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The photochemistry of (μ_2-RC_2H)$Co_2(CO)_6$ species (R = H or C_6H_5), important intermediates in the Pauson–Khand reaction

Sylvia M. Draper [a], Conor Long [b,*], Bronagh M. Myers [b]

[a] *Department of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland*
[b] *Inorganic Photochemistry Centre, Dublin City University, Dublin 9, Ireland*

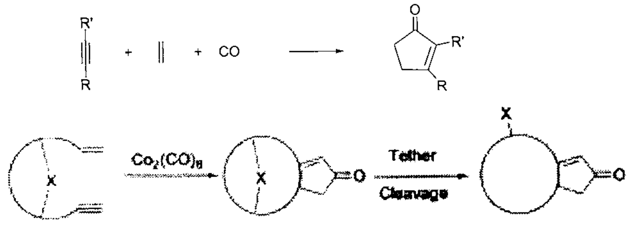
Abstract

The photochemistry of (μ_2-RC_2H)$Co_2(CO)_6$ (R = H or C_6H_5) has been investigated by both time-resolved and steady-state techniques. Pulsed excitation in cyclohexane solution with $\lambda_{exc} = 355$ nm causes Co–Co bond homolysis while photolysis at $\lambda_{exc} = 532$ nm results in CO loss. Steady-state photolysis ($\lambda_{exc} > 500$ nm) in the presence of suitable trapping ligands (L) produced the monosubstituted complexes (μ_2-RC_2H)$Co_2(CO)_5$(L) (L = C_5H_5N or PPh_3) in high yields. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cobalt; Carbonyl; Photochemistry; Flash photolysis; Pauson–Khand

1. Introduction

We are currently interested in investigating the possibility of using photochemical techniques to promote the Pauson–Khand reaction [1], i.e. the cocylisation of an alkyne, an alkene and carbon monoxide (Reaction 1). The products of the Pauson–Khand reaction can be highly regio- and stereo-chemically pure, explaining its enormous potential in the synthesis of biologically important molecules such as hirsutic acid [2], prostaglandins [3], *trans*-dihydrojasmonate [4], stemodin [5], and (±)-pentalene [6], amongst others.



(Reaction 1)

However, the high temperatures required for the Pauson–Khand process is a considerable disadvantage, particularly if the olefin substrates undergo thermally induced rearrangements. Consequently, techniques that reduce the thermal demands of this process will significantly expand the range of its application.

The carbonyl functionality of the product enone is usually supplied by a metal carbonyl fragment, generally derived from dicobalt octacarbonyl, although alternative sources such as tungsten [7], and iron [8] carbonyl compounds have also been successfully used. Many reactions to date require that the metal carbonyl fragment be supplied in stoichiometric amounts, which is undoubtedly a significant problem for commercialisation of the Pauson–Khand process. Consequently, there is growing interest in the development of systems which use only catalytic amounts of the metal carbonyl compound [9]. Recently it has been shown that visible light effectively promotes catalytic Pauson–Khand reactions [10], however the precise role the photon plays in the reaction remains uncertain.

In the case of the cobalt system, and based on studies of the regio- and stereo-chemical control of the products, it has been proposed that decarbonylation of an initally formed (μ_2-alkyne)$Co_2(CO)_6$ species, is a prerequisite to the overall reaction sequence. Confirmation of this comes from the work of Krafft and co-workers [11] who have successfully trapped such a CO-loss species by a sulphur atom of a thio-substituent on the alkyne,

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[*] Corresponding author. Tel.: +353-1-7048001: fax: +353-1-7048002.

E-mail address: conor.long@dcu.ie (C. Long)

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Table 1
The ν_{CO} band positions (cm^{-1}; ± 1 cm^{-1}) in pentane solution for the dicobalt carbonyl compounds in this investigation

Compound	ν_{CO}
$(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_6$	2094, 2056, 2033, 2029, 2014(sh)
$(\mu_2\text{-}C_2H_2)Co_2(CO)_6$	2100, 2060, 2035, 2029, 2018(sh)
$(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_5$ (pyridine)	2069, 2018, 2005, 1994, 1966,
$(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_5(PPh_3)$	2065, 2016, 2006, 1997, 1972
$(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_4(PPh_3)_2$	2021, 2004, 1972, 1949
$(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_4$ $(\text{pyridine})_2$	2018, 2002, 1967, 1942
$(\mu_2\text{-}C_2H_2)Co_2(CO)_5(\text{pyridine})$	2064, 2019, 2002, 1996, 1968
$(\mu_2\text{-}C_2H_2)Co_2(CO)_4(\text{pyridine})_2$	2021, 2004, 1970, 1941
$(\mu_2\text{-}C_2H_2)Co_2(CO)_5(PPh_3)$	2069, 2017, 2009, 1998, 1975
$(\mu_2\text{-}C_2H_2)Co_2(CO)_4(PPh_3)_2$	2028, 1982, 1965, 1948

yielding an isolable pentacarbonyl complex amenable to spectroscopic and structural analyses.

