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Elucidating the mechanism of the photochemical Pauson–Khand reaction: matrix photochemistry of phenylacetylenehexacarbonyldicobalt

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Abstract

Short wavelength UV irradiation of (phenylacetylene)$Co_2(CO)_6$ (**3**) in argon matrices at 12 K results in loss of CO to form (phenylacetylene)$Co_2(CO)_5$ (**4**). Reversal of this reaction occurs on longer wavelength irradiation. When the reaction is instead carried out in mixed argon/nitrogen matrices (phenylacetylene)$Co_2(CO)_5(N_2)$ (**5**) is formed as an additional product. Irradiation at $\lambda = 390$ nm allows selective reversal of photoproduct **4** to the parent species, leaving photoproduct **5** unaffected. When **3** is irradiated in pure nitrogen matrices photoproduct **4** is not formed, but two photoproducts containing coordinated dinitrogen are observed. One of these may confidently be assigned as **5**, but the identity of the second cannot at present be specified with certainty. The results gained are discussed in the light of the much more widely studied and better understood thermal chemistry of such complexes. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Carbonyl; Cobalt; Alkyne; Photochemistry; Matrix isolation

1. Introduction

The Pauson–Khand reaction, a cobalt-mediated (2 + 2 + 1) cycloaddition involving an alkyne, alkene and carbon monoxide, is a highly useful synthetic technique for the preparation of functionalised cyclopentenones [1–5]. Indeed, this methodology has now been widely employed as the key transformation in the formation of a range of natural products and molecular targets possessing an array of cyclic and polycyclic skeletal frameworks [6]. The initial stage of the annulation process involves reaction of the alkyne with $Co_2(CO)_8$ to form an (alkyne)$Co_2(CO)_6$ complex. The alkyne ligand bridges the two Co atoms, orientated perpendicularly to the Co–Co bond [7–10]. The currently accepted mechanism for the next step of the reaction involves loss of CO followed by coordination of the alkene to one of the cobalt atoms to give a pentacarbonyl intermediate species [1–3,11–20]. However, little experimental evidence exists to support this, or any of the following steps of the reaction.

More recent advances in Pauson–Khand chemistry have focused on the development of both enantioselective [18,20–36] and catalytic [37–39] versions of the reaction. With respect to the asymmetric cyclisations, the most direct and efficient strategies have focused on the selective replacement of an individual CO ligand from the prochiral parent hexacarbonyl complexes [23]. The mildest and most effective catalytic processes depend on photochemical initiation [37].

Surprisingly, the general photochemistry of the (alkyne)$Co_2(CO)_6$ system has received little attention. To date, the only reports have been preparative in

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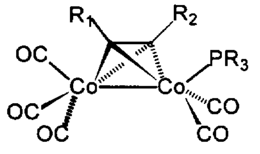
nature [40] and, to our knowledge, no mechanistic work has been carried out. In contrast, the thermal substitution chemistry of such complexes has been well studied. An extensive investigation showed that the thermal reaction of (alkyne)$Co_2(CO)_6$ complexes with phosphines and arsines resulted in displacement of from one to four carbonyl groups, depending on the reaction conditions employed [41–43]. Temperatures of up to ca. 70°C resulted in formation of only the monophosphine product **1**. Higher temperatures resulted in the formation of diphosphine products, **2**, with one phosphine group substituting at each cobalt atom. In these compounds the phosphine groups were always located in axial positions rather than at equatorial sites pointing away from the alkyne [44]. Tri- and tetra-substituted products were formed only with certain cobalt complexes, and required corresponding stoichiometric quantities of phosphine along with still higher temperatures. Additionally, variations from the above structures occurred when bidentate substituents were employed, giving mixtures of chelating and bridging structures [41].



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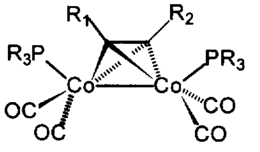

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With the emerging importance of selective decarbonylation of (alkyne)$Co_2(CO)_6$ complexes in enantioselective processes and the discovery of photochemically-induced catalytic techniques, it is considered important that the reactions of the parent complexes be further probed in a mechanistic sense. In this respect, matrix isolation techniques, in combination with infrared spectroscopy, have been found to be an efficient and widely used method for identifying reactive intermediates formed on photolysis of transition metal carbonyl complexes [45]. We now wish to report on the use of this technique in the identification of the primary photoproducts of (phenylacetylene)$Co_2(CO)_6$; these intermediates should also be present in Pauson–Khand processes and, in particular, the photochemically-induced catalytic variant.

