Supporting Information

For

An Approach to Carbide-Centered Cluster Complexes

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2: Physical Measurements

**NMR spectroscopic studies** were carried out using a 500 MHz Bruker instrument with a broad-band probe (\(^1\)H, \(^{13}\)C{\(^1\)H} and \(^{31}\)P{\(^1\)H} NMR measurements), or a 500 MHz Bruker instrument with a cryoprobe (\(^1\)H and \(^{13}\)C{\(^1\)H} NMR measurements). For \(^1\)H and \(^{13}\)C, residual solvent signals were used for calibration (\(\text{C}_6\text{D}_6\): 7.16 and 128.06 ppm; \(\text{CD}_2\text{Cl}_2\): 5.33, and 54.24 ppm for \(^1\)H and \(^{13}\)C, respectively). For \(^{31}\)P, the signals were referenced to the deuterium resonances arising from the solvents.

**IR spectroscopic studies** were carried out using an Agilent Technologies Cary 630 FTIR instrument.

**X-ray crystallographic studies** were carried out on a single crystal of \(\text{RuCl}_2(\text{CO})_2(\text{PCy}_3)_2\) coated with mineral oil and mounted on a nylon loop, which was transferred to the nitrogen cold stream of the diffractometer. The X-ray diffraction studies were performed at 122(2) K on a Bruker D8 VENTURE diffractometer equipped with a Mo \(\text{Ka}\) high-brilliance \(\text{I} \upmu \text{S} \text{S}3\) radiation source (\(\lambda = 0.71073\) Å), a multilayer X-ray mirror and a PHOTON 100 CMOS detector, and an Oxford Cryosystems low temperature device. The instrument was controlled with the APEX2 software package using SAINT. Final cell constants were obtained from least squares fits of several thousand strong reflections. Intensity data were corrected for absorption using intensities of redundant reflections with the program SADABS. The structures were solved in Olex2 using the olex2.solve\(^3\) program (Charge Flipping) and refined using SHELXL. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters (\(U_{\text{iso}} = 1.2 U_{\text{eq}}\) of the parent atom for \(\text{CH}_2\) and \(\text{CH}\) groups). Disorder among the chloride and carbonyl ligands was modelled with a minor component (ca. 8.6%) with isotropic displacement parameters; bond distances in the minor component were restrained to be similar to those in the major component using the SADI command. The disorder may either reflect co-crystallization of \(\text{cis}\) and \(\text{trans}\) isomers or rotational disorder of the \(\text{trans}\) isomer. Selected crystallographic details are listed in Table S8. CCDC entry 1833487 contains the crystallographic data reported herein. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
$^{57}$Fe Mössbauer spectroscopic studies were carried out using a resonant gamma-ray spectrometer (See Co.) equipped with a Janis Research Model SVT-400 cryostat. All spectra were collected at a temperature of 80 K over 48 hours in the absence of an applied magnetic field. Spectra were fit using WMOSS4 (ver.F, See Co.). The velocity scale was calibrated using an Fe foil spectrum collected at room temperature. All data were fit using a theoretical model which incorporated quadrupole splitting (MODEL3_QS). The amount of random starting positions of fits were set to 100. Errors represent the standard deviation of Monte Carlo simulations for spectral parameters. The data were plotted along with calculated fits and residuals using Igor Pro (v. 6.73).

Preliminary mass spectrometric studies were carried out using a Bruker Solarix XR ESI/MALDI FT-ICR MS instrument operated in both positive and negative modes. Various soft ionization techniques (MALDI, ESI), solvents (ESI: acetonitrile, dichloromethane, methanol, toluene), matrices (MALDI: neat, DHB, DIT), as well as reagents (natural abundance vs. $^{13}$C-labelled RuC, LiOTf, AgOTf) were employed. However, the observed ions did not correspond to RuCFe$_2$, RuCCo$_2$, or (RuCCo)$_2$ (or simple derivatives thereof such as Li$^+$, Ag$^+$ or H$^+$ adducts). We speculate that the electrically neutral nature of the complexes along with their inclination towards decomposition prevent identification by means of mass spectrometry.
3: Syntheses and Spectral Data

3.1: (Cy3P)2Cl2Ru=CFe2(CO)8, RuCFe2

Samples for EXAFS characterization
Under a N2 atmosphere, Ru13C (11.4 mg, 15.3 μmol, 1.11 eq.) was dissolved in 1 ml dichloromethane, added to solid Fe2(CO)9 (5.0 mg, 14 μmol, 1.0 eq.), and stirred for 15 minutes. The solution was cooled to 77 K and analyzed by Fe K-edge EXAFS.
Under a N2 atmosphere, Ru13C (10.8 mg, 14.5 μmol, 1.00 eq.) was dissolved in 1 ml dichloromethane, added to solid Fe2(CO)9 (11.9 mg, 32.7 μmol, 2.26 eq.), and stirred for 15 minutes. The solution was cooled to 77 K and analyzed by Ru K-edge EXAFS.

Figure S1. 1H NMR spectrum of Ru13CFe2.
Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of Ru$^{13}\text{CFe}_2$.

Figure S3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of Ru$^{13}\text{CFe}_2$. 

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**Stoichiometry:** variation of the Ru\textsuperscript{13}C : Fe\textsubscript{2}(CO)\textsubscript{9} ratio indicates an 1:1 adduct.

1) Ru\textsuperscript{13}C (4.9 mg, 6.6 μmol) and Fe\textsubscript{2}(CO)\textsubscript{9} (1.2 mg, 3.3 μmol, 0.5 eq.) were dissolved in 0.4 ml CD\textsubscript{2}Cl\textsubscript{2}. Ru\textsuperscript{13}C and Ru\textsuperscript{13}CFe\textsubscript{2} carbide resonances displayed a 1 : 1 intensity ratio.

2) Ru\textsuperscript{13}C (4.9 mg, 6.6 μmol) and Fe\textsubscript{2}(CO)\textsubscript{9} (2.4 mg, 6.6 μmol, 1.0 eq.) were dissolved in 0.4 ml CD\textsubscript{2}Cl\textsubscript{2}. Ru\textsuperscript{13}C and Ru\textsuperscript{13}CFe\textsubscript{2} carbide resonances displayed a 1 : 4 intensity ratio.

