

- (22) "Apparent" is used because it is not clear that this is not just another basis set problem.
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## The Solution Photosubstitution Chemistry of Triphenylphosphine Derivatives of Molybdenum Hexacarbonyl

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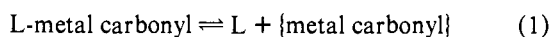
Contribution from the Department of Chemistry, Tulane University, New Orleans, Louisiana 70118. Received July 15, 1977

**Abstract:** The ligand photosubstitution chemistry of  $\text{Mo}(\text{CO})_5\text{PPh}_3$  has been demonstrated to proceed with a high quantum efficiency for CO loss ( $\Phi_{366} = 0.58$ ). When this reaction was carried out in the presence of either  $\text{PPh}_3$  or  $^{13}\text{CO}$  both *cis* and *trans* primary photoproducts were observed, presumably resulting from incoming ligand trapping of the  $[\text{Mo}(\text{CO})_4\text{PPh}_3]$  intermediate in its  $C_s$  or  $C_{4v}$  isomeric forms, respectively. On the other hand, the quantum efficiency for unique ligand loss,  $\text{PPh}_3$ , was only 0.11 at 366 nm. The *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  complex was found to undergo photoisomerization to the *cis*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  derivative via loss of  $\text{PPh}_3$  followed by subsequent rearrangement of the  $[\text{Mo}(\text{CO})_4\text{PPh}_3]$  ( $C_{4v}$ ) intermediate to its  $C_s$  analogue prior to recapture of  $\text{PPh}_3$ . Photolysis of either pure *cis*- or *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  in the presence of  $^{13}\text{CO}$  afforded primarily *cis*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{PPh}_3$  with a smaller quantity of *trans*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{PPh}_3$ . The latter  $^{13}\text{CO}$ -labeled species was observed in larger quantities from photolysis of *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  with  $^{13}\text{CO}$  as would be anticipated. These experiments further demonstrate the facile rearrangement of the  $C_{4v}$  structure of  $[\text{Mo}(\text{CO})_4\text{PPh}_3]$  to the  $C_s$  structure prior to recombination with an incoming ligand.

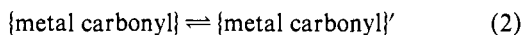
### Introduction

Ligand substitution is probably the most important photochemical reaction of metal carbonyl derivatives.<sup>1-5</sup> This is primarily due to the fact that photosubstitution chemistry is an essential aspect of photoinitiated transition metal carbonyl catalysis. The three steps in the photo- or thermal-substitution processes are illustrated below:

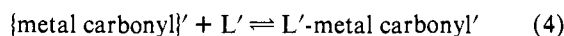
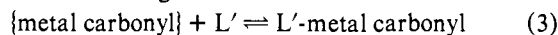
Ligand dissociation



Intermediate transformation

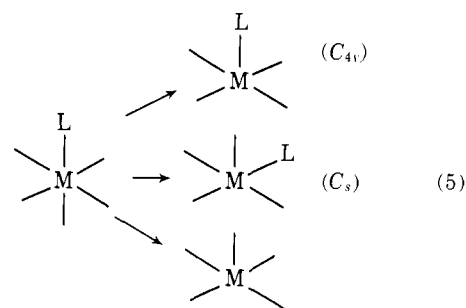


Ligand combination



As indicated in eq 1, during the photochemical process coordinatively unsaturated species can be produced under rather mild conditions. The nature of these intermediates and the stereochemical position of the ligand dissociated is a point of much interest since this information leads to an understanding of the structure and reactivity of these coordinatively unsaturated species which are ubiquitous in homogeneous catalysis. It is important to note that these intermediates can exhibit isomerization in photoexcited states. For example, Poliakoff has shown that the five-coordinate intermediate resulting from CO loss in matrix-isolated *trans*- $(^{13}\text{CO})\text{-W}(\text{CO})_4\text{CS}$ ,  $[(^{13}\text{CO})\text{W}(\text{CO})_3\text{CS}]$ , undergoes rearrangement in an electronic or vibrational excited state.<sup>6</sup> Black and Bra-

terman have also reported that the axial square-pyramidal isomer of  $[\text{Mo}(\text{CO})_4\text{P}(\text{C}_6\text{H}_{11})_3]$  generated by photolysis of  $\text{Mo}(\text{CO})_5\text{P}(\text{C}_6\text{H}_{11})_3$  in a hydrocarbon matrix isomerizes to the equatorial isomer via a photochemical process.<sup>7</sup> In addition it is also apparent that thermal rearrangements of unsaturated transition metal carbonyls often occur.<sup>8-10</sup>