2. Results and discussion

2.1. (Phenylacetylene)$Co_2(CO)_6$ in Ar matrices

The UV-visible spectrum of (phenylacetylene)$Co_2(CO)_6$ (**3**), isolated in an argon matrix, is shown in Fig. 1a; this corresponds closely to the reported solution spectra of similar complexes [46]. In particular, two weak bands appear in the visible region, a stronger band at $\lambda_{max} = 350$ nm (presumably MLCT), and a very strong ligand field band at $\lambda_{max} < 290$ nm. The matrix was irradiated at $\lambda = 254$ nm, resulting in depletion of the parent bands and appearance of new features at $\lambda_{max} = 330$ and 390 nm (Fig. 1b). Further irradiation at $\lambda > 400$ nm resulted in depletion of these product bands accompanied by corresponding regrowth of the parent bands, as shown in Fig. 1c. However, complete reversal could not be achieved even on extended irradiation. Photolysis into the band at $\lambda_{max} = 350$ nm resulted in no change in the UV-visible spectrum.

The ν(CO) region of the infrared spectrum of **3** isolated in an argon matrix is shown in Fig. 2a. The bands observed coincide very closely with the spectrum reported for a hexane solution [47] (see Table 1). Irradiation of the matrix at $\lambda = 254$ nm resulted in depletion of the parent, accompanied by the appearance of new bands at 2081, 2016 and 1981 cm^{-1}, as well as a build-up in intensity between the two strongest parent bands at ca. 2035 cm^{-1}. These changes are shown in Fig. 2b and listed in Table 2. The difference spectrum

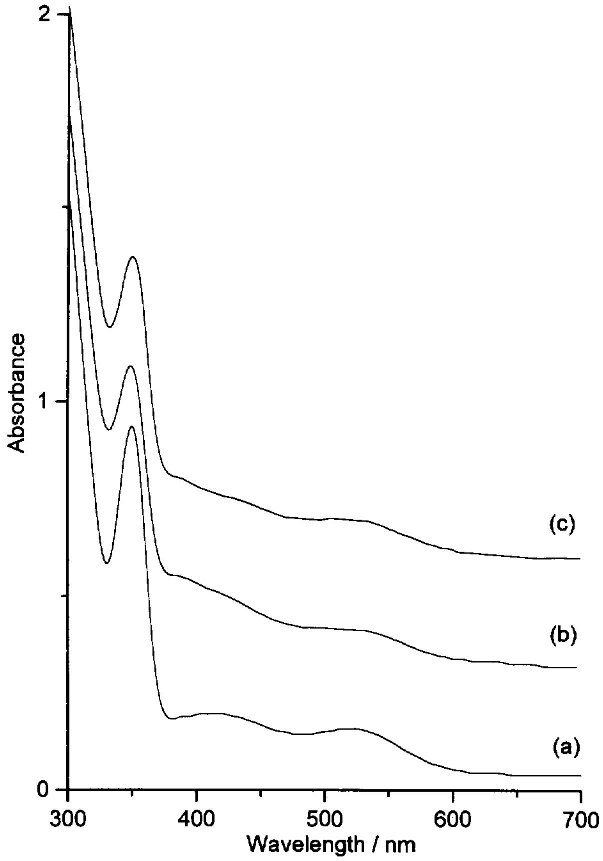


Fig. 1. UV-visible spectrum of (phenylacetylene)$Co_2(CO)_6$ and its photoproducts isolated in an argon matrix at 12 K (a) before photolysis; (b) after 30 min photolysis at $\lambda = 254$ nm; and (c) after a further 45 min photolysis at $\lambda > 400$ nm.

