Low-Temperature FTIR Study of the Photochemistry of $CpMo(CO)_3-Co(CO)_4$ and Related Heterodinuclear Complexes

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Received December 27, 1994®

Low-temperature flash photolysis of $CpMo(CO)_3-Co(CO)_4$ (**A**) or $CpMo(CO)_3-Co(CO)_3(P(n\text{-}Bu)_3)$ (**B**) in 3MP glass results in loss of CO as the only IR-detectable photoprocess. Flash photolysis of $CpMo(CO)_2(P(n\text{-}Bu)_3)-Co(CO)_3(P(n\text{-}Bu)_3)$ (**C**), however, results in loss of $P(n\text{-}Bu)_3$ as the major photoprocess with loss of CO as a minor process. An initially observed solvento species, **1**, produced in photolysis of **A** at 92 K rearranges to form a symmetrically bridging species, **2**. Symmetrically bridging species, **3** and **4**, and linear semibridging species, **5** and **6**, are observed initially in the photolysis of **B** at 93 K. When the temperature is raised, **3** and **4** rearrange to form **6** while **5** isomerizes to form another linear semibridging species, **7**. When **B** is photolyzed at 143 K, only **6** and **7** are still observable. All CO-loss intermediates recombine with expelled free CO to re-form the starting compound. If **B** is photolyzed in the presence of $P(n\text{-}Bu)_3$ at 93 K, the four initially formed intermediates, **3**−**6**, are observed to react with $P(n\text{-}Bu)_3$ when the glass is warmed, yielding compound **C** through intermediates **8**−**10**. Photolysis of **C** at 93 K yields initially the same four intermediates, **3**−**6**, as photolysis of **B** and another intermediate, **11**, upon loss of $P(n\text{-}Bu)_3$ and CO, respectively. Some of the four intermediates react with expelled free CO, giving rise to compound **B**; some react with the lost free $P(n\text{-}Bu)_3$, re-forming **C**, also through the same intermediates, **8**−**10**. All the experimental observations, together with results from thermal reactions with ^{13}CO, can be explained by the selective loss of CO or $P(n\text{-}Bu)_3$ from the Mo end of the molecule for **B** and **C**, respectively. A detailed mechanism of the photochemical behaviors of the substituted compounds and structures of the observed intermediates (including ring-slippage structures) are proposed. Steric and electronic effects on formation and stabilities of linear semibridging species are discussed.

Introduction

In recent years there has been a considerable interest in the rearrangements occurring within dinuclear or higher nuclearity metal carbonyl compounds upon photochemical loss of CO or other ligand.[1−5] Such rearrangements represent forms of intramolecular "self-repair", driven by the formation of a site of coordinative unsaturation. Among the most commonly observed structure motifs are the linear CO semibridge, symmetrically bridging CO group, or metal−metal multiple bonds.

While the behavior of homonuclear metal systems has been reasonably well-characterized, heterobimetallic systems have received relatively less attention. Pope and Wrighton have reported the results of photolysis of $CpMo(CO)_3Mn(CO)_5$ at low temperatures.[1g] Two isomers of the CO-loss product were observed after UV irradiation in rigid methylcyclohexane at 93 K. The two isomers of $CpMoMn(CO)_7$ were proposed to have a symmetrically bridging CO (μ-CO, 1680 cm^{-1}) and a linear semibridge (μ-η^1,η^2-CO, 1760 cm^{-1}), respectively. The origin of the expelled CO has not been determined.

The photolysis of $MnRe(CO)_{10}$ was first reported to result in loss of CO from Mn, with formation of a linear semibridge.[4a] More recent work indicates that the predominant photoproduct in a low-temperature 3-methylpentane (3MP) glass is a solvento species, which recombines with CO without intermediate formation of a semibridge. A minor fraction of the photoproduct is the linear semibridge. The two forms of the CO-loss species behave differently toward attacking ligand such as phosphines.[6]

To shed further light on the behavior of heterodinuclear systems, we have studied the low-temperature photochemical behavior of $CpMo(CO)_3-Co(CO)_4$. This compound, first prepared in 1978 by Abrahamson and Wrighton,[7] has been shown in our laboratories to undergo a rather complex set of thermal reactions with phosphorus ligands.[8] For phosphines of moderate steric requirement, e.g., $P(n\text{-}Bu)_3$, a radical chain reaction occurs; it involves fast substitution of a $CpMo(CO)_3$ radical, followed by fast electron transfer to $CpMo(CO)_3-Co(CO)_4$ to yield predominantly $CpMo(CO)_2L_2^+,Co(CO)_4^-$. The radical chain reaction is initiated by homolysis of the Mo−Co bond; thus the reaction is extremely sensitive to the presence of light.

In this contribution we report on studies of the photochemistry of $CpMo(CO)_3-Co(CO)_4$ (**A**) and related phosphine-substituted compounds, $CpMo(CO)_3-Co(CO)_3(P(n\text{-}Bu)_3)$ (**B**) and $CpMo(CO)_2(P(n\text{-}Bu)_3)-Co(CO)_3(P(n\text{-}Bu)_3)$ (**C**), in 3-methylpentane at temperatures of 92 K and above. The reactions of the intermediates formed in the photochemical processes are observed as the rigid 3MP glass is warmed. Under the

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® Abstract published in *Advance ACS Abstracts,* May 15, 1995.

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conditions of the experiment, radicals formed through metal–metal bond homolysis undergo rapid geminate recombination within the solvent (glass) cage. Thus, radical formation leads to no lasting consequences in the time scale of the experiments reported here, other than possible formation of isomers of the parent compound on radical recombination. (A precedent for such isomer formation is seen in the low-temperature photolysis of $[CpMo(CO)_3]_2$; the gauche isomer, present only in very small fractional concentration in the equilibrium solution, is formed in substantial amounts when the radicals recombine.[2c])

The CO expelled from the starting compound in the photochemical event can, at least in small measure, diffuse into the 3MP glass, even at 92 K. Thus, it is possible to form the CO-loss product in the glass and to observe its behavior as the glass is warmed. One of the most interesting questions to address in heterobimetallic carbonyl compounds, unlike homodinuclear compounds, is whether there is a preference or selectivity for CO loss with respect to the two different metal centers. By comparing the photochemical behavior of related substituted compounds, without resorting to a complicated stereospecific ^{13}CO-labeling experiment,[4b] we show an alternative way of answering this question. In addition, our results show that a variety of bridging types and geometries are formed. When the Co center is substituted by a phosphine, the presence of geometric isomers, based on the location of phosphine, is evidenced in the low-temperature spectra.

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of purified argon (or $CO/^{13}CO$ when indicated) employing Schlenk techniques. Hamilton gastight syringes were used for transferring liquids under positive gas pressure using carefully purged equipment. Except where irradiation is indicated, exposure to light other than red photographic safelight was rigorously minimized in all experiments.

Materials. The $Co_2(CO)_8$ (Strem Chemicals) was used after sublimation at 35 °C under vacuum. $[CpMo(CO)_3]_2$ (Pressure Chemicals) was used without further purification. $P(n\text{-}Bu)_3$ (n-Bu = n-butyl) was obtained from Strem Chemicals and distilled over CaH_2 before use. $[Co(CO)_3P(n\text{-}Bu)_3]_2$ was prepared by R. Sullivan in these laboratories.[9] Preparations of $CpMo(CO)_3-Co(CO)_4$ (**A**), $CpMo(CO)_3-Co(CO)_3(P(n\text{-}Bu)_3)$ (**B**), and $CpMo(CO)_2(P(n\text{-}Bu)_3)-Co(CO)_3(P(n\text{-}Bu)_3)$ (**C**) have been reported in a previous paper.[8] IR absorption bands in 3MP at low temperature and at room temperature are listed in Table 1.

Solvents. Hexane was purified as described previously.[9] 3-Methylpentane was distilled over CaH_2 under Ar atmosphere and stored over 4 Å molecular sieves in a Schlenk flask. The solvent was further degassed via three freeze–pump–thaw cycles before use. Toluene was purified by distillation over Na under nitrogen before use.

Argon, obtained from Linde Specialty Gas Co., was passed through columns of activated 4 Å molecular sieves and an MnO oxygen trap prior to use.

Carbon monoxide, CO (Matheson purity grade, minimum purity 99.99%), was obtained from Matheson Gas Products, Inc. Trace $Fe(CO)_5$ was removed by passing the CO through an activated charcoal trap in a sand bath at 180 °C, followed by passage through a second activated charcoal trap cooled in a dry ice–acetone bath, a column of activated 4 Å molecule sieves, and an oxygen trap purchased from American Scientific.

Variable-Temperature IR Cell. A SPECAC variable-temperature cell, Model 21500, equipped with CaF_2 windows (1-mm path length) was used. Liquid nitrogen or a dry ice–acetone bath was used as coolant.

Instrumentation. All IR spectra were collected on a Perkin-Elmer 1710 FTIR spectrometer (2-cm^{-1} resolution; each spectrum, which requires about 40 s, is an average of four scans). Data transfer to a PC was accomplished with the program 17DX provided by Perkin-Elmer. IR spectra were processed and analyzed using a locally developed program. A library of 3MP solvent spectra at different temperatures (one spectrum at each degree Celsius) from 90 to 298 K were collected and stored as the solvent background file. The spectrum of complex or product in 3MP is obtained by subtracting the solvent background at the same temperature from the original spectrum. Flash irradiations were conducted using high-pressure xenon flash lamps (EG&G FX-142C-4.5).[2]

Table 1. IR Absorption Band Frequencies for the Complexes and Intermediates in 3MP

compd[a]	$\nu(CO)/cm^{-1}$
A	2076 (m), 2022 (s), 1996 (sh, w), 1986 (sh, s), 1978 (s), 1949 (m), 1941 (m)[b]
	2076 (m), 2021 (s), 1994 (sh, w), 1984 (s), 1976 (s), 1947 (m), 1937 (m)[c]
B	2024 (m), 1966 (s), 1937 (vs), 1923 (sh, m), 1909 (sh, w)[b]
	2024 (m), 1964 (s), 1941 (sh, s), 1934 (vs), 1919 (sh,w), 1904 (vw)[c]
C	1993 (m), 1925 (vs), 1914 (vs), 1900 (sh, m), 1943 (s)[b]
	1990 (m), 1922 (vs), 1910 (vs), 1839 (s)[c]
D	2019 (m), 1984 (vw), 1962 (s), 1937 (vs), 1923 (sh, s), 1907 (m), 1894 (sh, m), 1881 (sh, w), 1860 (vw), 1852 (vw)
1	2068, 2004, 1973, 1957, 1946, 1914
2	2088, 2043, 1845 (bridging)
3, 4	1999, 1973, 1896, 1818 (bridging), 1803 (bridging)
5	1997, 1896, 1755 (bridging)
6	2024, 1978, 1905, 1862, 1730 (bridging)
7	1964, 1934, 1912, 1900, 1714 (bridging)
8, 9	2020, 2000, 1886, 1740 (bridging), 1721 (bridging)
10	2021, 1997, 1926, 1957, 1882, 1729 (bridging)

[a] See text for definitions of compounds and intermediates. [b] 298 K. [c] 93 K.

