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Supplementary material

Evidence for Cobalt-Cobalt bond homolysis and wavelength dependent CO loss in (μ₂-alkyne)Co₂(CO)₆ complexes

Nicola M. Boyle, Anthony C. Coleman, Conor Long, Kate L. Ronayne, Wesley R. Browne, Ben L. Feringa, Mary T. Pryce*

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1. General Experimental Details

All manipulations were carried out under an atmosphere of argon or nitrogen using standard Schlenk techniques. Silica Gel (Merck) was used as received. All mobile phases for column chromatography were dried over MgSO$_4$ before use. All solutions were deoxygenated by purging with argon or nitrogen for ~10 min. Column chromatography was carried out using neutral silica gel or neutral aluminum oxide. Diphenyl acetylene, 1-ethynylferrocene, and dicobalt octacarbonyl were obtained from Sigma-Aldrich and used without further purification. Carbon monoxide was obtained from Air Products Ltd. Steady state IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer (2 cm$^{-1}$ resolution) in a 0.1 mm sodium chloride liquid cell using spectroscopic grade pentane, cyclohexane, and dichloromethane. NMR spectra were recorded on a Varian VXR-300 ($^1$H NMR at 300 MHz, $^{13}$C NMR at 75.5 MHz), or on a Varian Mercury Plus 400 ($^1$H NMR at 400 MHz, $^{13}$C NMR at 100 MHz). Chemical shifts (δ) are denoted in ppm and referenced to the residual solvent peak unless stated otherwise (CDCl$_3$, 1H δ = 7.24, $^{13}$C δ = 77.0). The splitting patterns are designated as follows: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Coupling constants (J) between two nuclei separated by n chemical bonds are denoted in hertz (Hz). Chemical ionisation mass spectra (MS-CI+), electron impact (MS-EI+), and exact mass determination (HRMS) were recorded on a AEI MS-902 or Applied Biosystems Q-STAR mass spectrometer. Electrospray ionisation mass spectrometry (MS-ESI+) was performed on a Triple Quadrupole LC-MS-MS mass spectrometer (API 3000, Perkin-Elmer Sciex Instruments). UV-vis spectra were recorded on a Hewlett-Packard 8453 diode array. Picosecond time resolved infra-red spectroscopy were carried out as described previously.\textsuperscript{i}
2. Synthesis

2-(Phenylethynyl)thiophene was prepared via the Sonogashira coupling reaction. Anhydrous triethylamine was added to a round bottom flask, purged with argon for 10 min and then charged with 2-bromothiophene (3.0 mmol, 0.29 ml). Following this a catalytic quantity of bis(triphenylphosphine)palladium(II)chloride (0.06 mmol, 42 mg, 2 %), triphenylphosphine (0.12 mmol, 32 mg, 4%) and cuprous iodide (0.06 mmol, 11 mg, 2 %) were added to the flask followed by 1-phenylacetylene (4.5 mmol, 0.63 ml) in rapid succession. The reaction mixture was heated under a gentle reflux overnight under an inert atmosphere and then allowed to cool to room temperature. Solvent and excess aryl alkyne were removed in vacuo. The crude product was extracted from the brown oil by first washing in ca. 5 ml of dichloromethane followed by the addition of ca. 25 ml of hexane. The solvent was then decanted off. This process was repeated several times until the washings remained colourless. The washings were combined and dried over magnesium sulphate. The solvent was then removed in vacuo affording a viscous oil. The crude product was purified by Kugelrohr distillation (160 ºC, 0.04 mmHg) affording a white solid. Yield: 502 mg, 2.73 mmol, 91 %. Spectroscopic data were in agreement with reported data.iii 1H-NMR (CDCl$_3$): $\delta$ 7.54 – 7.51 (2H, m), 7.37 – 7.34 (3H, m), 7.30 – 7.29 (2H, m), 7.01 (1H, dd, $J = 4.8, 3.9$ Hz). 13C-NMR (CDCl$_3$): $\delta$ 131.93, 131.44, 128.45, 128.40, 127.29, 127.13, 123.34, 122.94. IR (pentane) $\nu$ (C≡C): 2130 cm$^{-1}$, m.p. = 51-52 ºC.

