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Photochemical or Electrochemical Bond Breaking – Exploring the Chemistry of (μ_2 -alkyne)Co₂(CO)₆ Complexes using Time-Resolved Infrared Spectroscopy, Spectro-electrochemical and Density Functional Methods

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The phorochemistry of $(\mu_2$ -CRCR')Co₂(CO)₆ complexes (R=pyrenyl, R'=H; R=pyrenyl, R'=ferrocenyl; R=ferrocenyl,R=H) was investigated by ps-time-resolved infrared spectroscopy at room temperature in dichloromethane solution. The main focus of these studies was to determine the primary photoprocess relevant to the light assisted Pauson-Khand reaction. These studies were supported by spectro-electrochemical investigations and density functional calculations which suggest that the primary process to initiate the Pauson-Khand reaction involves a homolytic cleavage of the Co-Co bond forming a high-spin diradical species and not CO-loss as previously thought.

Introduction

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Soon after the emergence of organometallic chemistry as a discrete topic in chemistry, photochemical methods were used to probe the unique properties of this molecular class.^{1, 2} In particular the photoinduced heterolytic cleavage of metalligand bonds, for example a metal carbonyl bond, where the bonding electrons leave with the ligand, provides the opportunity to investigate the chemistry of highly electron deficient and reactive metal complex fragments. The newly developed time-resolved (flash photolysis)³ and low-temperature techniques such as matrix isolation⁴ were ideally suited to study these systems. Homolytic cleavage, of a bond to produce radical species, is also an important process in many catalytic systems including polymerisations.^{5, 6}

The Group 6 metal hexacarbonyl complexes, and in particular $Cr(CO)_6$, emerged as a prototypical system, mainly because of the exceptionally high quantum yield (Φ_{CO}) for CO loss, and also the fact that the photochemical reaction was observed even at very low temperatures (10 K). In addition, the spectroscopic properties of the photoproducts $Cr(CO)_5$ and molecular CO are quite distinct from those of the starting complex, making detection and identification of the photoproduct relatively unambiguous. The pioneering work of Turner and Perutz⁷⁻¹⁴ who investigated the low-temperature matrix photochemistry of $Cr(CO)_6$ in a variety of matrix media revealed two important

features: firstly the photochemical reaction occurred under conditions where the thermal energy is scarce, suggesting that the photo-expulsion occurs from an excited state which presents an accelerating potential with respect to CO-loss. Secondly the resulting 16-electron $Cr(CO)_5$ fragment interacts with the isolating medium, indicating exceptional reactivity.¹² These two features were subsequently confirmed by timeresolved spectroscopic techniques which showed that photoinduced CO-loss from $Cr(CO)_5$ occurs very rapidly, on the timescale of molecular vibrations, a so-called ultrafast process.¹⁵⁻¹⁸ The $Cr(CO)_5$ photofragment is also very reactive interacting even with alkanes, hitherto considered chemically inert.¹⁹ Thus a general consensus developed that photoinduced CO-loss from all homoleptic metal carbonyl complexes are ultrafast.

More recently the development of *ab initio* quantum chemical methods provided a theoretical basis to explain the ultrafast nature of CO-loss from homoleptic metal carbonyl complexes. Both wavefunctional^{20, 21} and Density Functional Theory (DFT)^{22,} ²³ were used to model the development of the lowest energy singlet excited state of Cr(CO)₆ along productive vibrational modes, which explained both the high quantum yield and the time-scale of the CO-loss processes. Of these methods, DFT is the more computationally reasonable for most organometallic systems. The application of Time-Dependent Density Functional Theory (TDDFT) to heteroleptic metal carbonyl complexes such as $(\eta^6$ -benzene)Cr(CO)₃, revealed "bound" excited states on the singlet surface.^{24, 25} These excited states can be detected using Time-Resolved InfraRed spectroscopy with pico-second time-resolution (ps-TRIR) as they exist for many tens of pico-seconds. CO-loss is achieved by traversing a small thermal barrier, a process called "arrested" CO-loss. The timescale of CO-loss can therefore range from tens of femto-

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seconds to hundreds of pico-seconds depending on the electronic structure of accessible exited states, and CO-loss can also compete with the formation of electronic excited states.²⁶ There are many organometallic systems where the role of light in promoting chemical process remains poorly understood. One of these is the Pauson-Khand Reaction (PKR) which involves a [2+2+1] cycloaddition of an alkene, an alkyne and CO to form a cyclopentenone.²⁷ It is generally accepted that the reaction mechanism involves the initial reaction of the reagent alkyne with $Co_2(CO)_8$, to form (μ_2 -alkyne) $Co_2(CO)_6$. The $Co_2(CO)_6$ fragment supplies the CO required in the subsequent cyclisation reaction. Typically the PKR is initiated thermally,²⁸ however some examples of visible light/thermal or light-assisted reactions are known in which the reaction mixture is irradiated with little regard to which step in the overall reaction is promoted by photon absorption. There are few reports of purely light-driven PKR.²⁹ An intriguing feature of these investigations, is the fact that experiments have revealed little about the chemical or indeed photochemical behaviour of (μ_2 alkyne)Co₂(CO)₆ complexes. Once the $(\mu_2$ -alkyne)Co₂(CO)₆ complex is formed it proceeds to product without trace of observable intermediates apart from one example where a pendant alkene is present on the alkyne ligand.^{30, 31} Matrix isolation experiments indicated that CO-loss occurs upon photolysis but at photon energies far in excess of those used in the light-assisted PKR.^{32, 33} Light activation of the PKR can be useful as it facilitates the synthesis of thermally sensitive cyclopentenones.³⁴ Consequently a better understanding of the electronic structure of the $(\mu_2-alkyne)Co_2(CO)_6$ complexes and accessible excited states is important.