Infrared Spectra at Low Temperatures following Flash Photolysis. Solutions of complexes (the absorbance of the most intense IR peak is adjusted to about 1.0) in 3MP are prepared in a Schlenk tube under argon and degassed by three freeze–pump–thaw cycles. When CO is used as the cover gas, the solution is first degassed and then CO is added to a total pressure of 1 atm. A portion of the solution is then transferred by a gastight syringe into the IR cell under a positive pressure of argon in a bell jar attached to a vacuum/argon manifold. The cell is loaded into a SPECAC variable-temperature cell holder and cooled to the appropriate temperature with liquid nitrogen or dry ice–acetone coolant. After the sample reaches thermal equilibrium with the cell holder, the spectrum is recorded and stored as the spectrum-before-flash. The sample is then flash-photolyzed using the xenon flash lamp. Depending on the sample, one to ten flashes are typically used. However, sometimes as many as 60 flashes are needed to generate a sufficient absorbance change. After the photolysis, the cell assembly is quickly moved to the IR spectrometer and spectra are recorded either at constant temperature or in a warmup routine. The spectra are saved as spectra-after-flash. For experiments at constant temperature, only one spectrum-before-flash is needed and the difference spectra are obtained by subtracting the spectrum-before-flash from the spectra-after-flash. For warmup experiments, a series of spectra-before-flash are needed, because the solute spectra vary with temperature. The spectra-before-flash are collected using the same warmup routine as that for the spectra-after-flash.

Results and Discussion

1. Photochemistry of $CpMo(CO)_3-Co(CO)_4$ at 93 K.

Figure 1 shows the difference spectra of $CpMo(CO)_3-Co(CO)_4$ (**A**) after flash photolysis at 92 K in 3MP glass under an argon atmosphere. Negative IR bands at 2076, 2021, 1994, 1984, 1976, 1947, and 1937 cm^{-1} are due to the consumption of starting compound **A**. A band at 2132 cm^{-1} is due to free CO generated in the low-temperature glass.[10] Other positive bands are due to CO-loss intermediates. The time dependencies of

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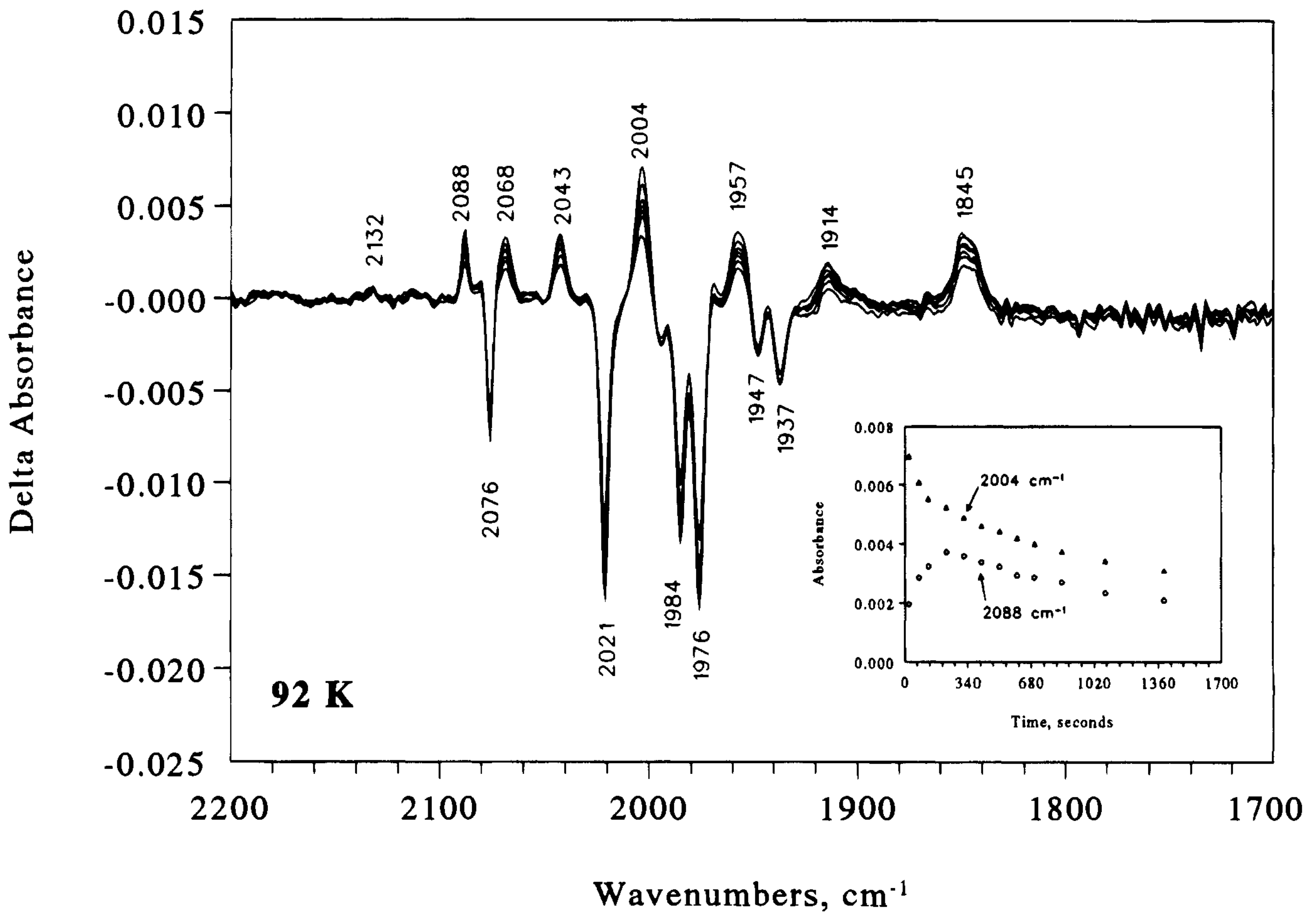

Figure 1. Difference IR spectra of $CpMo(CO)_3-Co(CO)_4$ (**A**) in rigid 3MP glass under argon before and after one flash irradiation at 92 K collected at different times after flash. The insert shows the time dependence of representative absorbances of species **1** at 2004 cm^{-1} and **2** at 2088 cm^{-1}, respectively.

the IR absorption changes show that the positive absorbances belong to two different intermediates. The first intermediate (**1**) has six terminal CO IR bands at 2068, 2004, 1973, 1957, 1946, and 1920 cm^{-1}; the second intermediate (**2**) exhibits terminal CO bands at 2088 and 2043 cm^{-1}, as well as a bridging-CO band at 1845 cm^{-1}. Even at 92 K, recombination of the CO-loss products with ejected free CO in the glass is fast. The first set of bands was observed to decay soon after flash photolysis and totally disappeared over a period of 5 min. Concurrently, the intensity of the second set of bands increased during the initial 5 min after flash irradiation and then started to decay (Figure 1, insert). All the positive absorbances due to CO-loss products decayed in 2 h at 92 K with >95% recovery of the negative absorbances due to the starting complex.

Under an atmosphere of added CO, no net absorbance change was observed 30 s after flash irradiation, indicating that all the intermediates have reacted with CO to form the starting complex.

Species **1** has six terminal CO IR bands and no absorbance assignable to bridging CO, consistent with a solvento species of the formula $CpMoCo(CO)_6(S)$, in which a solvent molecule has filled in the vacancy created by CO loss. The solvento species can either recombine with CO to form the starting material or rearrange to form a CO-bridging species, which subsequently picks up a CO to form the starting material.

The CO-bridging species, **2**, probably has a symmetrical bridging structure. The frequency of the bridging CO, at 1845 cm^{-1} for $CpMoCo(CO)_5(\mu\text{-}CO)$ (**2**), is close to those of the symmetrical bridging CO groups in $Co_2(CO)_6(\mu\text{-}CO)_2$ (1863, 1853 cm^{-1})[11] and $Cp_2Mo_2(CO)_3(\mu\text{-}CO)_2$ (1868 cm^{-1}).[5c]

Photolysis of **A** with an excess of $P(OPh)_3$ in 3MP at 143 K leads to substitution at both Mo and Co, with the Co-substituted form as the major product. The difference spectrum shows positive absorbances at 2064, 2038, 1954, 1933, and 1923 cm^{-1} due to formation of products and negative absorbances at 2076, 2021, 1984, 1976, and 1947 cm^{-1} due to the consumption of the starting compound **A**. Among the positive bands, 2064 cm^{-1} is a characteristic band of the Mo-substituted compound $CpMo(CO)_2(P(OPh)_3)-Co(CO)_4$ and the rest are due to the Co-substituted compound $CpMo(CO)_3-Co(CO)_3(P(OPh)_3)$.[6] The formation of both substituted products is consistent with the presence of a symmetrically bridged intermediate, which is subject to ligand attack at either unsaturated metal center. The relative quantum yields for formation of the two products, however, are different depending on the steric and electronic factors controlling the substitution processes. It is worth noting that in both the thermal and photochemical reactions of **A** with $P(OPh)_3$, the Mo-substituted compound is the minor product.[8]