($\mu_2$-C$_6$H$_5$CCC$_6$H$_5$)Co$_2$(CO)$_6$ (I)

($\mu_2$-C$_6$H$_5$CCC$_6$H$_5$)Co$_2$(CO)$_6$ (I) was prepared according to the method outlined by Champeil and Draperiv with minor modifications. Diphenylacetylene (1.12 mmol / 200 mg) was dissolved in 30 ml of hexane and purged with nitrogen for 10 min. Dicobalt octacarbonyl (1.12 mmol / 384 mg) was added to the reaction vessel and stirred under a stream of nitrogen for 20 h (in the dark). The product mixture (deep red) was purified by column chromatography on silica using petroleum ether (40:60) as mobile phase. A deep red fraction was collected and the solvent removed in vacuo. Yield: 483 mg, 1.04 mmol, 93 %. 1H-NMR (400 MHz, CDCl$_3$): $\delta$ 7.60 (2H, m), 7.58 (2H, m), 7.39-7.37 (3H, m), 7.35-7.33 (3H, m), IR (n-pentane): $\nu$ (CO) 2026, 2055, 2089 cm$^{-1}$. 
(µ₂-C₆H₂CCC₄H₄S)Co₂(CO)₆ (2)

(µ₂-C₆H₂CCC₄H₄S)Co₂(CO)₆ (2) was prepared in a manner similar to that described above. 2-phenylethynyl-thiophene (0.80 mmol / 150 mg) was dissolved in 30 ml of hexane and purged with nitrogen for 10 min. Dicobalt octacarbonyl (0.85 mmol / 290 mg) was then added to the reaction vessel and stirred under a stream of nitrogen for 20 h (in the dark). The product mixture (deep red) was purified by column chromatography on silica using petroleum ether (40:60) as mobile phase. A deep red fraction was collected and the solvent removed in vacuo. Yield: 338 mg, 0.72 mmol, 90 %.

¹H-NMR (600 MHz, CDCl₃): δ 7.70-7.68 (2H, m), 7.42-7.35 (5H, m), 7.06-7.04 (1H, m); ¹³C-NMR (CDCl₃), δ 198.6, 141.6, 137.2, 137.6, 128.9, 128.7, 128.4, 127.9, 126.7, 91.6, 82.0. IR (η-pentane): ν (CO) 2034, 2062, 2095 cm⁻¹.

(µ₂-Ethynylferrocene)Co₂(CO)₆ (3)

(µ₂-Ethynylferrocene)Co₂(CO)₆ (3) was prepared in a similar manner. Ethynylferrocene (0.95 mmol / 200 mg) was dissolved in 30 ml of hexane and purged with nitrogen for 10 min. Dicobalt octacarbonyl (0.93 mmol / 320 mg) was added to the reaction vessel and stirred under a stream of nitrogen for 18 h (in the dark). The product mixture (deep green) was purified by column chromatography on silica using petroleum ether (40:60) as mobile phase. A deep green fraction was collected and the solvent removed in vacuo. Yield: 210 mg, 0.42 mmol, 44 %. Spectroscopic data were in good agreement with reported data.

