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Photochemical studies of $Co_2(CO)_6$(acetylene) complexes and their phosphine derivatives in frozen Nujol matrices

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Abstract

Photolysis of $Co_2(CO)_6$(alkyne), where alkyne = H_2C_2 (**I**), $(C_2H_5)_2C_2$ (**II**) $(C_6H_5)_2C_2$ (**III**) and $C_6H_5C_2H$ (**IV**) in frozen Nujol at ca. 90 K results in loss of CO to give $Co_2(CO)_5$(alkyne) in which CO-loss appears to be from the axial position. Complete conversion to a second isomer, presumed to have a vacancy in an equatorial position, or to starting material is observed for all compounds upon annealing the matrices to ca. 140 K. The second isomer is also formed by $Co_2(CO)_5[(C_6H_5)_2C_2]$ upon photolysis at $\lambda < 280$ nm. Photolysis of $Co_2(CO)_6As_2$ (**V**), gave photochemical and annealing products whose spectra were analogous to those of the alkyne compounds. Photolysis of phosphine substituted derivatives such as $axial$-$Co_2(CO)_5(PR_3)(C_2R'_2)$, where R = Bu; R′ = H (**VI**), R = Ph; R′ = H (**VII**), R = OPh, R′ = H (**VIII**), R = Ph; R′ = Ph (**M**) yields two isomeric CO-loss products. Annealing samples of **V**–**IX** to ca. 140 K results in simple reaction reversal. Solution photolysis of **IX** with PPh_3 gives $Co_2(CO)_4(PPh_3)_2(Ph_2C_2)$. Photolysis of $Co_2(CO)_4(PPh_3)_2(H_2C_2)$ (**X**) yields two products. Annealing the sample reforms the starting material and also generates a new species. Photolysis of $Co_2(CO)_4(Ph_2P)_2CH_2][(C_2H_5)_2C_2]$ (**XI**) forms a single product that reforms **XI** upon annealing. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: Photochemical studies; Acetylene; Phosphine derivatives

1. Introduction

Compounds of the $Co_2(CO)_6$(alkyne) series are among the earliest known organometallic compounds [1] and their application to organic chemistry has been well studied [2]. With symmetric alkynes the molecules have been shown to have C_{2v} symmetry with distorted octahedral symmetry about the individual cobalt atoms. As shown in Fig. 1, two axial carbonyl ligands
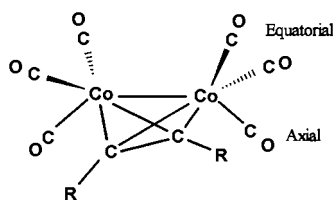

Fig. 1. Geometry of $Co_2(CO)_6$(alkyne).

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are approximately co-linear with the Co–Co 'bent' bond, while the remaining equatorial carbonyl ligands are coplanar with the acetylene. Hoffmann has reported molecular orbital calculations for these compounds carried out at the extended Hückel level [3] while Van Dam obtained similar results in an ab initio SC MO calculation [4]. In Hoffmann's model, the HOMO a_2 orbital corresponds to alkyne to metal back-bonding, while the HOMO-1 a_1 orbital corresponds to the Co–Co 'bent' bond. The LUMO, b_2, and LUMO + 1, a_1, levels are anti-bonding counterparts of the alkyne to metal bonds. The relative order of the a_2 and a_1, bonding orbitals determined by Hoffmann have been confirmed by photoelectron spectroscopy [5].

Thermal reactions in which one or more carbon monoxide ligands may be replaced by phosphines to yield stable derivatives have been reported with all simple phosphines giving mono and disubstituted products in which the phosphine appears in the axial position [6]. Bidentate ligands such as $(Ph_2P)_2CH_2$ and $(Ph_2As)_2CH_2$ have been found to bridge equatorial positions of the cobalt atoms [7]. Heck examined the

Table 1
Electronic spectral data for $Co_2(CO)_6$(alkyne) derivatives and $Co_2(CO)_6As_2$ in petroleum ether