Simple wave functional methods such as Hartree-Fock calculations cannot accurately model the ground state electronic structure of $(\mu_2$ -alkyne)Co₂(CO)₆ complexes.^{35, 36} Multi-configuration methods suggest that the ground state of $(\mu_2$ -alkyne)Co₂(CO)₆ complexes are best described as singlet (or low-spin) diradical species with less than optimal overlap of the cobalt d orbitals involved in the Co-Co bond. This results in a so-called "bent" Co-Co bond where the volume of maximum electron density does not lie on the vector joining the two cobalt nuclei. However multi-configuration calculations are computationally expensive, and their use quickly becomes unrealistic when many calculations are required to model excited state behaviour along specific reaction coordinates. Consequently both Density Functional (BLYP)^{37, 38} or Hybrid Density Functional (B3LYP)³⁹ methods can be used to provide reasonable models for the bonding in this complex at moderate computational cost. These methods when coupled with Time Dependent (TD)⁴⁰⁻⁴⁶ calculations can then model the dynamic behaviour of the ground and excited states along chosen reaction coordinates. Energy profiles which steadily reduce are described as "unbound" states with respect to the chosen reaction coordinate, while those exhibiting a local minimum are dubbed "bound" states.

In addition to quantum chemical calculations, we have used time-resolved spectroscopic techniques to gain a fuller understanding of the mechanism of light-assisted PKR. Three alkyne-substituted complexes were synthesized as represented in Figure 1. In addition, spectro-electrochemical methods baye been used to determine the stability ቦሪቶ የከይባሪዮር መንሰብ reduced complexes.



Figure 1. The (μ₂-R,R'-alkyne)Co₂(CO)₆ complexes in this investigation, 1 R=pyrenyl,R'=H; 2 R=pyrenyl, R'=ferrocenyl; 3 R=ferrocenyl; R'=H

Results

As a starting point, the UV/visible characteristics of the unsubstituted $(\mu_2-C_2H_2)Co_2(CO)_6$ complex was modelled using DFT and TDDFT methods. Dichloromethane (DCM) was selected as solvent for most calculations.⁴⁷ The lowest energy, and very weak transition centred at 500 nm, consists mainly of a cobaltcentred σ to σ^{*} transition of the Co-Co bond with minor contributions from a Co to CO(axial) charge-transfer, forming the lowest energy singlet Excited State (ES1).^{33, 48} By following this excited state along the axial CO-loss reaction coordinate it is clear that ES1 is bound with respect to this reaction (see supporting information Figure SI1). The second singlet excited state (ES2) is mainly ligand-field in character and is unbound with respect to axial CO loss, but this excited state cannot be directly populated from the ground-state as the transition is formally symmetry forbidden. The more intense absorption at 350 nm (ES8) is also mainly Co-based but with greater contributions from a Co to alkyne charge-transfer transition which has the effect of increasing the oscillator strength. This excited state is bound with respect to axial CO loss but offers the possibility of crossing to the lower ligand field state in a nonadiabatic description which can result in axial CO-loss. This process will be ultrafast as it is achieved by population of an excited state which presents an accelerating energy profile towards CO-loss but the efficiency of the process is low because of crossing to lower energy bound excited states in particular Examination of the energetics of equatorial CO-loss ES1. confirmed that no optically accessible excited states leads to this reaction. This conclusion is consistent with published results where only axial CO loss was observed following photolysis.32,33

The effect of varying the Co-Co distance on the excited state energies of $(\mu_2\text{-HCCH})\text{Co}_2(\text{CO})_6$ was then calculated to determine if population of the accessible singlet excited states result in a lengthening of the Co-Co bond. The results of these calculations are presented in Figure 2 and show that population of the lowest energy singlet state will tend to lengthen the Cobalt-Cobalt distance to 2.56397 Å (downward arrow in Figure 2(a)). Published on 02 September 2019. Downloaded by University of Glasgow Library on 9/3/2019 11:23:59 AM

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The experimental and simulated UV/visible spectra of the alkyne-substituted complexes which are the subject of this study were then investigated. The UV/visible spectra of **1**, **2**, and **3** complexes are presented as Figure SI2 with extinction parameters in Table SI1 of the supporting information.