Upon photolysis of  $\text{M}(\text{CO})_5\text{L}$  species under conditions of ligand substitution, three reaction pathways are available (eq 5). When photoejection of carbon monoxide occurs, the loss of an axial CO group affords the  $C_{4v}$  isomer, whereas the loss of an equatorial CO group leads to the  $C_s$  isomer.

We have previously shown via stereospecific  $^{13}\text{CO}$  labeling that the  $[\text{Mo}(\text{CO})_5]$  intermediate afforded thermally from  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_9$  in solution readily rearranges CO ligands, presumably through the square-pyramidal equivalent of the Berry pseudorotation ( $C_{4v} \rightarrow D_{3h} \rightarrow C_{4v}$ ).<sup>11</sup> Similar observations have also been made in the matrix photochemistry of group 6B hexacarbonyl species.<sup>12</sup> In cases where one of the isomeric forms of  $[\text{M}(\text{CO})_4\text{L}]$  ( $C_s$  or  $C_{4v}$ ) is produced pref-

erentially and further is stable toward isomerization, it is possible to prepare stereospecifically  $^{13}\text{C}$ -labeled derivatives upon recombination of the intermediate with labeled carbon monoxide. This process has been observed in  $\text{Mo}(\text{CO})_5\text{NHC}_5\text{H}_{10}$ <sup>11</sup> and  $\text{M}(\text{CO})_4(\text{NBD})$  ( $\text{M} = \text{Mo}, \text{W}$  and  $\text{NBD} = \text{bicyclo}[2.2.1]\text{hepta-2,5-diene}$ ).<sup>9,10</sup> Alternatively, it is as well feasible to prepare  $^{13}\text{C}$ -labeled derivatives stereoselectively in cases where there is no preferential photodissociation of carbon monoxide ligand, but where isomerization to the more stable intermediate species occurs more rapidly than CO recombination.

In this correspondence we wish to discuss quantitatively the solution photochemistry of  $\text{Mo}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$  and *cis*- and *trans*- $\text{Mo}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2$ .

## Experimental Section

**Materials.** All solvents were reagent grade chemicals by Matheson Coleman and Bell. Hexane was distilled under nitrogen from calcium sulfate. Tetrahydrofuran was distilled under nitrogen from the purple sodium benzophenone dianion. Diglyme (bis(2-methoxyethyl) ether) was dried by overnight reflux with excess sodium, followed by distillation.

Molybdenum hexacarbonyl (a gift of Climax Molybdenum Corp.) was vacuum sublimed at 50 °C for analytical application. Triphenylphosphine was recrystallized from hot methanol and dried in vacuo.  $^{13}\text{C}$ O gas enriched to >90% was obtained from Prochem, B.O.C. Ltd., London.

**Compound Preparations. A.  $\text{Mo}(\text{CO})_5\text{PPh}_3$ .**  $\text{Mo}(\text{CO})_6$  was refluxed in dry diglyme with a slight molar excess of  $\text{PPh}_3$  for 2 h under nitrogen. Diglyme was removed under vacuum at 35 °C and the product,  $\text{Mo}(\text{CO})_5\text{PPh}_3$ , was recrystallized from chloroform/ethanol yielding white crystals (mp 138 °C).

**B. *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$ .**  $\text{Mo}(\text{CO})_6$  and a twofold excess of  $\text{PPh}_3$  were refluxed in diglyme under nitrogen for 4 h. Upon cooling the reaction mixture to room temperature, a large quantity of a greenish-yellow precipitate crystallized and it was collected by filtration. These crystals were washed with methanol to remove any unreacted  $\text{PPh}_3$  and recrystallized from THF/methanol.

