2892 *Inorganic Chemistry, Vol. 15, No. 11, 1976* Martyn Poliakoff

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A New Experimental Approach to the Identification of Rearrangement Modes in Fluxional Square-Pyramidal Molecules. Photolysis of Matrix-Isolated *trans*-(^{13}CO)W(CO)$_4$CS

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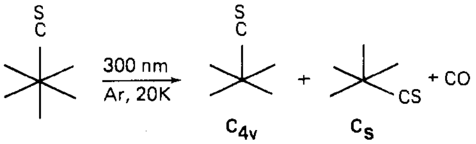
Received March 22, 1976 AIC60220V

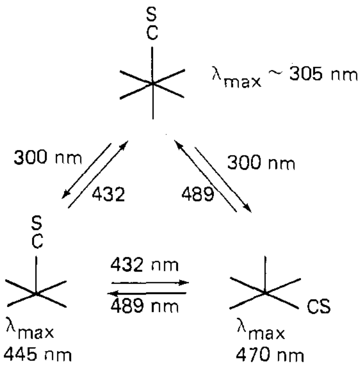
It is shown that the photolysis of W(CO)$_5$ CS proceeds in two stages: loss of CO, followed by an excited-state rearrangement of the photoproduct, W(CO)$_4$CS. Uv photolysis ($\lambda \sim 300$ nm) of sterospecifically ^{13}CO-labeled *trans*-(^{13}CO)W(CO)$_4$CS in Ar and CH$_4$ matrices at 20 K yields, as the major product, square-pyramidal *cis*-(^{13}CO)W(CO)$_3$CS, with the CS group in the axial position. The process involves not only loss of a CO group but also trans → cis rearrangement of the ^{13}CO and CS groups. Subsequent irradiation with visible light ($\lambda > 375$ nm) regenerates (^{13}CO)W(CO)$_4$CS but principally as the cis isomer. Ir band intensities suggest that the loss of an axial or equatorial CO group during uv photolysis of W(CO)$_5$CS is equally probable. Comparison of the product distributions obtained by uv photolysis of *trans*-(^{13}CO)W(CO)$_4$CS and a statistical mixture (4:1 cis:trans) of (^{13}CO)W(CO)$_4$CS shows that a rearrangement is occurring in an electronic or vibrational excited state of the product, (^{13}CO)W(CO)$_3$CS, after loss of CO from the parent molecule. Evidence is presented for an interaction between the (^{13}CO)W(CO)$_3$CS fragment and the photoejected CO molecule. The symmetry of this interaction allows the permutation cis-eexea to be eliminated as a possible rearrangement mode for the excited-state isomerization. The experiments show how matrix isolation can provide valuable insights into reaction pathways, by "freezing out" molecules which would be fluxional at higher temperatures.

Introduction

(a) Photochemistry of M(CO)$_5$CS. We have previously described the low-temperature photochemistry[1] of the thiocarbonyl complexes M(CO)$_5$CS (M = Cr or W) originally prepared by Angelici and Dombek.[2] Uv photolysis of these molecules in inert matrices produced molecular carbon monoxide and a mixture of the two isomers of square-pyramidal, SPY, M(CO)$_4$CS.

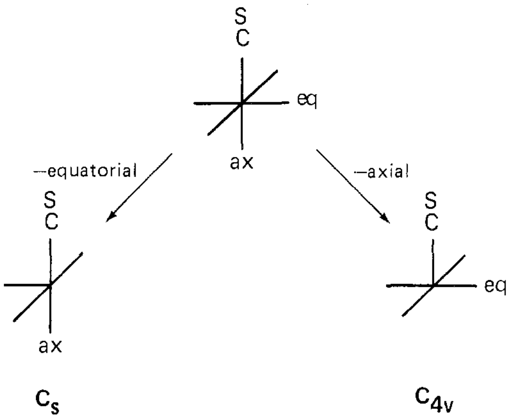


The relative amounts of the two isomers varied from one matrix to another but, in an Ar matrix, the C_{4v} isomer was in considerable excess. The two isomers are formally derived from SPY M(CO)$_5$,[3,4] by replacing either an axial or an equatorial CO group with a CS group. Their spectra and photochemical behavior are very similar to those of M(CO)$_5$,[3-5] and in many ways the CS group can be imagined to be a labeled CO group. This labeling, for example, enables the photochemical isomerization[1] of M(CO)$_4$CS to be followed. The overall photochemistry of these thiocarbonyls is summarized below, the specific photolysis wavelengths referring to the tungsten compounds in a CH$_4$ matrix.



In this paper we describe how the use of stereospecifically ^{13}CO-enriched[6] *trans*-(^{13}CO)W(CO)$_4$CS provides an insight into the mechanism of the uv photolysis of M(CO)$_5$CS. In particular we show that the formation of the two isomers of M(CO)$_4$CS involves the rearrangement of the M(CO)$_4$CS species in an excited state.

(b) Stereochemistry of Uv Photolysis. The simplest pathway for the photolysis of M(CO)$_5$CS assumes that loss of an *axial* CO group leads to the C_{4v} isomer of M(CO)$_4$CS and loss of an *equatorial* CO group produces the C_s isomer.