Figure 2. (a) The adiabatic behaviour of the five lowest energy singlet excited states relative to the singlet ground-state energy (blue) as the Co-Co distance is varied in (μ_2 -HCCH)Co₂(CO)₆. The data interval is indicated by the data markers on the singlet ground-state profile but are omitted from the excited state profiles for clarity, (b) The adiabatic behaviour of the lowest energy triplet excited state (red) and the singlet ground state (blue) indicating the accelerating profile of the lowest energy triplet excited state towards a high spin di-radical species (red plot).

Both pyrenyl-substituted complexes (1 and 2) exhibit an absorbance maximum close to 400 nm, the excitation wavelength used in the ps-TRIR experiments. In the case of 1 there is excellent agreement between the simulated and experimental spectrum (Figure 3) particularly in terms of the lowest energy absorption maximum.



Figure 3. The simulated (dashed) and experimental (solid line) spectra of **1** in dichloromethane (1.2 × 10⁻² M) with the principal vertical transition energies and associated electron density difference maps for the resulting excited states, blue volumes indicating regions where the electron density is lower in the excited state compared to the ground-state, and red volumes regions where the electron density is greater in the excited state compared to the ground-state compared to the ground state, the inset is a ball-and-stick diagram for **1** showing the orientation of the molecule



Figure 4. (a) The behaviour of ES1 to ES5 for $(\mu_2-1-pyrenylethyne)Co_2(CO)_6$ (1) along the Cobalt-Cobalt stretch reaction coordinate showing the non-bonding character of all low-lying singlet excited states; (b) the behaviour of the five lowest energy singlet excited states with respect to the axial Co-CO bond length, the dashed curve represents the non-adiabatic description showing the crossing to lower states, with the branching region highlighted with a circle.

The lowest energy absorption at approximately 590 nm is predominantly pyrene to cobalt charge-transfer in character with some electron density moving to the carbonyl ligands but also with substantial σ to σ^* character. A similar description applies to the absorption at 433 nm. The intense feature at 387 nm is mainly a ligand-field transition which is non-bonding with respect to the Co-Co interaction (Figure 4(a)), but ES3, ES4 and ES5 singlet excited states present an accelerating profile towards axial CO loss (Figure 4(b)). This process must compete with crossings to lower energy bound states reducing the efficiency of the CO-loss process (see dashed curve in Figure 4(b)). These calculations suggest that population of, for example, ES5 will result in ultrafast axial CO-loss but will also populate lower energy excited states.

Turning to the ferrocenyl-substituted derivative (**3**), the simulated UV/vis spectrum is compared to the experimental spectrum in Figure 5. Again, the simulated spectrum agrees well with the experimental one despite the weakness of the features in the visible region. The lowest energy transitions can be classified as ferrocenyl to cobalt carbonyl charge-transfer in nature and have small oscillator strengths, i.e. they are very weak. Plotting the behaviour of these states along the Co-CO (axial) reaction coordinate, (supporting information Figure SI3) confirmed that these states are bound with respect to axial CO-loss. It is only when the 10th excited state is reached that an accelerating profile towards CO-loss is predicted. This state

This is reassuring, as it confirms that the constituent transitions, derived from the TDDFT calculations, are 9eanst 2000 and 1000 and 10000 and 1000 and 10

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must cross nine lower energy states in progressing to CO-loss and each of these lower energy states are bound with respect to CO-loss. Consequently, the ferrocenyl derivative is not a good candidate for ultrafast CO loss and this reaction is likely to be very inefficient. This is very surprising given the observation of high yielding visible light induced PKR when **3** is irradiated in the presence of excess norbornene. This calls into question whether the proposal that photoinduced CO-loss is the primary step in the PKR is correct.²⁹



Figure 5. A comparison of the simulated and experimental UV/vis spectrum of (μ_2 -1-ferrocenylethyne)Co₂(CO)₆(**3**) (1.6 × 10⁻² M) showing the weak visible absorptions at 580 (yellow transition) and 480 nm (green transition) which are mainly iron to Co₂(CO)₆ charge transfer in character and a mainly Cobalt-based ligand field transition at 380 nm (red transition) corresponding to population of ES10.