3) Ru\textsuperscript{13}C (4.9 mg, 6.6 μmol) and Fe\textsubscript{2}(CO)\textsubscript{9} (5.1 mg, 14 μmol, 2.1 eq.) were dissolved in 0.4 ml CD\textsubscript{2}Cl\textsubscript{2}. Only Ru\textsuperscript{13}CFe\textsubscript{2} displayed a carbide resonance.

**Figure S4.** \textsuperscript{13}C\{\textsuperscript{1}H\} NMR spectra showing carbide resonances from titrations of Ru\textsuperscript{13}C with Fe\textsubscript{2}(CO)\textsubscript{9} in CD\textsubscript{2}Cl\textsubscript{2} (Ru\textsuperscript{13}C: 472.8 ppm, Ru\textsuperscript{13}CFe\textsubscript{2}: 438.1 ppm). 1) 0.5 equivalents of Fe\textsubscript{2}(CO)\textsubscript{9}, 2) 1 equivalent of Fe\textsubscript{2}(CO)\textsubscript{9}, 3) 2 equivalents of Fe\textsubscript{2}(CO)\textsubscript{9}.
Metallation with Fe₃(CO)₁₂

Ru¹³C (4.2 mg, 5.6 μmol) and Fe₃(CO)₁₂ (2.8 mg, 5.6 μmol) were dissolved in 0.4 ml C₆D₆ and analyzed by NMR. Immediately after mixing, no conversion had occurred as determined by ¹³C and ³¹P NMR. After 24 h, Ru¹³CFe₂ appeared in the reaction mixture, which contained predominantly Ru¹³C.

Figure S5. ¹³C{¹H} NMR spectrum of Ru¹³CFe₂ (437.6 ppm) generated from Ru¹³C (473.2 ppm) and Fe₃(CO)₁₂.
Figure S6. $^{31}P\{^1H\}$ NMR spectrum of Ru$^{13}$CFe$_2$ (26.0 ppm) generated from Ru$^{13}$C (38.4 ppm) and Fe$_3$(CO)$_{12}$. 
Decomposition: in C₆D₆, excess Fe₂(CO)₉ slowly converts Ru¹³C to Ru¹³CFe₂, which subsequently transforms to the all-trans complex, RuCl₂(CO)₂(PCy₃)₂. The reaction is nearly complete within 24 h. Crystals suitable for X-ray crystallography form in the NMR tube within days.

Figure S7. $^{13}$C{¹H} NMR spectra showing the progress of the reaction between Ru¹³C and Fe₂(CO)₉ in C₆D₆ (Ru¹³C: 473.2 ppm, Ru¹³CFe₂: 437.6 ppm).
**IR spectroscopy:** RuC (8.8 mg, 12 μmol) and Fe$_2$(CO)$_9$ (2.0 mg, 5.5 μmol) were dissolved in 1 ml CH$_2$Cl$_2$, stirred for 15 minutes, and analyzed by IR spectroscopy. For comparison, an IR spectrum of solid RuC was collected as well. CO stretching frequencies (cm$^{-1}$): 2070, 2003, 1993-1991, 1979, 1962.

**Figure S8.** IR spectrum of RuCFe$_2$ (black) and RuC (gray).

The IR spectrum of RuCFe$_2$ does not reveal bands indicative of bridging CO ligands (1800 – 1900 cm$^{-1}$). Typically, if two isomers are present, NMR spectroscopy will be likely to show a time-averaged single resonance, representing both terminal and bridging carbonyl ligands. On the other hand, both isomers are in principle observable by IR spectroscopy (if sufficiently abundant).

The bridging and terminal CO ligands in Fe$_2$(CO)$_8$(μ-L) complexes (μ-L = μ-CH$_2$, μ-CF$_2$) interconvert via an equilibrium between {Fe(CO)$_3$}$_2$(μ-L)(μ-CO)$_2$ (three bridging ligands) and {Fe(CO)$_4$}$_2$(μ-L) (one bridging ligand). Here, DFT$^6$ has revealed low energetic barriers for interconversion: for μ-CH$_2$, the {Fe(CO)$_4$}$_2$(μ-L) isomer is 1.2 – 5.9 kcal/mol above the {Fe(CO)$_3$}$_2$(μ-L)(μ-CO)$_2$ isomer, while for μ-CF$_2$, the isomers are nearly energetically degenerate (within 4 kcal/mol). Notably, solutions of the Fe$_2$(CO)$_8$(μ-L) complexes do not exhibit IR bands indicative of bridging CO ligands,
suggesting the isomerization barriers to be low enough for rapid interconversion on the IR timescale.

Based on the relative energies for the $\mu$-CH$_2$ and $\mu$-CF$_2$ complexes, the energetic barrier for interconversion between $\{\text{Fe(CO)}_3\}_2(\mu-$RuC)$\mu$-$\text{CO})_2$ and $\{\text{Fe(CO)}_4\}_2(\mu-$RuC) isomers is likely to be low, accounting for the lack of bands indicative of bridging CO ligands.
**57Fe Mössbauer spectroscopy:** RuCFe$_2$ was generated under an inert N$_2$ atmosphere in a glove box with a liquid N$_2$ cold-well. RuC (38.0 mg, 51.0 µmol, 1.11 eq.) was dissolved in 500 µL dichloromethane, added to a vial containing solid Fe$_2$(CO)$_9$ (16.7 mg, 45.9 µmol, 1.00 eq.), and allowed to stir for 15 minutes. Delrin Mössbauer sample cups were placed in the cold well and allowed to cool. The solution was divided into two 250 µL aliquots, and each aliquot was added dropwise to the center of a sample cup. The cups were sealed, brought out of the glove box, and introduced into liquid N$_2$ while frozen to ensure sample integrity. The sample cups were then placed in the Mössbauer spectrometer and analyzed. Absorption features were visible within hours, and the spectrum was collected over 48 hours. For comparison, solid Fe$_2$(CO)$_9$ was used to record a reference Mössbauer spectrum.