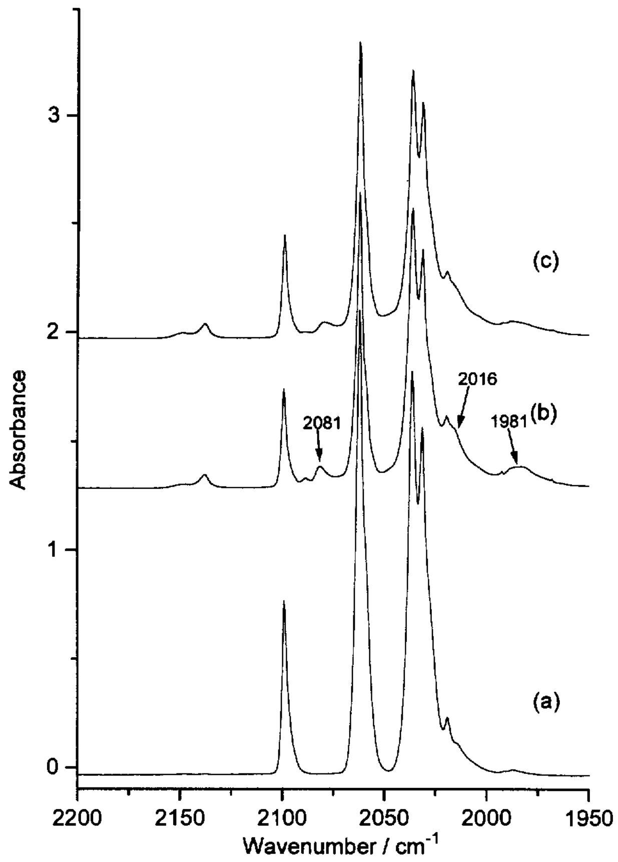


Fig. 2. Infrared spectrum of (phenylacetylene)$Co_2(CO)_6$ and its photoproducts isolated in an argon matrix at 12 K (a) before photolysis; (b) after 3 h photolysis at $\lambda = 254$ nm; and (c) after a further 60 min photolysis at $\lambda > 400$ nm. In this and subsequent figures, the positions of significant bands are indicated by their wavenumber values.

in Fig. 3a demonstrates the changes more clearly, as well as revealing three further weak features at 2005, 2021 and 2088 cm^{-1}. The new band at 2139 cm^{-1} can be assigned to free CO. Yields of the product were always relatively low, since the reaction appeared to reach a photostationary point once ≈25% of the starting material had been converted. Irradiation of the matrix at $\lambda > 400$ nm resulted in depletion of the new bands, accompanied by regeneration of the parent species, as shown in Fig. 2c and Fig. 3b. As with the UV-visible experiment, complete photo-reversal could never be achieved.

Table 1
Wavenumbers of the ν(CO) bands of $[PhCCH][Co_2(CO)_6]$

n-Hexane[a]	Ar matrix[b]	10% N_2/Ar matrix[b]	N_2 matrix[b]	Assignment[a]
2094.5	2099	2099	2099	ν_1 (a_1)
2057.7	2062	2062	2062	ν_4 (b_1)
2032.3	2036	2036	2035	ν_6 (b_2)
2027.9	2031	2031	2032	ν_2 (a_1)
2016.2	2019	2019	2019	ν_5 (b_1)
2011 (sh)	2015 (sh)	2014	2011	ν_3 (a_2)
		1987		^{13}CO satellite

[a] Data taken from [47].

[b] All values recorded at 12 K. Accuracy of band positions ±1 cm^{-1}.

The positions and intensities of the major ν(CO) product bands at 2081, ca. 2035, 2016 and 1981 cm^{-1} suggest that the principal photoproduct is a pentacarbonyl species, presumably (phenylacetylene)$Co_2(CO)_5$ (**4**). One potential structure for this species which could be ruled out was that involving a CO ligand bridging the two cobalt atoms, since no bands were observed at < 1950 cm^{-1}. Thus the structure can be thought of as containing one formally unsaturated cobalt atom, although in fact there will be very weak interactions with the argon atoms [48].

The band positions and intensities are similar to those observed for (phenylacetylene)$Co_2(CO)_5PR_3$ complexes prepared thermally, although shifted 10–15 cm^{-1} to higher energy [49]. The weaker band at 2005 cm^{-1} can also be tentatively assigned to this product as a similar weak band was observed in the phosphine complexes. The remaining two weak bands at 2021 and 2088 cm^{-1} are more difficult to assign. One possibility is that they simply arise from matrix splitting of the bands to which they are adjacent. This is unlikely, as such matrix splitting is rarely observed for product bands, and the shift in wavenumber is too large. Another explanation is that a minor CO loss photoproduct is also formed, which is a different isomer of **4**. If this is the explanation, then the remaining bands of this species may simply be unresolved from those of **4**. This seems a more likely explanation, owing to the presence of three distinct carbonyl ligands in **3**: axial and two equatorial (*cis*- and *trans*- to C-phenyl), giving three possible isomers of **4**. Thus, although the axial-substituted product is the more stable at ambient temperatures, at 12 K it is unlikely that one isomer will rearrange to form the other. Unfortunately, it seems likely that the ν(CO) spectrum of the equatorial CO loss products would be difficult to distinguish from that of the axial product, so any structural assignment of **4** must be tentative.

In the experiments carried out in an argon matrix there was no evidence for formation of a tetracarbonyl species resulting from loss of a second CO ligand, even on extended irradiation. By analogy with known phosphine complexes, such products would be expected to have ν(CO) bands at lower wavenumber than the pentacarbonyl species [41].