One question still remains: From which metal is CO lost, or is the CO lost from both metals? Although not entirely definitive, careful analysis and comparison of the IR bands of $CpMo(CO)_3-Co(CO)_4$ and the solvento species $CpMoCo(CO)_6(S)$ indicate that the CO is lost only from Mo. Figure 2 summarizes the positions of the terminal CO bands for a series of related compounds. One evident trend is that the CO stretch frequencies are generally higher in the $Co(CO)_4$ moiety than in the $CpMo(CO)_3$ moiety. It is also clear that the two lower-frequency stretch modes have similar values in many of the $CpMo(CO)_3$-containing compounds. One thus can reasonably assign the seven bands of $CpMo(CO)_3-Co(CO)_4$ as follows:

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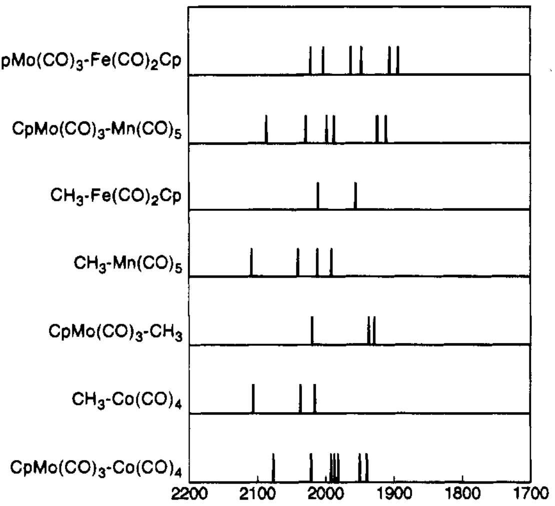


Figure 2. Summary of IR vibration frequencies of CO for related compounds.

$CpMo(CO)_3{-}Co(CO)_4$

2076, *2021*, 1994, 1984, 1976, *1947*, *1937* cm^{-1}

$CpMoCo(CO)_6(S)$

2068, 2004, 1973, 1957, *1946*, *1914* cm^{-1}

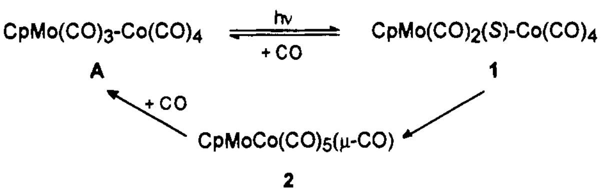
where the band frequencies in *italics* are assigned to $CpMo(CO)_3$ and the other four to $Co(CO)_4$. From the above comparison, it is clear that the totally symmetric stretching band of $Co(CO)_4$, at 2068 cm^{-1}, is still present in the spectrum of the solvento species, only slightly shifted in comparison to 2076 cm^{-1} for $CpMo(CO)_3{-}Co(CO)_4$. By contrast, the 2021 cm^{-1} band assignable to the totally symmetric CO stretch mode of $CpMo(CO)_3$ is absent. Thus, the spectrum of the solvento species is consistent with the formulation $CpMo(CO)_2(S){-}Co(CO)_4$. Scheme 1 summarizes the photochemical processes of **A** in 3MP glass at low temperature.

2. Photochemistry of $CpMo(CO)_3{-}Co(CO)_3P(n\text{-}Bu)_3$ in 3MP. (i) Flash Photolysis under Argon Atmosphere at Different Temperatures. Figure 3 shows the difference spectra of $CpMo(CO)_3{-}Co(CO)_3P(n\text{-}Bu)_3$ (**B**) before and after 10 flash irradiations in 3MP glass at 96 K under argon at different time delays after the irradiation. Four bands in the bridging-CO region, at 1818, 1803, 1755, and 1730 cm^{-1}, as well as bands in the terminal region, are seen after flash irradiation. These can be assigned to at least three different bridging-CO intermediates on the basis of their kinetic characteristics. At constant temperature, bands at 1818 and 1803 cm^{-1} gradually decay, with a concurrent increase in intensity of the bands at 1730 and 1861 cm^{-1}. The fourth band at 1755 cm^{-1} remains at constant intensity at this temperature for at least 20 min.

When the flash-photolyzed glass sample is gradually warmed (Figure 4), bands at 1818, 1803, and 1755 cm^{-1} start to decay. The decay rates for the two bands at 1818 and 1803 cm^{-1} are approximately the same and are faster than that of the 1755 cm^{-1} band. The band at 1730 cm^{-1} initially increases in intensity and then starts to decrease. During the warmup process, a new band at 1714 cm^{-1} appears and increases in intensity as the other bands decay. Bands at 1818, 1803, and 1755 cm^{-1} totally disappear upon continuous warming to 120 K. At this temperature, only two bands, at 1730 and 1714 cm^{-1}, are still present in the bridging-CO region.

When the sample is irradiated at 113 K, the two bands at 1818 and 1803 cm^{-1} are still observable with very low intensities when the spectrum is collected within 25 s after the flash, but they disappear from the spectrum collected 1 min later. At this temperature, the 1755 cm^{-1} band decays over a period of 35 min, while the 1714 cm^{-1} band is observed to increase initially and then decrease a few minutes later. Difference spectra reveal that the species giving rise to the 1714 cm^{-1} band is at least partially formed via consumption of the species absorbing at 1755 cm^{-1}.

Scheme 1



When the semiglassy sample of **B** is flash-photolyzed at a still higher temperature, 143 K, only two bands in the CO-bridging region, namely 1730 and 1714 cm^{-1}, are seen (Figure 5). At this temperature, the other three CO-loss species have already disappeared in this time domain. The two observed bands decay monotonically in about 20 min to re-form the starting compound. The first-order rate constants at 143 K for the 1730 and 1714 cm^{-1} band decays are 2.6×10^{-3} and 1.8×10^{-3} s^{-1}, respectively.

No CO-loss product is detected following flash photolysis of **B** at 200 K. In this time domain (i.e., 30 s), all the photochemical intermediates have disappeared. However, since the solvent is no longer a rigid glass at this temperature, and the radical species resulting from metal−metal bond rupture can easily escape the solvent cage, radical cross-recombination products, the respective homonuclear dimers $[Co(CO)_3P(n\text{-}Bu)_3]_2$ and $[CpMo(CO)_3]_2$, are seen. The same results are obtained when the flash photolysis is carried out at higher temperatures up to room temperature.

(ii) Flash Photolysis under 1 atm of Added CO at Different Temperatures. Under added CO, only three bridging-CO bands at 1818, 1755, and 1730 cm^{-1} are observed following flash photolysis of **B** at 94 K (Figure 6). All three bands begin to decay immediately after the flashes, even at constant temperature. The absorption at 1803 cm^{-1}, one of the two closely related bands at 1818 and 1803 cm^{-1}, as shown previously under argon atmosphere, is not seen in this case, suggesting that the two bands at 1818 and 1803 cm^{-1} are due to two different species, rather than to two bridging CO's in one species. The fact that the two bands at 1818 and 1803 cm^{-1} decay at similar rates under an argon atmosphere and at different rates in the presence of excess CO suggests that the rate-determining step is CO diffusion in the former case and different reactivities of the two bridging species with CO in the latter case. The three CO-loss products disappear over a period of 60 min, recombining with CO to re-form the starting compound without forming any other intermediates. More than 99% of the initial bleaching due to the consumption of starting compound in photolysis is recovered.

When flash photolysis is carried out at 113 K under CO, two CO-bridging bands, at 1730 and 1714 cm^{-1}, are observed, with similar intensities, without the presence of other bands that were observed at lower temperatures. The two bands decay over about 30 min at slightly different rates to re-form the starting material.

All of these observations taken together make it clear that the six CO stretching absorptions described above arise from five different CO-bridging species. They react with CO at different rates and can be assigned as follows: 1818 cm^{-1} (**3**), 1803 cm^{-1} (**4**), 1755 cm^{-1} (**5**), 1860, 1730 cm^{-1} (**6**), and 1714 cm^{-1} (**7**). These and other bands for each species in the terminal region are listed in Table 1.

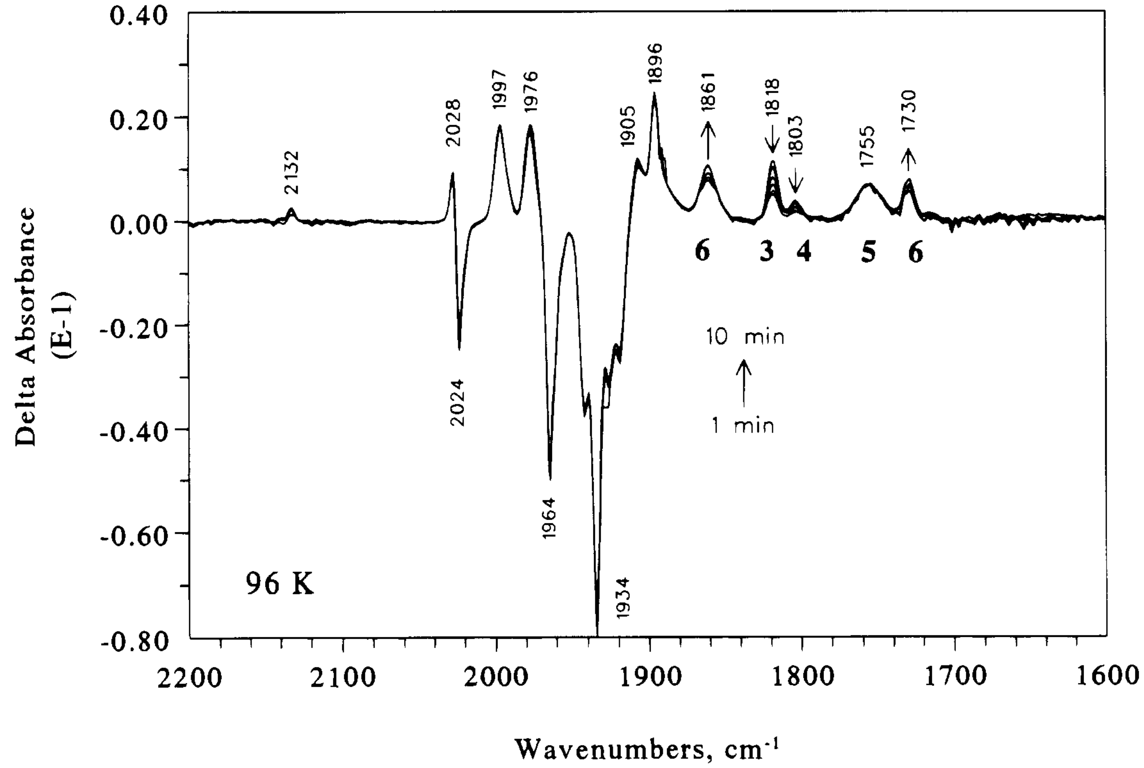


Figure 3. Difference IR spectra of $CpMo(CO)_3-Co(CO)_3(P(n\text{-}Bu)_3)$ (**B**) in rigid 3MP glass under argon before and after 10 flash irradiations at 96 K collected at different times between 1 and 10 min after flash. Up and down arrows indicate increases and decreases in peak intensities.

