

Electronic Supporting Information for:

Visible Light Driven Room Temperature Pauson-Khand Reaction

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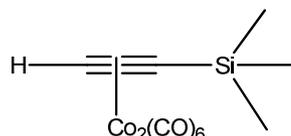
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1. General Experimental Details

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 mins. Column chromatography was carried out using neutral silica gel or neutral aluminum oxide. Trimethylsilylacetylene, 1-ethynylferrocene, dicobalt octacarbonyl and norbornene were obtained from Sigma-Aldrich and used without further purification. Carbon monoxide was obtained from Air Products Ltd. 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 (^1H NMR at 300 MHz, ^{13}C NMR at 75.5 MHz), or on a Varian Mercury Plus 400 (^1H 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). Diastereomeric ratios were determined by Chiral HPLC (Shimadzu LC-10AD) using a chiralcel OD column and a *n*-heptane:*iso*-propanol 95:5 eluent mixture. Elemental analysis was determined using a EuroVector CHNS-O Elemental Analyzer Euro EA 3000. Melting points were recorded on a Büchi B-545 melting point apparatus. UV-Vis spectra were recorded on a Hewlett-Packard 8453 diode array or Jasco V-570 spectrophotometer.

2. Synthesis

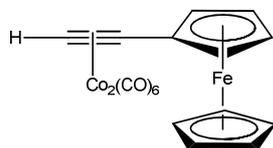
$[(\mu_2\text{-Me}_3\text{SiCCH})\text{Co}_2(\text{CO})_6]$ (1a)



The procedure used was similar to that described by Schore¹, with minor modifications.

$\text{Co}_2(\text{CO})_8$ (0.95 g, 2.7 mmol) was added to a solution of trimethylsilylacetylene (0.5 mL, 7.3 mmol) in 20 ml of *n*-pentane (argon purged). The mixture was stirred under an argon stream for 20 h (in the dark). The product mixture (deep red) was placed on a 15 cm neutral aluminium oxide column and eluted with *n*-pentane. A deep red fraction was collected and the solvent removed in vacuo. Yield: 0.44 g (43 %, 1.16 mmol). ¹H-NMR (400 MHz, CDCl_3): δ 0.3 (s, 9H), 6.4 (s, 1H); ¹³C-NMR (100 MHz, CDCl_3): 0.8, 84.3; IR (*n*-pentane): 2092, 2054, 2029, 2022 and 2010 cm^{-1} . Mass Spec.: EI m/z M^+ 384, 356 (-1 x CO), 272 (-4 x CO), 244 (-5 x CO) and 216 (-6 x CO); Anal. Calcd. for $\text{C}_{11}\text{H}_{10}\text{Co}_2\text{O}_6\text{Si}$: C 34.39 %, H 2.62 %, Found C 34.03 %, H 2.42 %

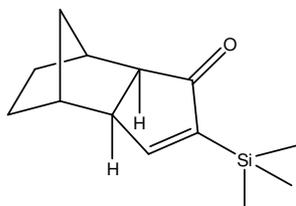
[(μ_2 -Ethynylferrocene)Co₂(CO)₆] (2a)



The procedure was according to the method outlined by Champeil and Draper² with minor modifications.

Ethynylferrocene (0.200 g, 0.95 mmol) was added to [Co₂(CO)₈] (0.320 g, 0.95 mmol) in 20 ml of HPLC grade *n*-pentane. The solution was left stirring for 18 h under an argon stream after which the solvent was removed in vacuo and the residue eluted from a silica gel column with a 70%:30% *n*-pentane:CH₂Cl₂ mobile phase to yield a dark green product. Solvent was then removed under reduced pressure to yield dark green crystals. Yield 0.21 g (44 %, 0.42 mmol). IR (CH₂Cl₂): 2091, 2053, 2030, 2024 and 2210 cm⁻¹; 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): ppm 75-76 (C≡C), 69.2 (α, Cp), 70.1 (Cp), 70.5 (β, Cp); Mass Spec.: E.I m/z 328 (-6 x CO), 356 (-5 x CO); HRMS (E.I.) calcd. for C₁₈ H₁₀O₆Co₂Fe: 495.8491, found 495.8514; Anal. Calcd. for C₁₈ H₁₀O₆Co₂Fe: C 43.59 %, H 2.03 %, Found C 43.46 %, 1.99 %

Trimethylsilyl-tricyclo[5.2.1.0]deca-4,8-dien-3-one (1b)

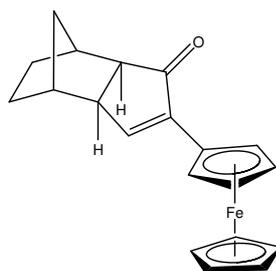


This was synthesized according to a method similar to that described by Schore¹, with minor alterations.