¹H NMR (400 MHz, CDCl₃): 6.28 (s, 1H), 4.38 (d, 2H), 4.32 (s, 5H), 4.16 (d, 2H); ¹³C-NMR (100 MHz, CDCl₃): δ 75-76 (C≡C), 69.2 (α, Cp), 70.1 (Cp), 70.5 (β, Cp); IR (CH₂Cl₂): ν (CO) 2091, 2053, 2030, 2024 and 2210 cm⁻¹; Mass Spec.: E.I m/z 328 (-6 x CO), 356 (-5 x CO); HRMS (E.I.) calcd. for C₁₈H₁₀O₆Co₂Fe: 495.8491, found 495.8514; Anal. Calcd. for C₁₈H₁₀O₆Co₂Fe: C 43.59 %, H 2.03 %, Found C 43.46 %, 1.99 %
3. Quantum yield determinations

Photochemical quantum yields were determined by actinometry using potassium ferrioxalate as the reference reaction. Solutions of complexes 1-3 were irradiated at each excitation wavelength in pentane, with PPh₃ (10% molar excess) as trapping agent. Irradiation was achieved using band pass filtering of the output of a 150 W Hg arc lamp. Conversions of the starting materials were driven to a maximum of 10%, to minimize the effect of product absorption at the excitation wavelength. Changes in absorbance were monitored at 400 nm, which corresponds to $\lambda_{\text{max}}$ of the photoproduct, as displayed in figure 1.

![UV-vis spectra](image.png)

**Figure 1.** UV-vis spectra for ($\mu_2$-C₆H₅CCC₄H₄S)Co₂(CO)₆ (2) (solid dark line) and ($\mu_2$-C₆H₅CCC₄H₄S)Co₂(CO)₅(PPh₃) (dashed line) in pentane.

<table>
<thead>
<tr>
<th>Irradiation wavelength</th>
<th>313 nm</th>
<th>365 nm</th>
<th>405 nm</th>
<th>546 nm</th>
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<tr>
<td><strong>compound</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.078</td>
<td>0.035</td>
<td>0.027</td>
<td>0.045</td>
</tr>
<tr>
<td>2</td>
<td>0.145</td>
<td>0.080</td>
<td>0.045</td>
<td>0.106</td>
</tr>
<tr>
<td>3</td>
<td>0.269</td>
<td>0.071</td>
<td>0.047</td>
<td>0.233</td>
</tr>
</tbody>
</table>

**Table 1** Quantum yields for CO-loss for the ($\mu_2$-alkyne)Co₂(CO)₆ complexes studied.
(a) Quantum yield determinations of CO loss for \([\mu_2-C_6H_5CCC_6H_5]Co_2(CO)_6\) \(\text{(1)}\)

Molar excitation coefficients at 400 nm

\[
\begin{align*}
(\mu_2-C_6H_5CCC_6H_5)Co_2(CO)_6 & \quad (\text{1}) & \quad 1,140 \text{ L mol}^{-1} \text{ cm}^{-1} \\
(\mu_2-C_6H_5CCC_6H_5)Co_2(CO)_5(PPh_3) & \quad & \quad 8,179 \text{ L mol}^{-1} \text{ cm}^{-1}
\end{align*}
\]

Irradiation of 1 at 313 nm (21 mins)

Increase in intensity of band at 400 nm = 0.16

Molar increase = \(2.34 \times 10^{-5}\) molar

Moles converted per second = \(1.9 \times 10^{-8}\) moles/s

For a 3 cm³ sample, number of molecules photolysed per second = \(3.35 \times 10^{13}\) molecules/s

Change in absorbance of actinometer solution at 510 nm

Absorbance at 510 nm = 0.8228

Number of Fe\(^{2+}\) ions = \(6.70 \times 10^{17}\) ions

Using a quantum yield for Fe\(^{2+}\) production of 1.24 at 313 nm

Number of photons emitted by the source at 313 nm = \(5.40 \times 10^{17}\)

Number of photons emitted per second by the source at 313 nm = \(4.29 \times 10^{14}\) photons/s

Number of photons absorbed by the sample = \(4.29 \times 10^{14}\) photons/s

Quantum yield of photochemical reaction is \((3.35 \times 10^{13}) / (4.29 \times 10^{14}) = 0.078\)

Irradiation of 1 at 365 nm (20 mins)