Conveniently, the $(\mu_2\text{-alkyne})Co_2(CO)_6$ intermediates are readily isolated, and while their thermal chemistry is well known [12], few detailed studies of their photochemical properties have appeared to date [13]. Of particular importance, in this regard, is a recent matrix isolation study, which demonstrated that CO-loss occurs following short-wavelength ($\lambda_{exc} = 250$ nm) photolysis of $(\mu_2\text{-alkyne})Co_2(CO)_6$ [14]. This work demonstrated that $(\mu_2\text{-alkyne})Co_2(CO)_6$ is photochemically inert when irradiated with $\lambda_{exc} = 350$ nm. However, it would not be feasible to use photons of wavelengths less than 300 nm in the Pauson–Khand reaction because of the risk of photochemical damage to the unsaturated substrates.

A fuller investigation, in particular of the wavelength-dependent nature of the photochemistry of $(\mu_2\text{-alkyne})Co_2(CO)_6$ compounds, might provide both further evidence for the importance of the CO-loss process to the Pauson–Khand reaction, and present an alternative and more attractive means of promoting the reaction particularly when thermally sensitive substrates are required.

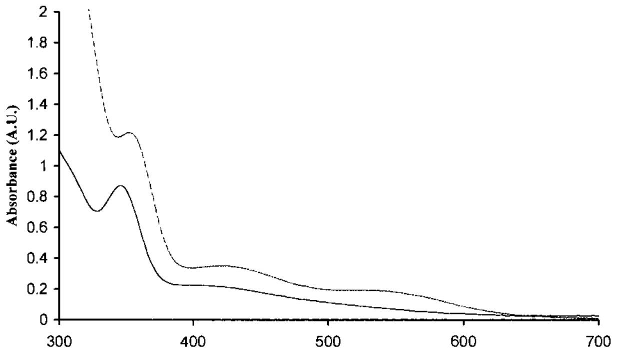


Fig. 1. The UV–vis spectra of $(\mu_2\text{-}RC_2H)Co_2(CO)_6$ (R = H, —, conc. = 1.6×10^{-3} M; R = C_6H_5, - - - - -, conc. = 3.2×10^{-4} M) in pentane solution at room temperature.

This paper reports the results of our investigation into the photochemistry of a range of $(\mu_2\text{-alkyne})Co_2(CO)_6$ compounds by both steady-state and laser flash photolysis techniques and demonstrates the importance of correct selection of excitation wavelengths in promoting the desired CO-loss process.

2. Results and discussion

Table 1 contains the band positions in the carbonyl stretching region for the compounds used in this study. Typical UV–vis spectra for the dicobalt hexacarbonyl compounds are presented in Fig. 1. In general these compounds absorb across a broad range of wavelengths up to 630 nm providing the photochemist with a wide choice of excitation wavelengths. Preliminary experiments were conducted using broad-band photolysis techniques in order to identify which spectral region produced the desired CO-loss process.

2.1. Steady-state photolysis of $(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_6$ in the presence of trapping ligands

Broad-band photolysis of $(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_6$ with $\lambda_{exc} > 340$nm in the presence of a trapping ligand L (L = C_5H_5N or PPh_3) produced the monosubstituted $(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_5(L)$ species. Product assignment in each case was based on a comparison of the ν_{CO} bands with those of authentic samples of the appropriate monosubstituted hexacarbonyl species (cf. Table 1). Prolonged photolysis of $(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_5(PPh_3)$ however, also produced the disubstituted species $(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_4(PPh_3)_2$. Qualitatively similar results were obtained in experiments using $\lambda_{exc} > 400$ nm, however, in general the photolysis times required were longer under similar experimental conditions owing to the lower optical density of the parent hexacarbonyl compound within this spectral range. These results clearly demonstrate that CO-loss can be achieved under photochemical conditions, and these results prompted a fuller investigation of this system using monochromatic light sources.