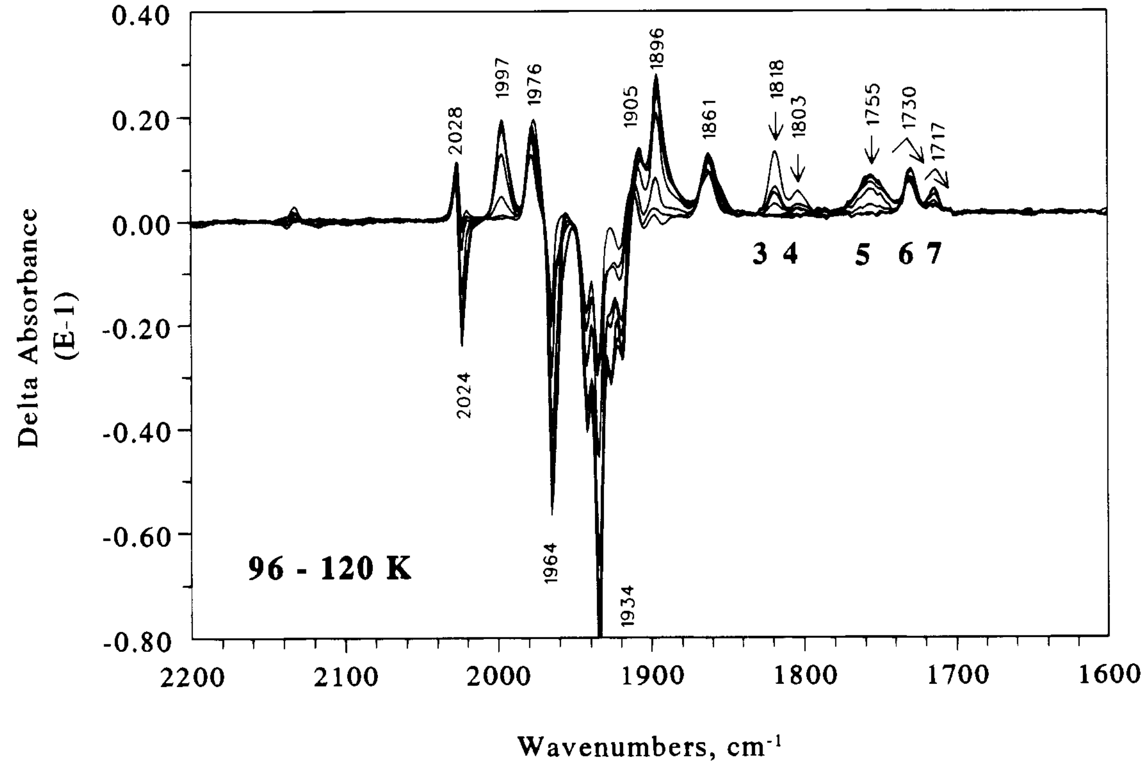


Figure 4. Difference IR spectra of **B** at different temperatures when the glass is photolyzed at 96 K and subsequently warmed to 120 K.

(iii) Flash Photolysis with Added ^{13}CO at Different Temperatures. Flash photolysis of **B** under 1 atm of added ^{13}CO at 96 K produces three CO-bridging intermediates, just as described above under ordinary CO. In addition, new bands at 2015, 1959, and 1911 cm^{-1} are observed in the terminal-CO region. These bands grow in as the three bridging-CO bands decay (Figure 7). We assign this new product as the ^{13}CO-substituted compound **D**. Because the concentration of added ^{13}CO present in the solvent glass cage is much higher than that of the expelled CO, nearly all the CO-loss intermediates recombine with ^{13}CO to form product **D**. The CO stretching IR bands of **D** at 96 K are at 2018 (s), 1959 (s), 1938 (vs), 1932 (s, sh), 1916 (vs), and 1889 cm^{-1} (w, sh). As shown in Figure 7, the bleaching due to loss of starting material is not recovered following photolysis, because **D** rather than **B** is formed. The positive peak at 2132 cm^{-1} is due to the expelled CO, and the negative peak at 2086 cm^{-1} is due to consumption of ^{13}CO. Note also that as the bridging-CO intermediates decay,

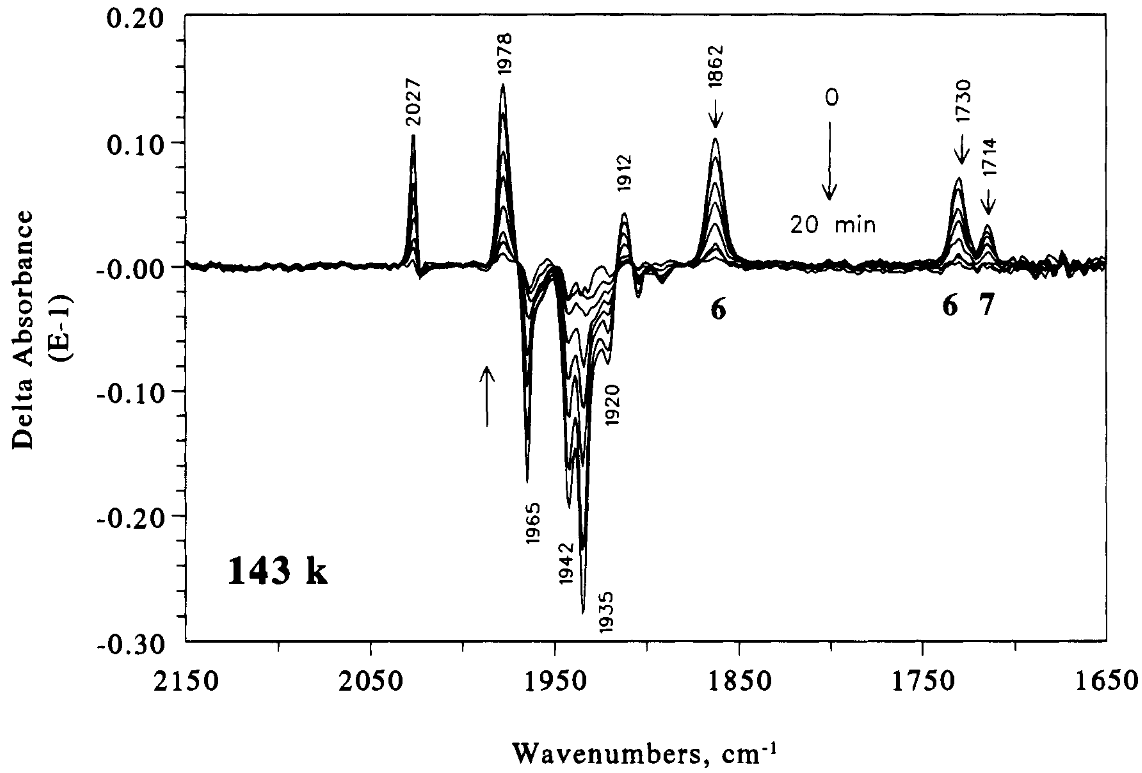


Figure 5. Difference IR spectra of **B** in 3MP under argon before and after three flash irradiations at 143 K collected at different times between 30 s and 20 min after flash.

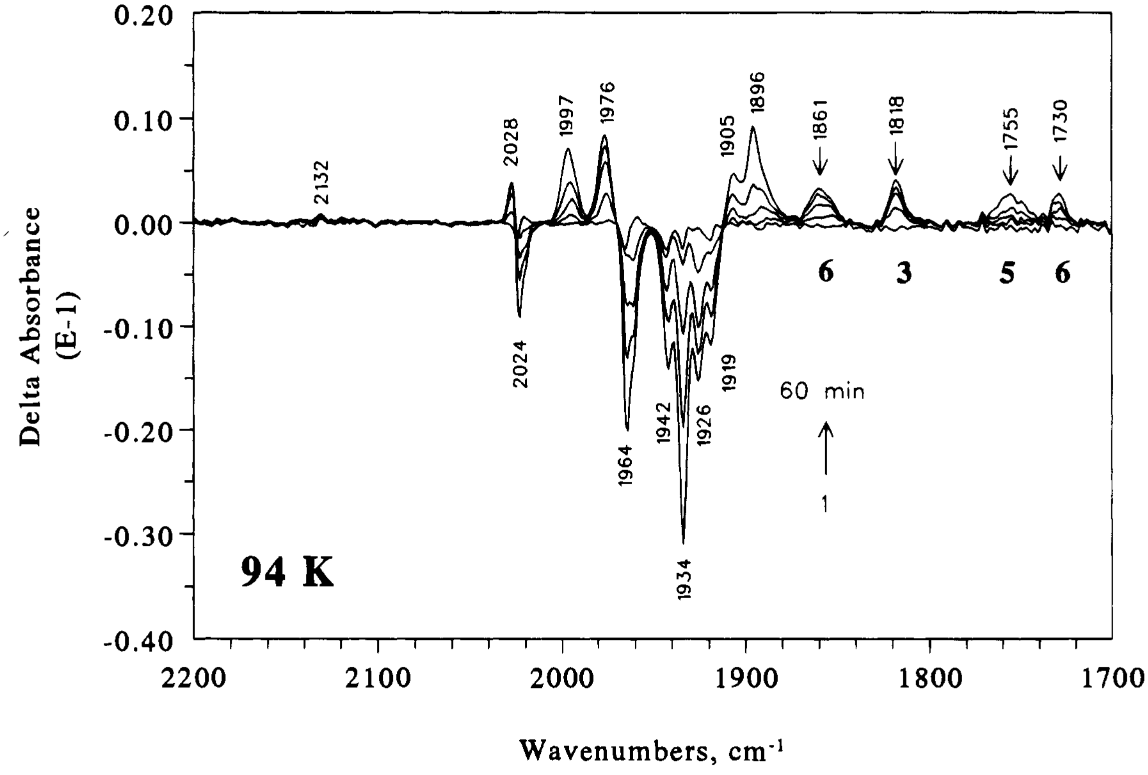


Figure 6. Difference IR spectra of **B** in 3MP under 1 atm of CO before and after five flash irradiations at 94 K collected at different times between 1 and 60 min after flash.

the negative intensity of the 2086 cm^{-1} peak increases, indicating that more ^{13}CO is consumed.