Increase in intensity of band at 400 nm = 0.15

Molar increase = \(2.19 \times 10^{-5}\) molar

Moles converted per second = \(1.8 \times 10^{-8}\) moles/s

For a 3 cm³ sample, number of molecules photolysed per second = \(3.30 \times 10^{13}\) molecules/s

Change in absorbance of actinometer solution at 510 nm

Absorbance at 510 nm = 1.70

Number of Fe\(^{2+}\) ions = \(1.39 \times 10^{18}\) ions
Using a quantum yield for Fe$^{2+}$ production of 1.21 at 365 nm

Number of photons emitted by the source at 365 nm = 5.40 x 10$^{17}$

Number of photons emitted per second by the source at 313 nm = 9.56 x 10$^{14}$ photons/s

Number of photons absorbed by the sample = 9.56 x 10$^{14}$ photons/s

Quantum yield of photochemical reaction is ($3.30 \times 10^{13}$) / (9.56 x 10$^{14}$) = 0.035

Irradiation of 1 at 405 nm (15 mins)

Increase in intensity of band at 400 nm = 0.074

Molar increase = 1.09 x 10$^{-5}$ molar

Moles converted per second = 1.2 x 10$^{-8}$ moles/s

For a 3 cm$^3$ sample, number of molecules photolysed per second = 2.19 x 10$^{13}$ molecules/s

Change in absorbance of actinometer solution at 510 nm

Absorbance at 510 nm = 1.02

Number of Fe$^{2+}$ ions = 8.31 x 10$^{17}$ ions

Using a quantum yield for Fe$^{2+}$ production of 1.14 at 405 nm

Number of photons emitted by the source at 405 nm = 7.29 x 10$^{17}$

Number of photons emitted per second by the source at 405 nm = 8.10 x 10$^{14}$ photons/s

Number of photons absorbed by the sample = 8.10 x 10$^{14}$ photons/s

Quantum yield of photochemical reaction is (2.19 x 10$^{13}$) / (8.10 x 10$^{14}$) = 0.027

Irradiation of 1 at 546 nm (60 mins)

Increase in intensity of band at 400 nm = 0.114

Molar increase = 1.69 x 10$^{-5}$ molar

Moles converted per second = 5.0 x 10$^{-9}$ moles/s

For a 3 cm$^3$ sample, number of molecules photolysed per second = 8.47 x 10$^{12}$ molecules/s
*Change in absorbance of actinometer solution at 510 nm*

Absorbance at 510 nm = 0.123

Number of Fe\(^{2+}\) ions = 1.00 x 10\(^{17}\) ions

Using a quantum yield for Fe\(^{2+}\) production of 0.15 at 546 nm

Number of photons emitted by the source at 546 nm = 6.68 x 10\(^{17}\)

Number of photons emitted per second by the source at 546 nm = 1.87 x 10\(^{14}\) photons/s

Number of photons absorbed by the sample = 1.87 x 10\(^{14}\) photons/s

Quantum yield of photochemical reaction is \((8.47 \times 10^{12}) / (1.87 \times 10^{14}) = 0.045\)
(b) Quantum yield determinations of \([\mu_2-C_6H_5CCC_4H_4S]Co_2(CO)_6\) (2)

Molar excitation coefficients at 400 nm
\[
\begin{align*}
(\mu_2-C_6H_5CCC_4H_4S)Co_2(CO)_6 & \quad 2,314 \text{ L mol}^{-1}\text{ cm}^{-1} \\
(\mu_2-C_6H_5CCC_4H_4S)Co_2(CO)_5(PPh_3) & \quad 4,829 \text{ L mol}^{-1}\text{ cm}^{-1}
\end{align*}
\]

**Irradiation of 2 at 313 nm (10 mins)**

Increase in intensity of band at 400 nm = 0.077
Molar increase = \(3.07 \times 10^{-5}\) molar
Moles converted per second = \(5.1 \times 10^{-8}\) moles/s
For a 3 cm\(^3\) sample, number of molecules photolysed per second = \(9.21 \times 10^{13}\) molecules/s