Alkyne	λ (nm)	ε (M^{-1} cm^{-1})
C_2H_2 (**I**)	515	188
	405	530
	342	2700
$(C_2H_5)C_2$ (**II**)	540	252
	400	1024
	350	4640
$(C_6H_5)C_2H$ (**III**)	530	86
	428	834
	358	3220
$(C_6H_5)_2C_2$ (**IV**)	560	702
	435	1140
	360	3420
$Co_2(CO)_6As_2$ (**V**)	460	Not determined
	377	Not determined

kinetics of the reactions of **I** and **II** with triphenylphosphine in toluene and found the reactions to be first order in cobalt compound. **I** was found to have activation parameters of $\Delta E^* = 17.0$ kcal mol^{-1} and $\Delta S_{25}^* = -23.0$ cal mol^{-1} deg^{-1}. The negative value for the entropy of activation prompted Heck to suggest a symmetric transition state with a bridging carbonyl [8].

Photochemical substitution of $Co_2(CO)_6(RC_2H)$, where R = Ph, *n*-Bu, CH_3, CH_2, CH_3O_2C, or CH_3CO, by PPh_3 has been reported by Anderson using the 351.1, 351.4 and 363.8 nm lines from an Ar ion laser [9].

Thermal loss of CO is postulated as a first step in the Pauson–Khand synthesis of cyclopentenone derivatives [10] and as the initiating step in alkyne trimerization [11]. The Pauson–Khand reaction has been observed to proceed stoichiometrically under photochemical conditions [12] and recently Livinghouse has described visible light conditions for a catalytic Pauson–Khand reaction [13].

Gordon et al., have photolyzed $Co_2(CO)_6(C_6H_5C_2H)$ (**IV**), in argon, mixed argon–nitrogen, and nitrogen matrices at 12 K and have observed the formation of $Co_2(CO)_5(C_6H_5C_2H)$ (Ar matrix) or $Co_2(CO)_5(N_2)$-$(C_6H_5C_2H)$ (Ar–N_2 or N_2 matrices). Trace amounts of what appeared to be a second species were also observed in the argon matrix [14].

As part of an extended investigation into the photochemistry of tetrahedrane complexes in frozen Nujol matrices we have reexamined the photolysis of **IV**, three other members of this class of compounds and the analogous arsenic compound (**V**). The high quality spectra obtained from this method and the ease with which samples may be annealed to examine possible thermal reactions allow new details to be extracted from the data that bear on the identity of the photoproducts. Further, the excellent solubility of the phosphine derivatives in Nujol allowed investigation of their photochemistry as well.

2. Results and discussion

Photochemical studies were carried out using a glass cryostat as previously described [15]. Samples are dissolved in Nujol and frozen to ca. 90 K with liquid nitrogen. A 350 W high pressure mercury lamp was the primary light source with wavelength selectivity being achieved through the use of optical filters.

2.1. Photolysis of $Co_2(CO)_6$(acetylene) (**I**–**IV**) and $Co_2(CO)_6As_2$ (**V**)

Electronic spectra of compounds **I**–**V** exhibit two weak bands (about 530 and 420 nm), a strong band (about 350 nm) attributed to a MLCT transition, and an intense ligand field band at $\lambda < 290$ nm (Table 1). IR spectra of these compounds have four or five bands in the carbonyl stretching region consistent with their C_{2v} symmetry [16,17]. Photolysis at wavelengths greater than 450 nm resulted in no change in the IR spectra as determined by difference spectral methods. IR spectral changes were noted for $\lambda < 450$ nm. Incremental decreases in wavelength using a series of graduated filters established that photochemistry was associated with excitation of either the MLCT or ligand field bands.

Photolysis of compounds **I**–**V** in the range $250 < \lambda < 380$ nm resulted in the decrease in intensity of the bands of the starting material and growth of new bands. This is illustrated in Figs. 2 and 3 for **II**. IR data are presented in Table 2. Fig. 2 presents 1:1 subtraction spectra while in Fig. 3 the bands of starting material are nulled thus revealing bands that overlap with those of the starting material. As observed by Gordon [14], some product bands overlap with those of the starting material thus it was necessary to examine difference spectra with the starting material bands canceled out to locate all product bands. Small shifts of as little as 2 cm^{-1} between spectra occasionally result in artificial splitting of the product bands. The band at 2131 cm^{-1} observed in all cases is associated with 'free' CO indicating that in each case CO is lost from the molecule. Loss of CO from these C_{2v} molecules results in reduction of symmetry to give either a C_s (axial loss) or C_1 (equatorial loss). In either case five IR active carbonyl bands are expected and observed for **I**–**V**. Both **I** and **V** were found to have six distinct photoproduct bands in the carbonyl stretching region. In both cases the extra band was at the high frequency end. A possible explanation for this effect is discussed below.