In addition to the homonuclear dimers, $[CpMo(CO)_3]_2$ and $[Co(CO)_3P(n\text{-}Bu)_3]_2$, the above mentioned ^{13}CO-substituted product **D** is also formed when the flash irradiation is carried out at room temperature under ^{13}CO. IR bands of **D** at room temperature occur at 2019, 1963, 1937, 1923, 1907, 1893, and 1881 cm^{-1}.

(iv) Flash Photolysis with Excess of $P(n\text{-}Bu)_3$ under Argon Atmosphere. Flash photolysis of **B** with 10 mM $P(n\text{-}Bu)_3$ at 94 K does not produce as large positive and negative absorbance changes as in the absence of $P(n\text{-}Bu)_3$ for the same numbers of flashes employed. A possible reason is absorption of UV radiation by the phosphine, which reduces the number of photons absorbed by the carbonyl molecules. Nevertheless, the intermediates initially formed are the same as when no phos-

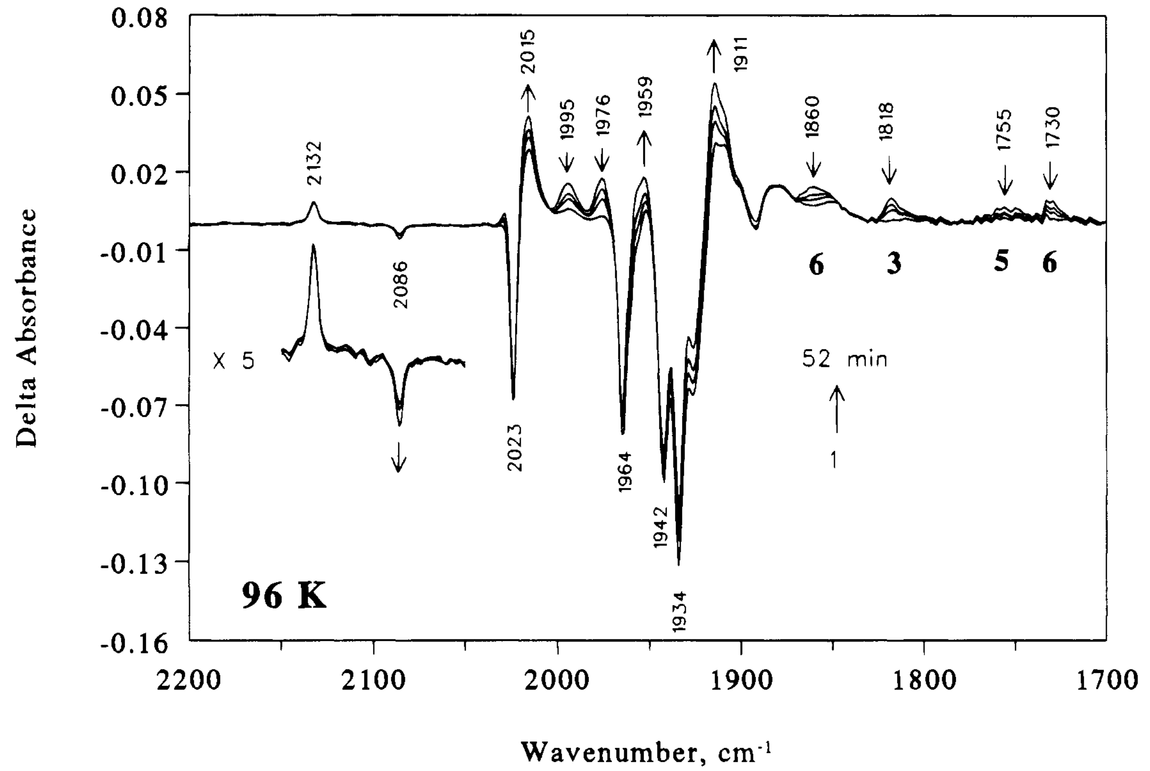


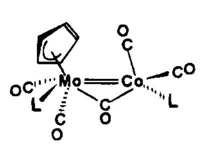
Figure 7. Difference IR spectra of **B** in 3MP under ^{13}CO before and after 12 flash irradiations at 96 K collected at different times between 1 and 52 min after flash. $\nu(^{13}CO) = 2086\ cm^{-1}$.

phine is present. After about 60 min at this temperature, the expelled CO recombines with the intermediates, re-forming the starting material. No other detectable quantities of products are formed, which indicates that the phosphine does not migrate in the glass at 94 K to react with the CO-loss intermediates. However, when the mixture is allowed to warm slowly after irradiation, up to room temperature, a new product is formed, with a concomitant loss of **B**. The CO stretching IR bands of this new product occur at 1992, 1913, 1898 (sh), and 1843 cm^{-1} at 25 °C. Another band at 1925 cm^{-1}, obscured in the difference spectrum, is revealed after correcting for the negative bands due the loss of **B**. The IR absorptions of this product precisely match those of a known disubstituted compound **C**, CpMo(CO)$_2$-(P(n-Bu)$_3$)−Co(CO)$_3$(P(n-Bu)$_3$), previously synthesized and characterized.[8] When a solution of **B** with 10 mM P(n-Bu)$_3$ is photolyzed (one flash) at room temperature, **C** is formed as the major product along with small amounts of [Co(CO)$_3$P(n-Bu)$_3$]$_2$ and much smaller amounts of [CpMo(CO)$_3$]$_2$. Therefore, at either 94 or 298 K, a CO on Mo is replaced by a P(n-Bu)$_3$ upon flash photolysis of **B**. Whether or not the replaced CO is originally bound to Mo is not absolutely clear at this stage, but additional experimental evidence suggests that this is the case.

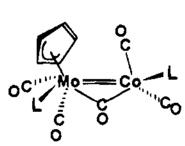
Following photolysis at a slightly higher temperature (96 K) and lower concentration of P(n-Bu)$_3$ (1.0 mM), we observe two new bands, due to species **8** and **9**, at 1740 and 1721 cm^{-1}, that grow in at the same rate as the 1818 cm^{-1} (**3**) and 1803 cm^{-1} (**4**) bands decay (Figure 8). The other two species, **5** (1756 cm^{-1}) and **6** (1861 and 1730 cm^{-1}), are persistent for up to 40 min at this temperature.

The conversion of **3** and **4** to **8** and **9** is more clearly shown in Figure 9, in which the flash photolysis is carried out at 113 K. Species **6** disappears over about 10 min, as shown by decay of one of its terminal CO bands at 1861 cm^{-1}. At the same time, the band at 1729 cm^{-1} actually increases in intensity. In this interval the absorbance at 1730 cm^{-1} due to the bridging-CO band of **6** has disappeared. The new band at 1729 cm^{-1} is assigned to another species **10**, which in turn may be a product derived from **5** (1755 cm^{-1}), because it grows in as **5** decays.

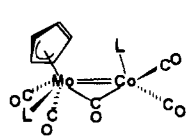
The two new features seen at 1740 and 1721 cm^{-1}, assigned to **8** and **9**, may arise from a double-CO-bridging structure, since the two absorptions decay at similar rates. However, it is also possible that the two bands belong to two different symmetrically bridging isomers derived directly from **3** and **4** when they react with a P(n-Bu)$_3$ ligand. Because **8**−**10** are seen only when P(n-Bu)$_3$ is present, they can be assigned as the products of P(n-Bu)$_3$ addition to CO-loss intermediates, **3**−**5**. The phosphine-substituted products are presumably saturated molecules, yet they contain a bridging CO group. The likely structures involve a phosphine-induced η^5 to η^3 ring slippage:[12-14]



8



9



10

When the flash photolysis is carried out at 143 K, species **3**, **4**, and **6** have already disappeared by the time the first spectrum is collected (Figure 10). Species **8** and **9** disappear over a 10 min period, while about half of **5** and **10** are still present after 30 min. As the CO-loss intermediates decay in the presence of excess P(n-Bu)$_3$, compound **C** is formed, as shown by the appearance of a band at 1843 cm^{-1}, as well as bands in the terminal-CO stretch region. **C** is the only product present in the solution upon warming to room temperature.

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(12) (a) Casey, C. P.; Widenhoefer, R. A.; O'Connor, J. M. *J. Organomet. Chem.* **1992**, *428*, 99. (b) Jones, W. D.; Kuykendall, V. L.; Selmeczy, A. D. *Organometallics* **1991**, *10*, 1577. (c) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.

(13) Basolo, F. *New. J. Chem.* **1994**, *18*, 19.

(14) Bang, H.; Lynch, T. J.; Basolo, F. *Organometallics* **1992**, *11*, 40.