2.2. Laser flash photolysis of $(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_6$ in cyclohexane solution ($\lambda_{exc} = 355$ nm)

Pulsed photolysis ($\lambda_{exc} = 355$ nm) of $(\mu_2\text{-}RC_2H)Co_2(CO)_6$ (R = C_6H_5 or H) in cyclohexane solution results in a depletion of the absorption of the hexacarbonyl compound within the rise-time of the monitoring system (~ 20 ns). The depletion is followed by a rapid recovery of the absorption to the pre-irradiation level. This behaviour is observed at all monitoring wavelengths where the parent hexacarbonyl has significant absorbance.

The recovery of the depleted absorption followed first-order kinetics, and this provided an observed first-order rate constant of 4×10^7 s^{-1} at 298 K. Addition of CO to the solution had no effect on the rate of recovery of the depleted absorption. This is strong evidence that the depletion of the parent absorption was not the result of CO-loss. No transient absorption signals were detected out to monitoring wavelengths of 600 nm, indicating that the photoproduct has a lower extinction across the entire accessible spectral range when compared to that of the parent compound. Such observations have precedence in the literature [15].

A series of experiments was conducted in which a trapping ligand (C_5H_5N) was added to the photolysis solution in a 20-fold excess over the parent carbonyl compound (typical concentration of parent compound $= 1 \times 10^{-5}$ M). Again the only spectral change observed was depletion of the parent hexacarbonyl which recovered with an observed rate constant identical to that measured in the presence of CO. This demonstrated that the intermediate produced does not react with pyridine. However, an IR spectrum recorded after flash photolysis experiments confirmed the presence of $(\mu_2\text{-}RC_2H)Co_2(CO)_5(C_5H_5N)$. Clearly the photochemical changes observed were the result of excitation by the monitoring lamp rather than the laser output. This result is consistent with the recently published results of matrix isolation studies, which demonstrated that no photochemistry results from irradiation with $\lambda_{exc} = 350$ nm [14].

To explain the depletion of the parent absorption observed in these experiments, following laser excitation, without resulting photochemical change, we propose that homolytic cleavage of the cobalt–cobalt bond occurs, which rapidly undergoes efficient recombination. Consequently further time-resolved experiments were conducted using the second harmonic of the Nd-YAG fundamental at 532 nm.

2.3. *Laser flash photolysis of $(\mu_2\text{-}RC_2H)Co_2(CO)_6$ in cyclohexane solution with $\lambda_{exc} = 532$ nm*

Pulsed photolysis of $(\mu_2\text{-}RC_2H)Co_2(CO)_6$ ($R = C_6H_5$ or H) with $\lambda_{exc} = 532$ nm resulted in the formation of a transient species which absorbs with a λ_{max} at 400 nm. The position of this absorption compared well to that observed in matrix isolation experiments on the same system [14]. Addition of CO ($[CO] = 9 \times 10^{-3}$ M) reduced the lifetime of the transient species while its yield was not affected. A typical transient signal is presented in Fig. 2. This behaviour is typical of the reaction of CO-loss intermediates. Under these conditions the system is fully reversible i.e. repeated exposure to the laser radiation did not result in the build-up of high concentrations of photoproducts. The k_{obs} was linearly dependent on the concentration of CO, yielding the second-order rate constant ($k_2 = 1.2 \times 10^6$ dm^3 mol^{-1} s^{-1} at 298 K) as the slope.

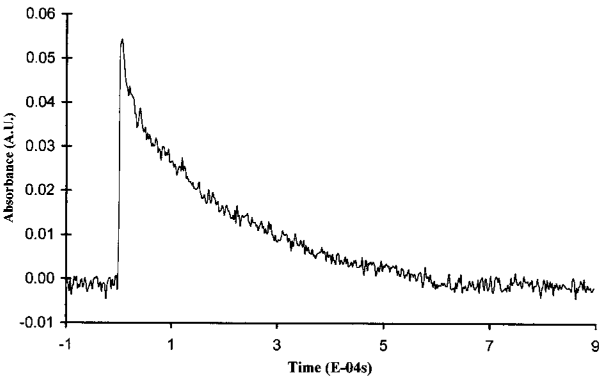


Fig. 2. A typical transient absorption signal observed at 400 nm following pulsed photolysis of $(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_6$ in pentane solution with $\lambda_{exc} = 532$ nm at 298 K in the presence of CO (conc. $= 9 \times 10^{-3}$ M).

Experiments were then conducted in the presence of a trapping ligand (PPh_3). Again a transient absorption was observed with λ_{max} at 400 nm assigned to $(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_5$(solvent). The lifetime of this transient species depended on the concentration of added PPh_3, and again the analysis of this dependence yields an estimate of the second order rate constant for the reaction of $(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_5$(solvent) with PPh_3 of 3.0×10^6 dm^3 mol^{-1} s^{-1} at 298 K. Examination of the resulting solution by IR spectroscopy confirmed the presence of $(\mu_2\text{-}C_6H_5C_2H)Co_2(CO)_5(PPh_3)$.