$[(\mu_2\text{-Me}_3\text{SiCCH})\text{Co}_2(\text{CO})_6]$ (0.200 g, 0.520 mmol) and norbornene (0.097 g, 1.04 mmol) were added to 30 mL toluene and the flask sealed using a septum. This solution was then purged with CO for 20 min. A 3 mL aliquot of the solution was withdrawn via syringe and placed in a sealed container under a CO atmosphere and covered to exclude light. This served as the control sample and showed no change in its UV/vis or IR spectrum over the period of the photolysis. The reaction flask was placed in front of a Kodak Ektapro 3000 slide projector at a sufficient distance so as to minimize thermal effects and irradiated for 45 h at 25 °C after which time the solution became clear with the formation of a white/brown precipitate. Another reaction flask exposed to filtered (pyrex) sunlight for 2 months. For both solutions the toluene was removed in vacuo and the residue dissolved in diethylether. The residue was placed on a neutral alumina column and the first dark fraction eluted with n-pentane followed by a second colorless fraction with diethylether. The diethylether fractions were combined and solvent removed to yield a fine white powder.

Yield (white light source): 0.090 g, 78 %; Yield (sunlight, 2 months): 0.050g, 59 %; M.P.:64 – 66 °C ; IR (CDCl₃): 1735, 1686 cm⁻¹; UV-Vis (pentane):244, 276, 346 nm; ¹H-NMR (400 MHz, CDCl₃): δ 7.56 (d, J = 2.8 Hz, 1H); 2.37 (d, J = 4 Hz, 2H), 2.12 (d, J = 5.2 Hz, 2H), 1.54 (s, 2H), 1.25 (m, 4H), 0.5 (s, 9H); ¹³C-NMR and DEPT 135 (100.21 MHz, CDCl₃) δ 173.1 (C-H), 150.1 (C), 54.3 (C-H), 51.9 (C-H), 39.1 (C-H), 37.9 (C-H), 31.0 (CH₂), 29.0 (CH₂), 28.3 (CH₂), -2.8 (Si-CH₃); M.S. E.I m/z 221.13; HRMS (EI) Calcd. for C₁₃H₂₁OSi: 221.1356. found 221.1357

4-ferrocenyl-tricyclo[5.2.1.0]deca-4,8-dien-3-one (2b)



[(μ₂-ethynylferrocene)Co₂(CO)₆] (**2a**) (0.210 g, 0.422 mmol) and norbornene (0.148 g, 1.58 mmol) were added to 30 mL of hexane and the intensely green solution was purged with CO for 20 min. A 3 ml aliquot of the solution was withdrawn via syringe and placed in a sealed container under a CO atmosphere and covered to exclude light. This served as the control sample and showed no change in its UV/vis or IR spectrum over the period of the photolysis. The reaction mixture was then irradiated as for **1a** yielding the corresponding cyclopentenone product after 45 h and 1 month with projector or filtered sunlight, respectively. Over this time the solution become light brown-green in colour and an orange-brown precipitate formed. Solvent was removed by rotary evaporation and the crude residue

purified by column chromatography on neutral alumina with hexane and diethyl ether. The hexane fraction contained two light blue-green bands with close retention times while the band eluted with diethyl ether contained a single intense orange coloured compound identified to be the desired product. Solvent was removed by rotary evaporation to yield the product as an orange-red solid. Yield (Projector Light, 45 h): 0.110 g, 78%; Yield: (sunlight, 1 month): 0.032g, 23%; M.P.:150 – 152 °C; IR (CHCl₃): 1737 and 1695 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): 7.33 ppm (s, 1H); 4.78 ppm (s, 2H); 4.72 ppm (s, 1H); 4.26 ppm (s, 1H); 4.06 ppm (s, 5H); 2.55 ppm (s, 1H); 2.45 ppm (s, 1H); 2.25 ppm (d, J = 30 Hz, 1H); 2.20 ppm (d, J = 22 Hz, 1H); 1.7-0.9 ppm (m); ¹³C-NMR (100 MHz, CDCl₃): 208.8, 155.9, 145.7, 69.5, 54.7, 48.21, 39.27, 38.19, 31.36, 29.08, 28.45; Mass Spec.: EI m/z 332; HRMS (ED): Calcd. for C₂₀H₂₀FeO 332.0864, found 332.0845; Anal. Calcd. for C₂₀H₂₀FeO: C 72.30 %, H 6.07 %; Found C 72.33 %, H 6.17 %.