In this, and indeed all of the other experiments in this project, no useful information was gained from the bands involving the coordinated phenylacetylene ligand. A weak band at 1599 cm^{-1} in the spectrum of **3** could be assigned to the ν(CC) mode of the acetylene ligand, agreeing with previous workers' approximation

Table 2
Wavenumbers of the ν(CO) bands of photoproducts of $[PhCCH][Co_2(CO)_6]$ generated in gas matrices at 12 K

Photoproduct	Ar matrix[a]	10% N_2/Ar matrix[a]	N_2 matrix[a]	$[PhCCH][Co_2(CO)_5PPh_3]$[b]
4	2081	2081	—	2067 *s*
	ca. 2035	ca. 2035	—	2017 *vs*
	2016	2016	—	2007 *vs*
	2005	2005	—	1997 *w*
	1981	1981	—	1973 *m*
5	—	2249	2249	
	—	2088	2089	
	—	ca. 2040	2045	
	—	2025	2025	
	—	2016	2017	
	—	2003	2000	

[a] All values recorded at 12 K. Accuracy of band positions ± 1 cm^{-1}.
[b] Hexane solution. Data taken from [41].

of this to a carbon–carbon double bond [50]. Unfortunately, in this region strong bands arising from water vapour prevented reliable assignment of any bands arising from photoproducts.

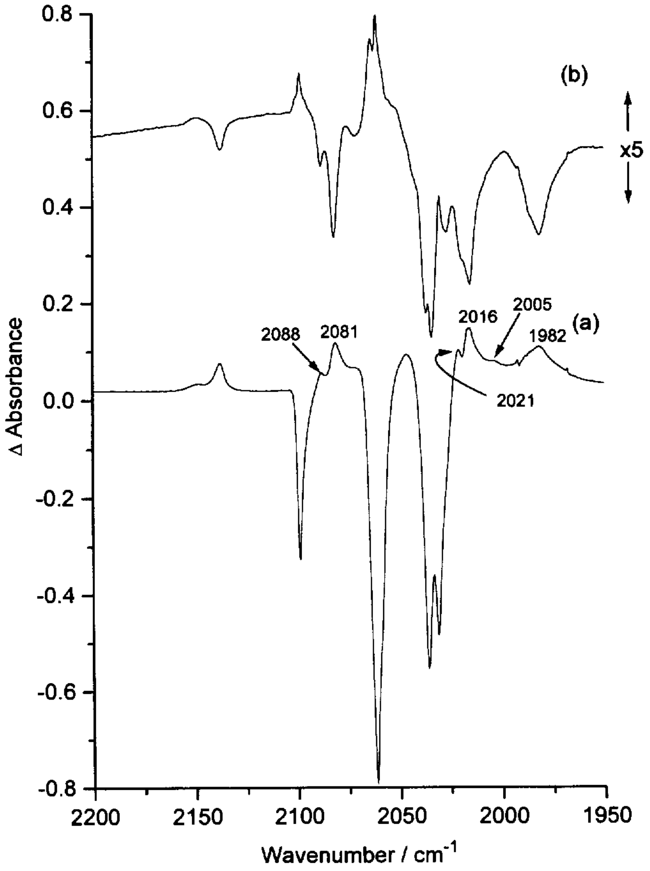


Fig. 3. Infrared difference spectra of the data shown in Fig. 2 showing the effect of (a) 3 h photolysis at λ = 254 nm; and (b) 60 min photolysis at λ > 400 nm. Note that the absorbance scale in spectrum (b) has been increased by a factor of five for added clarity

2.2. *(Phenylacetylene)$Co_2(CO)_6$ in mixed Ar/N_2 matrices*

The photochemistry of **3** was investigated in Ar matrices doped with 2 and 10% of dinitrogen. In this manner it was hoped to both identify the bands that arose from the 'naked' CO loss species **4**, and also to investigate whether a dinitrogen adduct was formed.

The ν(CO) region for **3** in the 10% N_2 matrix is shown in Fig. 4a. It can be seen that this spectrum is very similar to that obtained in a pure Ar matrix, although the slightly sharper bands mean that the lowest energy feature at 2014 cm^{-1} is now resolved from the more intense feature at 2019 cm^{-1}. As before the matrix was irradiated at λ = 254 nm; in this experiment it was found that photoproducts appeared more quickly than in the pure Ar matrix, and with a greater amount of parent band depletion, indicating a higher yield of product. The effect of this photolysis can be seen in Fig. 4b, where, as well as depletion of the parent, a number of new bands may be seen, mostly similar to those observed in argon. The most notable difference is the broad feature at 2249 cm^{-1}, attributable to a ν(NN) band of coordinated N_2. In addition, a new product band can clearly be seen at 2046 cm^{-1}, where in the Ar matrix there was simply a build-up of intensity between the two parent bands in this region. The appearance of more than five new ν(CO) bands clearly suggests that two or more photoproducts are being formed.