**Notes:** CH$_2$Cl$_2$ is known to absorb up to 80% of the 14.4 keV radiation used for $^{57}$Fe Mössbauer spectroscopy,$^7$ resulting in relatively low-intensity spectra. The CH$_2$Cl$_2$ solutions tended to cling to the walls of the sample cups, preventing effective absorption by the sample. Consequently, we used a minimal sample volume to increase the concentration of Fe-containing species, cooled the sample cups to 77 K prior to sample addition, and added the samples dropwise to the center of the cups. This located the samples on path with the beam.
The $^{57}$Fe Mössbauer spectrum of solid Fe$_2$(CO)$_9$ reveals a quadrupole doublet with high photon absorbance (Figure S3.1.9). The spectrum is centered at an isomer shift ($\delta$) of 0.18 ± 0.01 mm/s with a quadrupole splitting ($|\Delta E_q|$) of 0.40 ± 0.01 mm/s. The quadrupole splitting is consistent with the value reported by Gibb et al.$^8$ (0.42 mm/s). While Fe$_2$(CO)$_9$ is a highly symmetric molecule, the presence of any quadrupole splitting implies asymmetry about the electric field gradient (EFG) on the iron center(s). Indeed, the inequivalence of bridging and terminal carbonyls engenders this asymmetry in the EFG and manifests itself as minor quadrupole splitting.

The value of the isomer shift for Fe$_2$(CO)$_9$ may warrant a comment. Herber, Kingston and Wertheim$^9$ reported this isomer shift to be 0.282 mm/s, while Gibb et al.$^8$ reported isomer shifts between 0.31 – 0.44 mm/s, depending on sample thickness, temperature, and preparation method. The literature values are referenced to 310 stainless steel and sodium nitroprusside, respectively, (versus Fe foil used here) accounting for the variation.

Figure S9. Mössbauer spectrum of solid Fe$_2$(CO)$_9$ collected at 80 K. In black are the raw data, fit to the red calculated spectrum. The residual spectrum is in gray. The spectrum was fit to one Fe species with the following parameters: $\delta = 0.18 \pm 0.01$ mm/s, $|\Delta E_q| = 0.40 \pm 0.01$ mm/s.
The Mössbauer spectrum of the reaction mixture reveals resonances from two iron-containing compounds (Figure S3.1.10). Upon fitting, one resonance was identified as unconverted Fe$_2$(CO)$_9$ ($\delta = 0.21 \pm 0.01$ mm/s, $|\Delta E_q| = 0.35 \pm 0.02$ mm/s). The other resonance arises from a single new species (RuCFe$_2$) with $\delta = -0.09 \pm 0.01$ mm/s and $|\Delta E_q| = 2.34 \pm 0.01$ mm/s. The relative areas of the RuCFe$_2$ and Fe$_2$(CO)$_9$ components display an approximate 3:2 ratio.

Figure S10. Mössbauer spectrum of reaction mixture (showing Fe$_2$(CO)$_9$ + RuCFe$_2$) collected at 80 K. In black are the raw data, fit to the red calculated spectrum. The residual spectrum is in gray. The spectrum was fit to two Fe species (Fe$_2$(CO)$_9$ and RuCFe$_2$) with the following parameters: $\delta_1 = 0.21 \pm 0.01$ mm/s, $|\Delta E_q|_1 = 0.35 \pm 0.02$ mm/s; $\delta_2 = -0.09 \pm 0.01$ mm/s, $|\Delta E_q|_2 = 2.34 \pm 0.01$ mm/s.
A difference spectrum with the resonance of Fe$_2$(CO)$_9$ subtracted (Figure S3.1.11), was fit independently and returned parameters identical to those of RuCFe$_2$ in the reaction mixture ($\delta = -0.09 \pm 0.01$ mm/s, $|\Delta E_q| = 2.35 \pm 0.01$ mm/s).

RuCFe$_2$ displays a smaller isomer shift than Fe$_2$(CO)$_9$. This may reflect the change in coordination environment about the Fe nuclei. Namely, a marked decrease in $\delta$ may reflect less d-$\pi$ backbonding involving the RuC ligand. This would push more electron density about the Fe nuclei and, in turn, decrease the isomer shift. The large quadrupole splitting likely manifests from the descent in symmetry from $D_{3h}$ of Fe$_2$(CO)$_9$ to $C_{2v}$ of RuCFe$_2$.

Figure S11. Difference Mössbauer spectrum of reaction mixture (showing RuCFe$_2$) collected at 80 K. In black are the raw data, fit to the red calculated spectrum. The residual spectrum is in gray. The spectrum was fit to one Fe species (RuCFe$_2$) with the following parameters: $\delta = -0.09 \pm 0.01$ mm/s, $|\Delta E_q| = 2.35 \pm 0.01$ mm/s.
3.2: (Cy₃P)₂Cl₂Ru=CCO₂(CO)₇, RuCCO₂

Samples for EXAFS characterization

Under a N₂ atmosphere, Ru¹³C (4.0 mg, 5.4 μmol, 1.0 eq.) was dissolved in 0.5 ml toluene, added to solid Co₂(CO)₈ (6.6 mg, 19 μmol, 3.6 eq.), and stirred for 5 minutes. The solution was cooled to 77 K and analyzed by Ru K-edge EXAFS.

Figure S12. ¹H NMR spectrum of Ru¹³CCO₂.
Figure S13. $^{13}$C\{$^1$H\} NMR spectrum of Ru$^{13}$CCo$_2$.

Figure S14. $^{31}$P\{$^1$H\} NMR spectrum of Ru$^{13}$CCo$_2$. 
Decomposition: Ru$^{13}$CCo$_2$ decomposes slowly in C$_6$D$_6$, as judged from the appearance of new $^1$H and $^{31}$P NMR resonances after 24 h.