3. Triphenylphosphine trapping Studies

3.1. Photolysis of $[(\mu_2\text{-Me}_3\text{SiCCH})\text{Co}_2(\text{CO})_6]$ in the presence of PPh_3

Broad band photolysis in the presence of the trapping ligand triphenylphosphine (PPh_3) was employed to explore photochemical CO loss in the complex $[(\mu_2\text{-Me}_3\text{SiCCH})\text{Co}_2(\text{CO})_6]$. Irradiation of a hexane solution of $[(\mu_2\text{-Me}_3\text{SiCCH})\text{Co}_2(\text{CO})_6]$ containing excess PPh_3 with $\lambda_{\text{exc}} > 500 \text{ nm}$ over 25 mins resulted in no spectral changes in either the UV/vis or IR spectra. In contrast irradiation with $\lambda_{\text{exc}} > 410 \text{ nm}$ resulted in a bleaching of the parent IR absorption bands at 2092, 2054, 2029, 2022 and 2010 cm^{-1} together with concomitant formation of new IR bands at 2062, 2018, 2005, 1989 and 1964 cm^{-1} . The absorption bands at 2062, 2018 and 2005 cm^{-1} initially grow in quickly but reached a steady state after a number of minutes. The absorption bands at 1989 and 1964 cm^{-1} appeared slowly over the same time period. In the UV/vis spectrum a shoulder grew in at $\sim 375 \text{ nm}$, with a small decrease in the intensity of the 346 nm band observed following 30 min photolysis.

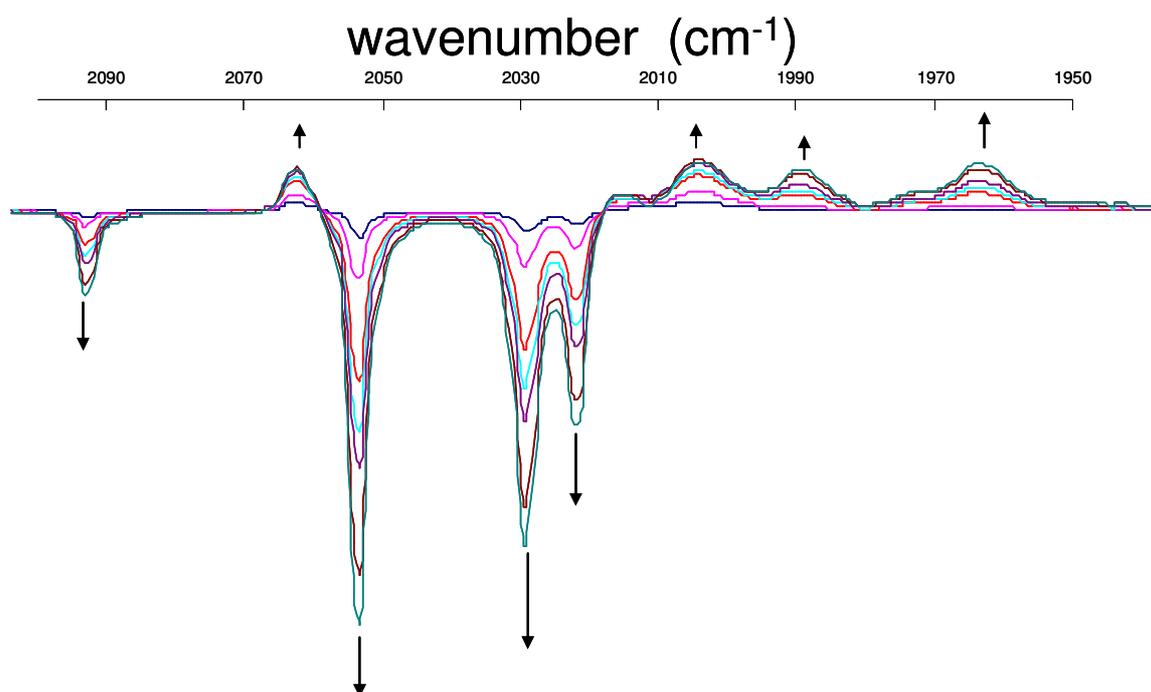


Figure 1 *Difference spectra obtained following the irradiation of $[(\mu_2\text{-Me}_3\text{SiCCH})\text{Co}_2(\text{CO})_6]$ in the presence of excess PPh_3 with $\lambda > 400$ nm. Spectra collected after 1, 2, 5, 7, 10, 15, and 20 min irradiation.*