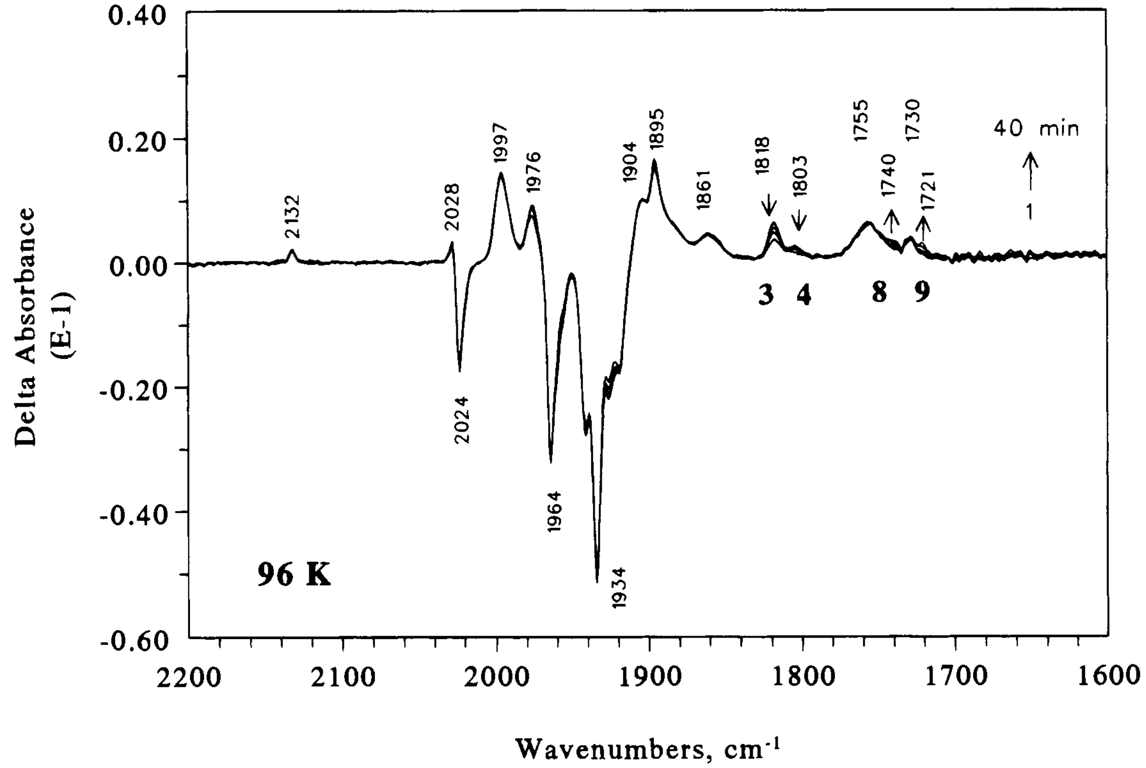


Figure 8. Difference IR spectra of **B** and 1.0 mM P(n-Bu)$_3$ in 3MP under argon before and after eight flash irradiations at 96 K collected at different times between 1 and 40 min after flash.

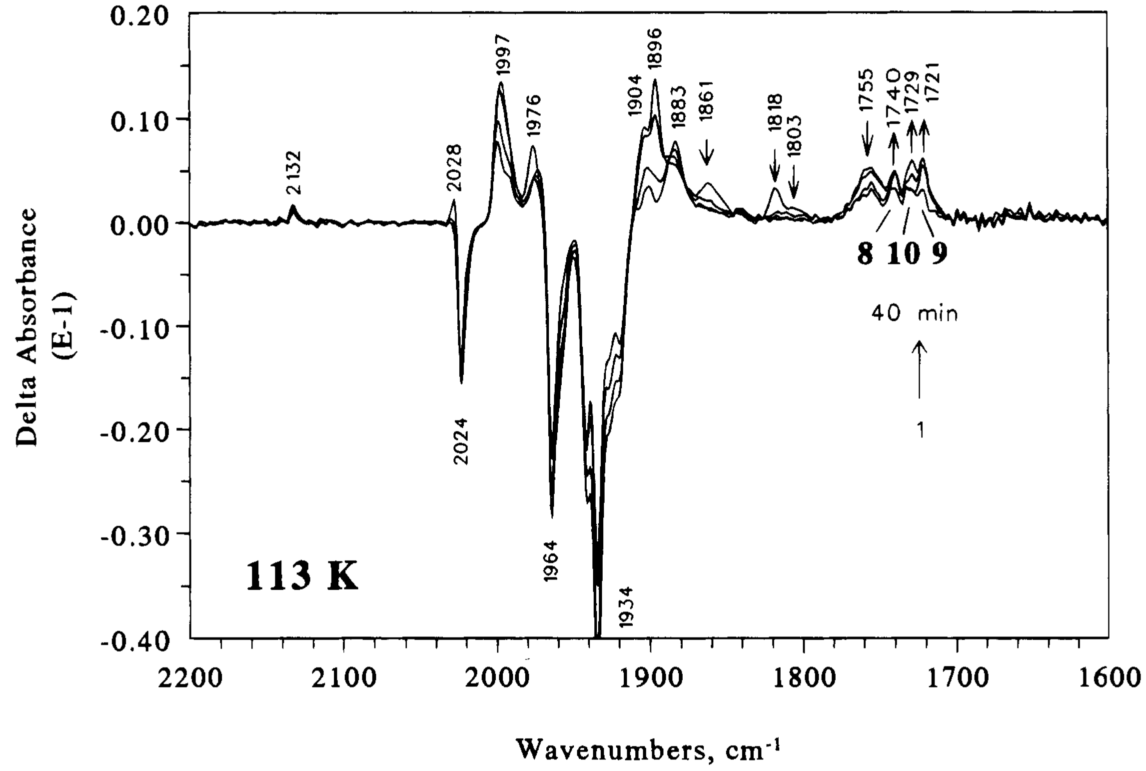


Figure 9. Difference IR spectra as in Figure 8, except photolysis is at 113 K.

3. Photochemistry of CpMo(CO)$_2$(P(n-Bu)$_3$)−Co(CO)$_3$(P(n-Bu)$_3$), C. Many more flashes are required to generate significant absorbance change upon irradiation of CpMo(CO)$_2$(P(n-Bu)$_3$)−Co(CO)$_3$(P(n-Bu)$_3$) (**C**), as compared with compounds **A** and **B** described above. Figure 11 shows the difference IR spectra after 20, 40, and 60 flash irradiations at 96 K. Interestingly, species **3**−**6**, intermediates formed in the photolysis of **B**, are also formed in this case, as indicated by IR bands at 1816, 1802, 1751, and 1730 cm^{-1}, respectively. The fact that we observe the same four original intermediates from two different compounds provides us a clear picture as to the photochemical processes involved. To form the same intermediate, CpMo*(CO)$_2$−Co(CO)$_3$(P(n-Bu)$_3$), in which Mo* denotes a vacancy on Mo created by the loss of a ligand, requires a CO loss from Mo in CpMo(CO)$_3$−Co(CO)$_3$(P(n-Bu)$_3$) (**B**) and P(n-Bu)$_3$ loss from Mo in CpMo(CO)$_2$(P(n-Bu)$_3$)−Co(CO)$_3$(P(n-Bu)$_3$) (**C**).

A very low-intensity positive band at 1682 cm^{-1}, assigned

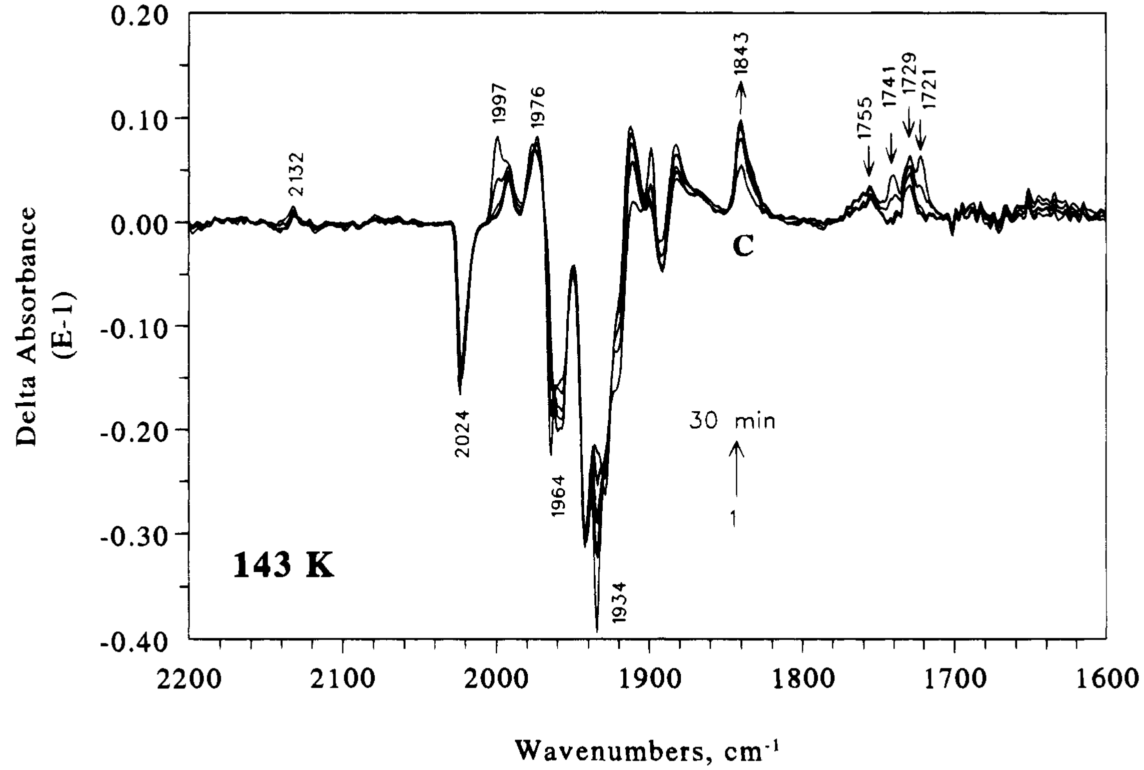


Figure 10. Difference IR spectra as in Figure 8, except photolysis is at 143 K.