![Figure S15. $^1$H NMR spectra showing the decomposition of Ru$^{13}$CCo$_2$.](image)

![Figure S16. $^{31}$P{$^1$H} NMR spectra showing the decomposition of Ru$^{13}$CCo$_2$.](image)
3.3: [(Cy3P)2Cl2Ru≡C–Co(CO)3]2, (RuCCo)2

Figure S17. 1H NMR spectrum of (Ru13CCo)2.
Figure S18. $^{13}\text{C}^{\text{1}H}$ NMR spectrum of (Ru$^{13}\text{CCo}$)$_2$. Minor carbide resonances: Ru$^{13}\text{C}$ at 473.2 ppm and Ru$^{13}\text{CCo}$ at 423.0 ppm.
Figure S19. $^{31}P\{^1H\}$ NMR spectrum of (Ru$^{13}$CCo)$_2$. Minor resonances: Ru$^{13}$C at 38.4 ppm and Ru$^{13}$CCo at 30.7 ppm.
4: EXAFS Experiments and Computational Details

Ruthenium and iron K-edge extended X-ray absorption fine structure (EXAFS) was used to characterize two analogous reaction products of a RuC and a bimetallic Fe or Co core: (Cy₃P)₂Cl₂Ru=CFe₂(CO)₈ (RuCFe₂) and (Cy₃P)₂Cl₂Ru=CCo₂(CO)₇ (RuCCo₂). Geometry optimizations were conducted at the BP86/ZORA-def2-TZVPP level of theory. While a multitude of potential products were proposed (Scheme S4.1), we confidently assign the major reaction product as a C₂ᵥ symmetric molecule where the RuC acts as a bridge between the Fe/Co centers.

Scheme S1. Potential [RuC–Fe] complexes arising from the reaction between RuC and Fe₂(CO)₉.

Materials and Methods

XAS Measurements

(Cy₃P)₂Cl₂Ru=CFe₂(CO)₈ (RuCFe₂) and (Cy₃P)₂Cl₂Ru=CCo₂(CO)₇ (RuCCo₂) were prepared in solution under an inert nitrogen atmosphere. These solutions were injected into Delrin sample holders with 38 µm Kapton tape windows and held at 77 K until data collection. Fe and Ru K-edge XAS spectra were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) at beamline 7-3 under ring conditions of 3 GeV and 500 mA. A Si(200) double-crystal monochromator was used for energy
selection and a Rh-coated mirror (set to an energy cutoff of 9 keV) was used for harmonic rejection. Internal energy calibration was performed by assigning the first inflection point of a Fe and Ru foil spectrum to 7111.2 eV and 22117 eV, respectively. Fe samples were measured in transmission mode using N$_2$-filled ionization chambers with the sample maintained at 10 K in an Oxford liquid helium flow cryostat. Fe data were collected from 6784 to 8127 eV (k = 16 Å$^{-1}$). Ru samples were measured under identical conditions, and data were collected in fluorescence mode using a Ge30 detector. Ru data were collected from 21893 to 23115 eV (k = 14 Å$^{-1}$). 2-6 scans were averaged and processed using the MAVE and PROCESS modules of EXAFSPAK$^{10}$ software package. A smooth pre-edge background was removed from each averaged spectrum by fitting a first-order polynomial to the pre-edge region and subtracting this polynomial from the entire spectrum. A polynomial spline was subtracted above 7130 eV and 22135 eV for Fe and Ru, respectively, and normalized to a post-edge absorption of 1. Extended X-ray absorption fine structure (EXAFS) fitting was performed using the OPT module of the EXAFSPAK software package. Coordinates from DFT geometry optimizations were used to generate models for scattering path calculations by FEFF7.$^{11}$ Paths were optimized by least-squares fitting, where floated parameters included R and $\sigma^2$.

Calculations

All geometry optimizations were performed using version 4.0 of the ORCA computation chemistry package.$^{12}$ Geometry optimizations were performed using the BP86$^{13}$ functional and the zeroth-order regular approximation for relativistic effects as implemented by van Wüllen.$^{14}$ The ZORA-def2-TZVPP basis set$^{15}$ was used on all atoms. Numerical frequencies were calculated to ensure that the geometry optimization converged to a global minimum. A single point calculation was carried out on the optimized geometry using the PBE0 hybrid density functional$^{16}$ and with the same aforementioned basis set on all atoms. Solvation was modeled using a conductor-like polarizable continuum model (CPCM$^{17}$) with an infinite dielectric. To minimize computational
expense, model structures were truncated at the PCy$_3$ ligands on Ru to PMe$_3$. Initial coordinates were obtained from a previous computational study by Krapp and Frenking.$^{18}$

**Results**

*Extended $X$-ray Absorption Fine Structure*

Both Ru EXAFS were collected to $k = 14$ Å$^{-1}$ and Fe EXAFS were collected to $k = 16$ Å$^{-1}$. All EXAFS were fit using scattering paths calculated by FEFF7 using geometry optimized coordinates. The raw data were used for fitting the Ru EXAFS. Fe spectra showed significant glitching, so the smoothed data were used in the fitting procedure. Fitted EXAFS including Fourier transforms are presented in Figures S20 – S22. Fit parameters are compiled in Tables S1 – S3.

**Figure S20.** Ru EXAFS of RuCFe$_2$. Red traces represent experimental data, while dashed black lines correspond to simulated data from fits producing F-factors.
EXAFS were fit in OPT using paths calculated by FEFF7. Coordination numbers (CN) were held constant while distances (R) and Debye-Waller factors ($\sigma^2$) were allowed to float. Errors in distances are estimated to be 0.02-0.03 Å and 25% for coordination numbers. Fits were performed over the entire (0 to 6.0 Å) Fourier transform window. Goodness of fit is measured by $F$, defined as $\left[ \frac{\sum_i \left( k^3 (EXAFS_{obs} - EXAFS_{calc})_i \right)^2 / n \right]^{1/2}$.

| Fit | Path  | Coordination # | R (Å)  | $\sigma^2$ | $F$  |
|-----|-------|----------------|--------|------------|------|
| 1   | Ru-Cl | 4              | 2.383  | 0.00339    | 40.40|
| 2   | Ru-Cl | 4              | 2.384  | 0.00339    | 38.78|
|     | Ru=C  | 1              | 1.713  | 0.00303    |      |
| 3   | Ru-Cl | 4              | 2.381  | 0.00334    | 23.95|
|     | Ru=C  | 1              | 1.710  | 0.00236    |      |
|     | Ru-Fe | 2              | 3.606  | 0.00202    |      |

Table S1. Ru EXAFS simulations for RuCFe$_2$.