ps-TRIR studies

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Quantum chemical calculations described above indicated that the most likely system to observe photoinduced CO loss was the pyrene substituted complex 1. This complex absorbs strongly at excitation wavelength used in the ps-TRIR apparatus ($\lambda_{exc.}$ = 400 nm) and progression of the accessible excited states (Figure 4(b)) would lead, at least in part, to ultrafast CO loss. The spectral changes observed in the ν_{CO} region following pulsed photolysis of 1 in hexane solution at 19°C are presented in Figure 6 (IR spectral features are presented in the supporting information Table SI2). These are presented as difference spectra (Δ absorbance) where the negative absorbances indicate bleaching of the parent hexacarbonyl absorptions following excitation. Product bands are evident as positive absorbances, and the spectrum measured within 7.64 ps of the excitation pulse exhibits three broad features, each approximately 10 cm⁻¹ to the low energy side of each parent band. Their broadness, relative to the width of the parent bands, suggesting excess vibrational energy which is dissipated in approximately 10 ps. The features decay over the subsequent 40 ps with concomitant recovery of the parent absorptions, as indicated by the arrows in Figure 6. It is reasonable to assign the three broad product features to a "hot" species but whether this species is electronically excited or on the ground-state will be discussed later. A residual bleach of the parent features persists for over 1 ns, and the largest residual bleach is observed for the 2053 cm⁻¹ feature at approximately 14% of the initial bleach. In addition, persistent (> 500 ps) features are evident at 1975, 2005, and 2071 cm 3046d a further band at 2028 cm⁻¹ is implied because the intensities of the bleach signals do not correspond to the v_{CO} band intensities of the parent. These new features are indicated by asterisks in the inset in Figure 6, and agree well with the calculated v_{CO} positions (B3LYP/6-31G(d)) of the CO-loss species, (µ2pyrenylethyne)Co₂(CO)₅ (the red spectrum) and the band positions observed in matrix isolation studies for the initially produced axial CO-loss species in related systems.^{32, 33} The ps-TRIR data were analysed using a global analysis approach, and this confirmed the presence of the CO-loss features in the early timescale data (blue spectrum in the insert of Figure 6). Excitation of 1 at 400 nm produces both a hot ground-state species with a lifetime of 40 ps and a CO-loss species formed in an ultrafast process.



Figure 6. The ps-TRIR spectra recorded following pulsed photolysis of 1 ($\lambda_{exc.}$ = 400 nm) in hexane solution at 19°C, spectra were recorded at delay times of 7.64, 11.8, 16.22, 25.98, 37.34, 50.9, 67.72, 89.94, 104.42, 122.68, 147.46, 186.16, 280.0 and 500.0 ps after the excitation pulse with arrows indicating the time-dependent behaviour of the features, and the insert shows the spectrum obtained at 500 ps with an expanded Δ absorbance scale with persistent features marked with asterisks at 1975, 2005, ca 2028, and 2071 cm⁻¹ (black spectrum in insert), the lower red spectrum, in both the main plot and in the inset is the calculated spectrum at the B3LYP/6-31g(d) level of 1 and the CO-loss species (μ_2 -pyrenylethyne)Co₂(CO)₅ respectively, while the blue spectrum was extracted by global analysis of the time-dependent data (see text).

A ps-TRIR study of the spectral changes observed following 400 nm excitation of **3** showed similar features to those obtained for **1**, however features which could be associated with the CO-loss product are considerably weaker (Figure 7). The residual depletion of the 2050 cm⁻¹ band, measured 500 ps after the excitation pulse, is approximately 5% of the initial depletion. This represents the maximum yield of any CO-loss species. It is clear therefore that photoinduced CO-loss from **3** is less efficient than in the case of **1**. Global analysis of the of the spectral data revealed a long-lived species which is formed within the excitation pulse (blue spectrum in the inset in Figure 7) which has characteristics like the CO-loss species obtained following photolysis of **1**, for example the band indicated with an asterisk. However, the global analysis indicated that the

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lifetime of this species was considerably shorter than the lifetime of the CO-loss species obtained from species 1 (220 ps vs 1200 ps supporting information Figure SI3). In addition, the calculated IR spectrum of the CO-loss species at its optimum geometry (red spectrum in the inset in Figure 7) shows the presence of a bridging carbonyl band just below 1900 cm⁻¹ which is not observed in the ps-TRIR data. The green spectrum in the inset in Figure 7 shows the calculated spectrum of the COloss species at a local minimum on the potential energy hypersurface close to the initially produced CO-loss species, and this spectrum correlates well with both the final spectrum obtained in the ps-TRIR experiment (500 ps after excitation, black spectrum) and the initially produced component extracted from the global analysis treatment of the ps-TRIR data (blue spectrum). The features indicated with asterisks are common to all three spectra. This suggests that the initially produced CO-loss species may then isomerise over the subsequent 200 ps but it is not clear from the ps-TRIR data what is the ultimate product of this isomerisation.



Figure 7. The ps-TRIR spectra recorded following pulsed photolysis of **3** ($\lambda_{exc.}$ = 400 nm) in hexane solution at 19°C, spectra were recorded at delay times of 7.64, 11.8, 16.22, 20.92, 31.42, 43.78, 67.72, 89.94, 122.68, 186.16, and 500 ps after the excitation pulse with arrows indicating the time-dependent behaviour of the features, the insert shows the final spectrum obtained 500 ps after the excitation pulse (black) the decay adjusted spectrum of the long-lived species (blue) and the calculated spectrum (red) of the optimized CO-loss species and (green) the calculated spectrum of the initially produced CO-loss species.

The calculated structure indicates an asymmetric coordination of the alkyne ligand to the two Co centres. Bitterwolf and coworkers suggested a structural rearrangement of the carbonyl ligands from the initially produced axial CO-loss species to the equatorial CO-loss to explain the spectroscopic changes observed upon annealing a Nujol matrix to 140 K.³³ It is clear from the global analysis data that the axial CO-loss species produced from **1** and especially **3** are labile (Figure SI4). However, in no case did the calculations indicate the formation of a CO-loss photoproduct in which the vacant coordination site is in the equatorial position. The dominant product following 400 nm photolysis of **3** is a vibrationally excited species and that the very low yield of the CO-loss species could only have a minor role in promoting the PKR.