Since there are four equatorial CO groups and only one axial group, one would predict a product ratio C_s:C_{4v} 4:1. It has been shown,[1] however, that for Cr(CO)$_4$CS in an Ar matrix, this ratio (C_s:C_{4v}) is only 1:2 and similar results were found for W(CO)$_4$CS. To explain this excess of the C_{4v} isomer, it must be assumed that there is either (a) a preferential loss of the axial CO group, leading to formation of the C_{4v} isomer, or (b) an excited-state isomerization of the M(CO)$_4$CS fragments after ejection of CO from the M(CO)$_5$CS molecule. In principle one can distinguish between these alternative explanations by using a molecule specifically labeled with ^{13}CO in the axial position.

In order to simplify the following discussion, we shall refer to *trans*- and *cis*-(^{13}CO)W(CO)$_4$CS as *trans*-[6] and *cis*-[6]. The various isomers of W(^{12}CO)$_4$CS and (^{13}CO)W(CO)$_3$CS are shown in Figure 1 together with the nomenclature used in this paper. Those isomers with an axial CS group are named with letters (i.e., A, B) and those with an equatorial CS group with numbers (i.e., **1**, **2**, **3**, **4**).

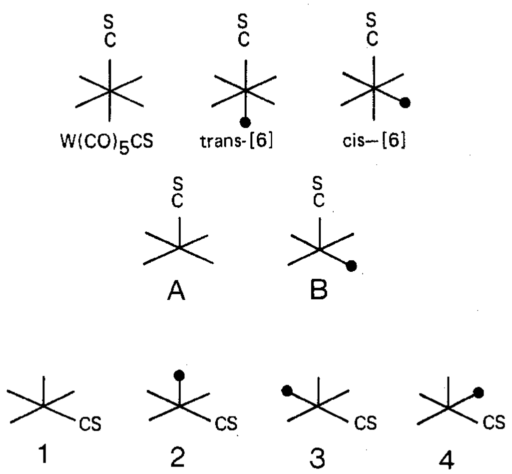
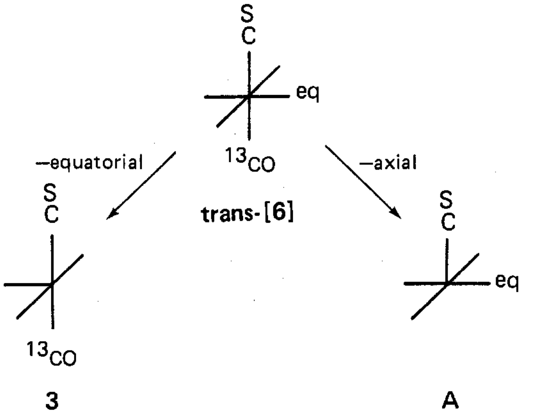


Figure 1. Structures of the different W(^{13}CO)$_x$(^{12}CO)$_y$CS species, illustrating the nomenclature used in this paper. The black circle represents ^{13}CO.

If loss of an axial CO group really does lead to the C_{4v} isomer and loss of an equatorial group to the C_s isomer, photolysis of *trans*-[6] should produce *only* **3** and A in the same ratio as that found for **1**:A in the photolysis of the unlabeled M(CO)$_5$CS (i.e., 1:2).



In particular there should be no formation of B, which should be easily distinguishable from A, since it has a ^{13}CO group and four ir-active C–O stretching modes (3 a′ + a″) while A has only two (a$_1$ + e), with the e mode coincident with the a″ mode of B. However, it should be remembered that so-called "matrix effects" can cause a single mode to give rise to several closely spaced ir bands.[1,3]

In the next section we describe experiments performed using *trans*-[6] prepared by stereospecific ^{13}CO enrichment[6] of [*trans*-(I)W(CO)$_4$CS]$^-$ in the presence of Ag$^+$ ions

$$[\textit{trans}\text{-(I)W(CO)}_4\text{CS}]^- \xrightarrow[\text{Ag}^+]{93\%\ ^{13}\text{CO}} \textit{trans}\text{-(}^{13}\text{CO)W(CO)}_4\text{CS} + \text{AgI}$$

Results

(a) Photolysis of *trans*-(^{13}CO)W(CO)$_4$CS. Figure 2a shows the C–O stretching region of the ir spectrum of the 93% (^{13}CO)W(CO)$_4$CS, after deposition in an Ar matrix at 20 K, at a dilution of 1:15 000. The group of strong bands in the center of the diagram (~1990 cm^{-1}) is due to the coincident modes of W(CO)$_5$CS (e), *trans*-[6] (e), and *cis*-[6] (a″). The two other groups of bands shown in broken lines are the split a$_1$ modes of *trans*-[6]. The weak bands, u, are the split low-frequency a$_1$ mode of W(CO)$_5$CS, and the weak bands, c, are the split lowest frequency a′ mode of *cis*-[6]. There is also a very weak band, d, assigned to the disubstituted species (^{13}CO)$_2$W(CO)$_3$CS, and another weak doublet, 6, due to a trace impurity of W(CO)$_6$. These and subsequent band assignments are justified in the Appendix given as supplementary material. The bands of *trans*-[6], broken lines, are far more intense than those of any other species, and it is clear that this specifically labeled molecule was the predominant species in the matrix.