Light yellow crystals were isolated by filtration and vacuum dried (mp 235 °C). Anal. Calcd for  $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$ : C, 65.58; H, 4.13. Found: C, 65.83; H, 4.25.

**C. *cis*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$ .** *cis*- $\text{Mo}(\text{CO})_4[\text{NHC}_5\text{H}_{10}]_2$ , prepared from  $\text{Mo}(\text{CO})_6$  and piperidine in heptane, was reacted with a slightly greater than twofold excess of triphenylphosphine in benzene under nitrogen at 50 °C to afford yellow crystals of *cis*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$ .<sup>13</sup> These were purified by recrystallization from  $\text{CHCl}_3$ /methanol. Anal. Calcd for  $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$ : C, 65.58; H, 4.13. Found: C, 65.68; H, 4.12.

**D. *cis*- $\text{Mo}(\text{CO})_4(^{13}\text{C})[\text{PPh}_3]_2$ .** *cis*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]\text{NHC}_5\text{H}_{10}$ <sup>14</sup> was reacted with  $^{13}\text{C}$ O in hexane at 25 °C for 2.5 h. The product was purified by column chromatography on a 10-in. alumina column eluting with hexane.

**Instrumentation.** The infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer equipped with a linear absorbance potentiometer. The spectra were calibrated against a water vapor spectrum below 2000  $\text{cm}^{-1}$  and against a CO spectrum above 2000  $\text{cm}^{-1}$ . Sodium chloride solution cells (0.1-mm path length for THF solutions, 1.0 mm for other solutions) were used with appropriate solvent in the reference cell. Ultraviolet/visible spectra were recorded on either a Cary 14 or Beckman DK-1H recording spectrophotometers using 1-cm quartz cells.

**Sample Preparation.** All samples were handled under red photographic safe light from mixing through analysis. Typically, a 25-mL solution of reactants was prepared and mixed thoroughly. Three-milliliter aliquots of solution were pipetted into 13 × 100 mm Pyrex test tubes, which were sealed with tight-fitting rubber serum caps secured by copper wire. The tubes were then degassed by three freeze-thaw cycles. Pumping was accomplished by inserting syringe needles connected to a common vacuum line through the serum caps. Tubes for a particular experiment were simultaneously degassed in a batch of four to six. Upon completion of degassing, dry nitrogen or the appropriate gaseous reactants ( $^{12}\text{C}$ O or  $^{13}\text{C}$ O) were admitted at a pressure slightly greater than atmospheric.

Samples were temperature equilibrated (25 °C) prior to irradiation. An unirradiated blank was always employed in establishing the baseline for the analytical procedures. Reactant concentrations were arranged so as to yield optical densities much greater than 2 in a 1.0-cm cell at the appropriate wavelength.

**Quantum Yield Determination.** Quantum yields were determined using a photochemical reactor with merry-go-round feature. The turntable photochemical reactor was purchased from Ace Glass Inc. and was fitted with a Pyrex water jacket through which circulated coolant (water or filter solutions) between the lamp and the samples.

The light source was a 450-W Hanovia medium-pressure mercury-vapor lamp. For the irradiations at 366 nm, the extraneous lines of the lamp were filtered out using (a) a uranium glass filter sleeve from Ace Glass Inc. and (b) Corning plate glass filters no. 5840. Ultraviolet/visible spectra indicated very good isolation of the 366-nm line. Light intensity at this wavelength was approximately  $2 \times 10^{15}$  quanta  $\text{s}^{-1} \text{cm}^{-2}$ .

Isolation of the 313-nm line was achieved employing a set of Corning filters no. 9863 in addition to a three-component solution consisting of 0.89 M  $\text{NiSO}_4$ ,  $2.5 \times 10^{-3}$  M  $\text{K}_2\text{CrO}_4$ , and 0.123 M potassium biphthalate in water.<sup>15</sup> This filter solution was circulated through the water jacket by means of a small tubing pump. The circulation system was closed with a filter flask serving as heat exchanger as well as reservoir. The transmission characteristics of the filter solution were carefully monitored spectroscopically. Light intensity at this wavelength was  $8 \times 10^{14}$  quanta  $\text{s}^{-1} \text{cm}^{-2}$ .