**Change in absorbance of actinometer solution at 510 nm**

Absorbance at 510 nm = 0.5862
Number of Fe\(^{2+}\) ions = \(4.77 \times 10^{17}\) ions
Using a quantum yield for Fe\(^{2+}\) production of 1.24 at 313 nm
Number of photons emitted by the source at 313 nm = \(3.85 \times 10^{17}\)
Number of photons emitted per second by the source at 313 nm = \(6.41 \times 10^{14}\) photons/s
Number of photons absorbed by the sample = \(6.41 \times 10^{14}\) photons/s
Quantum yield of photochemical reaction is \((9.21 \times 10^{13}) / (6.41 \times 10^{14}) = 0.145\)

**Irradiation of 2 at 365 nm (15 min)**

Increase in intensity of band at 400 nm = 0.099
Molar increase = \(3.94 \times 10^{-5}\) molar
Moles converted per second = \(4.4 \times 10^{-8}\) moles/s
For a 3 cm\(^3\) sample, number of molecules photolysed per second = \(7.91 \times 10^{13}\) molecules/s

**Change in absorbance of actinometer solution at 510 nm**
Absorbance at 510 nm = 1.3191
Number of Fe$^{2+}$ ions = 1.07 x 10$^{18}$ ions

Using a quantum yield for Fe$^{2+}$ production of 1.21 at 365 nm
Number of photons emitted by the source at 365 nm = 8.87 x 10$^{17}$
Number of photons emitted per second by the source at 313 nm = 9.85 x 10$^{14}$ photons/s
Number of photons absorbed by the sample = 9.85 x 10$^{14}$ photons/s
Quantum yield of photochemical reaction is (7.91 x 10$^{13}$) / (9.85 x 10$^{14}$) = 0.080

*Irradiation of 2 at 405 nm (15 mins)*

Increase in intensity of band at 400 nm = 0.046
Molar increase = 1.83 x 10$^{-5}$ molar
Moles converted per second = 2.0 x 10$^{-8}$ moles/s
For a 3 cm$^3$ sample, number of molecules photolysed per second = 3.67 x 10$^{13}$ molecules/s

*Change in absorbance of actinometer solution at 510 nm*
Absorbance at 510 nm = 1.02
Number of Fe$^{2+}$ ions = 8.31 x 10$^{17}$ ions
Using a quantum yield for Fe$^{2+}$ production of 1.14 at 405 nm
Number of photons emitted by the source at 405 nm = 7.29 x 10$^{17}$
Number of photons emitted per second by the source at 405 nm = 8.10 x 10$^{14}$ photons/s
Number of photons absorbed by the sample = 8.10 x 10$^{14}$ photons/s
Quantum yield of photochemical reaction is (3.67 x 10$^{13}$) / (8.10 x 10$^{14}$) = 0.045

*Irradiation of 2 at 546 nm (40 mins)*
Increase in intensity of band at 400 nm = 0.073
Molar increase = 2.91 x 10$^{-5}$ molar
Moles converted per second = 1.2 x 10$^{-9}$ moles/s
For a 3 cm$^3$ sample, number of molecules photolysed per second = $2.19 \times 10^{13}$ molecules/s

*Change in absorbance of actinometer solution at 510 nm*

Absorbance at 510 nm = 0.0907
Number of Fe$^{2+}$ ions = $7.38 \times 10^{16}$ ions
Using a quantum yield for Fe$^{2+}$ production of 0.15 at 546 nm
Number of photons emitted by the source at 546 nm = $4.92 \times 10^{17}$
Number of photons emitted per second by the source at 546 nm = $2.05 \times 10^{14}$ photons/s
Number of photons absorbed by the sample = $2.05 \times 10^{14}$ photons/s
Quantum yield of photochemical reaction is $(2.19 \times 10^{13}) / (2.05 \times 10^{14}) = 0.106$
(e) Quantum yield determinations of [(µ₂-Ethynylferrocene)Co₂(CO)₆] (3)