Figure S21. Ru EXAFS of RuCCo$_2$. Red traces represent experimental data, while dashed black lines correspond to simulated data from fits producing F-factors.
Table S2. Ru EXAFS simulations for RuCCo₂.

| Fit | Path      | Coordination # | R (Å)   | σ²      | F    |
|-----|-----------|----------------|---------|---------|------|
| 1   | Ru-Cl     | 4              | 2.379   | 0.00396 | 44.36|
| 2   | Ru-Cl     | 4              | 2.377   | 0.00393 | 42.73|
|     | Ru=C      | 1              | 1.693   | 0.00511 |      |
| 3   | Ru-Cl     | 4              | 2.373   | 0.0039  | 23.51|
|     | Ru=C      | 1              | 1.688   | 0.00446 |      |
|     | Ru-Co     | 2              | 3.588   | 0.00197 |      |
| 4   | Ru-Cl     | 4              | 2.380   | 0.00383 | 18.80|
|     | Ru=C      | 1              | 1.693   | 0.00453 |      |
|     | Ru-Co     | 2              | 3.570   | 0.00082 |      |
|     | RuCCo (MS)| 4              | 3.646   | 0.00069 |      |
|     | RuPC (MS) | 6              | 3.691   | 0.00487 |      |

EXAFS were fit in OPT using paths calculated by FEFF7. Coordination numbers (CN) were held constant while distances (R) and Debye-Waller factors (σ²) were allowed to float. Errors in distances are estimated to be 0.02-0.03 Å and 25% for coordination numbers. Fits were performed over the entire (0 to 6.0 Å) Fourier transform window. Goodness of fit is measured by F, defined as $F = \left[ \frac{\sum_{i} k_i^3 (\text{EXAFS}_{\text{obs}} - \text{EXAFS}_{\text{calc}})_i^2}{n} \right]^{1/2}$. 
**Figure S22.** Fe EXAFS of RuCFe₂. Red traces represent experimental data, while dashed black lines correspond to simulated data from fits producing F-factors.

**Table S3.** Fe EXAFS simulations for RuCFe₂.

| Fit | Path                        | Coordination # | R (Å)  | σ²    | F     |
|-----|------------------------------|----------------|--------|-------|-------|
| 1   | Fe-C (terminal carbonyl)     | 3              | 1.799  | 0.00702 | 82.58 |
| 2   | Fe-C (terminal carbonyl)     | 3              | 1.832  | 0.00755 | 46.47 |
|     | Fe-Fe                        | 1              | 2.768  | 0.00321 |       |
|     | *Treat bridges the same*     |                |        |        |       |
| 3   | Fe-C (terminal carbonyl)     | 3              | 1.841  | 0.00744 | 46.16 |
|     | Fe-Fe                        | 1              | 2.777  | 0.00314 |       |
|     | Fe-C (bridging carbonyl)     | 3              | 2.166  | 0.02054 |       |
|     | *Treat bridges differently*  |                |        |        |       |
| 4   | Fe-C (terminal carbonyl)     | 3              | 1.847  | 0.00621 | 43.97 |
|     | Fe-Fe                        | 1              | 2.781  | 0.00337 |       |
|     | Fe-C (bridging carbonyl)     | 2              | 2.065  | 0.00485 |       |
|     | Fe-C (bridging carbonyl)*    | 1              | 2.189  | 0.00207 |       |
| 5   | Fe-C (terminal carbonyl)     | 3              | 1.846  | 0.00617 | 37.55 |
| Bond Type                        | Coordination Number | Distance (Å) | Debye-Waller Factor |
|---------------------------------|---------------------|--------------|---------------------|
| Fe-Fe                           | 1                   | 2.779        | 0.00341             |
| Fe-C (bridging carbonyl)        | 2                   | 2.066        | 0.00494             |
| Fe-C (bridging carbonyl)*       | 1                   | 2.191        | 0.00222             |
| Fe-Ru                           | 1                   | 3.650        | 0.0057              |
| Fe-C (terminal carbonyl)        | 3                   | 1.813        | 0.00524             |
| Fe-Fe                           | 1                   | 2.756        | 0.00446             |
| Fe-C (bridging carbonyl)        | 2                   | 1.993        | 0.00619             |
| Fe-C (bridging carbonyl)*       | 1                   | 2.143        | 0.00411             |
| Fe-Ru                           | 1                   | 3.619        | 0.00616             |
| Fe-O (terminal carbonyl)        | 3                   | 3.069        | 0.00208             |
| Fe-O (bridging carbonyl)        | 2                   | 3.221        | 0.00138             |

EXAFS were fit in OPT using paths calculated by FEFF7. Coordination numbers (CN) were held constant while distances (R) and Debye-Waller factors ($\sigma^2$) were allowed to float. Errors in distances are estimated to be $0.02-0.03$ Å and 25% for coordination numbers. Fits were performed over the entire (0 to 6.0 Å) Fourier transform window. Goodness of fit is measured by $F$, defined as $[(\sum_i [k_i^3 (\text{EXAFS}_{\text{obs}} - \text{EXAFS}_{\text{calc}})]^2 / n)^{1/2}$.

Good fits were obtained for all datasets. It should be noted that models used in scattering path calculations and fitting procedures feature PMe$_3$ ligands on Ru, and thus are truncated versions of the compounds synthesized, which feature PCy$_3$ ligands. While we cannot rule out the contributions of additional C scatterers interacting with the photoabsorbing Ru or Fe, the truncated models are sufficient to fit the data as demonstrated by the statistical fitting parameter $F$ of each fit. The fits establish bridging rather than terminal Ru=C coordination.

During Ru EXAFS fitting simulations on RuCFe$_2$ and RuCCo$_2$, a coordination number of four was chosen to model both Cl and P, as EXAFS cannot accurately distinguish between scatterers in close proximity on the periodic table. Fitting these data consistently yields an inner-sphere, Ru-C bond distance of ~1.7 Å. This bond distance is within statistical error of the RuC starting material (1.66 Å) and our geometry optimized model (1.73 Å). While multiple scattering (MS) paths were
incorporated into EXAFS fitting of RuCCO₂, these paths proved troublesome in modeling RuCFe₂ and yielded physically unrealistic Debye-Waller factors. Fits presented in Tables S1 – S2 reflect a single photoabsorbing Ru equally interacting with two identical Fe or Co scatterers in RuCFe₂ and RuCCO₂, respectively. Judging from the raw data, no significant scatterers appear to be omitted from these fits, aiding the argument that the Fe and Co centers are at the same distance from Ru.