Irradiation of this matrix was then carried out at λ = 390 nm as this had been identified as the position of one λ_{max} of **4** (see Fig. 1b). As can be seen in Fig. 4c, and more clearly in Fig. 5a, this resulted in depletion of the product bands at 2081, 2016 and 1981 cm^{-1}, but not the ν(NN) feature or the band at 2088 cm^{-1}. In addition, the observation that the parent band at 2031 cm^{-1} increased in intensity, but not that at 2036 cm^{-1},

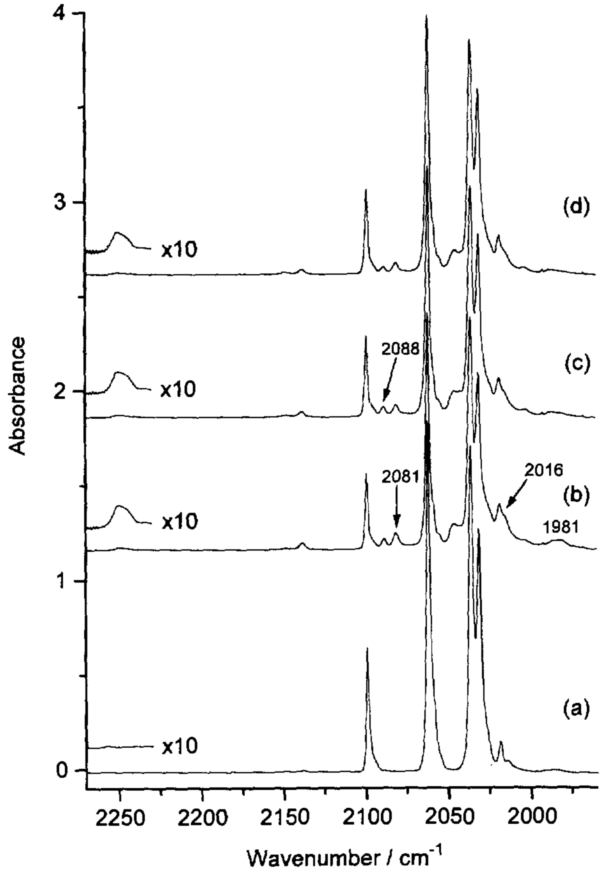


Fig. 4. Infrared spectrum of (phenylacetylene)$Co_2(CO)_6$ and its photoproducts isolated in a mixed argon/10% dinitrogen matrix at 12 K (a) before photolysis; (b) after 45 min photolysis at $\lambda = 254$ nm; (c) after 90 min photolysis at $\lambda = 390$ nm; and (d) after 20 min photolysis at $\lambda > 400$ nm. In each spectrum the absorbance scale of the ν(NN) region is also increased by a factor of ten for extra clarity.

suggested that a product band was overlapping with the latter, cancelling out its intensity. These bands were assigned to photoproduct **4**, the 'naked' CO loss species observed in the pure Ar matrix experiments. Subsequently irradiation was carried out using a $\lambda > 400$ nm cut-off filter. This resulted in considerable depletion of the ν(NN) band, along with ν(CO) bands at 2088, 2045, 2025, 2016 and 2003 cm^{-1}. These bands were therefore assigned to the dinitrogen adduct (phenylacetylene)$Co_2(CO)_5(N_2)$ (**5**). Some depletion of the bands assigned to **4** was also observed.

Thus, using these spectra it was possible to separate the bands resulting from **4** and **5**. The bands assigned to each photoproduct are listed in Table 2. Although the ν(CO) bands of the N_2 adduct are shifted slightly to higher wavenumber, it is clear that the relative positions and intensities of ν(CO) bands arising from the two photoproducts are similar, suggesting a similar molecular structure. The observation of just one ν(NN) band indicated clearly that only a single carbonyl ligand was being displaced, and that, under the photolysis conditions employed, no secondary photolysis was occurring. As discussed in the previous section, however, it is impossible at present to state definitively which of the three possible isomers of **5** is being formed.

The position of the ν(NN) band, at 2249 cm^{-1}, indicates that the NN bond remains strong compared with the uncoordinated state (ν(NN) for gaseous $N_2 =$ 2330 cm^{-1}) [51], and thus the Co–N_2 interaction is relatively weak. This is in accordance with an analogous cobalt–dinitrogen complex (η^3-allyl)$Co(CO)_2(N_2)$, formed in pure N_2 matrices on UV irradiation of (η^3-allyl)$Co(CO)_3$, for which ν(NN) occurs at 2241 cm^{-1} [52].