Reactant complexes were always  $5 \times 10^{-3}$  M in THF solutions. When  $\text{PPh}_3$  was the incoming ligand its concentration was  $5 \times 10^{-2}$  M unless otherwise noted. Product quantum yields were determined by quantitative infrared spectroscopy in the  $\nu(\text{CO})$  region. Since the  $\nu(\text{CO})$  spectra of *cis*- and *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  (the products resulting from photolysis of  $\text{Mo}(\text{CO})_5\text{PPh}_3$  in the presence of  $\text{PPh}_3$ ) are grossly overlapped, it was necessary to measure the absorbance of the unknown mixtures afforded of these two species at two different wavelengths. The wavelengths employed were the maxima at 1899  $\text{cm}^{-1}$  (E mode) for the *trans* derivative and 1887  $\text{cm}^{-1}$  (B<sub>2</sub> mode) for the *cis* derivative. Other quantum yields were computed from the appearance of well-isolated  $\nu(\text{CO})$  absorptions. All quantum efficiencies were measured before 10% reaction had occurred.

**Actinometry.** Light intensity was gauged by potassium ferrioxalate actinometry using the procedure described by Calvert and Pitts.<sup>16</sup> A Beer's law plot for the absorption of the iron(1,10-phenanthroline)<sub>3</sub>- $\text{Fe}^{+2}$  complex was constructed which yielded an extinction coefficient of  $1.06 \times 10^4$  L/mol-cm as compared to the reported value of  $1.11 \times 10^4$  L/mol-cm.<sup>16</sup> In practice the actinometer system showed good linearity with irradiation time and good reproducibility.

**Isolation of *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  Produced Photochemically from  $\text{Mo}(\text{CO})_5\text{PPh}_3$  and  $\text{PPh}_3$ .** The near total insolubility of *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  in hydrocarbon solvents provides a ready means for its separation from  $\text{Mo}(\text{CO})_5\text{PPh}_3$  and *cis*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$ . Four 3-mL samples of  $\text{Mo}(\text{CO})_5\text{PPh}_3$  and  $\text{PPh}_3$  were prepared and irradiated in an identical manner with that used in the quantum yield determination. The resulting samples were combined and the THF was removed under vacuum at room temperature. After two washings of the solid with hexane, the unreacted  $\text{Mo}(\text{CO})_5\text{PPh}_3$  and  $\text{PPh}_3$  starting materials as well as the *cis*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  product were removed as evidenced by infrared spectroscopy. The remaining hexane-insoluble solid was dissolved in dichloromethane and its  $\nu(\text{CO})$  spectrum recorded. In this way the material was shown to be pure *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  by comparison with an authentic sample. It should be noted that thermal isomerization (*cis* → *trans*) does not occur at 25 °C.<sup>17</sup>

**$^{13}\text{C}$  Labeling Experiments.** Experiments in which  $^{13}\text{C}$ O was used as the incoming ligand were carried out in a manner exactly analogous to an equivalent quantum yield experiment where  $^{12}\text{C}$ O or  $\text{PPh}_3$  were employed. After the last pumping cycle of tubes prepared for irradiation, 90%  $^{13}\text{C}$ O was admitted to a positive pressure and the solutions were allowed to thermally equilibrate with intermittent shaking. Experiments involving prolonged irradiation indicated that the  $^{13}\text{C}$ O concentration was sufficient to trap all unsaturated species produced via photolysis. In general,  $^{13}\text{C}$ O-labeled molecules were examined spectroscopically both in their initial THF reaction solutions and also in hexane solution after removal of THF. In experiments where  $\text{Mo}(\text{CO})_4(^{13}\text{C})\text{PPh}_3$  was the product, the samples were chromatographed on a 1-ft alumina column using 90% hexane/10%