Annealing each sample to ca. 140 K followed by its return to ca. 90 K for recording of its spectrum was found to result in complete loss of the bands associated with the photoproducts and some reduction of the 'free' CO band. In addition to bands of the starting materials additional bands were observed to grow in. In the case of **II**, Figs. 2c and 3c clean conversion of the photolysis product to the anneal product occurred without

concurrent appearance of starting material *or change of CO*. Back photolysis at $\lambda > 500$ nm results in simple reversal of the forward photolysis as observed by Gordon [14]. In the case of **IV** it was found that photolysis in the range $285 < \lambda < 380$ nm produced the expected photoproduct while expanding this range to $250 < \lambda < 380$ nm gave rise to the species observed upon annealing as well as the primary photoproduct.

The strong similarities in spectra of photoproducts and anneal products for all five compounds indicate

that all compounds undergo CO loss to form an unsaturated species (**A**), of similar structure, and that all of these photoproducts undergo isomerization upon warming to form a thermodynamically preferred species (**B**). Four of the five carbonyl bands in the IR spectra of species **A** and **B** are similar in both position and relative intensity, but the spectra of species **A** are characterized by a medium intensity carbonyl band at about 1970 cm^{-1}, while the lowest frequency bands of the **B** species are weak and are found at about 2000
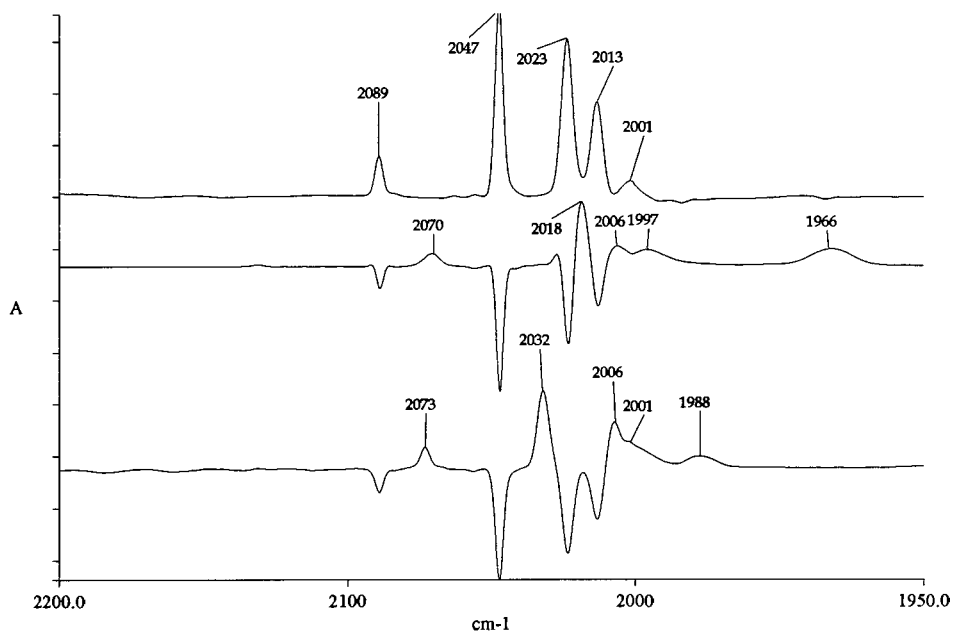