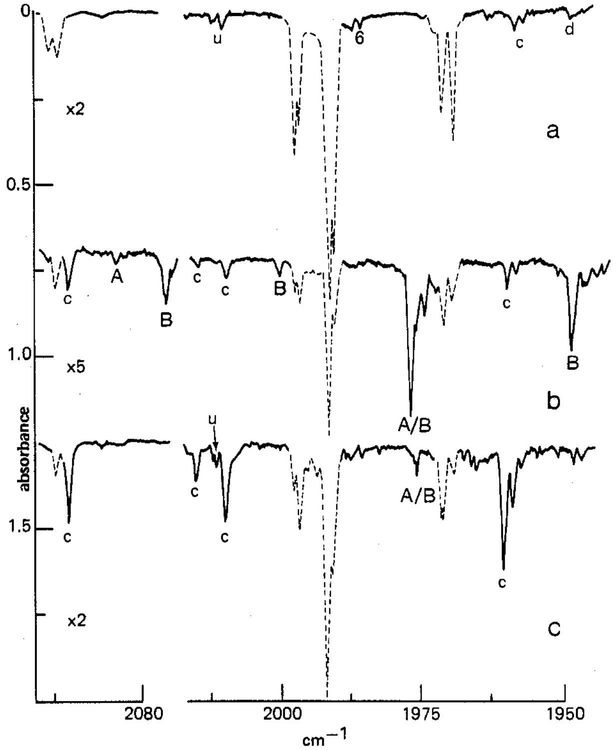


Figure 2. The C–O stretching region of the ir spectra of stereospecifically ^{13}CO-enriched W(CO)$_5$CS in an Ar matrix (1:15 000) at 20 K: (a) after deposition; (b) after 135-min photolysis (λ 302 ± 10 nm); (c) after 60-min photolysis with a tungsten lamp + λ 489 nm filter, showing the growth of bands c due to *cis*-[6]. Bands are labeled as follows: *trans*-[6], broken lines; *cis*-[6], c; C_{2v} (^{13}CO)$_2$W(CO)$_3$CS, d; W(^{12}CO)$_5$CS, u; W(CO)$_6$, 6; A and B refer to structures in Figure 1.

Uv photolysis (λ 302 ± 10 nm, 135 min) produced several changes, Figure 2b. The bands of *trans*-[6] all substantially decreased in intensity, while those of *cis*-[6] increased by only a small amount. At the same time several new bands appeared, the strongest of which were due to A and B. Comparison of the relative intensities of the two most intense bands ~1975 cm^{-1} (coincident modes of A and B) and ~1948 cm^{-1} (B) shows that there is an almost equal probability of losing the CO groups which were *originally* in the axial and equatorial positions in *trans*-[6]. Details of these intensity measurements are given in the Appendix (Table VI). B is a molecule, which, on the simplest model, should not have been produced at all by photolysis of *trans*-[6]. *Thus trans → cis isomerization of the CS and ^{13}CO groups occurs at some stage during the uv photolysis.* A more detailed analysis of the weaker bands in Figure 2b shows that, apart from the major products A and B, uv photolysis of *trans*-[6] also produced **1**–**4**. The formation of **2** and **4** provides further evidence for trans → cis isomerization.

Subsequent irradiation of the matrix with visible light (λ 489 nm, 60 min) destroyed nearly all of the products and regenerated the parent (^{13}CO)W(CO)$_4$CS. Furthermore, Figure 2c shows that it was predominantly *cis*-[6] which was regenerated. Since light of this wavelength does not isomerize *trans*-[6], the regeneration of *cis*-[6] is the consequence of the trans → cis isomerization of the ^{13}CO and CS groups during the uv photolysis. Thus the results of the experiment can be

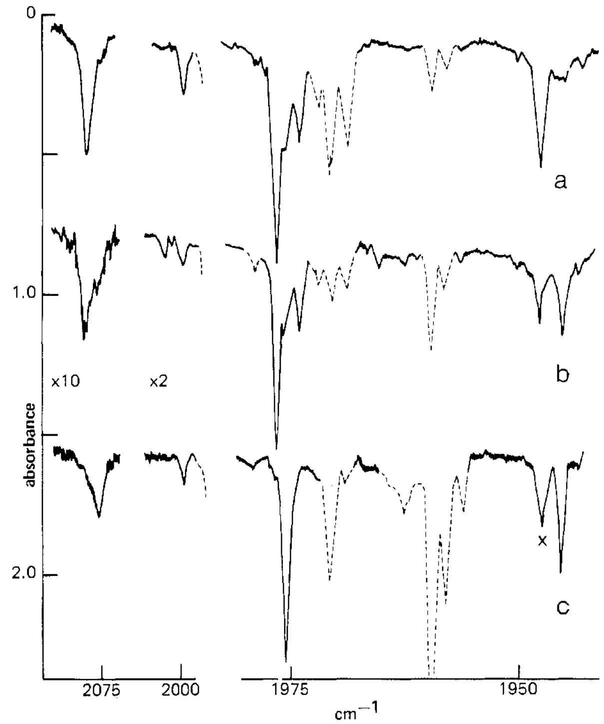
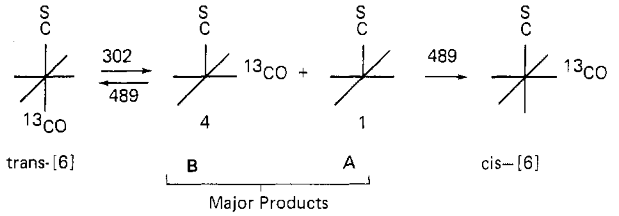


Figure 3. Illustration of the different splittings of the bands of B (solid lines) generated from *trans*-[6] and *cis*-[6] in an Ar matrix (1:5000). The bands shown in broken lines are due to species other than B: (a) 100-min photolysis (λ 302 ± 10 nm) of *trans*-[6]; (b) 105-min photolysis (λ 302 ± 10 nm) of a 4:1 mixture of *cis*-[6]/*trans*-[6], produced by thermal isomerization of *trans*-[6] in solution at 373 K; (c) "irreversible" B produced by 20-min photolysis (unfiltered Hg arc) of same matrix as in (a), followed by 5-min photolysis (Hg arc + λ >375 nm filter). The band X is due to $(^{13}CO)_2W(CO)_3CS$.

summarized as follows.