2.4. *Steady-state photolysis of $(\mu_2\text{-}RC_2H)Co_2(CO)_6$ ($R = C_6H_5$ or H) in alkane solution*

Steady-state experiments using visible light ($\lambda_{exc} >$ 500 nm) in the presence of a trapping ligand (L) gave

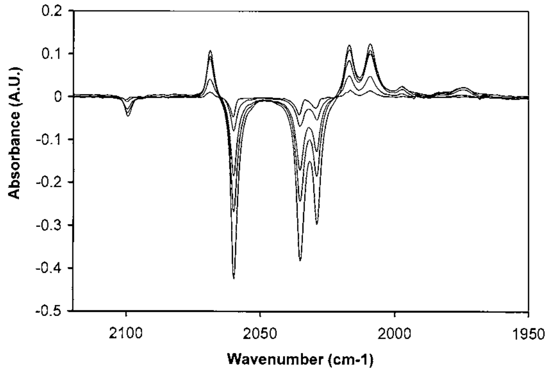
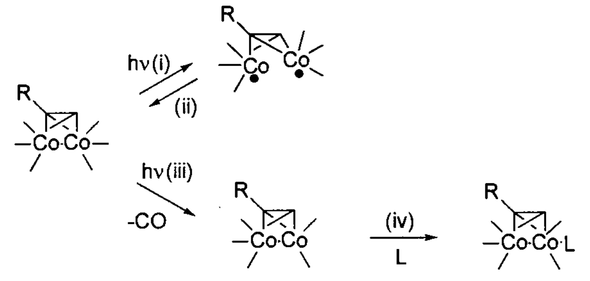


Fig. 3. Difference IR spectra obtained following broad-band photolysis ($\lambda_{exc} > 500$ nm) of $(\mu_2\text{-}C_2H_2)Co_2(CO)_6$ in cyclohexane, acquired at 10, 30, 120, 300 and 600 s, respectively. The negative bands, indicate depletion of the parent absorptions; while the positive bands are assigned to $(\mu_2\text{-}C_2H_2)Co_2(CO)_5(PPh_3)$ (see text).



Scheme 1. (i) $\lambda_{exc} = 350$ nm in alkane solvent, (ii) $\tau_{\frac{1}{2}} = 2.5 \times 10^{-8}$ s at 298 K, (iii) $\lambda_{exc} > 400$ nm, (iv) $k_2 = 1.2 \times 10^6$ dm^3 mol^{-1} s^{-1} at 298 K for L = CO (carbonyl ligands are indicated thus — for clarity).

rise exclusively to the monosubstituted pentacarbonyl complexes (μ_2-RC_2H)$Co_2(CO)_5$(L) (L = C_5H_5N or PPh_3). Fig. 3 shows the appearance of new bands and the continual depletion of parent bands upon photolysis of (μ_2-RC_2H)$Co_2(CO)_6$ in the presence of PPh_3. While reducing the excitation wavelengths ($\lambda_{exc} > 340$ nm) increased the yield of the substituted product, short wavelength photolysis also increased the yield of the disubstituted derivatives particularly for L = PPh_3.

3. Summary and conclusions

This work demonstrates the importance of the correct selection of excitation wavelength in inducing the photochemical decarbonylation of (μ_2-RC_2H)$Co_2(CO)_6$ complexes. Excitation at 355 nm does not result in CO-loss and the time resolved behaviour can be interpreted in terms of a Co–Co bond cleavage followed by a rapid reformation. In this respect, the compound acts as a ‘photon sink’ in this region of the spectrum. Long-wavelength excitation at 532 nm results in the desired CO-loss process and consequently facilitates the next step in the Pauson–Khand reaction. This explains why Livinghouse et al. [10] observed the photochemical promotion of the Pauson–Khand reaction following visible light photolysis.

The overall photochemistry is summarised in Scheme 1.

4. Experimental

4.1. Reagents

$Co_2(CO)_8$ (Fluka Chemicals), the alkynes phenylacetylene (Aldrich Chemical) and acetylene gas (Air Products), triphenylphosphine (Aldrich Chemical), pyridine, cyclohexane, hept-1-ene, and pentane (spectroscopic grade, Aldrich Chemical) were used as received. All manipulations involving $Co_2(CO)_8$ were conducted under an argon atmosphere.