Fig. 2. Nujol matrix photolysis of $Co_2(CO)_6$(3-hexyne). (a) Starting material; (b) 30 min photolysis ($250 < \lambda < 380$ nm) minus starting material; (c) 10 min anneal minus starting material.
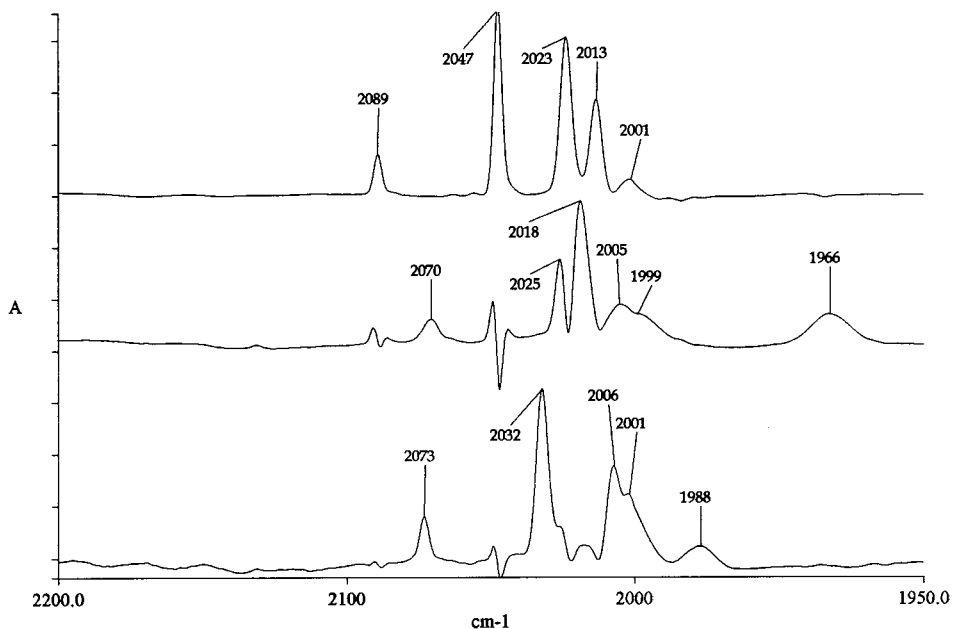

Fig. 3. Nujol matrix photolysis spectra of $Co_2(CO)_6$(3-hexyne). (a) Starting material; (b) 30 min photolysis ($250 < \lambda < 380$ nm) with starting material bands nulled out; (c) 10 min anneal with starting material bands nulled out. The peak at 2025 cm^{-1} in 3(b) is a subtraction artifact as is the broad feature at 1900 cm^{-1} in 3(c).

Table 2
IR spectral data for $Co_2(CO)_6$(alkyne) derivatives and $Co_2(CO)_6As_2$ (cm^{-1}) in frozen Nujol at ca. 90 K [a]

Alkyne	Parent spectrum	Photoproduct (A)	Anneal product (B)
C_2H_2 (I)	2099 (w)	2084 (w)	2084 (w)
	2058 (s)	2080 (w)	2043 (s)
	2032 (s)	2034 (s)	2019 (m)
	2027 (sh)	2019 (m)	2014 (sh)
	2016 (w)	2011 (sh)	2000 (w)
		1980 (m)	
$(C_2H_5)_2C_2$ (II)	2088 (w)	2070 (w)	2073 (w)
	2047 (s)	2018 (s)	2032 (s)
	2023 (s)	2004 (s)	2006 (m)
	2013 (m)	1999 (sh)	2001 (sh)
	2002 (w)	1966 (m)	1988 (w)
$(C_6H_5)C_2H$ (III)	2095 (w)	2077 (w)	2080 (w)
	2057 (s)	2029 (s)	2042 (s)
	2030 (s)	2015 (m)	2018 (m)
	2026 (sh)	1976 (m)	1998 (w)
$(C_6H_5)_2C_2$ (IV)	2091 (w)	2073 (m)	2076 (w)
	2056 (s)	2028 (s)	2042 (s)
	2028 (m)	2013 (m)	2017 (s)
	2025 (sh)	2005 (sh)	2012 (sh)
		1975 (m)	
$Co_2(CO)_6As_2$ (V)	2094 (m)	2082 (m)	2078 (w)
	2058 (s)	2074 (w)	2047 (s)
	2038 (s)	2035 (s)	2025 (m)
	2031 (m)	2030 (sh)	2017 (w)
		2017 (m)	
		1990 (m)	

[a] Free CO band at 2032 cm^{-1} observed in all cases.