Spectro-electrochemical Studies

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Spectro electrochemistry with monitoring in both the de and UV-Vis regions was used to detect products that and to any following either reduction or oxidation of the complexes. These studies were undertaken to gauge the stability of these complexes with respect to a one electron change to the overall configuration. The studies were performed at applied potentials of -1.5 V (vs Ag/Ag+) for complexes 1, 2, and 3 where the radical anion is formed. Two oxidising potentials were applied, a 1 V potential for complexes 2 and 3 to observe the oxidation of the ferrocenyl substituent, and at 1.7 V for 1, 2, and 3 where the radical cations based on the cobalt centres are formed.

IR Spectro-electrochemistry

When a potential of -1.5 V was applied to solutions of complexes **1**, **2**, or **3**, a decrease in the absorbance of the all cobalt-carbonyl v_{CO} bands (down arrows in Figure 8(a)) was observed. A broad feature at 1900 cm⁻¹ is produced indicating the formation of Co(CO)₄⁻ as the only observable metal carbonyl fragment.⁴⁹ Evidence for the release of the alkyne ligand was obtained by monitoring in the UV/vis region (Figure 8(b)) where the structured features of the free ligand are produced (up arrows).



Figure 8. (a) the spectral changes observed in the IR region following reduction (-1.5 V) of 2 in DCM showing the loss of metal carbonyl features (down arrows) and formation of $Co(CO)_4^-$ (* up arrow); (b) The UV/vis absorption changes observed following reduction (-1.5 V) of 2 in DCM showing the decay of 2 (down arrows) and the liberation of uncoordinated pyrene ligand (up arrows)

At an applied potential of 1 V, **1** appeared to be stable because this potential was insufficient to form the cobalt-centred radical cation. In the case of complexes **2** or **3**, both of which contain

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a ferrocene moiety, a decrease in the parent bands in the carbonyl region was observed with concomitant formation of new bands at 2097, 2065, and circa 2040 cm⁻¹ for 2 and 2033 and 2002 cm⁻¹ for **3** (Figure 9) The product bands appear at slightly higher wavenumbers to those of the parent cobaltcarbonyl complexes and these new stretching vibrations result from the oxidation of the ferrocenyl substituent (Fe^{II}/Fe^{III}).

Figure 9. The IR spectral changes following electrolysis at 1V for (a) 1 and (b) 2 in DCM solution

It would appear, at least gualitatively, that these complexes are more stable with respect to oxidation than reduction. Reduction of all complexes results in ligand loss and the formation of inorganic cobalt species and free alkyne ligand. The structure and reactivity of the singly reduced 1 (i.e. 1.) were modelled. In the reduced species the Co-Co bond length is greater than in the parent (2.755 and 2.442 Å respectively). There is also evidence for a slight asymmetric binding of the alkyne ligand to the Co, Co-C1 2.01617 compared to Co-C2 1.99427 Å. Several possible reaction coordinates were selected to model decomposition routes for this complex and the energy changes along these reaction coordinates are presented in the supporting information Figure SI5. The Co-Co bond stretching is the lowest energy pathway which perhaps explains the formation of the $Co(CO)_4$ decomposition fragment.

Discussion

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The ps-TRIR studies supported by TDDFT calculations on 1 or 2 showed that axial CO-loss occurs upon photolysis at 400 nm.

This process is ultrafast but very inefficient. In addition, global analysis of the ps-TRIR data suggests that the CO21639 Species are themselves labile. Photolysis of 3 at 400 nm also produced the axial CO-loss product but with a greatly reduced efficiency even compared to 1 or 2. This contrasts with the observation that 3, in particular, catalyses the PKR when irradiated with visible light.²⁹ This would suggest, contrary to the common belief, that CO-loss is not the primary process in the photoassisted PKR. The spectro-electrochemical studies indicate that a single electron reduction of all complexes in this study is sufficient to decompose the di-cobalt complexes, producing uncoordinated alkyne ligand and a rupture of the Co-Co bond. Clearly a relatively minor change to the electron configuration can have a dramatic effect on the overall stability of these complexes particularly with respect to weakening of the Co-Co bond. The ps-TRIR studies indicate that the dominant photochemical pathway following photolysis of 1 at 400 nm is the formation of a vibrationally hot species as indicated by the broadness of the ν_{CO} bands (30 $\text{cm}^{\text{-1}}$ Full Width at Half Maximum) when compared to the parent (7 cm⁻¹ FWHM). The nature of this species is worthy of discussion, in particular whether it is an electronically excited or a ground state species. Time-resolved investigations by Harris and co-workers,⁵⁰ using both IR pump;IR probe and UV pump;IR probe methods on a related diiron system, $(\mu_2$ -benzene-1,2-dithiolate)Fe₂(CO)₆, produced similar transient features to those observed here. It was concluded that the transient IR features were the result of processes on the electronic ground state. In common with our results, the initially produced broad IR features relaxed to the parent in two stages, the first a cooling process where excess energy is dissipated to the solvent occurs quickly, within 20 ps. A second slower process involving the vibrational relaxation of the isolated metal carbonyl modes takes place over 80 to 300 ps. With our systems, and using only UV-pump;IR-probe, we also observed two relaxation processes that occur on similar, if slightly shorter, timescales of 10 ps and 57 ps. We propose a similar explanation for the faster decay process, i.e. vibrational cooling by dissipation of thermal energy to the solvent. However, we can offer an alternative explanation for the slower process namely the formation of a ground-state species in which the Co-Co bond distance is longer than in the parent, possibly a high-spin diradical species (Figure 2(b). Such a proposal is not without precedent; a transient lengthening of the Fe-Fe bond in $(\mu_2-S_2C_3H_6)Fe_2(CO)_6$ was proposed following visible light excitation.⁵¹