Molar excitation coefficients at 400 nm
(µ₂-Ethynylferrocene)Co₂(CO)₆ (3)  1,497 L mol⁻¹ cm⁻¹
(µ₂-Ethynylferrocene)Co₂(CO)₅(PPh₃)  2,717 L mol⁻¹ cm⁻¹

Irradiation of 3 at 313 nm (20mins)
Increase in intensity of band at 400 nm = 0.072
Molar increase = 1.21 x 10⁻⁴ molar
Moles converted per second = 1.0 x 10⁻⁷ moles/s
For a 3 cm³ sample, number of molecules photolysed per second = 1.81 x 10¹⁴ molecules/s

Change in absorbance of actinometer solution at 510 nm
Absorbance at 510 nm = 1.2258
Number of Fe²⁺ ions = 9.98 x 10¹⁷ ions
Using a quantum yield for Fe²⁺ production of 1.24 at 313 nm
Number of photons emitted by the source at 313 nm = 8.04 x 10¹⁷
Number of photons emitted per second by the source at 313 nm = 6.71 x 10¹⁴ photons/s
Number of photons absorbed by the sample = 6.71 x 10¹⁴ photons/s
Quantum yield of photochemical reaction is (1.81 x 10¹⁴) / (6.71 x 10¹⁴) = 0.269

Irradiation of 3 at 365 nm (25 mins)
Increase in intensity of band at 400 nm = 0.084
Molar increase = 6.68 x 10⁻⁵ molar
Moles converted per second = 4.6 x 10⁻⁸ moles/s
For a 3 cm³ sample, number of molecules photolysed per second = 8.26 x 10¹³ molecules/s

Change in absorbance of actinometer solution at 510 nm
Absorbance at 510 nm = 1.993
Number of Fe$^{2+}$ ions = 1.62 x 10$^{18}$ ions
Using a quantum yield for Fe$^{2+}$ production of 1.21 at 365 nm
Number of photons emitted by the source at 365 nm = 1.34 x 10$^{18}$
Number of photons emitted per second by the source at 365 nm = 1.16 x 10$^{15}$ photons/s
Number of photons absorbed by the sample = 1.16 x 10$^{15}$ photons/s
Quantum yield of photochemical reaction is \(\frac{8.26 \times 10^{13}}{1.16 \times 10^{15}} = 0.071\)

**Irradiation of 3 at 405 nm (25 mins)**

Increase in intensity of band at 400 nm = 0.044
Molar increase = 3.61 x 10$^{-5}$ molar
Moles converted per second = 2.4 x 10$^{-8}$ moles/s
For a 3 cm$^3$ sample, number of molecules photolysed per second = 4.35 x 10$^{13}$ molecules/s

**Change in absorbance of actinometer solution at 510 nm**

Absorbance at 510 nm = 1.952
Number of Fe$^{2+}$ ions = 1.59 x 10$^{18}$ ions
Using a quantum yield for Fe$^{2+}$ production of 1.14 at 405 nm
Number of photons emitted by the source at 405 nm = 1.39 x 10$^{18}$
Number of photons emitted per second by the source at 405 nm = 9.30 x 10$^{14}$ photons/s
Number of photons absorbed by the sample = 9.30 x 10$^{14}$ photons/s
Quantum yield of photochemical reaction is \(\frac{4.35 \times 10^{13}}{9.30 \times 10^{14}} = 0.047\)

**Irradiation of 3 at 546 nm (35 mins)**

Increase in intensity of band at 400 nm = 0.133
Molar increase = 5.27 x 10$^{-5}$ molar
Moles converted per second = 2.5 x 10$^{-8}$ moles/s
For a 3 cm$^3$ sample, number of molecules photolysed per second = $4.54 \times 10^{13}$ molecules/s