**Table I.** Calculated and Observed Infrared Frequencies in the  $\nu(\text{CO})$  Region for  $\text{Mo}(\text{}^{12}\text{CO})_{5-n}(\text{}^{13}\text{CO})_n\text{PPh}_3$  Species<sup>a</sup>

Molecule	Frequencies, $\text{cm}^{-1b}$				
1. $\text{Mo}(\text{}^{12}\text{CO})_5\text{PPh}_3$	2073.8 (2072.0)	1989.3	1950.5 (1951.4)	1950.5 (1951.4)	1950.4 (~1947)
2. $\text{Mo}(\text{}^{12}\text{CO})_4(\text{}^{13}\text{CO})\text{PPh}_3$ eq	2065.7 (2064.8)	1982.1 (1982.6)	1950.4	1950.5	1917.8 (1921.2)
3. $\text{Mo}(\text{}^{12}\text{CO})_4(\text{}^{13}\text{CO})\text{PPh}_3$ ax	2069.5	1989.3	1950.5	1950.5	1907.3 (1909.5)
4. $\text{Mo}(\text{}^{12}\text{CO})_3(\text{}^{13}\text{CO})_2\text{PPh}_3$ cis-eq	2056.1 (2055.7)	1976.7	1950.4	1919.8	1915.6
5. $\text{Mo}(\text{}^{12}\text{CO})_3(\text{}^{13}\text{CO})_2\text{PPh}_3$ trans-eq	2057.7	1965.0	1903.5	1950.5	1942.0

<sup>a</sup> Observed frequencies are listed in parentheses directly below the calculated values. <sup>b</sup> Force constants calculated were  $k_1 = 15.59$ ,  $k_2 = 15.96$ ,  $k_c = 0.28$ ,  $k_c' = 0.321$ , and  $k_t = 0.597$ .  $k_1$  and  $k_2$  are the stretching force constants of the axial and equatorial CO groups, respectively, and  $k_c$ ,  $k_c'$ , and  $k_t$  refer to the interaction constants for *cis*- $\text{CO}_{\text{eq}}-\text{CO}_{\text{ax}}$ , *cis*- $\text{CO}_{\text{eq}}-\text{CO}_{\text{eq}}$ , and *trans*- $\text{CO}_{\text{eq}}-\text{CO}_{\text{eq}}$ , respectively.

$\text{CHCl}_3$  as elutant. This was done so as to assure that the product was not contaminated with *cis*- or *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$ .

**Vibrational Analysis in  $\nu(\text{CO})$  Region.** Initial CO stretching force constant calculations on  $\text{Mo}(\text{CO})_5\text{PPh}_3$  species were performed using the Cotton-Kraihanzel approach<sup>18</sup> employing the  $^{12}\text{CO}$  frequency data obtained in hydrocarbon solvent. The low-frequency  $A_1$  vibration and the E vibration are essentially accidentally degenerate. However, since there is some asymmetry on the low-frequency side of this absorption which is centered at  $1951.4 \text{ cm}^{-1}$ , the  $A_1$  vibrational mode was assigned a value of  $1947 \pm 1 \text{ cm}^{-1}$ . The trial force constants were refined using the  $^{13}\text{CO}$  frequency data and an iterative computer program<sup>19</sup> that adjusts a set of force constants common to a group of isotopically substituted molecules to give simultaneously a least-squares fit between the observed and calculated frequencies for all the molecules. The five trial force constants were refined to reproduce the observed  $^{12}\text{CO}$  and  $^{13}\text{CO}$  vibrations to within an average error of  $<1.8 \text{ cm}^{-1}$ .