This experiment indicates that the isomerization is occurring in some excited state[7] but it does not show whether it is occurring before or after the ejection of a CO group from *trans*-[6]. Thus, using the notation [6] = $^{13}(CO)W(CO)_4CS$ and [5] = $(^{13}CO)W(CO)_3CS$, we have two possible reaction schemes

$$[6] \xrightarrow{h\nu} [6]^* \xrightarrow{\text{isomerize}} [6]^* \xrightarrow{-CO} [5]$$

$$[6] \xrightarrow{h\nu} [6]^* \xrightarrow{-CO} [5]^* \xrightarrow{\text{isomerize}} [5]$$

These two schemes are distinguishable in theory at least, since the first requires that the product distribution from photolysis of *trans*-[6] and *cis*-[6] should be essentially the same,[7] as a consequence of the trans ⇌ cis isomerization in the excited state, which does not occur in the second.

(b) Comparison of Photolysis of *trans*- and *cis*-(^{13}CO)-W(CO)$_4$CS. (1) Major Products. Figure 3a shows the ir bands (solid lines) corresponding to the four C–O stretching modes of B, the major photolysis product of *trans*-[6] in an Ar matrix. Notice that three of the bands, the a′ modes, are sharp, while the a″ mode, which is coincident with the e mode of A, is split into three closely spaced lines, ~1975 cm^{-1}, by "matrix effects".

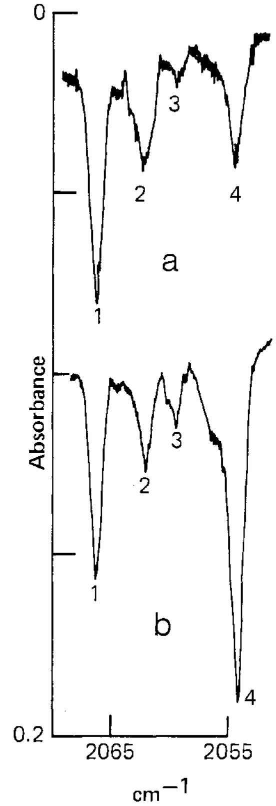


Figure 4. Illustration of different minor product distributions obtained by photolysis of *trans*-[6] and *cis*-[6] in CH$_4$ matrices (1:5000) at 20 K. The bands are assigned by numbers which refer to the structures in Figure 1. Only the highest frequency C–O stretching mode of each species is shown. Note the highly expanded ordinate scale. All uv photolysis used λ 302 ± 10 nm: (a) 45-min uv photolysis of *trans*-[6]; (b) 45-min uv photolysis of a 4:1 mixture of *cis*-[6]/*trans*-[6], produced photochemically in situ in matrix (cf. Figure 2).

When the experiment was repeated using a statistical (4:1) mixture of *cis*-[6] and *trans*-[6], produced by the thermal isomerization of a solution of *trans*-[6], the spectrum in Figure 3b was obtained. Although the group of a″ bands, ~1975 cm^{-1}, is identical with that observed on photolysis of the pure *trans*-[6], Figure 3a, the high-frequency band has developed a low-frequency shoulder and the other two bands have been split into doublets. These split bands are apparently also due to B.[10] Similar splittings of the bands of B were observed in CH$_4$ matrices. The lowest frequency a′ band was a singlet (1942.4 cm^{-1}) when generated from *trans*-[6] and a doublet (1942.4 and 1940.3 cm^{-1}) when generated from a *cis*-[6]/*trans*-[6] mixture.

It is important to realize that whatever the origin of these splittings, the spectra in Figure 3a and b show that photolysis of *trans*-[6] does not produce the same result as the photolysis of the statistical *cis*-[6]/*trans*-[6] mixture.

(2) Minor Products. Even more striking confirmation of the differences between the photolysis of *trans*-[6] and *cis*-[6] comes from the analysis of the spectra of the minor products, with equatorial CS groups. Unlike the previous sections, this section emphasizes experiments in CH$_4$ matrices, because, although qualitatively identical results were obtained in Ar matrices, the minor product bands were more intense[1] in CH$_4$. Figure 4a shows the highest frequency bands of **1**–**4**, obtained by uv photolysis (λ 302 ± 10 nm, 45 min) of *trans*-[6] in a CH$_4$ matrix. Details of the band assignment and force constant calculations are given in the Appendix. Figure 4b illustrates the same absorptions produced in a different experiment, by photolysis of a statistical (4:1) mixture of *cis*-[6] and *trans*-[6] under identical conditions. Comparison of the relative intensities of bands for **2**, **3**, and **4** in Figure 4a and b shows that the distribution of ^{13}CO among the products is substantially different in the two experiments. In particular, photolysis of *trans*-[6] produces considerably more **2** and very much less **4** than the statistical *cis*-[6]/*trans*-[6] mixture. These conclusions are supported by the relative intensities of the other C–O stretching bands of **2** and **4**.

