

Evidence for Cobalt–Cobalt Bond Homolysis and Wavelength-Dependent CO Loss in (μ_2 -Alkyne) $\text{Co}_2(\text{CO})_6$ Complexes

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Time-resolved infrared spectroscopy was used to probe the photochemistry of three (μ_2 -alkyne) $\text{Co}_2(\text{CO})_6$ complexes. The data indicate the formation of a triplet diradical species, with lifetimes in the range 38–71 ps. Theoretical calculations support these experimental findings. No evidence for the CO loss species, (μ_2 -alkyne) $\text{Co}_2(\text{CO})_5$, was observed, and this is rationalized by the low quantum yield for this process at the excitation wavelengths used.

Time-resolved infrared (TRIR) spectroscopy is particularly suited to studying metal carbonyls because subtle differences in the electron density at the metal center and/or the ligands will induce changes in the positions of the IR bands. To the best of our knowledge, there are no reports detailing the photochemical properties of (μ_2 -alkyne) $\text{Co}_2(\text{CO})_6$ -type complexes (Figure 1), using TRIR. This is somewhat surprising given the direct application of such complexes to the Pauson–Khand reaction (PKR).¹ The PKR is a versatile route to the synthesis of natural products² and pharmaceutically active compounds.³ The reaction is typically performed as a thermally driven reaction; however, several examples of photochemically assisted thermal PKRs have been reported.⁴ Recently, we have demonstrated that



Figure 1. (μ_2 -alkyne) $\text{Co}_2(\text{CO})_6$ complexes used in the present study.

the PKR can be driven using visible-light irradiation at ambient temperatures.⁵ Laser flash photolysis with UV–vis spectroscopic detection, together with matrix isolation studies,^{6,7} has suggested two possible photochemical pathways for (μ_2 -alkyne) $\text{Co}_2(\text{CO})_6$ complexes following excitation: Co–Co bond homolysis ($\tau_{\text{recomb}} = 25$ ns; $\lambda_{\text{exc}} = 355$ nm) and reversible CO loss (in an argon matrix, $\lambda_{\text{exc}} = 254$ nm). Although the former process, Co–Co bond homolysis, can be considered to be a nonproductive process because of efficient Co–Co recombination, the latter process, i.e., that of CO loss, is important because it is presumed to be the initial step in the PKR.^{2a,8,9} The possibility of Co–Co cleavage playing a role in the PKR was recently highlighted by Gibson and co-workers, who indicated that cleavage may be a facile process.¹⁰ It was proposed that Co–Co cleavage competes with CO loss and alkene binding in an (alkyne)-(binap)tetracarbonyldicobalt intermediate in the PKR [binap = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl].

Here we report the first picosecond TRIR study of the photochemical activation of (μ_2 -alkyne) $\text{Co}_2(\text{CO})_6$ complexes. We show that the dominant photochemical pathway following photoexcitation of complexes 1–3 is Co–Co bond homolysis, providing initially a vibrationally hot species that relaxes over 10 ps to an intermediate species.

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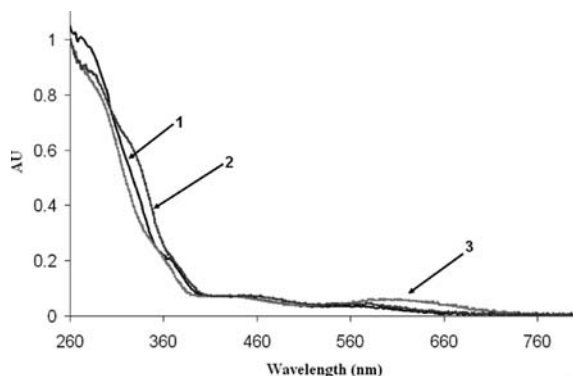


Figure 2. UV-vis spectra for compounds **1–3** in pentane.

decays on the picosecond time scale with concomitant recovery of the parent (μ_2 -alkyne) $\text{Co}_2(\text{CO})_6$ species. Importantly, no evidence for CO loss was observed in the transient IR spectra upon 400 or 532 nm excitation despite the fact that steady-state photolysis yields CO loss products.¹¹

The synthesis of compounds **1–3**⁵ is available as Supporting Information. The UV-vis absorption spectra for complexes **1–3** exhibit a ligand field band at <280 nm, in addition to a band at ~ 350 nm and two further weak bands in the range 380–730 nm assigned to metal-to-ligand charge-transfer transitions (Figure 2).¹² Molecular orbital calculations carried out by Hoffmann and co-workers¹³ on (μ_2 -alkyne) $\text{Co}_2(\text{CO})_6$ complexes at the Hückel level demonstrate that the highest occupied molecular orbital (HOMO) a_2 corresponds to alkyne-to-metal back-bonding, while the HOMO-1 a_1 corresponds to a Co-Co bond. The lowest unoccupied molecular orbital (LUMO) b_2 and LUMO+1 a_1 levels are antibonding with respect to the alkyne-to-metal bonds. These results are similar to those obtained by Van Dam et al.¹⁴ using ab initio molecular orbital calculations. Photoelectron spectroscopy subsequently confirmed the relative order of the bonding orbitals proposed using molecular orbital calculations.¹⁵

