- S. Harder and J. Brettar, *Angew. Chem. Int. Ed*., 2006, **45**, 3473-3478.

5- A. Causero, G. Ballmann, J. Pahl, C. Färber, J. Intemann and S. Harder, *Dalton. Trans*., 2017, **46**, 1822-1831.

6- O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

7- SHELXTL v5.1, Bruker AXS, Madison, WI, 1998.

8- SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

9- A.L. Spek (2003, 2009) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. See also A.L. Spek, *Acta. Cryst.*, 2015, **C71**, 9-18.

10- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. A. Peterson, Gaussian 09; Revision D.01, Gaussian Inc. 2009.

11- J. Da Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys*., 2008, **10**, 6615–6620.

12- W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys*., 1972, **56**, 2257–2261.

13- P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213–222.

14- T. Clark, J. Chandrasekar, W. Spitznagel, Gunther and P. von R. Schleyer, *J. Comput. Chem*., 1983, **4**, 294–301.

15- J. M. Parr, A. Phanopoulos, A. Vickneswaran, M. R. Crimmin, *Chem. Sci*., 2023, **14**, 1590-1597.

16- J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev*., 2005, **105**, 2999–3093.

17- R. Dennington, T. Keith and J. Milliam, GaussView 5.0, Semichem Inc., Shawnee Mission, KS., 2009.

18- E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis and F. Weinhold, NBO 6.0., 2013.

19- F. Weinhold and C. R. Landis, *Chem. Educ. Res. Pr*., 2001, **2**, 91–104.

20- T. A. Keith, AIMALL (Version 19.10.12). TK Gristmill Software, Overland Park KS, USA., 2019.

21- F. Cortés-Guzmán and R. F. W. Bader*, Coord. Chem. Rev*., 2005, **249**, 633–662.

22- E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W. Yang, J*. Am. Chem. Soc.*, 2010, **132**, 6498–6506.

23- M. P. Mitoraj, A. Michalak and T. Ziegler, *J. Chem. Theory. Comput*., 2009, **5**, 962-975.

24- F. Neese, WIREs Comput Mol Sci 2018, 8:e1327.

25- F. Neese, F. Wennmohs, U. Becker and C. Riplinger, *J. Chem. Phys*., 2020, **152**, 1–18.

26- J. Da Chai and M. Head-Gordon, *J. Chem. Phys*., 2008, **128**, 084106.