Since photolysis of the statistical mixture must produce a statistical distribution of ^{13}CO among the photolysis products, the spectra show that photolysis of *trans*-[6] results in a nonstatistical product distribution. This means that there must be *considerable stereospecificity* in the photolysis process.

These experiments confirm that there are substantial differences between the photolysis of pure *trans*-[6] and a statistical *cis*-[6]/*trans*-[6] mixture, in the distribution of both the major and the minor products. Such differences are inconsistent with a photolysis mechanism which involves isomerization of (^{13}CO)W(CO)$_4$CS prior to the loss of CO, and it is likely that an excited-state rearrangement occurs in the five-coordinate species after the CO has been ejected from the parent carbonyl

$$[6] \xrightarrow{h\nu} [6]^* \xrightarrow{-\mathrm{CO}} [5]^* \xrightarrow{\text{isomerize}} [5]$$

Of course, the experiment provides no evidence as to whether the rearrangement is occurring in an electronic excited state or a vibrationally excited ground state. Nevertheless, although thermal rearrangements of unsaturated transition metal carbonyls (e.g., Mn(CO)$_4$Br[11]) have been reported previously, this is the first time that an excited-state rearrangement has been shown to be an integral part of a photolytic process. *Thus rearrangement is occurring between the ejection of the CO from the parent carbonyl and the arrival of the products in the vibrational ground state.* Furthermore, if the rearrangement process were occurring a large number of times before the molecules reached the nonfluxional ground state, one would expect the same product distribution from *trans*-[6] and *cis*-[6]. Different distributions were observed which means that *only a small number of consecutive rearrangements can be occurring between the ejection of CO and the attainment of the final ground state.*

Interaction with the Photoejected CO Molecule. In this section we present evidence showing that there is appreciable interaction between the carbonyl fragments and the photoejected CO molecule, which we shall term the "p-CO", and then discuss the stereochemical consequences of this interaction. Figure 5a shows the ir absorption of the p-CO produced by irradiation of *trans*-[6] in an Ar matrix at 21 K with monochromated uv light (λ 302 ± 10 nm, 60 min). There is a weak band at 2135.5 cm^{-1} and a stronger sharp band at 2137.6 cm^{-1}. This frequency is significantly lower[12] than 2138.6 cm^{-1}, the frequency reported for molecular CO, isolated in an Ar matrix.[13] At this stage, the photolysis of the *trans*-[6] is almost completely reversible. That is, irradiation of the matrix with visible light (λ >375 nm) regenerates the parent carbonyl and the p-CO absorption disappears. After prolonged uv irradiation with an unfiltered Hg arc, the photolysis is only partially reversible. The absorption of this "irreversible" p-CO at 12 K is shown in Figure 5b. The band is not only much broader than that of "reversible" p-CO, Figure 5a, but also shifted to higher frequency. Furthermore, the band becomes weaker and even broader as the matrix temperature is raised from 12 to 21 K, Figure 5c. The band becomes narrower again on recooling the matrix. Such broadening is also observed with matrix-isolated molecular CO, where it has been ascribed to restricted rotation of the CO molecule.[13] There are corresponding differences between the C–O stretching bands of the "reversible" and "irreversible" forms of B (see Figure 3).

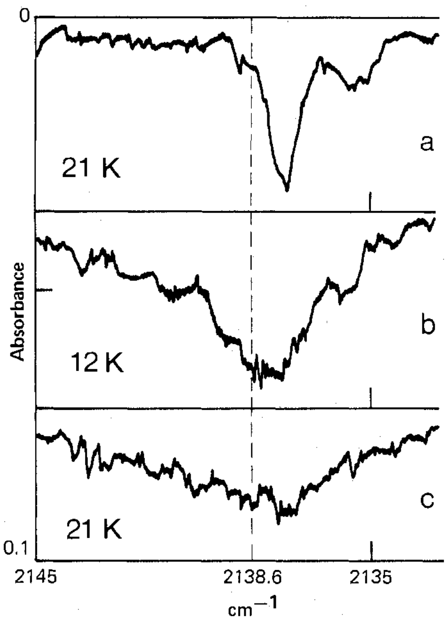
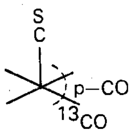
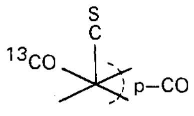


Figure 5. Ir bands of photoejected CO in an Ar matrix, showing the difference between "reversible" and "irreversible" p-CO: (a) "reversible" at 21 K p-CO produced by uv photolysis (λ 302 ± 10 nm 60 min) of *trans*-[6]; (b) irreversible p-CO at 12 K produced by 25-min further photolysis with an unfiltered Hg arc, followd by 5-min photolysis (λ >375 nm); (c) the same sample as (b) warmed to 21 K. The dotted line shows the band position of isolated molecular CO.[13]

Thus, after mild uv irradiation of *trans*-[6], the p-CO has a sharp ir band and is apparently in a well-defined site, while after prolonged irradiation, the band is broad similar to that of an isolated rotating CO molecule. This change, together with the changes in the spectrum of B, suggests that the "reversible" p-CO is interacting with B sufficiently strongly to prevent rotation of the p-CO and to shift the ir bands of both species. Prolonged uv irradiation, on the other hand, allows some of the p-CO to diffuse away from B, thus preventing interaction and photochemical reversal of the photolysis. Similar interactions with p-CO have been reported for iron tetracarbonyl[14] and chromium pentacarbonyl.[5,15] The interaction is unlikely to be occurring via the vacant sixth coordination site of B, since the behavior of the uv–visible absorption band of B indicates that this site is occupied by a matrix atom (or molecule) interacting with the tungsten atom.[1,5,15] Thus the p-CO is probably interacting unequally with the four carbonyl groups of B.