4.2. Equipment

IR spectra were recorded on a Perkin–Elmer 2000 FTIR spectrometer, solution cells were fitted with NaCl windows ($d = 0.1$ mm), and spectroscopic grade cyclohexane or pentane was used. ^{1}H- and ^{13}C-NMR spectra were obtained using a Bruker model AC400 spectrometer and were calibrated with respect to the residual proton resonances of the solvent or with an internal TMS standard. UV spectra were measured on a Hewlett–Packard 8453A photodiode array spectrometer using 1 cm quartz cells. Photolysis was performed using an Applied Photophysics medium-pressure Xe arc lamp (275 W). Wavelength selection was achieved using Corning cut-off filters.

The laser system used was a pulsed Nd:YAG laser capable of generating the second, third or fourth harmonic at 532, 355 or 266 nm as required, with typical energies of 150, 30, and 45 mJ per pulse, respectively. The pulse duration was approximately 10 ns. The apparatus has been described in detail elsewhere with the excitation and monitoring beams arranged in a cross-beam configuration [16]. All samples were prepared for laser flash photolysis in a degassing bulb attached to a fluorescent cell and protected from light. The solutions were subjected to three cycles of a freeze–pump–thaw procedure to 10^{-2} torr. The solution, at room temperature, was then subjected to a dynamic vacuum, a process which has been shown to remove traces of water [17]. The required atmosphere of Ar or CO was then admitted to the sample cell.

4.3. Synthesis of (μ^2-alkyne)hexacarbonyldicobalt complexes

The (μ_2-alkyne)$Co_2(CO)_6$ complexes were prepared by the standard method, which involves the slow addition of the alkyne to a degassed solution of $Co_2(CO)_8$ in pentane [18]. The solution was stirred overnight at room temperature, following which the solvent was removed under reduced pressure yielding the dark red products.

Spectroscopic and analytical data for (μ_2-C_2H_2)$Co_2(CO)_6$: ^{1}H-NMR ($CDCl_3$): 6.01(s, 2H, C–H) ppm. ^{13}C-NMR ($CDCl_3$): 59.358 (C–H), 198.99 (C–O) ppm. UV(C_5H_{12}): 346, 447 nm. M.p. 13–13.5°C. Yield 95%. Anal. Calc. C 30.80%, H 0.65%. Found C 31.07%, H 0.65%. The ν_{CO} data are presented in Table 1. Spectroscopic and analytical data for (μ_2-$C_6H_5C_2H$)$Co_2(CO)_6$: ^{1}H-NMR (CD_3CN): 6.66(1H, s, =C–H), 7.36–7.59(5H, m, Ar CH) ppm. ^{13}C-NMR ($CDCl_3$): 128.1(s), 128.85(s), 130.21(s), (C_6H_5) ppm. UV(C_5H_{12}): 352, 422, 536 nm. M.p. 52–53°C. Anal. Calc. C 43.33%, H 1.56%. Found C 43.06%, H 1.65%. The ν_{CO} data are presented in Table 1.

4.4. Synthesis of (μ_2-RC_2H)$Co_2(CO)_5(C_5H_5N)$ and (μ_2-RC_2H)$Co_2(CO)_5(PPh_3)$

The thermal syntheses of (μ_2-RC_2H)$Co_2(CO)_5$(L) complexes where L = PPh_3 or pyridine were carried out according to the method of Manning and co-workers [19]. Equimolar amounts of the desired ligand and (μ_2-RC_2H)$Co_2(CO)_6$ were added to benzene (5 cm^3) and brought to reflux temperature for 4 h yielding dark red solutions. The solvent was then removed under reduced pressure, followed by chromatography on silica gel. The unreacted starting materials were removed by elution with petroleum ether. The products were eluted by diethylether–petroleum ether (1:1 v/v). Evaporation of the solvent in an Ar stream yielded the crystalline products. Typical yields were in the range 90–95%. IR ν_{CO} data for these compounds are provided in Table 1. UV (μ_2-C_2H_2)$Co_2(CO)_5(PPh_3)$ (C_5H_{12}): λ_{max} 322, 376, and 506 nm.

4.5. Steady-state photochemical experiments: photochemical synthesis of (μ_2-RC_2H)$Co_2(CO)_5$(L) (L = C_5H_5N or PPh_3)

The relevant alkyne compound was dissolved in cyclohexane together with a four-fold excess of the desired trapping ligand L. The solution was purged with argon gas for 15 min, before being transferred to an IR solution cell for irradiation with light of selected wavelengths. The reaction was then followed by IR spectroscopy

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