The fundamental problem remains, how does visible light absorption promote the PKR? By populating the lowest energy excited state either directly or through internal conversion from higher optically accessible excited states, the Co-Co bond length increases. This provides a pathway to move from the initially formed low-spin diradical excited state to a high-spin diradical such as that described in Figure 2(b). This would have a lifetime sufficiently long to engage in bimolecular reactions with alkene substrates.^{52, 53} To confirm that a high spin diradical is consistent with the spectral changes in the IR, the ps-TRIR spectrum was obtained 90 ps after 532 nm excitation of 1 in hexane solution. This spectrum is presented in Figure 10 which



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Figure 11.

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compares the experimental spectrum to the calculated difference spectrum obtained by subtracting the simulated spectrum of the parent complex from that of the high spin diradical. Despite the significant overlap of features, particularly the middle feature, the 90 ps difference spectrum is an excellent fit to the simulated spectrum. It is worth noting also, that the broadness of the low energy feature is the result of the overlap of four fundamental modes and not an indication of vibrational relaxation. The symmetry of the high-spin diradical is reduced to C_1 which exhibits in six vCO bands only two of which (the two high energy bands) are fully resolved.



Figure 10. The experimental difference spectrum obtained 78 ps after 532 nm excitation of 1 in hexane (red) and the simulated difference spectrum obtained by subtracting the parent spectrum from that of the high-spin diradical species (assuming 90% conversion) (blue)

We can propose a slight modification to the accepted catalytic cycle for the thermal PKR to explain the visible light promoted PKR.^{30, 54} This scheme does not involve photoinduced CO-loss as the primary step (Scheme)

The initial photochemical step involving cleavage of the Co-Co bond forming the high-spin diradical. This is followed by an insertion of the alkene into one Co-alkyne bond. The reaction then proceeds in the conventional manner involving CO insertion uptake of CO, release of the product cyclopentenone and regeneration of the di-cobalt alkyne complex. It is noteworthy that this scheme involves insertion of CO into a COalkyl bond from a coordinatively saturated cobalt centre. The inserted CO originates on the original $Co_2(CO)_6$ fragment. This is consistent with mass spectrometry experiments using ¹³CO enrichment which confirmed that the carbonyl unit in the resulting cyclopentenone originated in the Co₂(CO)₆ unit.⁵⁵ Notwithstanding the primary focus of this work to elucidate the photochemical initiation of the PKR, at the suggestion of a reviewer, the proposed catalytic cycle in the Scheme was modelled using B3LYP/6-31G(d) in acetonitrile. The species modelled were the alkene insertion, CO-insertion, and cyclopentenone formation when bound to a $Co_2(CO)_6$ fragment starting with complex **1** in the presence of prop-1-ene and CO. Both high-spin and low-spin configurations were examined, and their energies expressed relative to the energy of the starting



mixture defined at zero kJ mol⁻¹. These results are presented in

Scheme. The proposed reaction scheme for the light assisted Pauson-Khand reaction (metal carbonyl ligands are represented as simple lines for clarity), the Co to Co interaction indicated with a single bond for low-spin and two radicals high-spin configurations, the shading indicates the principal intermediate species in the catalytic cycle.



Figure 11. The energies of 1 (low-spin blue; high-spin red) and the alkene-insertion, COinsertion and cyclopentenone species as indicated in the Scheme, showing an energy cascade from the high-spin starting complex through to the cyclopentanone product species, the shading colour indicates the corresponding intermediate steps in the Scheme.

These calculations indicate that once the high-spin species is produced in the initiation step, the insertion reactions and the product formation occur in a cascade of energetically favourable intermediates. No activation parameters were calculated for these steps, as these will be the subject of future

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work. These results also suggest that the displacement of the cyclopentenone from the coordination sphere of the cobalt is likely to be the rate determining step in the catalytic cycle, and that the relaxation from the high-spin to low-spin surface happens at the CO-insertion step. A full description of the structures and energies of these intermediates is available in the supporting information as .mol files.