Such an asymmetrical interaction can be used to explain the strange band splittings of B (Figure 3a and b). For example, if the p-CO lay somewhere on a plane between two cis CO groups, there would be two possible positions for the ^{13}CO group in B: either close to or far from the p-CO.





If there were significant interaction between the p-CO and the adjacent bound CO groups, these two molecules would have slightly different C–O stretching frequencies. Photolysis of the statistical 4:1 cis-[6]/*trans*-[6] mixture would necessarily produce equal amounts of these two molecules, and the frequencies of the split a′ modes, illustrated in Figure 3b, can be *quantitatively* reproduced using a CO-factored force field

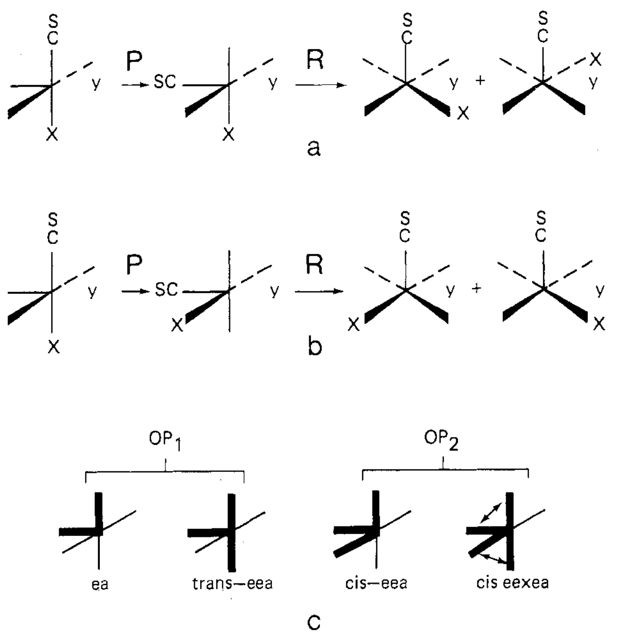
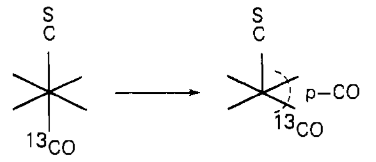


Figure 6. (a, b) Possible rearrangements of **3** to **B** illustrating the permutation, P, of the CO and CS groups, and the reorientation, R, of the fragment relative to the p-CO. X represents the ^{13}CO and Y the p-CO. For simplicity the p-CO has been drawn as if it remained fixed in the matrix. This is not necessarily so in reality. (c) The permutations included in OP_1 and OP_2 (see ref 17).

based on this model (see Appendix). The differences between the spectra in Figure 3a and b can then be explained if *photolysis of trans-[6] produces molecules of B with all* ^{13}*CO groups in the same position relative to the p-CO.*



The force constant calculations suggest that only molecules of **B** with the ^{13}CO group close to the p-CO are produced, but the precise position of the ^{13}CO relative to the p-CO is not important in the discussion which follows.

Thus, if it is accepted (1) that the p-CO is interacting asymmetrically with **B** and (2) that the ^{13}CO groups of all molecules of **B**, produced by photolysis of *trans*-[6], are in equivalent positions relative to the p-CO, then interesting conclusions can be drawn about the symmetry of the rearrangement process occurring during the photolysis of *trans*-[6].

Since **B** contains a ^{13}CO group, it must be formed by loss of an equatorial ^{12}CO group from *trans*-[6]. If the dissociative state of *trans*-[6] were pseudooctahedral,[16] then, immediately after ejection, the p-CO would be in a symmetrical position relative to the excited molecule of **3**. In particular, the p-CO would lie in the mirror plane, defined by the axial CO, the CS, and the ^{13}CO groups; see Figure 6a. (In Figure 6a the mirror plane lies in the plane of the page, and X represents ^{13}CO and Y the p-CO.)

The excited-state rearrangement of **3** to **B** can be imagined as occurring in two steps. These steps are illustrated in Figure 6a. They are (1) permutation, P, of the CO and CS groups of **3** to form **B**, without any change in the orientation of the SPY molecule, and (2) reorientation, R, of **B** relative to the p-CO. In reality this reorientation would be the combined result of the permuting mechanism and thermal motion of both the fragment and the p-CO. However, for clarity, Figure 6 has been drawn as if the p-CO remained fixed.

Table I. The Four Observable Rearrangment Processes of a C_{4v} SPY Molecule[a]

OP_0	I ≡ trans-ee
OP_1	ea(4) ≡ trans-eea(4)
OP_2	cis-eea(8) ≡ cis-eexea(8)
OP_3	cis-ee(4)

[a] Taken from ref 17. The figures in parentheses give the number of equivalent permutations.