cm^{-1}. A careful search was made for additional bands associated with bridging carbonyl groups, but no additional bands were found. Symmetry arguments provide no clues as to the likely structural assignment of the two species. The carbonyl band at 1970 cm^{-1} is well above the region associated normally with semi-bridging carbonyl groups, thus there is no experimental support for the bridging carbonyl intermediate species proposed by Heck.
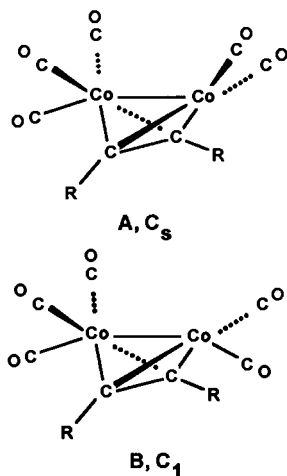
As noted, the pentacarbonyl fragments may have C_s (*axial* CO loss) or C_1 (*equatorial* CO loss) symmetry with theory predicting five carbonyl stretching bands for each of these isomers. There is a strong similarity between the spectra of the **A** species and those of axial $Co_2(CO)_5(PR_3)$(alkyne). For example, *axial*-$Co_2(CO)_5(PBu_3)(C_2H_2)$ has bands in frozen Nujol at 2064 (m), 2008 (s), 2001 (s), 1989 (m), and 1966 (m) cm^{-1}, while the bands of the **A** species of $Co_2(CO)_5(C_2H_2)$ are at 2084 (w), 2080 (w), 2034 (s), 2019 (m), 2011 (sh), and 1980 (m) cm^{-1}. It is generally observed that carbonyl loss fragments have the same pattern of carbonyl bands as the corresponding phosphine derivatives with the bands of the carbonyl loss species shifted to higher frequency by 20–40 cm^{-1}. Keeping with this pattern we have assigned A as the *axial*-CO loss species.

Assuming the above analysis to be correct, the most likely identity of the **B** species would be the corresponding equatorial species, however, all thermal and photochemical reactions of $Co_2(CO)_6$(alkyne) and $Co_2(CO)_6As_2$ compounds with simple phosphine ligands yield products in which the phosphine is in the axial position. It is possible that an equilibrium between the two structural isomers occurs in solution and that reaction between ligands and the axial isomers is favored for steric reasons. It should be noted that photolysis of $Fe_2(CO)_6(SR)_2$ compounds in frozen Nujol yields a pentacarbonyl intermediate with an IR spectrum essentially identical to those of the **A** species described here [18]. In the case of the iron compounds there is no evidence of a thermal rearrangement.

The additional carbonyl bands observed for **I** and **V** cannot be explained by the formation of simple isomers since in both cases annealing results in the formation of a clear second species. We propose that the additional bands arise from splitting of the highest energy symmetric stretch as the result of vibrational coupling between these bands and the $Co_2(C_2H_2)$ or Co_2As_2 tetrahedrane unit. For compounds **II–IV**, with alkyl or aryl substituents on the acetylene group these vibrational couplings may be damped.

2.2. Photolysis of $Co_2(CO)_5(PR_3)$(alkyne) (VI–IX), $Co_2(CO)_4(PBu_3)(H_2C_2)$ (XI) and $Co_2(CO)_4(DMPM)(C_2Et_2)$ (XII)

Multiple substitution of carbon monoxide by phosphines is well known for $Co_2(CO)_6$(alkyne) compounds [6]. We sought to establish whether phosphine substituted compounds undergo photolysis and CO-loss in a manner similar to that of the parent carbonyl compounds. Table 3 presents electronic spectral data for these substituted compounds and Table 4 presents IR data of the compounds and photoproducts. Compounds **VI–IX** are strongly colored as a result of a

Table 3
Electronic spectral data for phosphine and phosphite derivatives in petroleum ether