Irradiation of the sample with $\lambda_{\text{exc}} > 300$ nm resulted in similar spectral changes to that described above. The IR stretching vibrations at 2062, 2018 and 2005 cm^{-1} are assigned to $(\mu_2\text{-Me}_3\text{SiCCH})\text{Co}_2(\text{CO})_5(\text{PPh}_3)$, and those at 1989 and 1964 cm^{-1} to $[(\mu_2\text{-Me}_3\text{SiCCH})\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2]$. The assignments in this study are based on comparisons with ν_{CO} bands for similar systems, such as $[(\mu_2\text{-C}_2\text{H}_2)\text{Co}_2(\text{CO})_5(\text{PPh}_3)]$ which has stretching vibrations at 2069, 2017, 2009, 1998, 1975 cm^{-1} and, the tetracarbonyl analogue, $[(\mu_2\text{-C}_2\text{H}_2)\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2]$ which displays ν_{CO} bands at 2028, 1982, 1965, and 1948 cm^{-1} .³

3.2. Photolysis of $[(\mu_2\text{-ethynylferrocene})\text{Co}_2(\text{CO})_6]$ in the presence of PPh_3

Irradiation ($\lambda_{\text{exc}} > 500$ nm) of a hexane solution of $[(\mu_2\text{-ethynylferrocene})\text{Co}_2(\text{CO})_6]$ containing excess PPh_3 resulted in bleaching of the parent bands together with concomitant formation of five new IR bands at 2061, 2012, 2005, 1989, and 1964 cm^{-1} , with the latter two peaks showing only a modest increase. When the excitation source was changed to $\lambda_{\text{exc}} > 410$ nm a dramatic decrease in the intensity of the parent bands was observed with a concomitant increase in six peaks at 2061, 2012, 2005, 1989, 1970 (too weak to be observed at $\lambda > 500$ nm) and 1964 cm^{-1} . The growth of the absorption bands was not concomitant throughout the experiment with no increase observed at 2061, 2012 and 2005 cm^{-1} after 15 min and peaks at 1989, 1970 and 1964 cm^{-1} continuing to rise over the 28 min.

Irradiation with $\lambda_{\text{exc}} > 300$ nm, led to the same spectral changes at that previously described following photolysis at $\lambda_{\text{exc}} > 410$ nm. However, the peaks at 2061, 2012 and 2005 cm^{-1} grew quickly (up to 2.5 min) but then gradually decreased in intensity, disappearing entirely after 30 mins irradiation. In contrast the peaks at 1989, 1970 and 1964 cm^{-1} which up to 2.5 min showed modest growth grew quickly throughout the remainder of the experiment. The IR stretching vibrations at 2061, 2012 and 2005 cm^{-1} are assigned to $[(\mu_2\text{-ethynylferrocene})\text{Co}_2(\text{CO})_5(\text{PPh}_3)]$, and those at 1989, 1970 and 1964 cm^{-1} to $[(\mu_2\text{-ethynylferrocene})\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2]$. The assignments in this study are based on comparisons with ν_{CO} bands for similar systems, such as $(\mu_2\text{-C}_2\text{H}_2)\text{Co}_2(\text{CO})_5(\text{PPh}_3)$ which has stretching vibrations at 2069, 2017, 2009, 1998, 1975 cm^{-1} and, the tetracarbonyl analogue, $[(\mu_2\text{-C}_2\text{H}_2)\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2]$ which displays ν_{CO} bands at 2028, 1982, 1965, and 1948 cm^{-1} .²

The primary aim of the photolysis experiments was to trap the pentacarbonyl (e.g. $[(\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_5(\text{PPh}_3)]$) as the monophosphine product. In both complexes, this was observed, however the pentacarbonyl itself also underwent photochemical ligand substitution to form the disubstituted species ((e.g. $[(\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_4(\text{PPh}_3)_2]$).

¹ N. E. Schore, *Organic Reactions*, John Wiley & Sons, Hoboken, **1991**, 40

² E. Champeil, S.M. Draper, *J. Chem. Soc., Dalton Trans.*, **2001**, 1440-1447

³ S.M Draper, C. Long, B. M. Myers, *J. Organomet. Chem.*, **1999**, 588, 195-199