2.3. (Phenylacetylene)$Co_2(CO)_6$ in N_2 matrices

The infrared spectrum of **3** isolated in a pure N_2 matrix exhibited sharper ν(CO) bands than in the Ar matrix spectrum, but was almost identical to that recorded in the mixed Ar/N_2 matrix, as can be seen in Fig. 6a. On irradiation at $\lambda = 254$ nm, the system proved to be extremely photosensitive. The effect of just 15 min photolysis at this wavelength can be seen in Fig. 6b: the parent bands were reduced to less than half

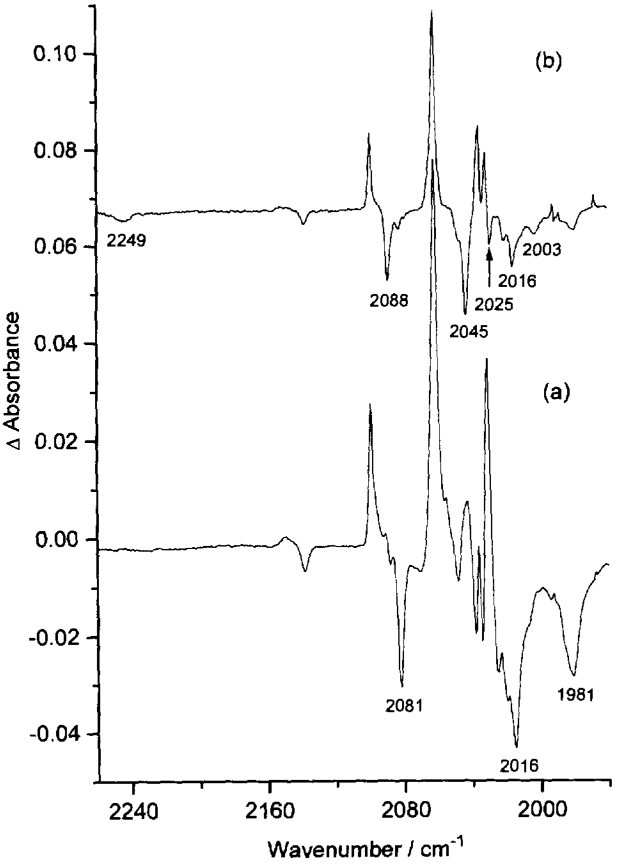


Fig. 5. Infrared difference spectra of the data shown in Fig. 4 showing the effect of (a) 90 min photolysis at $\lambda = 390$ nm; and (b) 20 min photolysis at $\lambda > 400$ nm.

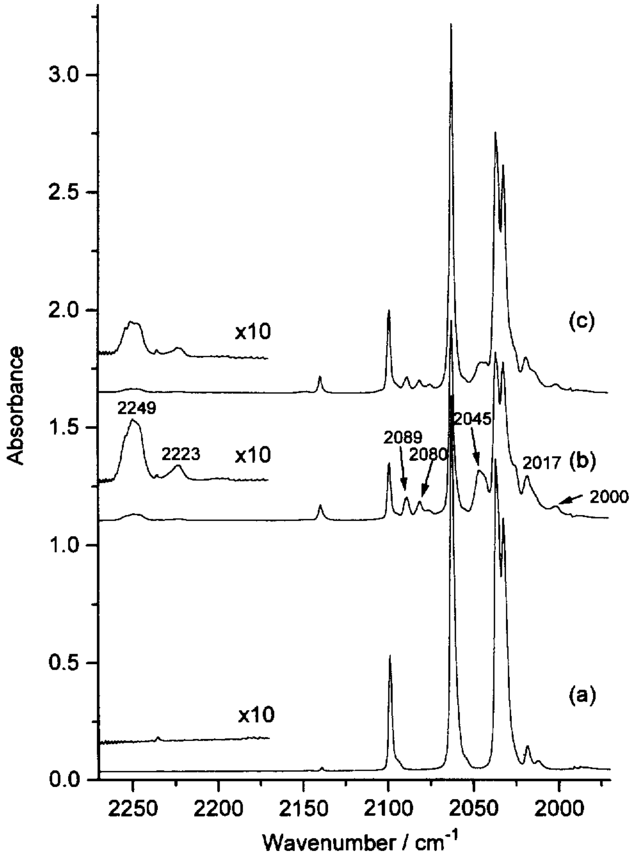


Fig. 6. Infrared spectrum of (phenylacetylene)$Co_2(CO)_6$ and its photoproducts isoalted in a pure dinitrogen matrix at 12 K (a) before photolysis; (b) after 15 min photolysis at $\lambda = 254$ nm; and (c) after 35 min photolysis at $\lambda > 400$ nm. In each spectrum the absorbance scale in the ν(NN) region is also increased by a factor of ten for extra clarity.

their initial intensity, and a considerable number of product bands were observed. As in the mixed Ar/N_2 matrix a ν(NN) band was observed at 2249 cm^{-1}, but with much greater intensity. In addition a weaker band was also seen at 2223 cm^{-1}, presumably also ν(NN). The observation of seven new bands in the ν(CO) region indicated once again that more than one photoproduct was formed.