*Change in absorbance of actinometer solution at 510 nm*

Absorbance at 510 nm = 0.075

Number of Fe$^{2+}$ ions = $6.14 \times 10^{16}$ ions

Using a quantum yield for Fe$^{2+}$ production of 0.15 at 546 nm

Number of photons emitted by the source at 546 nm = $4.09 \times 10^{17}$

Number of photons emitted per second by the source at 546 nm = $1.95 \times 10^{14}$ photons/s

Number of photons absorbed by the sample = $4.09 \times 10^{14}$ photons/s

Quantum yield of photochemical reaction is \((4.54 \times 10^{13}) / (1.95 \times 10^{14}) = 0.233\)
4. Theoretical methods

Initial coordinates for the structural optimization of \((\mu\text{-C}_2\text{H}_2)\text{Co}_2(\text{CO})_6\) were obtained from Platts et al.\(^vi\) The B3LYP/LANL2DZp model chemistry was used for all the calculations as implemented in Gaussian03.\(^vii\)

The Hessian matrix was calculated to predict the infrared spectrum of \((\mu\text{-C}_2\text{H}_2)\text{Co}_2(\text{CO})_6\). The predicted \(\nu_{\text{CO}}\) bands of this complex were corrected by comparison with the published IR spectrum.\(^viii\) This yielded a correction factor of 1.0222 which was then used to correct the calculated \(\nu_{\text{CO}}\) bands of the equivalent ground state triplet species.

<table>
<thead>
<tr>
<th></th>
<th>(\nu_{\text{CO}}) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obs.</td>
<td>2097.8  2058.5  2033.7  2028.1  2016.6</td>
</tr>
<tr>
<td>Singlet</td>
<td>2097.9  2051.3  2037.6  2035.1  2012.7</td>
</tr>
<tr>
<td>Triplet</td>
<td>2087.5  2057.9  2024.1  2021.7  2015.2</td>
</tr>
<tr>
<td>(\Delta \nu)</td>
<td>10.3    0.6     9.6     6.3     1.4</td>
</tr>
</tbody>
</table>

Table 1. Observed spectrum and calculated singlet and triplet state spectra for \((\mu\text{-C}_2\text{H}_2)\text{Co}_2(\text{CO})_6\)

Mulliken atomic spin densities:

\[
\begin{align*}
1 & \text{ Co} & 1.092758 \\
2 & \text{ Co} & 1.092758 \\
3 & \text{ C} & -0.052279 \\
4 & \text{ C} & -0.052279 \\
5 & \text{ H} & -0.009581 \\
6 & \text{ H} & -0.009581 \\
7 & \text{ C} & -0.007863 \\
8 & \text{ O} & -0.017921 \\
9 & \text{ C} & -0.007863 \\
10 & \text{ O} & -0.017921 \\
11 & \text{ C} & -0.007863 \\
12 & \text{ O} & -0.017921 \\
13 & \text{ C} & -0.007863 \\
14 & \text{ O} & -0.017921 \\
15 & \text{ C} & 0.044255 \\
16 & \text{ O} & -0.023586 \\
17 & \text{ C} & 0.044255 \\
18 & \text{ O} & -0.023586 \\
\end{align*}
\]

Sum of Mulliken spin densities= 2.00000

Table 2. Mulliken atomic spin densities: for \(^3(\mu\text{-C}_2\text{H}_2)\text{Co}_2(\text{CO})_6\) at UB3LYP/LANL2DZp
**TD DFT Results for Singlet to Singlet transitions** in \((\mu-\text{C}_2\text{H}_2)\text{Co}_2(\text{CO})_6\)

Excitation energies and oscillator strengths:

Excited State 1: Singlet-B1 2.1748 eV 570.09 nm  f=0.0013
59 -> 67 -0.12921
66 -> 67 0.64946

This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-B2 2.9485 eV 420.50 nm  f=0.0006
57 -> 67 -0.10783
64 -> 67 0.66633
65 -> 67 0.10100