Compound	λ (nm)	ε (M^{-1} cm^{-1})
$Co_2(CO)_5(PBu_3)(C_2H_2)$ (VI)	460	1010
	370	8500
$Co_2(CO)_5(PPh_3)(C_2H_2)$ (VII)	369	2330
$Co_2(CO)_5[P(OPh)_3(C_2H_2)$ (VIII)	420	838
	355	4350
$Co_2(CO)_5(PPh_3)(C_2Ph_2)$ (IX)	565	1880
	382	27 600
$Co_2(CO)_4(PBu_3)_2(C_2H_2)$ (XI)	480	2560
	372	22 800
	315	13 600
$Co_2(CO)_4(DPPM)(C_2Et_2)$ (VI)	525	1100
	325	24 700

MLCT band in the region of 370 nm that tails into the visible region. A very strong ligand field absorption is found at $\lambda < 300$ nm. The band maxima for the MLCT transition were found to be sensitive to the electron donor ability of the phosphorus ligand with the order being $CO > P(OPh)_3 > PPh_3 > PBu_3$. The carbonyl stretching bands within this series decrease in the order

$P(OPh)_3 > PPh_3 > PBu_3$ paralleling the decrease in π-acceptor capacity of the ligand.

Photolysis into the high energy electronic bands of these compounds resulted in IR bands of the starting materials decreasing in intensity while new bands grew in. In each case a band at 2131 cm^{-1} associated with 'free' CO was observed while five or six well-defined band maxima were found. Asymmetries in the shapes of some of these bands suggest that there might be additional, unresolved bands. Annealing of the photolyzed sample of VIII resulted in reduction of bands at 2047, 1986, and 1962 cm^{-1} and growth of bands at 2052, 2046, 2016, and 1990 cm^{-1} as well as bands of the starting material. Annealing of photolyzed samples of VI, VII and IIX results in reversal of the photochemical reaction.

Photolysis of mono-phosphine compounds, VII–IX, results in CO-loss and the appearance of a complex set of carbonyl bands. Although these compounds have three unique CO groups, *axial*-$Co(CO)_3$, *equatorial*-$Co(CO)_3$, and *equatorial*-$Co(CO)_2(PPh_3)$, evidence from thermal reactions suggest that addition of a second phosphine to $Co_2(CO)_5(PR_3)$(alkyne) dominantly or exclusively occurs on the unsubstituted cobalt atom. It is

Table 4
IR spectral data (cm^{-1}) for $Co_2(CO)_5(L)$(alkyne), $Co_2(CO)_4(PBu_3)_2(C_2H_2)$ and $Co_2(CO)_4(DPPM)[(C_2H_5)_2C_2]$ in frozen Nujol at ca. 90 K [a]

Compound	Parent spectrum	Photoproduct	Anneal products
$Co_2(CO)_5(PBu_3)(C_2H_2)$ (VI)	2064 (w)	2053 (w)	
	2008 (s)	2034 (s)	
	2001 (m)	1988 (s)	
	1989 (w)	1971 (m)	
	1966 (s)	1948 (m)	
$Co_2(CO)_5(PPh_3)(C_2H_2)$ (VII)	2067 (s)	2053 (w)	
	2014 (s)	2038 (s)	
	2005 (s)	1994 (s)	
	1993 (w)	1977 (m)	
	1970 (w)	1954 (m)	
$Co_2(CO)_5[P(OPh)_3](C_2H_2)$ (VIII)	2075 (s)	2047 (w)	2052 (w)
	2025 (s)	2016 (s)	2046 (w)
	2012 (s)	2004 (s)	2016 (s)
	2000 (w)	1993 (sh)	1990 (m)
	1985 (w)	1990 (m)	
		1962 (m)	
$Co_2(CO)_5(PPh_3)(Ph_2C_2)$ (IX)	2062 (s)	2051 (m)	
	2016 (s)	2029 (s)	
	2002 (m)	1990 (s)	
	1994 (w)	1979 (w)	
	1970 (w)	1966 (m)	
		1951 (m)	
$Co_2(CO)_4(PBu_3)_2(C_2H_2)$ (XI)	2019 (s)	1992 (m)	1997 (m)
	1969 (m)	1976 (m0	1949 (m)
	1960 (s)	1937 (s)	1905 (w)
		1920 (w)	
$Co_2(CO)_4(DPPM)[(C_2H_5)_2C_2]$ (XII)	2020 (m)	2005 (s)	
	1990 (s)	1955 (s)	
	1964 (m)	1931 (s)	
	1945 (w)		