Irradiation at $\lambda > 400$ nm resulted in depletion of most of the product bands, accompanied by re-growth of the bands of **3**, as can be seen from Fig. 6c. As usual in this system, even on extended irradiation, reversal of the reaction was incomplete. One surprising observation was that the band at 2139 cm^{-1}, generally assigned to free CO, displayed both a depletion, as would be expected on reformation of starting material, and also a sharper band growing in the middle. One possibility is that the sharper growth arises from a coordinated N_2, although it is very sharp compared with the other ν(NN) bands observed. Another possibility is that free phenylacetylene was being formed: the ν(CC) stretch of this species was observed at 2124 cm^{-1} in an Ar matrix [53]. However, this would seem unlikely due to the intensity of the peak observed in our experiments, which is much greater than that expected for the free acetylene.

Among the most clear product bands are the two peaks at 2089 and 2080 cm^{-1}. By analogy with the mixed N_2/Ar matrix work described in the previous section, these might be expected to arise from photoproducts **5** and **4**, respectively. In the pure N_2 matrix no bands were observed below 2000 cm^{-1}, however, which would seem to rule out the formation of the unsaturated CO loss species **4** as this has a distinctive broad band at 1980 cm^{-1}. The most likely explanation therefore is that two isomeric products are being formed.

Extended irradiation at $\lambda = 254$ nm resulted in the appearance of a number of further bands, notably including a further weak band at 2201 cm^{-1}, presumably ν(NN), and some relatively broad features in the region 1960–2000 cm^{-1}. At this stage no attempt was made to assign these in detail, but it seems likely that they arise from further loss of CO from the photoproducts to form a tetracarbonyl (by way of comparison, the ν(CO) bands for (phenylacetylene)$Co_2(CO)_4(PPh_3)_2$ are at 1940, 1965, 1975 and 2021 cm^{-1} [41]). In addition, the band at 2138 cm^{-1} increased considerably in intensity on extended photolysis, indicating formation of a large amount of free CO.

3. Summary and conclusions

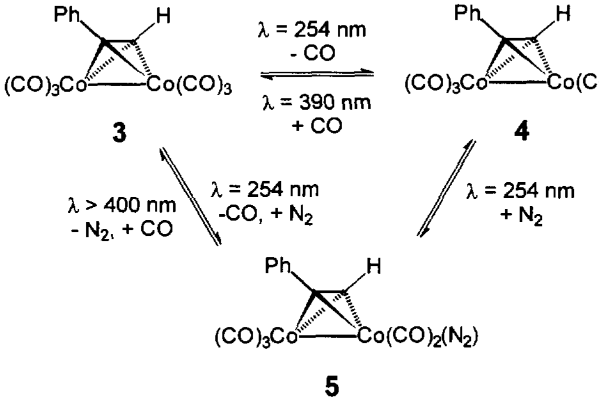
In this paper we have demonstrated that (phenylacetylene)$Co_2(CO)_6$ isolated in an argon matrix loses one carbonyl ligand on short wavelength photolysis. In the presence of N_2 the vacant site may be filled by a dinitrogen ligand. The rate of formation and yield of photoproducts increases markedly as the proportion of dinitrogen in the matrix increases. This would suggest that in a pure argon matrix in-cage recombination is an important process. The greater stability of the dinitrogen adduct prevents this species from undergoing this reaction.

It should be noted that no CO loss from **3** in gas matrices was observed on longer wavelength irradiation ($\lambda = 350$ nm). This fact is somewhat surprising, since phosphine complexes were prepared efficiently in solution using laser irradiation at $\lambda =$ ca. 350 nm [40]. It is likely, however, that this is simply an indication that the quantum yield for the photoreaction is greater at $\lambda = 254$ nm than at longer wavelengths. An additional consideration was that the intensity of irradiation available at $\lambda = 254$ nm was considerably greater than that at $\lambda = 350$ nm. For this reason an extensive investigation of the initial photolysis conditions was not carried out at this time.