Photoexcitation ($\lambda_{\text{exc.}} = 400$ nm; $\tau_{\text{fwhm}} = 150$ fs) of **1–3** (and in the case of **3** also at 532 nm) resulted in depletion of the ground-state ν_{CO} bands of **1–3** with the appearance of three new bands in the ν_{CO} region (Table 1 and Figure 3).¹⁶ For example, in the case of **3** (in CH_3CN), the parent bands at 2090, 2052, and 2024 cm^{-1} deplete and three new bands at 2071, 2042, and 2005 cm^{-1} appear within the laser pulse. The IR bands undergo vibrational cooling (over ~ 10 ps), with a shift in the wavenumber to higher frequency, to 2080, 2046, and 2009 cm^{-1} . These bands decay with complete recovery of the initial spectrum. In the case of complex **3**, the lifetime was calculated to be 50 ps. All complexes (**1–3**) exhibit similar spectral changes, and the kinetics (Table 1) are largely

Table 1. Lifetimes and IR Stretching Frequencies (Following Vibrational Cooling) Observed Following Excitation of Compounds **1–3** at 400 nm^a

	lifetime τ /ps ($\nu_{\text{CO}}/\text{cm}^{-1}$)		
	THF	CH_3CN	pentane
1	70 (2073, 2040, 2012)	69 (2082, 2048, 2019)	71 (2079, 2045, 2021)
2		63 (2077, 2049, 2011)	
3	38 (2084, 2046, 2007)	50 (2080, 2046, 2009)	

^a Lifetimes are for recovery of the parent complex (± 5 ps). See the Supporting Information for experimental details.

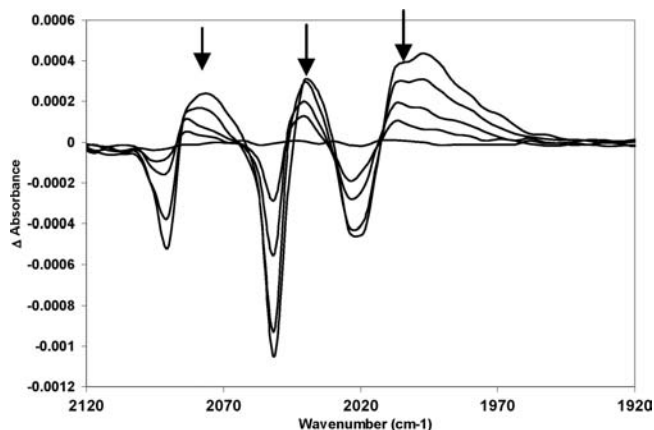


Figure 3. Transient absorption difference spectra at 1, 10, 25, 50, and 250 ps, following excitation of compound **3** in THF at 532 nm.

solvent-independent. To rule out the possibility of the solvent pentacarbonyl species (μ_2 -alkyne) $\text{Co}_2(\text{CO})_5(\text{solvent})$, absorbing either in a region similar to that of the parent complex or underneath the new bands observed in this study, PPh_3 was added to the solution. However, no new IR bands were observed on the nanosecond time scale that could be assigned to (μ_2 -alkyne) $\text{Co}_2(\text{CO})_5(\text{PPh}_3)$. This is in contrast to steady-state photolysis, where, in the presence of PPh_3 , the mono-substituted and, subsequently, disubstituted complexes form.¹¹ Previously, the IR bands for the CO-loss photoproduct, (μ_2 - $\text{C}_6\text{H}_5\text{CCH}$) $\text{Co}_2(\text{CO})_5$, were reported to occur at 2081, 2035, 2016, 2005, and 1981 cm^{-1} in an argon matrix.⁶