After reorientation **B** appears to interact asymmetrically with the p-CO. This means that the p-CO is not interacting equally with a given CO group and the CO group trans to it. The permutation step will either leave the ^{13}CO group lying in the mirror plane, Figure 6a, or remove the ^{13}CO group from the plane, Figure 6b. In the latter case the ^{13}CO group is symmetry related to the ^{12}CO group trans to it by the mirror plane. The final distribution of reoriented molecules will be symmetrical with respect to this mirror plane. This means that after reorientation of these molecules, Figure 6b, there would be two possible inequivalent sites for the ^{13}CO relative to the p-CO. Only if the permutation left the ^{13}CO group on the mirror plane, Figure 6a, could the ^{13}CO groups of all reoriented molecules occupy equivalent sites relative to the p-CO. Since the ^{13}CO groups of all molecules of **B** appear to be equivalent, the permutational process occurring in the excited state of **3** must leave the ^{13}CO group lying in the mirror plane.

Musher has classified the possible permutations for a five-coordinate square-pyramidal molecule, with nonchelating ligands, in terms of four observable processes, OP, which are listed in Table I. Only OP_1 and OP_2 allow the exchange of axial and equatorial groups which is required to convert **3** into **B**. The permutations constituting OP_1 and OP_2 are illustrated in Figure 6c. Since the permutation cis-eexea would not leave the ^{13}CO group of **3** lying in the mirror plane, it can be eliminated as a possible rearrangement. Thus it follows that *the rearrangement* **3** → *B could be occurring via* OP_1 *or the cis-eea component of* OP_2.

It is interesting to note that OP_1 contains the square-pyramidal equivalent[17] of the Berry pseudorotation ($C_{4v} \rightarrow D_{3h} \rightarrow C_{4v}$), which has already been invoked to rationalize several related aspects of the matrix photochemistry of d^6 transition metal carbonyl species.[18,19]

Experimental Section

All apparatus, spectrometers and photolysis sources have been described in an earlier paper.[1] The *trans*-(^{13}CO)W(CO)$_4$CS, *trans*-[6], was a gift from Professor Angelici, and the preparation is reported elsewhere.[6] Gas-phase mixtures of *trans*-[6] and Ar (1:15 000) were found to be stable for a few hours, but if they were left overnight, in the dark at 25 °C, significant isomerization and formation of W(CO)$_6$ were observed.

The statistical 4:1 mixture of *cis*-[6] and *trans*-[6] was prepared by heating a solution of 5 mg of *trans*-[6] in 1 ml of degassed methylcyclohexane under 37 cmHg pressure of CO for 4 h and 20 min at 100 °C and then removing the solvent under vacuum at −5 °C. There was no visible decomposition nor detectable formation of W(CO)$_6$. In the absence of added CO, there was considerable decomposition accompanied by formation of W(CO)$_6$.

Conclusions

These experiments show how the combination of matrix isolation and stereospecific isotopic labeling provides a powerful new method for tracing the pathways of photochemical reactions, by eliminating any subsequent thermal rearrangement of the products. Uv photolysis of matrix-isolated *trans*-(^{13}CO)W(CO)$_4$CS has demonstrated that the product, (^{13}CO)W(CO)$_3$CS, rearranges in a vibrationally or electronically excited state, following the loss of CO from the parent carbonyl. It is important to stress that this conclusion does not depend on the precise interpretation of spectra but merely on an overall assignment of bands to parent or product molecules.

It was shown previously that irradiation of M(CO)$_4$CS with visible light also caused an excited-state rearrangement.[1] Thus there are two independent ways of populating excited states of M(CO)$_4$CS and promoting isomerization. There is no a priori reason to suppose that the two isomerizations should have the same mechanism. However, for W(CO)$_4$CS, isomerization is promoted by visible light of ~500 nm, which is equivalent to 240 kJ/mol. The uv photolysis, which causes both the breaking of a W–CO bond and the isomerization of the W(CO)$_4$CS fragment, uses light of ~300 nm, equivalent to 400 kJ/mol. The difference in energy between the photons at these two wavelengths, equivalent to 160 kJ/mol, is close to the mean W–CO bond energy[20] of W(CO)$_6$, 178 kJ/mol. This suggests that very similar amounts of excess energy are available in the two isomerizations and therefore that the two mechanisms may also be similar.

The overall photochemistry of M(CO)$_5$CS closely resembles that of M(CO)$_6$,[1] and it seems reasonable to suppose that M(CO)$_5$ also undergoes an excited-state rearrangement during the course of uv photolysis of M(CO)$_6$. Unfortunately the experimental verification of this must await the preparation of a stereospecifically ^{13}CO-labeled M(CO)$_6$ molecule. Similar rearrangements may well occur during the photolysis of other pseudooctahedral d^6 systems, such as Mn(CO)$_5$Br or *cis*-Fe(CO)$_4$I$_2$, which are indeed known to undergo dissociative photochemical cis → trans isomerization.[21]

Acknowledgment. I thank the Science Research Council for supporting this research, Professor R. J. Angelici and Dr. B. D. Dombek for the gift of *trans*-(^{13}CO)W(CO)$_4$CS, and Professor J. J. Turner, Dr. J. K. Burdett, Dr. I. R. Dunkin, Professor W. G. Klemperer, Dr. J. C. Lockhart, and Dr. R. N. Perutz for stimulating discussions.