Experimental

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All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Mobile phases for column chromatography were dried over MgSO₄ before use. All solutions were deoxygenated by purging with nitrogen for ~10 min. Column chromatography was carried out using neutral silica gel. Silica Gel (Merck) was used as received. 1bromopyrene, 1-ethynylferrocene, TMS acetylene, and cobaltcarbonyl $(Co_2(CO)_8)$ were obtained from Sigma-Aldrich and used without further purification. IR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrophotometer (2 \mbox{cm}^{-1} resolution) in a 0.1 mm pathlength cell with NaCl plates using spectrophotometric grade DCM.56-58 1H NMR spectra were recorded using a Brüker AC 400 spectrophotometer in CDCl₃ and were calibrated by the residual proton resonances of the solvent peak. UV spectra were measured using an Agilent 8453 UV-Vis spectrophotometer in a 1 cm quartz cell using spectrophotometric grade DCM. ps-TRIR photolysis was carried out with λ_{exc} 400 nm , and τ_{FWHM} = 150 fs using the ULTRA facility at the Rutherford Applelton Laboratory. Details of the experimental setup have been presented elsewhere.59 Spectrophotometric grade DCM or *n*-hexane were used for these experiments. The photochemical quantum yields for COloss were determined using potassium ferrioxalate actinometry at irradiation wavelengths of 313, 365, 405 or 546 nm in spectrophotometric grade n-heptane (see supporting information Table SI3). Triphenylphosphine, present in excess, was used as the trapping ligand for the pentacarbonyl photoproduct.

All spectro-electrochemical measurements were performed at room temperature. Solutions were prepared under a nitrogen flow with a freshly prepared 0.1 M tetrabutylammonium hexafluorophosphate solution in either dichloromethane or acetonitrile. A 1 mm omni-cell (Specac) was used equipped with a platinum mesh working electrode, platinum mesh counter electrode and silver wire quasi-reference electrode. All spectroelectric experiments were conducted on a CHI 600E (CH Instruments) potentiostat. IR measurements used a Spectrum 65 FT-IR spectrometer (Perkin Elmer), while UV-Vis experiments measurements used an Agilent 8453 UV-Visible spectrometer.

Computational Studies

All quantum calculations were conducted using the Gaussian 16 suite of programmes (Revision B.01).⁶⁰ The computational studies initially focussed on the simplest alkyne complex (μ_2 -C₂H₂)Co₂(CO)₆ before attempting to model the larger pyrenyl and ferrocenyl substituted derivatives. Our initial calculations on (μ_2 -C₂H₂)Co₂(CO)₆ were centred on obtaining an accurate

molecular geometry at a convenient model chemistry Ainterms of computational cost) in order to କାନ୍ମାଧ୍ୟ ଅନ୍ୟୁନ୍ତି ସାମନେଶ୍ୱନିକର absorptions particularly in the v_{CO} region. In these calculations the ground state structure was optimized to tight convergence limits using a pruned (99,590) grid. Both the BLYP and B3LYP functionals were used with a 6-311G basis set,61,62 augmented with diffuse and polarisation functions (6-311++G(3df,3pd)).63, ⁶⁴ Geometry optimizations using unrestricted BLYP or B3LYP functionals yielded ground state singlet species with no evidence for significant spin contamination. For both functionals, the lowest energy triplet state occurs at higher energy than the singlet at the optimized geometry of the lowest energy singlet state (1.82 eV for BLYP and 1.58 eV for B3LYP). Both values are smaller than the singlet-triplet energy gap of 2.284 eV obtained from the computationally more expensive complete active space calculations using a molecular geometry derived from X-ray diffraction data. The optimized Co-Co distance was 2.551 Å for BLYP and 2.488 Å for B3LYP (a value of 2.442 Å was obtained using the B3LYP functional and the smaller 6-31G(d) basis set). These compare to the Co-Co distance of 2.463 Å in (μ_2 -HCCC₆H₁₀OH)Co₂(CO)₆^{65 36} or 2.476 Å in $(\mu_2-C_6H_5CCC_6H_5)Co_2(CO)_6^{66}$ both values were obtained by single crystal X-ray diffraction methods. Because of the respectable performance of the B3LYP functional in modelling the Co-Co distance coupled with the smaller 6-31G(d) basis set this model chemistry was selected to probe the ground and excited-state behaviour of all the complexes in this study. Complete descriptions of the optimised structures are available as .mol files in the supporting information.

Syntheses.

All the ligands used in this study were prepared using the Sonogashira coupling reaction,⁶⁷ using the following method. A 25 cm³ aliquot of di-isopropylamine was purged with nitrogen for 10 minutes, following which 1.77 mmol of the appropriate bromoalkane was added and the solution was purged with nitrogen for a further 10 minutes. Pd(PPh₃)₂Cl₂ 0.071 mmol (4%), CuI 0.071 mmol (4%) and PPh₃ 0.142 mmol (8%) and the required terminal alkyne 2.66 mmol were then added and the solution was brought to its reflux temperature (88°C) for 8 hours under a nitrogen atmosphere. The solvent was then removed under reduced pressure. The product was extracted into a mixture of DCM:hexane (1:5 v/v). The resulting solution was dried over anhydrous MgSO₄, filtered, and the solvent removed under reduced pressure. The product was purified using column chromatography on silica using n-hexane:DCM, 25:75 (v/v) as the mobile phase.