By comparison with the infrared spectra of known pentacarbonyl analogues it seems likely that the axial carbonyl is displaced. The presence of weak bands, unassigned to the principal products, indicates that more than one isomer of the CO loss species may be formed. In a mixed N_2/Ar matrix both the formally unsaturated CO loss and the dinitrogen adduct are identified. In a pure N_2 matrix, however, only N_2 adducts are identified. The exact structure of the various photoproducts is difficult to ascertain with the data obtained, since the ν(CO) spectra of the various isomeric alternatives would be quite similar. The primary photochemistry is illustrated in Scheme 1.

It should also be noted that, on extended irradiation, particularly in pure N_2 matrices, a number of weaker unattributed bands are observed. At this stage these were not assigned to any particular photoproduct, although it seems likely that further CO is being lost to form a tetracarbonyl species.

In this study we have shown clearly that loss of CO to form (PhCCH)($Co_2(CO)_5$) is the initial photoreaction on irradiation at short wavelengths. The parent complex appears to be much less reactive in inert gas matrices than in solution on irradiation at longer wavelengths. The CO loss reaction is partially reversible, and the unsaturated product can coordinate with dinitrogen. These results will now form the basis of further matrix investigations on complexes of the type studied here. The use of cobalt complexes containing more symmetrical alkynes may permit better characterisation of the pentacarbonyl products. Particularly important will be to follow the reaction of pentacarbonyl species with alkenes. These results and the eventual elucidation of the site of principal CO loss will have implications for the development of both the asymmetric and photolytically-induced catalytic versions of the Pauson–Khand reaction. The results of these studies will be published in due course.



Scheme 1.

4. Experimental

4.1. Equipment

The matrix isolation cold cell has been described previously [54,55]. It consists of a CsBr window enclosed in a stainless steel vacuum shroud (pumped to 10^{-6} mbar) fitted with external KBr windows. For the UV-visible experiments the central window was CaF_2, while the external ones were quartz. Cooling of the central window was achieved by means of an APD Cryogenics Displex Model HC-2 closed cycle helium refrigerator. The base temperature was 12 K, measured by means of a Chromel–Au–0.07% Fe thermocouple connected to the temperature controller.

Infrared spectra in the range 4000–400 cm^{-1} were recorded on a Bomem MB-100 Fourier Transform spectrometer interfaced with a Viglen 486SX PC via a DSP-100 fast Fourier transform interface card, and run under Labcalc software. A resolution of 1 cm^{-1} was employed for all experiments. UV-visible spectra were recorded on a Shimadzu UV-250 spectrophotometer, with a double monochromator.

Photolysis at $\lambda = 254$ nm was performed using a Vilber Lourmat low pressure Hg arc (2 × 4 W) lamp. Photolysis at longer wavelengths was performed with an Oriel 200 W high-pressure Hg arc, fitted with a quartz lens to effect rough collimation. When exact photolysis wavelengths were required (e.g. $\lambda = 390 \pm 10$ nm), an Applied Photophysics *f*/3.4 high-radiance monochromator with variable entrance and exit slits was employed. When the monochromator was not used, the photolysis beam was passed through a water filter of 13 cm path length with quartz windows to remove IR radiation which might warm the matrix. Wavelength selection was achieved using glass cut-off filters.

4.2. Materials

Research grade Ar ($\geq$99.9997%) and N_2 ($\geq$ 99.994%) were obtained from BOC, and were employed without further purification. Phenylacetylenehexacarbonyl-dicobalt (**3**) was prepared by a modification of the standard procedure for such complexes [56]. Dicobaltoctacarbonyl (4.19 g, 12.28 mmol) was dissolved in 30 ml petrol in a nitrogen purged Schlenk-type round bottomed flask. The solution was stirred for 5 min at room temperature and phenylacetylene (1.10 g, 10.78 mmol) in petrol (4 ml) was added, causing rapid evolution of CO. The reaction was purged with nitrogen and stirred at room temperature for 2.5 h. Solvent was then removed in vacuo to give an oily red residue which was purified by flash column chromatography using silica with petrol eluant, to yield 4.14 g (99%) of **3** as a red oil which solidified on storage at −25°C.

4.3. Matrix deposition

Matrices containing (phenylacetylene)$Co_2(CO)_6$ were prepared by subliming the compound from a glass side arm on the vacuum shroud (cooled to ca. 10°C), while a large excess of the matrix host was allowed to co-condense through a needle valve. In IR experiments, deposition was continued until the strongest ν(CO) bands of **3** had an absorbance of 1–2, typically 60–120 min. Using this method, matrix host:guest ratios could not be determined, although in all experiments adequate isolation appears to have been achieved. Mixtures of Ar and N_2 were prepared on a conventional vacuum line by standard manometric procedures.

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