Registry No. **1**, 59780-39-1; **2**, 60270-09-9; **3**, 60305-12-6; **4**, 60305-13-7; *trans*-[6], 60172-96-5; *cis*-[6], 60201-90-3; A, 59752-97-5; B, 60305-14-8; W(CO)$_5$CS, 50358-92-4; W(CO)$_3$(^{13}CO)$_2$CS, 60270-08-8.

Supplementary Material Available: Appendix, in which the assignment of ir bands to the different species is justified quantitatively using CO-factored force fields (16 pages). These assignments are presented in Table II [W(^{12}CO)$_{5-x}$(^{13}CO)$_x$CS], Tables III and IV [(^{13}CO)W(CO)$_3$CS (axial CS) and the interaction with p-CO], and Table V [(^{13}CO)W(CO)$_3$CS (equatorial CS group)]. The force constants are defined in Figure 7. Relative ir band intensity measurements are summarized in Table VI. Ordering information is given on any current masthead page.

References and Notes

(1) M. Poliakoff, *Inorg. Chem.*, **15**, 2022 (1976).

(2) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **95**, 7516 (1973).

(3) M. A. Graham, M. Poliakoff, and J. J. Turner, *J. Chem. Soc. A*, 2939 (1971).

(4) R. N. Perutz and J. J. Turner, *Inorg. Chem.*, **14**, 262 (1975).

(5) R. N. Perutz and J. J. Turner, *J. Am. Chem. Soc.*, **97**, 4791, 4800 (1975).

(6) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **98**, 4110 (1976).

(7) One can eliminate the possibility that nondissociative isomerization and loss of CO are alternative photochemical pathways, with a much higher quantum yield for isomerization than CO loss, since such a scheme implies that the bands of *cis*-[6] should grow much more rapidly than those of the products. This clearly did not happen (cf. Figure 2a and b). Photolysis even in the ligand field absorption at 367 nm (cf. ref 1, Figure 7) failed to provide any evidence of nondissociative isomerization, although irradiation of similar bands in other d^6 pseudooctahedral systems (e.g., cis[Co(CN)$_4$(H$_2$O)$_2$]$^-$) promotes isomerization.[8]

(8) L. Viaene, J. D'Olieslager, and S. de Jaegere, *Inorg. Chem.*, **14**, 2786 (1975).

(9) Strictly to get *identical* photolysis results from *trans*-[6] and *cis*-[6] would require isomerization to occur more than once. However only one isomerization would convert all *trans*-[6] to *cis*-[6]. This scheme would also require an additional mechanism to explain the product distribution from unlabeled M(CO)$_5$CS.

(10) The evidence for assigning the split bands to B is as follows: (1) The intensity of the ν_{C-S} bands (not illustrated) shows that approximately equal amounts of species with axial CS groups (i.e., A + B) were present in the two experiments. (2) The e mode of A has an extinction coefficient at ~1975 cm^{-1}, twice that of the a″ mode of B which is coincident with it. Since the bands at this frequency have almost the same intensity in Figure 3a and b, the amounts of A and B in the two cases must also be the same. (3) Although there are equal amounts of B in both spectra, the relative intensities of the "old" a′ bands relative to the a″ bands in Figure 3b are about half those in Figure 3a. However the *combined* intensities of the two components of each a′ doublet are the same relative to the a″ mode as the intensities of the single bands in Figure 3a (see Appendix—Table VI). (4) These band splittings can be explained both qualitatively and quantitatively in terms of a weak interaction with the photoejected CO group, using a CO-factored force field (see Appendix—Tables III and IV).

(11) J. D. Atwood and T. L. Brown, *J. Am. Chem. Soc.*, **97**, 3380 (1975).

(12) The shift, ~1 cm^{-1}, from molecular CO is equal to five standard deviations, 0.2 cm^{-1}, of our method of frequency measurement.

(13) H. Dubost, *Chem. Phys.*, **12**, 139 (1976).

(14) M. Poliakoff and J. J. Turner, *J. Chem. Soc., Dalton Trans.*, 1351 (1973).

(15) R. N. Perutz, Ph.D. Thesis, Cambridge University, 1974.

(16) If the dissociative excited state were a trigonal prism, the most probable alternative, immediately after dissociation there would have to be four different positions for the ^{13}CO relative to the p-CO, in order to explain the equal probability of losing CO groups from the axial and equatorial positions of the ground-state pseudooctahedron. Clearly it is hard to relate these four positions of the ^{13}CO to the single final position of the ^{13}CO in the ground state B. Similar arguments can be used to eliminate other excited-state geometries.

(17) J. I. Musher and W. C. Agosta, *J. Am. Chem. Soc.*, **96**, 1320 (1974).

(18) J. K. Burdett, R. N. Perutz, M. Poliakoff, and J. J. Turner, *J. Chem. Soc., Chem. Commun.*, 157 (1975).

(19) A detailed analysis of these rearrangements on a molecular orbital basis will be presented elsewhere: J. K. Burdett, R. N. Perutz, M. Poliakoff, and J. J. Turner, to be submitted for publication.

(20) D. S. Barnes, G. Pilcher, D. A. Pittam, H. A. Skinner, and D. Todd, *J. Less-Common Met.*, **38**, 53 (1974).

(21) M. Pankowski and M. Bigorgne, *J. Organomet. Chem.*, **19**, 393 (1969); B. F. G. Johnson, J. Lewis, P. W. Robinson, and R. Miller, *J. Chem. Soc. A*, 1043 (1968).