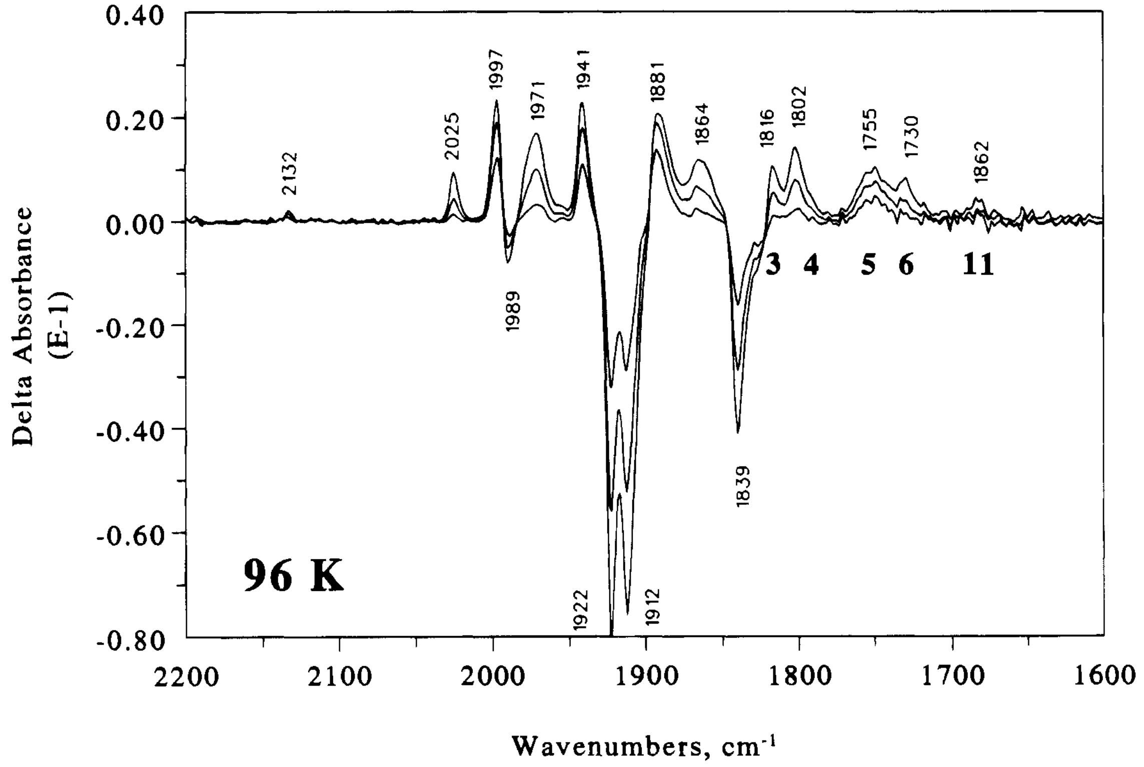
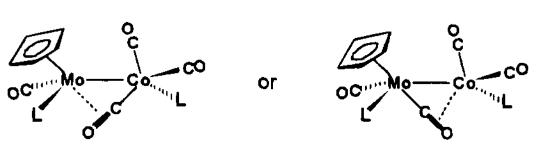


Figure 11. Difference IR spectra of $CpMo(CO)_2(P(n\text{-}Bu)_3)-Co(CO)_3(P(n\text{-}Bu)_3)$ (**C**) in 3MP under argon before and after 20, 40, and 60 flash irradiations at 96 K. Each spectrum is collected 30 s after flash.

to **11**, following photolysis of **C** is seen in the difference spectra.

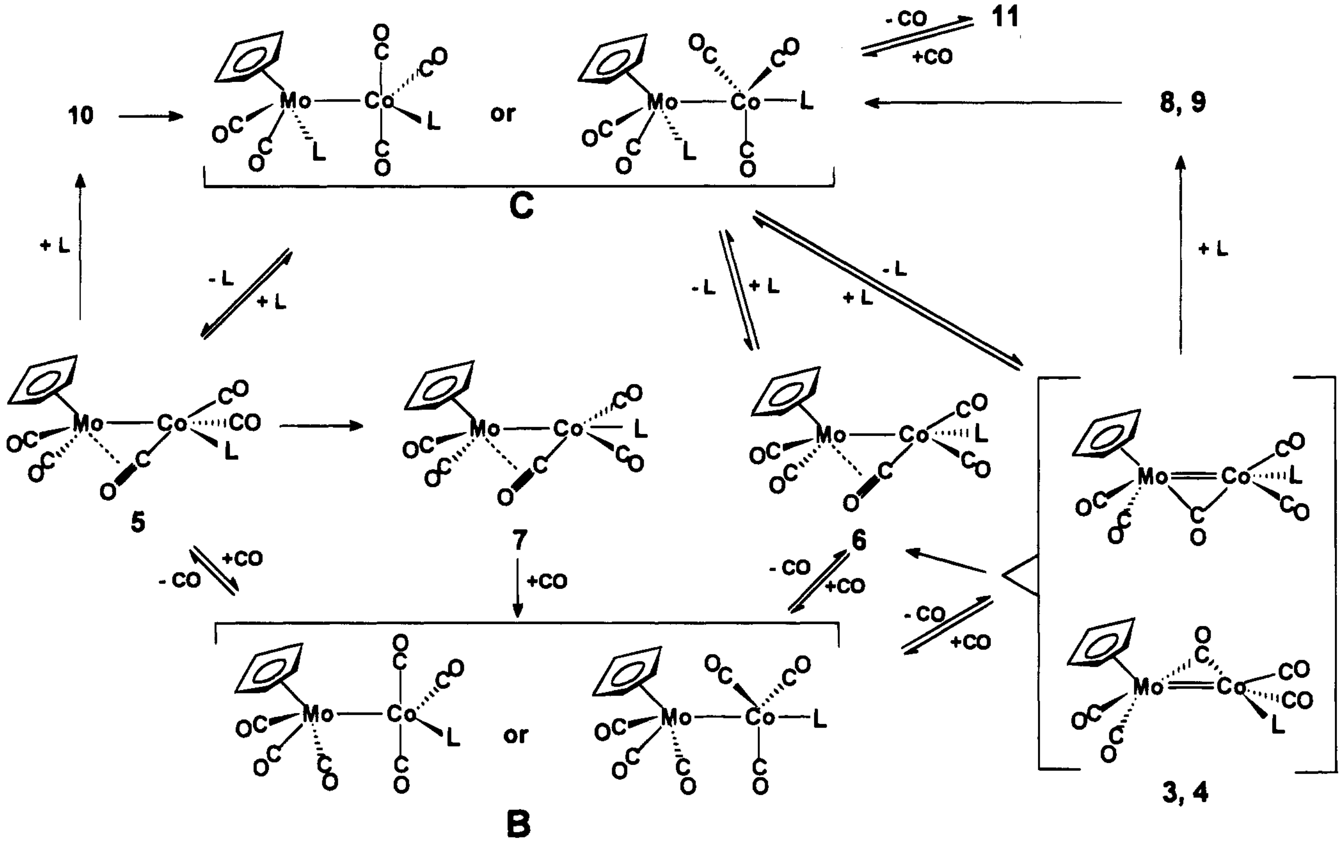


11

11 is most likely a CO-loss product containing a semibridging CO; it absorbs at a comparatively low frequency, which implies that neither of the two electron-donating phosphine ligands is lost. Yet the origin of the expelled CO is by no means clear in this case. A small band at 2132 cm^{-1} indicates that a small amount of free CO is indeed generated in the solvent glass.

When the above glass slowly warms from 96 to 112 K following irradiation of **C**, **3**–**6** decay, with partial recovery of **C** and increases in absorbances due to **8**–**10**. At 245 K, all the CO-bridging intermediates, including **11**, finally disappear. The negative absorbance due to the bleaching of **C** is partially

Scheme 2

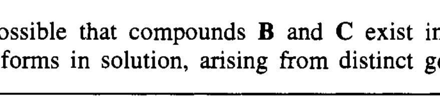


[a] L = P(n-Bu)$_3$.

recovered, with the appearance of positive absorption bands in the terminal-CO region due to **B**. The fact that **C** is partially recovered indicates that, as the temperature is slowly raised, some of the intermediates react with P(n-Bu)$_3$, re-forming **C** in competition with the reaction with CO, forming **B**. Small amounts of CO are present as a result of the formation of **11**. As discussed above, features at 1741 and 1722 cm^{-1} due to intermediates **8** and **9** are observed between 105 and 112 K as the result of the reactions of **3** and **4** with P(n-Bu)$_3$ present in their vicinity. The final net product at 245 K and up to room temperature is compound **B**, as indicated by the three of its strongest IR bands at 2024, 1966, and 1937 cm^{-1}. A weak band at 1868 cm^{-1} indicates the presence of an additional unidentified product.

Flash photolysis of **C** at higher temperatures (i.e., at 178, 189, and 245 K) results in formation of **B**, without the detection of any intermediates.

Scheme 2 outlines the possible intermediates and processes involved in the photochemistry of **B** and **C** in the presence of Ar, CO, ^{13}CO, and P(n-Bu)$_3$, respectively. It has been shown that there are three isomers of Co$_2$(CO)$_8$ in solution.[15] Two of them are nonbridged structures having D_{3d} and D_{2d} symmetries, respectively:



It is possible that compounds **B** and **C** exist in different isomeric forms in solution, arising from distinct geometrical locations of P(n-Bu)$_3$ on Co. Two likely isomers, analogous to those seen in Co$_2$(CO)$_6$L$_2$ compounds, are shown in Scheme 2, assuming a constant Mo moiety. However, we have no evidence for the existence of more than one isomer of either **B** or **C**, on the basis of the number of CO bands in the IR spectra.

In Scheme 2, geometrical isomer intermediates **3** and **4** are formed with loss of a CO from Mo in **B**. These two are the two most unstable intermediates, and they rearrange to form a more stable semibridging species, **6**. As seen in the difference spectra, a fraction of **6** may also be formed directly from the CO-loss precursor as well as from **3** and **4**. Also seen at low temperature is **5**, which converts, upon warming, to a more stable species **7**. Under argon or added CO, all the CO-loss intermediates recombine with CO to re-form **B**. In the presence of excess P(n-Bu)$_3$, species **8**–**10** are formed when the photolyzed sample is warmed from 96 K or when the photolysis is carried out at 113 K and above.