Excited State 3: Singlet-A2 3.0145 eV 411.29 nm  f=0.0000
58 -> 67 0.10349
62 -> 67 0.66856

Excited State 4: Singlet-A1 3.0321 eV 408.90 nm  f=0.0002
60 -> 67 0.52324
63 -> 67 0.41758

Excited State 5: Singlet-A1 3.0944 eV 400.67 nm  f=0.0012
60 -> 67 -0.44065
63 -> 67 0.50257

Excited State 6: Singlet-B2 3.2176 eV 385.33 nm  f=0.1090
59 -> 68 -0.10106
61 -> 67 -0.22033
64 -> 67 -0.10484
65 -> 67 0.53699
66 -> 72 0.11054
66 -> 76 -0.23921
66 -> 78 0.16302
MO63 HOMO-3
Energy calculations on parallel and perpendicular structures as per Hoffmann et al. (reference 13 in manuscript)

Repeated attempts to locate a parallel isomer on the singlet potential energy surface using both B3LYP/Lanl2dzp and B3LYP/Tzvp model chemistries failed. However the semi-empirical approach used by Hoffmann (reference 13 in manuscript) was used to estimate the energy of this species and this was compared to the energy of the optimized perpendicular structure at the B3LYP/Tzvp level. The results are outlined in the following table:

<table>
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<th></th>
<th>delta E</th>
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<tr>
<td></td>
<td>a.u.</td>
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<tr>
<td>Parallel</td>
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</table>

Coordinates used in calculation of energy

Perpendicular

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<th>Coordinates (Angstroms)</th>
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<tr>
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Parallel (using semi empirical approach cf Hoffmann reference 13 in Manuscript)

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<th>Coordinates (Angstroms)</th>
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5. Examples of Time Resolved IR kinetics for Compounds 1 and 2, and IR data for the parent compounds and intermediate produced

<table>
<thead>
<tr>
<th>Compound 1</th>
<th>CH$_3$CN cm$^{-1}$</th>
<th>THF cm$^{-1}$</th>
<th>Pentane cm$^{-1}$</th>
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<tbody>
<tr>
<td>Parent bands</td>
<td>2092, 2056, 2028</td>
<td>2084, 2050, 2022</td>
<td>2089, 2055, 2031</td>
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<tr>
<td>‘Hot’ species</td>
<td>2072, 2044, 2009</td>
<td>2064, 2036, 2008</td>
<td>2074, 2040, 2016</td>
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<td>Triplet diradical</td>
<td>2082, 2048, 2019</td>
<td>2073, 2040, 2012</td>
<td>2079, 2045, 2021</td>
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</table>

**Table 3.** IR data for compound 1, and the bands observed in the IR spectrum following excitation at 400 nm.

<table>
<thead>
<tr>
<th>Compound 2</th>
<th>CH$_3$CN cm$^{-1}$</th>
<th>THF cm$^{-1}$</th>
<th>Pentane cm$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>Parent bands</td>
<td>2093, 2058, 2029</td>
<td>-</td>
<td>-</td>
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<tr>
<td>‘Hot’ species</td>
<td>2078, 2049, 2008</td>
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<td>Triplet diradical</td>
<td>2083, 2052, 2018</td>
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</table>

**Table 4.** IR data for compound 2, and the bands observed in the IR spectrum following excitation at 400 nm.

<table>
<thead>
<tr>
<th>Compound 3</th>
<th>CH$_3$CN cm$^{-1}$</th>
<th>THF cm$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>Parent bands</td>
<td>2090, 2052, 2024</td>
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<td>2071, 2042, 2005</td>
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<td>2080, 2046, 2009</td>
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</table>

**Table 5** IR data for compound 3, and the bands observed in the IR spectrum following excitation at 400 nm.
Time resolved IR spectra and kinetics

**Compound 1 in Pentane**

**Compound 2 in THF**
6. References


v Monalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry*, 3rd Ed. Taylor and Francis, Boca Raton, **2006**