Pyrene-ethynylferrocene. Yield: 96%. ¹H NMR: (400 MHz, CDCl₃) 8.62 ppm (d, J= 9.2 Hz, 1H), 7.9 ppm (m, 8H), 4.665 ppm (dd, J_a = 1.6 Hz, J_b = 1.6 Hz, 2H), 4.33 ppm (s, 7H).⁶⁸

Removal of the TMS protection groups. 20 cm³ of freshly distilled methanol was purged with nitrogen for 10 min and 1.3 mmol of 1-trimethylsilylacetylene was then added followed by 0.17 mmol of K_2CO_3 . The solution was stirred under nitrogen for 4 hr and the solvent was then removed under reduced pressure. The residue was dissolved in 100 cm³ of dichloromethane and washed with 4 \times 25 cm³ of 5% (w/v)

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aqueous NaHCO₃. The organic phase was dried over anhydrous MgSO₄. The solvent was removed. The product was purified by chromatography using silica and hexane: DCM, 25:75 (v/v) as the mobile phase.⁶⁹

1-ethynylpyrene. Yield: 70%. ¹H NMR: (400 MHz, CDCl₃), 8.5 ppm (d, J = 8.8 Hz, 1H), 8.15 ppm (m, 8H), 3.6 ppm (s, 1H).

Synthesis of $(\mu_2$ -alkyne)Co₂(CO)₆ complexes. 25 cm³ of hexane was purged with N₂ for 10 min and 0.45 mmol of the alkyne ligand was then added and solution was purged with N₂ for a further 10 min. 0.9 mmol of cobaltcarbonyl was added to the reaction mixture and the vessel was sealed. The reaction mixture was allowed to stir for 8 hr under N₂. The solvent was removed and the pure product was obtained by column chromatography using a silica solid phase and DCM: hexane, 1:1 as the solvent.

(μ_2 -1-ethynylpyrene)Co₂(CO)₆ (**1**. Yield: 78%. ¹H NMR: (400 MHz, CDCl₃), 8.55 ppm (d, J= 9.2 Hz 1H), 8.15 ppm (m, 8H), 6.95 ppm (s, 1H). UV-Vis: (DCM) 274 nm (20.5 x 10³ M⁻¹ cm⁻¹), 392 nm (19.1 x 10³ M⁻¹ cm⁻¹), 577 nm (1.1 x 10³ M⁻¹ cm⁻¹). IR: (DCM) 2092, 2056, 2030 cm⁻¹.

 $(\mu_2-Pyrene-ethynylferrocene)Co_2(CO)_6 (2). Yield: 59\%. \ ^1H NMR: (400 MHz, CDCl_3), 8.7 ppm (d, J= 8.08 Hz, 1H), 8.24 ppm (m, 8H), 4.6 ppm (dd, J_a= 1.84 Hz, J_b= 1.84 Hz, 2H), 4.48 ppm (dd, J_a= 1.84 Hz, J_b= 1.84 Hz 2H), 4.32 ppm (s, 5H). UV-Vis: (DCM) 279 nm (18.7 x 10^3 M^{-1} cm^{-1}), 389 nm (11.7 x 10^3 M^{-1} cm^{-1}), 574 nm (1.3 x 10^3 M^{-1} cm^{-1}). \ IR: (DCM) 2085, 2048, 2023 cm^{-1}.$

 $\begin{array}{l} (\mu_2\text{-}1\text{-}ethynylferrocene)\text{Co}_2(\text{CO})_6 \ \textbf{(3)}. \ \text{Yield:} \ 98\%, \ ^1\text{H} \ \text{NMR:} \ (400 \ \text{MHz}, \text{CDCl}_3), \ 6.28 \ \text{ppm} \ (\text{s}, 1\text{H}), \ 4.33 \ \text{ppm} \ (\text{d}, \ J_a = 1.84 \ \text{Hz}, \ J_b = 1.84 \ \text{Hz}, \ 4\text{Hz}, \ 4$

Supporting Information.

Supporting information includes details of actinometric quantum yield experiment, TRIR spectra of **1b**, **2b** and **3b**, electrochemical data and details of quantum chemical calculations including atomic coordinates of all optimises structures in the form of embedded .mol files.

Conclusions

Contrary to previous proposals that photoinduced CO-loss from $(\mu_2$ -alkyne)Co₂(CO)₆ complexes was the primary photochemical step in the visible light assisted Pauson-Khand reaction, our investigations implicate a high-spin diradical species formed by homolytic cleavage of the Co-Co bond. Attempts to maximise the quantum efficiency of CO-loss by tuning the absorption profile of a series of alkyne-substituted complexes to the excitation wavelength in time-resolved spectroscopic studies failed to significantly increase the CO-loss efficiency. This, despite the increased efficiency of the visible light assisted Pauson-Khand reaction for the ferrocenyl substituted

Conflicts of interest

There are no conflicts to declare.

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The photoassisted Pauson-Khand reaction involves the formation of a high-spin diradical species of the online not CO loss as previously thought.



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