The Fe dataset was modeled with two identical Fe absorbers. Thus, coordination numbers reflect a single Fe photoabsorber. Sequential fitting show significant improvements measured by the decreasing statistical fit parameter F. As with the fitting of the Ru dataset, the Fe dataset is sufficiently modeled by a symmetric molecule with two identical Fe centers. This rules out the terminal binding motif of the di-iron core, which would display two chemically distinct Fe centers. This suggests that the Fe atoms in RuCFe₂, and by extension Co in RuCCO₂, are better described as being bridged by RuC.

Additional fits were made to see if the data were better modeled after three identical bridging carbons between Fe centers, or if one could be distinguished from the other two. Comparing fits 3 and 4 in Table S3 suggests that RuCFe₂ should be seen as having two identical carbonyl bridges with Fe-C distances of ~2.0 Å along with a unique carbon bridge with a slightly larger Fe-C distance of 2.1Å. This observation is reasonable when considering the molecular structure. Steric bulk surrounding RuC will clash with the terminally bound CO moieties on the bimetallic core. This should induce a slight elongation of the Fe-C distances between the Fe centers and RuC.

Collectively, the datasets support C₂v-symmetric molecules with Ru=C bridging the heterometals.
Figure S23. RuC Frontier Orbitals (ZORA-def2-TZVPP/B3LYP)
Table S4. Orbital parentage scheme for RuC Frontier Orbitals (ZORA-def2-TZVPP/B3LYP)

| MO       | OCCUPANCY | ENERGY (H)  | ENERGY (eV) | C_s | C_pz | C_px | C_py | Ru_dz^2 | Ru_dxy | Ru_dyz | Ru_dxy^2-y^2 |
|----------|-----------|-------------|-------------|-----|------|------|------|---------|--------|--------|-------------|
| HOMO-4   | 79        | -0.29793    | -8.1066753  | 0   | 0    | 17   | 0.8  | 0       | 11.1   | 0.5    | 0.3         | 3.6        |
| HOMO-3   | 80        | -0.26602    | -7.2384042  | 11.3| 17   | 0.5  | 7    | 5.3     | 0.4    | 8.6    | 0.1         | 0          |
| HOMO-2   | 81        | -0.25037    | -6.8125677  | 0   | 3.3  | 1.2  | 13.2 | 9.3      | 0      | 6      | 2.8         | 0.2        |
| HOMO - 1 | 82        | -0.25005    | -6.8038605  | 0   | 0.2  | 1    | 2.1  | 1.1      | 0.9    | 0.4    | 0           | 1          |
| HOMO     | 83        | -0.21008    | -5.7162768  | 0   | 0    | 0    | 0    | 13.2     | 0.4    | 7.4    | 39.1        |
| LUMO     | 84        | -0.0323     | -0.878883   | 0.1 | 15.3 | 1.6  | 5.6  | 4        | 0.1    | 13.2   | 7.7         | 1.9        |
| LUMO + 1 | 85        | -0.02667    | -0.7256907  | 0   | 10.6 | 0.3  | 38.7 | 16.4     | 0.1    | 13.6   | 15.0        | 0.2        |
| LUMO + 2 | 86        | -0.02333    | -0.6348093  | 0   | 0.7  | 52.1 | 1.3  | 0.1      | 20.2   | 0.1    | 1.1         | 5          |
Figure S24. RuCFe\textsubscript{2} Frontier Orbitals (ZORA-def2-TZVPP/PBE0) (schematic indication of bonding referring to RuC molecular orbitals)
| MO   | ENERGY (eV) | C s | C pz | C px | C py | C d | Ru pz | Ru px | Ru py | Ru d² | Ru dx²-y² | Ru dyz | Ru dxz | Fe pz | Fe px | Fe py | Fe d² | Fe dx²-y² | Fe dyz | Fe dxz | Fe dx²-y² | Fe dyz |
|------|-------------|-----|------|------|------|-----|-------|-------|-------|-------|-----------|--------|--------|-------|-------|-------|--------|-----------|--------|--------|-----------|--------|
| HOMO-4 | -7.394 | 0   | 0    | 7.4  | 0    | 0   | 0     | 0     | 0.2   | 0     | 5.4       | 0      | 0      | 1.4   | 0.4   | 0     | 8.2    | 17.2     | 0      | 17     | 0          | 0      |
| HOMO-3 | -7.262 | 0   | 0    | 6.2  | 0.9  | 0    | 0     | 6.7   | 0     | 0     | 0.9       | 0      | 0      | 0     | 0     | 0     | 0      | 0         | 5.8    | 0      | 1.8        | 0      |
| HOMO-2 | -6.209 | 0   | 0    | 0    | 0.6  | 0    | 0     | 0     | 0     | 0     | 0         | 0      | 0      | 42.6  | 0     | 0     | 1.6    | 0         | 1.2    | 0      | 7.4        | 0      |
| HOMO-1 | -6.153 | 0   | 0    | 0    | 0    | 0    | 0     | 0     | 0     | 0     | 0         | 0      | 0      | 15.1  | 0     | 0     | 5.4    | 0         | 0      | 2      | 26.4       | 0      |
| HOMO  | -5.412 | 0   | 0    | 0.6  | 0    | 4    | 0     | 0.1   | 0     | 0     | 28.8      | 0      | 0      | 4.2   | 0     | 0     | 10.2   | 20.2     | 0      | 0.2    | 0          | 0      |
| LUMO  | -2.021 | 6.2 | 1.6  | 0    | 0    | 1.1  | 9.4   | 0     | 0     | 18.5  | 0         | 0      | 0.6    | 0.8   | 0.2   | 0     | 9      | 8        | 0      | 15.8   | 0          | 0      |
| LUMO+1 | -1.644 | 0   | 0    | 10.9 | 0.8  | 0.2  | 0     | 0.2   | 0     | 9.6   | 0         | 0      | 0      | 2.4   | 0     | 8.6   | 0      | 22.4     | 0      | 0      | 22.4       | 0      |
| LUMO+2 | -1.367 | 0   | 0    | 18.9 | 1.2  | 0    | 0     | 0     | 0     | 0     | 0         | 0      | 13.5   | 0     | 0     | 0     | 1      | 0        | 0      | 10     | 0          | 0.6    |
| LUMO+3 | -1.161 | 0.7 | 5.4  | 0    | 0    | 0.5  | 3.4   | 0     | 0     | 3.2   | 0         | 0      | 1.2    | 0.8   | 0.4   | 0     | 3.6    | 6.2      | 0      | 0.8    | 0          | 0      |
| LUMO+4 | -0.920 | 0.9 | 0.8  | 0    | 0    | 0.2  | 0     | 0     | 0     | 1     | 0         | 0      | 0      | 3.8   | 0.2   | 0     | 17.8   | 0        | 0      | 0      | 0          | 0      |