[a] Free CO band at 2132 cm^{-1} is observed in all photolyses.

reasonable to propose that carbonyl groups may be lost from the $Co(CO)_3$ unit to give rise to both possible isomeric axial (**C**), and equatorial (**D**), CO-loss photoproducts. This implies that substitution of axial carbonyl by phosphine on one cobalt atom either facilitates CO-loss from both the equatorial and axial positions of the second $Co(CO)_3$ unit, or lowers the thermal barrier to rearrangement so that an equilibrium mixture is formed. In no instance was the phosphorus ligand lost upon photolysis.
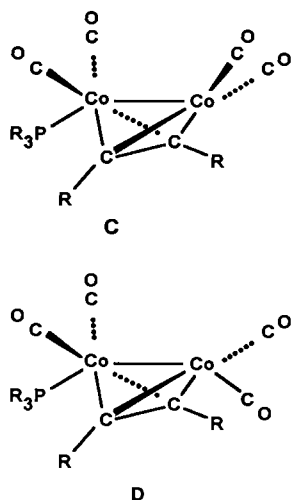
In the specific case of **VIII**, annealing clearly results in the conversion of one photoproduct isomer to the other. It is significant that the isomer which is depleted upon warming is the one with the lowest energy CO stretching band (1962 cm^{-1}). This parallels the behavior of the photoproducts from **I**–**V**, and argues that the symmetries of the pairs of species **A** and **C**, and **B** and **D** are the same. It is also important to note that the photochemistry and annealing behavior of the $P(OPh)_3$ derivative is most like the parent carbonyl derivatives, consistent with the π-acid character of phosphites.

To test the possibility of carrying out photochemical substitutions on monophosphine compounds, a sample of $Co_2(CO)_5(PPh_3(H_2C_2)$ was photolyzed in heptane with one equivalent of PPh_3. IR spectra of the reaction mixture indicated that $Co_2(CO)_5(PPh_3)(H_2C_2)$, had been formed. Concentration of the reaction mixture and recrystallization from dichloromethane–heptane gave the bis(triphenylphosphine) derivative in 10% yield.

As noted above, there was no evidence to suggest phosphine or phosphite loss from the cobalt compounds upon photolysis, nor was there any evidence that CO had been lost from the $Co(CO)_5(PR_3)$ unit. To examine whether the presence of a phosphine suppresses CO loss we photolyzed two derivatives, containing two phosphine ligands. The phosphine ligands in **X** are known to occupy axial positions while the bidentate

DPPM ligand of **XI** is known to span equatorial positions.

Photolysis of **X** was found to result in decreases in the intensities of its carbonyl bands, and the appearance of new bands at 2131, 1991, 1976, 1937, and 1918 (sh) cm^{-1}. Annealing of this sample resulted in loss of 'free' CO and regeneration of **X** and also appearance of new bands at 1997, 1949, and 1905 cm^{-1}.

Photolysis of **X** demonstrates that even a $Co(CO)_2(PR_3)$ unit may lose CO. The resulting species, $Co_2(CO)_3(PBu_3)_2(H_2C_2)$, would be expected to have three distinct carbonyl stretching bands. The small shoulder observed at 1918 cm^{-1} may be evidence for a rearrangement of phosphine to an equatorial position analogous to the axial to equatorial shift proposed for **A** to **B**. This latter possibility is reinforced by the appearance of a new species upon annealing that may be a structural isomer of **VIII**.

To explore the effect of phosphine position on the photochemistry we have examined the photolysis of $Co_2(CO)_4(DPPM)(C_2Et_2)$ (**XI**) in frozen Nujol. The IR spectrum of the photolyzed sample exhibits reduction in the intensity of the bands of the starting material and growth of new bands at 2131, 2005, 1955, and 1930 cm^{-1}. Annealing the sample results in simple reversal of the photoreaction.

The bidentate DPPM ligand in **XI** is known to bridge equatorial positions on the two cobalt atoms, thus photolysis could result in loss of CO from either an axial or equatorial position. Photolysis appears to result in only one of the two possible carbonyl-loss isomers being formed.