As shown in Figure 11, the same four primary intermediates, **3**–**6**, in the photolysis of **B** are also seen in the photolysis of **C**. In addition, intermediates **8**–**10** are also seen upon warming the glass. As shown in Scheme 2, these intermediates are formed as the result of P(n-Bu)$_3$ loss from Mo. Because there is P(n-Bu)$_3$ as well as a small amount of free CO in the solution after photolysis, the intermediates can recombine with P(n-Bu)$_3$ or CO to form **8**–**10** followed by re-forming **C** or to form small amounts of **B**.

4. Thermal Reaction of CpMo(CO)$_2$(P(n-Bu)$_3$)–Co(CO)$_3$(P(n-Bu)$_3$) with CO or ^{13}CO. We have shown that the P(n-Bu)$_3$ ligand on Mo in CpMo(CO)$_2$(P(n-Bu)$_3$)–Co(CO)$_3$(P(n-Bu)$_3$) (**C**) is photochemically labile toward substitution by CO. A similar substitution reaction is also observed under thermal conditions. Admittance of CO (1 atm) to a 3MP solution of **C** at room temperature in the dark results in slow formation of **B**

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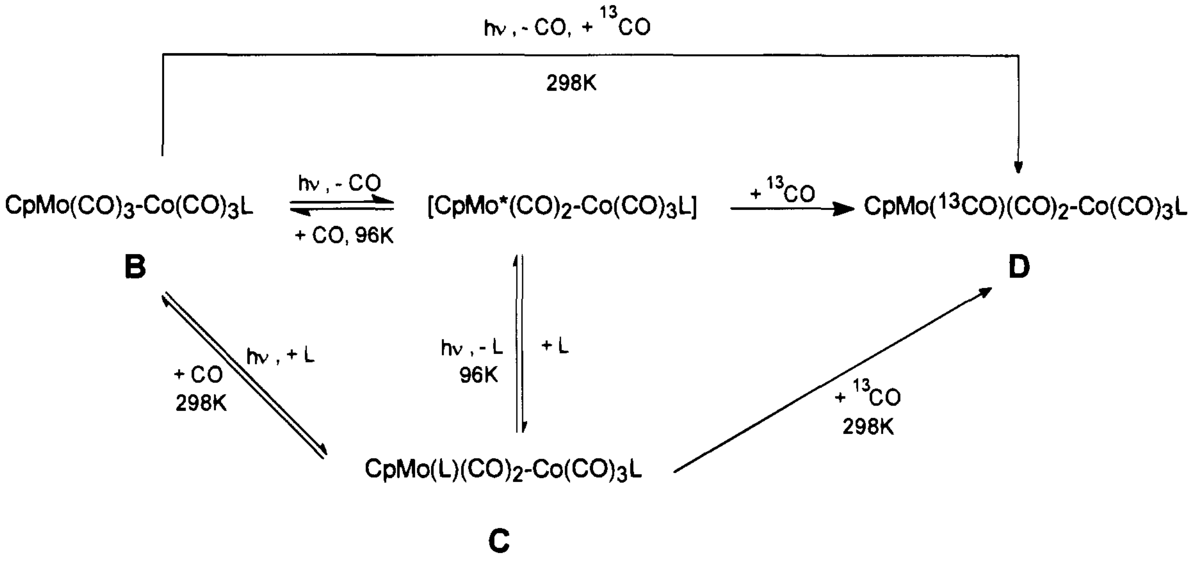
[15] (a) Bor. G.; Noack, K. *J. Organomet. Chem.* **1974**, *64*, 367. (b) Bor, G.; Dietler, U. K.; Noack, K. *J. Chem. Soc., Chem. Commun.* **1976**, 914. (c) Onaka, S.; Shriver, D. F. *Inorg. Chem.* **1976**, *15*, 915. (d) Lichtenberger, D. L.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 1381.

Scheme 3



* precursor with a vacant coordination site on Mo due to CO or L loss.

[a] L = P(n-Bu)$_3$.

via replacement of P(n-Bu)$_3$ by CO on Mo. The substitution reaction is rather slow; only about 15% of **C** has reacted with CO after about 20 h at 23 °C. The thermal reaction of **B** with P(n-Bu)$_3$, in which a P(n-Bu)$_3$ ligand replaces a CO on Mo to form **C**, does occur. However the rate is at least 10 times slower than that for the reaction of **C** with CO.

If ^{13}CO instead of ordinary CO is admitted to the solution of **C** under the same thermal conditions, a similar substitution reaction should occur, in which a ^{13}CO replaces the labile P(n-Bu)$_3$ on Mo in **C**, forming CpMo(^{13}CO)(CO)$_2$−Co(CO)$_3$(P(n-Bu)$_3$) (**D**). Although we have made no attempt to isolate and characterize this product, the IR spectrum with absorptions at 2019, 1962, 1937, 1923, and 1907 cm^{-1} closely resembles the spectrum of **B** (absorptions at 2024, 1966, 1937, 1923, and 1909 cm^{-1}), as one would expect. As we have described earlier, **D** is also formed under photochemical conditions in which the flash photolysis of **B** is carried out either at room temperature or at low temperature with excess of added ^{13}CO.

Scheme 3 summarizes the chemistry of **B**−**D** and shows how one compound can be converted to another. For example, **C** can be obtained via photolysis of **B** in the presence of P(n-Bu)$_3$ at either low temperature or room temperature, while **B** can be obtained from thermal or photochemical reactions of **C** with excess of CO. All these results are consistent with a CO or phosphine loss from Mo in **B** or **C**, respectively. Further evidence is obtained from the ^{13}CO experiments. The ^{13}CO-enriched species **D** is formed as an analog of **B** in which a ^{13}CO replaces the P(n-Bu)$_3$ on the Mo of **C**. Since photolysis of **B** leads to the ejection of a CO from Mo, product **D** is expected to form if the photolysis is carried out in the presence of added ^{13}CO. Scheme 3 shows that photolysis of **B** with added ^{13}CO at both low temperature and room temperature results in formation of product **D**.

The ring-slippage mechanism (η^5−η^3−η^5) is recognized as an important pathway for certain organometallic reactions.[12−14] We propose structures for the intermediates, **8**−**10**, in which the Cp ring is coordinated in an η^3 fashion to Mo. These intermediates, formed in the reaction of phosphine and CO-loss species, may represent another example of so-called η^5−η^3 ring-slippage intermediates. Similar intermediates are observed in the photochemistry of Cp$_2$Fe$_2$(CO)$_4$.[16]

We have shown that the presence of a phosphine on Co, as in compound **B**, leads to a complex assortment of intermediates upon CO loss. The presence of the phosphine on Co may affect the photochemical behavior in three ways: (1) different isomeric forms may arise due to geometrically distinct locations of the phosphine in the CO-loss intermediates; (2) an increase of steric crowding may favor the formation of semibridge carbonyls; and (3) a phosphine-induced change in the relative electron densities on the two metal centers may affect the relative stabilities of different kinds of bridging-CO structures. Four kinds of bridging-CO groups, symmetric bridging, linear semibridging, bent semibridging, and prone semibridging, have been proposed.[17,18] Simpson and Hall[17c] performed ab initio calculations on M−M closed-shell electronic configurations for M$_2$(CO)$_2$ (M = Sc and Mn) model systems and concluded that linear semibridging carbonyls are a consequence of steric crowding. It is also known that some coordinatively saturated metal carbonyl systems favor the CO-bridged structures while others exist only in nonbridged forms. For example, most polynuclear Fe carbonyl compounds, which tend to be electron-rich, exist in bridging forms.[19] We have shown here that photodissociation of CO from the unsubstituted compound **A** leads to a symmetric bridging species (**2**), while two symmetric bridging species (**3** and **4**) and three linear semibridging species (**5**−**7**) are observed among the CO-loss products of the substituted compound **B**. In the latter case, geometric isomers in both the symmetric and linear semibridging-CO groups can be accounted for in terms of stereochemically distinct locations of the phosphine, and formation of more stable linear semibridging species can be explained in terms of increasing steric and electronic effects.

In symmetrically substituted homodinuclear carbonyls, substitution of electron donors on both metal centers does not induce

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(16) Zhang, S.; Brown, T. L. *J. Am. Chem. Soc.* **1993**, *115*, 1779.

(17) (a) Crabtree, R. H.; Lavin, M. *Inorg. Chem.* **1986**, *25*, 805. (b) Shinn, N. D.; Trenary, M.; McClellan, M. R.; McFeely, F. R. *J. Chem. Phys.* **1981**, *75*, 3142. (c) Simpson, C. Q., II; Hall, M. B. *J. Am. Chem. Soc.* **1992**, *114*, 1641.

(18) Klinger, R. J.; Butler, W. M.; Curtis, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5034.

(19) Colton, R.; McCormick, M. J. *Coord. Chem. Rev.* **1980**, *31*, 1.

significant changes in the relative electron densities of the two metal centers. Thus, the electronic effect of phosphine substitution is expected to have a minimal influence on the stabilities of semibridging forms. For example, in the series $Mn_2(CO)_9$*, $Mn_2(CO)_7L_2$*, $Mn_2(CO)_5(\mu\text{-L-L})_2$* (where * denotes the presence of a linear semibridge), the increased stability of the semibridging form with increasing degree of phosphine substitution can be ascribed entirely to increasing steric stabilization.[6a] On the other hand, in a monosubstituted heterodinuclear compound, greater changes in relative electron densities of the two metal centers are expected upon phosphine substitution. In compound **B,** in which one CO is replaced by a $P(n\text{-Bu})_3$ on Co, the increase in electron density is expected to be greater on Co than on Mo, since the molecule is not a fully delocalized system, although there may be significant coupling between the two metal centers. In the photolysis of **B**, CO is expelled from Mo, which creates an electron-deficient Mo center. The more electron-rich substituted Co center may be able to donate more electron density to the Mo center by forming a semibridge (formally, 2e as compared to 1e for the symmetrically bridging CO), thus more effectively equilibrating electron density inside the molecule. However, we do not know the relative importance of steric and electronic effects on the stabilities of CO-bridging intermediates.

Acknowledgment. This research was supported by the National Science Foundation under Grant NSFCHE92-13531.

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