**Table S5.** Orbital parentage scheme for RuCFe₂ Frontier Orbitals (ZORA-def2-TZVPP/PBE0)

| Bond     | Distance (Å) |
|----------|--------------|
| Ru–C     | 1.713        |
| C–Fe     | 2.062        |
| Fe–Fe    | 2.525        |
| Fe–C bridging CO | 1.982 |
| Fe–C terminal CO | 1.787 |

**Table S6.** Selected Bond Distances from Frequency Calculation
Table S7. Vibrational frequencies (cm\(^{-1}\)) calculated for RuCFe\(_2\).

|   |     |     |     |     |     |     |     |
|---|-----|-----|-----|-----|-----|-----|-----|
| 0 | 0.00| 36: | 190.77 | 72: | 536.76 | 108: | 1391.70 |
| 1 | 0.00| 37: | 191.86 | 73: | 542.77 | 109: | 1393.00 |
| 2 | 0.00| 38: | 201.56 | 74: | 548.66 | 110: | 1396.56 |
| 3 | 0.00| 39: | 203.22 | 75: | 579.79 | 111: | 1398.08 |
| 4 | 0.00| 40: | 213.57 | 76: | 605.16 | 112: | 1398.81 |
| 5 | 0.00| 41: | 214.69 | 77: | 617.60 | 113: | 1400.32 |
| 6 | 30.07| 42: | 221.68 | 78: | 619.11 | 114: | 1401.11 |
| 7 | 31.40| 43: | 225.98 | 79: | 631.04 | 115: | 1402.39 |
| 8 | 38.43| 44: | 228.61 | 80: | 633.24 | 116: | 1413.32 |
| 9 | 43.84| 45: | 229.67 | 81: | 653.92 | 117: | 1414.89 |
| 10 | 55.27| 46: | 251.73 | 82: | 657.91 | 118: | 1785.34 |
| 11 | 63.29| 47: | 253.14 | 83: | 725.40 | 119: | 1813.45 |
| 12 | 64.36| 48: | 253.39 | 84: | 726.18 | 120: | 1955.25 |
| 13 | 64.53| 49: | 259.00 | 85: | 731.15 | 121: | 1956.36 |
| 14 | 65.05| 50: | 268.19 | 86: | 731.49 | 122: | 1967.61 |
| 15 | 76.51| 51: | 270.82 | 87: | 772.17 | 123: | 1969.57 |
| 16 | 81.92| 52: | 298.20 | 88: | 772.87 | 124: | 1997.81 |
| 17 | 85.92| 53: | 316.18 | 89: | 818.58 | 125: | 2053.33 |
| 18 | 88.67| 54: | 332.15 | 90: | 823.67 | 126: | 2971.75 |
| 19 | 91.21| 55: | 337.00 | 91: | 827.40 | 127: | 2972.07 |
| 20 | 91.90| 56: | 348.92 | 92: | 832.92 | 128: | 2982.21 |
| 21 | 93.94| 57: | 378.22 | 93: | 920.91 | 129: | 2982.48 |
| 22 | 98.61| 58: | 393.48 | 94: | 929.68 | 130: | 2982.72 |
| 23 | 101.24| 59: | 405.94 | 95: | 930.75 | 131: | 2982.83 |
| 24 | 107.98| 60: | 418.89 | 96: | 931.19 | 132: | 3059.59 |
| 25 | 108.54| 61: | 430.20 | 97: | 932.11 | 133: | 3059.70 |
| 26 | 108.91| 62: | 431.32 | 98: | 939.18 | 134: | 3068.62 |
| 27 | 115.39| 63: | 452.86 | 99: | 1032.35 | 135: | 3068.73 |
| 28 | 122.41| 64: | 454.58 | 100: | 1257.47 | 136: | 3069.52 |
| 29 | 141.92| 65: | 457.38 | 101: | 1258.37 | 137: | 3069.59 |
| 30 | 149.74| 66: | 476.72 | 102: | 1259.52 | 138: | 3069.76 |
| 31 | 156.98| 67: | 478.67 | 103: | 1260.40 | 139: | 3070.11 |
| 32 | 166.88| 68: | 498.20 | 104: | 1273.14 | 140: | 3088.08 |
| 33 | 172.48| 69: | 499.05 | 105: | 1275.07 | 141: | 3088.22 |
| 34 | 176.36| 70: | 499.59 | 106: | 1385.04 | 142: | 3088.88 |
| 35 | 182.22| 71: | 502.18 | 107: | 1385.70 | 143: | 3089.15 |
Input file from SP calculation using coordinates from frequency calculation

!PBE0 RIJCOSX ZORA-def2-TZVPP def2/J ZORA CPCM RKS PAL4
!NormalPrint VeryTightSCF SlowConv Grid4 NoFinalGrid
!PrintBasis

%output print[p_mos] 1 end

%basis
NewGTO P "ZORA-def2-TZVPP" end
NewGTO Cl "ZORA-def2-TZVPP" end
NewGTO Fe "ZORA-def2-TZVPP" end
NewGTO Ru

S 8
  1 93283.6692400000      0.0008767582
  2 13982.1477960000      0.0037777363
  3 31820.7919860000      0.0145163200
  4 9007.5776945000      0.0494502816
  5 2933.9513846000      0.1442783116
  6 1057.3914575000      0.3102364092
  7 412.0736383600      0.4200949705
  8 163.3737210300      0.2160171158
S 1
  1 958.8142400900      1.0000000000
S 1
  1 299.4506679900      1.0000000000
S 1
  1 52.7324868350      1.0000000000
S 1
  1 24.1566818200     -1.0000000000
S 1
  1 35.6482305180      1.0000000000
S 1
  1 7.4588193956      1.0000000000
S 1
  1 4.5066812748     -1.0000000000
S 1
  1 1.6110646956      1.0000000000
S 1
  1 0.6754002829     -1.0000000000
S 1
  1 0.0999396325      1.0000000000
S 1
  1 0.0396207977     -1.0000000000
P 6
  1 5281.5619152000     0.0038091900
newauxgto Ru "def2/J" end
newauxgto C "def2/J" end
newauxgto H "def2/J" end
end