3. Conclusions

Photolysis into the MLCT or ligand field bands of cobalt tetrahedrane compounds results in loss of CO to form one or two species in which the tetrahedrane core of the molecule is retained. Hexacarbonyl compounds appear to generate one species upon photolysis and a second upon annealing of the sample. Pentacarbonyllphosphine compounds appear to form two isomers upon photolysis while the tetracarbonylldiphosphine compounds give one dominant product.

These matrix observations indicate that the cobalt tetrahedrane compounds have a rich, mostly untapped photochemistry that may be useful in preparing derivatives with mixed ligands or intermediates for Pauson–Khand and acetylene trimerization reactions. As an illustration we have photochemically prepared the previously unknown tetrahydrothiofuran derivative, $Co_2(CO)_5(SC_4H_8)(C_2Et_2)$. A detailed description of synthetic applications of photochemistry to cobalt tetrahedrane compounds is in preparation.

4. Experimental

Matrix studies were performed using a liquid nitrogen cooled glass cryostat and techniques described previously [15]. Spectra are recorded on a Perkin–Elmer Spectrum 1000 FTIR Spectrometer at 4 cm^{-1} resolution. Compounds were prepared by literature procedures. Nujol (light mineral oil) was purchased from Aldrich and used as received.

4.1. Nujol matrix experiments

Compounds to be studied are dissolved in Nujol by grinding a 10 mg sample with 0.5 ml Nujol followed by centrifugation for at least ten min to ensure that all particles have been removed from the solution.

Nujol solutions are applied to the CaF$_2$ windows of the sample cell and the cell assembled. The cell is screwed onto the inner reservoir of the glass cryostat and the cryostat is assembled. Dry nitrogen is flushed through the cell to remove water vapor, then liquid nitrogen is introduced into the reservoir and the cell is evacuated using a vacuum line equipped with an oil diffusion pump. Ultimate vacuums of 4×10^{-3} torr are desired to avoid frosting of the exterior windows during the experiments.

Photolyses are carried out using a 350 W high pressure mercury lamp with optical filters used to control the irradiation wavelengths. Band pass filters have a roughly bell shaped window with the transmittance at the band center of about 63% and a band width of ± 70 nm. In some cases, particularly in the ultraviolet, pairs of filters are used together to narrow the actual irradiation wavelengths.

After recording an initial spectrum the sample is photolyzed at $\lambda_{irr} > 600$ nm. While it is rare to observe photochemistry at such low energies we have found that samples undergo minor photoannealing that may shift vibrational bands by 1–2 cm^{-1}. By conducting a long wavelength photoannealing step we avoid problems associated with these band shifts. In a typical photochemical series, samples are photolyzed for 30 min followed by recording of a spectrum. In the current studies photolyses were carried out at (1) $\lambda_{irr} > 600$, (2) $\lambda_{irr} = 550 \pm 70$, (3) $\lambda_{irr} = 500 \pm 70$, (4) $\lambda_{irr} = 450 \pm 70$, (5) $\lambda_{irr} = 400 \pm 70$, (6) $350 < \lambda_{irr} < 400$, (7) $250 < \lambda_{irr} < 380$ nm.

Annealing experiments involve removing the liquid nitrogen from the reservoir and allowing the cell to warm for about 10 min during which time the cell temperature rises to about 140 K. The sample is returned to 90 K for recording the spectrum.

4.2. Synthesis of $Co_2(CO)_4(PPh_3)_2(Ph_2C_2)$

Complex **VII** (32 mg, 59 μmol) and PPh$_3$ (31 mg, 118 μmol), were placed in a 50 ml microscale quartz photochemical cell outfitted with a cold finger. The cell was evacuated and flushed with N$_2$ and 20 ml of degassed benzene was added. The sample was irradiated for 30 min with a 350 W high pressure Hg lamp and filter such that $240 < \lambda_{irr} < 380$ nm. A water filter was used to remove infrared light to prevent warming of the sample. After photolysis the solvent as removed and the sample recrystallized from dichloromethane–heptane to yield the bis-phosphine derivative as red crystals. 4.7 mg, 10%. IR: (CH$_2$Cl$_2$) 2019, 1971 (sh), 1960, 1935 cm^{-1} [6b].

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