Conventional electron counting in organometallic chemistry implies that the cobalt compounds discussed here should have a Co-Co single bond; however, a recent charge density study on the bonding interactions in ($\text{HC}\equiv\text{CC}_6\text{H}_{10}\text{OH}$) $\text{Co}_2(\text{CO})_6$ indicates that the Co-Co bonding is weak, and a singlet diradical character is proposed for this compound.¹⁷ An earlier theoretical study by Platts et al.¹⁸ proposed that the more appropriate designation for μ_2 - $\text{C}_2\text{H}_2\text{Co}_2(\text{CO})_6$ is that of a singlet diradical, where the ground-state electronic structure has a partial occupation of both Co-Co bonding and antibonding orbitals. We have used quantum chemical calculations (B3LYP/LANL2DZp) to provide a model for the transient species observed following photoexcitation of the (μ_2 -acetylene) $\text{Co}_2(\text{CO})_6$ complexes to predict IR spectra of possible intermediate species (Table 2 and the Supporting Information). The IR properties of (μ_2 -alkyne) $\text{Co}_2(\text{CO})_6$ on both the singlet and triplet ground-state surfaces were calculated. It is apparent that in moving from the singlet to the

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Table 2. Observed and Calculated Singlet- and Triplet-State Data for $(\mu_2\text{-C}_2\text{H}_2)\text{Co}_2(\text{CO})_6^a$

	ν_{CO} (cm^{-1})				
obsd ²⁰	2097.8	2058.5	2033.7	2028.1	2016.6
singlet	2097.9	2051.3	2037.6	2035.1	2012.7
triplet	2087.5	2057.9	2024.1	2021.7	2015.2

^a A correction factor of 1.0222 was used to correct the calculated ν_{CO} bands of the ground-state triplet species.²⁰ See the Supporting Information for experimental details.

triplet surface the ν_{CO} bands of **1–3** move to lower energy. Indeed, the transient ν_{CO} bands observed in the TRIR experiments are all at lower energy compared with the parent bands (Figure 3). In addition, the calculated Co–Co bond length increases from 2.47 Å on the singlet surface (equal to about twice cobalt's covalent radius of 1.25 Å) to 3.10 Å for the triplet species. This suggests that the Co–Co interaction is considerably weaker in the triplet state. Consequently, we have tentatively assigned the transient species observed in the TRIR experiments to a $^3(\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6$ diradical species. The observation of the triplet species in the picosecond TRIR experiments requires fast intersystem crossing from the singlet surface of the order $1 \times 10^{12} \text{ s}^{-1}$. While this is fast, it is not without precedence in the literature.¹⁹

Other possibilities for the species observed in this study include the isomer in which the alkyne lies parallel to the Co–Co bond, a species where one Co–alkyne bond is cleaved, and a Co-to-CO charge-transfer excited state. Extended Hückel calculations, carried out by Hoffmann and co-workers,¹³ indicated that the parallel isomer lies at an energy 2.5 eV higher than that of the perpendicular isomer. In this study, density functional theory methods were used in an attempt to calculate the energy difference between the two isomers. Repeated attempts to locate the parallel isomer at a minimum on the singlet potential energy surface failed. It is therefore unlikely that the parallel isomer plays any significant role in the photochemistry of complexes **1–3**. An intermediate arising from cleavage of one of the Co–C alkyne bonds was also excluded based on the number of IR bands observed. Nevertheless, in addition to Co–Co bond cleavage consideration should be given to a Co-to-CO charge-transfer excited state. However, on the basis of our results, to date, Co–Co cleavage seems the most appropriate assignment.

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Table 3. Quantum Yields for CO Loss for the $(\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6$ Complexes Studied^a

compound	irradiation wavelength			
	313 nm	365 nm	405 nm	546 nm
1	0.078	0.035	0.027	0.045
2	0.145	0.080	0.045	0.106
3	0.269	0.071	0.047	0.233

^a See the Supporting Information for experimental details.

As there was no evidence for CO loss in picosecond TRIR experiments, the wavelength dependence of the quantum yield for CO loss under steady-state irradiation was determined at several excitation wavelengths (Table 3). The quantum yield for CO loss was both wavelength- and complex-dependent. For example, in the case of compound **1**, the quantum yield for CO loss ranged from 3 to 8%. Compound **3** showed higher quantum yields, except at 405 nm, which is close to the 400 nm picosecond excitation wavelength used in the present study. It is unlikely that a photochemical process with these low quantum efficiencies will be detected in the TRIR experiments.

In summary, combined picosecond TRIR studies and theoretical calculations allowed for identification of the radical species generated following excitation of the $(\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6$ complexes. The triplet diradical rapidly recombines to regenerate the parent complex, with no evidence for CO loss arising from this species. Lifetimes for the triplet diradical species ranged from 38 to 71 ps. The quantum yield for CO loss at 405 nm is low at < 5% and varies with the excitation wavelength. The observation of competing pathways to CO loss allows for a better understanding of the photochemical properties of $(\mu_2\text{-alkyne})\text{Co}_2(\text{CO})_6$ complexes in developing a photochemically driven catalytic approach in the PKR. Future studies will focus on approaches to improve the competitiveness of the CO loss pathway.

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Supporting Information Available: General experimental details and synthesis and characterization of complexes **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.