% tddft  NRoots 80
MaxDim 800
OrbWin[0] = 0, 0, -1, -1
OrbWin[1] = 0, 0, -1, -1
DoQuad true
end

%method SpecialGridAtoms 44
  SpecialGridIntAcc 7
end

%maxcore 10000

%SCF
  Directresetfreq 1
  DIIS MaxEq 15
end
  Shift Shift 0.5
  Erroff 0.1
end
  MaxIter 750
end

#coordinates from frequency calc from KML

| *   | xyz | 0 1 |
|-----|-----|-----|
| Fe  | -0.00096012069900 | 0.0000099648355 | -0.16345073147080 |
| Ru  | -0.00078004829870 | 0.00002236092596 | 1.54983862356304 |
| P   | 0.00080572140781 | 2.26332727450308 | 2.14250805708033 |
| Fe  | -1.26119787312199 | 0.0011703884452 | -1.79467300398935 |
| C   | -2.820411676925    | 1.3150818571997 | -1.10759166909129 |
| O   | -3.0324295456513   | 2.12734022585671 | -0.78062833174047 |
| C   | 0.0016209634357    | 1.36944774826821 | -2.47157449697563 |
| O   | 2.83551397272723   | 1.3145723741770 | -1.1046637562287 |
| C   | 3.0336097031434    | 2.1265848725111 | -0.7764623909214 |
| C   | -2.8159497466322   | -1.31509209715031 | -1.10747705688465 |
| O   | -3.03131654826604  | -2.12793562599865 | -0.78043640814523 |
| C   | 0.00154844937027   | -1.36918301773568 | -2.47187120467276 |
| O   | 0.00161718679473   | -2.43687029545882 | -2.9723097219255 |
| C   | -2.0459253566754   | 0.0000255218976 | -3.40058334204527 |
| O   | -2.58564641079934  | -0.000170287379 | -4.42194167790107 |
| C   | 0.00188769377755   | 2.4372443372214 | -2.9717844532678 |
| C   | 2.82382863064126   | -1.3152716322357 | -1.1054250274098 |
| C   | 3.03311796513270   | -2.12793341289623 | -0.77814907858210 |
| C   | 2.0502208009476    | 0.00009563516548 | -3.3984996097579 |
| C   | 2.59103326638538   | 0.00016857513058 | -4.4192867323070 |
| P   | -0.00135099871396  | -2.26323244914555 | 2.14262222443860 |
| Cl  | 2.30402645170643   | -0.0079904482080 | 2.01691282115394 |
| Cl  | -2.30521195789367  | 0.0000210991713 | 2.01652240839576 |
| C   | 1.4256269756925    | 3.31382898110795 | 1.73348674768368 |
| C   | 1.42448877699907   | -3.31365784664018 | 1.73255402318680 |
| C   | 0.00179638952022   | 2.17406919633206 | 3.96926387226729 |
C  -1.42925703757068  3.31202421412649  1.73705461786162
C  0.00245046418971  -2.17421870928160  3.96938721856609
C  -1.43042394047143  -3.31163618080654  1.73705461786162
H  -1.38094107553111  -4.23349649244047  2.33191235128301
H  -2.35682861176060  -2.77065695852693  1.9555985021728
H  -1.40207433057834  -3.56779234900977  0.67396772237805
H  0.00286495065279  -3.18701106496670  4.39304282197857
H  0.89821679131063  -1.63802685639652  4.30537395859396
H  -0.89111950824855  -1.63693457724955  4.30956142018681
H  1.37637464919429  -4.23561557703635  2.32593768782254
H  1.39159449877108  -3.56941283451060  0.6680335766432
H  2.35248835054973  -2.77404337090268  1.94613694835467
H  0.00079836586373  3.18682689916980  4.39301377160621
H  -0.89117904077477  1.63555010882783  4.30902975841433
H  0.89815318558044  1.63898737859554  4.30550580075501
H  -1.37953651957331  4.23431871443153  2.32977156875630
H  -1.39998864154206  3.56721309243736  0.67230139252266
H  -2.35610216249289  2.77182090659949  1.95409478261230
H  1.37665705529599  4.23544171615400  2.32739386373866
H  2.35335278336073  2.77448437169253  1.94727423132356
H  1.39228024430245  3.57032211227741  0.66913215994338

*
## 5: Crystallographic Data

**Table S8.** Crystallographic data for trans,trans,trans-RuCl$_2$(CO)$_2$(PCy$_3$)$_2$.

| CCDC entry | 1833487 |
|-------------|---------|
| Empirical formula | C$_{38}$H$_{66}$Cl$_2$O$_2$P$_2$Ru |
| Formula weight | 788.81 |
| $T / K$ | 122(2) |
| Crystal system | triclinic |
| Space group | P–1 |
| $a / \text{Å}$ | 9.8206(5) |
| $b / \text{Å}$ | 10.4764(4) |
| $c / \text{Å}$ | 10.8375(5) |
| $\alpha / ^\circ$ | 115.2290(10) |
| $\beta / ^\circ$ | 107.486(2) |
| $\gamma / ^\circ$ | 92.418(2) |
| $V / \text{Å}^3$ | 943.12(8) |
| $Z$ | 1 |
| $\rho_{\text{calc}} / \text{g cm}^{-3}$ | 1.389 |
| $\mu / \text{mm}^{-1}$ | 0.674 |
| $2\theta$ range / $^\circ$ | 4.384 – 50.694 |
| Reflections collected | 14301 |
| Independent reflections | 3428 [$R_{\text{int}} = 0.0302$] |
| Data / restraints / parameters | 3428 / 4 / 218 |
| Goodness-of-fit on $F^2$ | 1.042 |
| Final $R$ indexes [$I>2\sigma (I)$] | $R_1 = 0.0220$, $wR_2 = 0.0517$ |
| Final $R$ indexes [all data] | $R_1 = 0.0272$, $wR_2 = 0.0543$ |
| Largest diff. peak / hole / e $\text{Å}^{-3}$ | 0.34 / –0.51 |
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