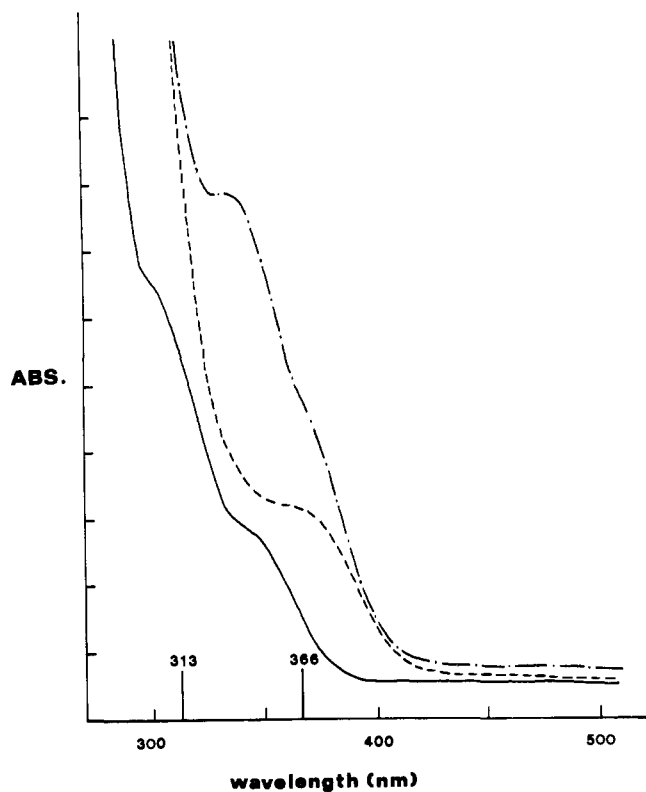
The observed and calculated  $\nu(\text{CO})$  values for the five isotopically substituted  $\text{Mo}(\text{}^{12}\text{CO})_{5-n}(\text{}^{13}\text{CO})_n\text{PPh}_3$  species ( $n = 0-2$ ) of interest are listed in Table I along with the approximate force field.

## Results and Discussion

**Electronic Structure.** Figure 1 contains the low-energy absorption bands in the room temperature electronic spectra of  $\text{Mo}(\text{CO})_5\text{PPh}_3$ , *cis*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$ , and *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  in tetrahydrofuran solvent. The first low-energy band maximum in the absorption spectrum of  $\text{Mo}(\text{CO})_5\text{PPh}_3$  which appears at 345 nm ( $\epsilon \sim 2000$ ) has been assigned to the  $^1A_1(b_2^2e^4) \rightarrow E(b_2^2e^3a_1^1)$ , whereas the higher frequency, more intense absorption at 305 nm ( $\epsilon \sim 6000$ ) is most likely  $M \rightarrow \pi^*$  CO charge transfer.<sup>3</sup> The weak spin-forbidden  $^1A_1 \rightarrow ^3E$  transition was not observed; however, this band has been noted in several analogous tungsten derivatives.<sup>20</sup>

The disubstituted *cis* and *trans* complexes have electronic transitions at slightly lower energies than those for  $\text{Mo}(\text{CO})_5\text{PPh}_3$  because of the lower average ligand field strength resulting from CO replacement by  $\text{PPh}_3$ . These band maxima were observed at 370 nm ( $\epsilon \sim 2000$ ) in the *cis*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  derivative, and at 370 (sh) and 330 nm ( $\epsilon \sim 6000$ ) in the corresponding *trans* derivative. Although these spectra have not been assigned, the excited states for the bands at 370 nm are undoubtedly the low-lying ligand field states. On the other hand, the 330-nm ( $\epsilon \sim 6000$ ) absorption in the *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  derivative is probably  $M \rightarrow \pi^*$  CO and LF in character.

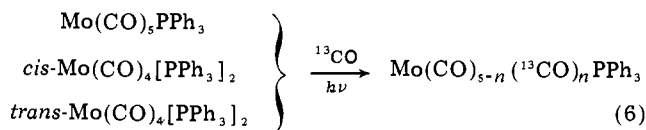
In all three derivatives investigated the lowest LF excitation results in population of a  $\sigma^*$  level (either  $d_{x^2-y^2}$  or  $d_{z^2}$ ), thus leading to a labilization of exclusively  $\sigma$  bonding ligands. This effect has indeed been observed in the photosubstitution chemistry of amine metal pentacarbonyl derivatives which is dominated by metal-amine bond dissociation.<sup>21,22</sup> In the case of  $\text{PPh}_3$  species the ligands (CO and  $\text{PPh}_3$ ) are less dissimilar as indicated by electronic and vibrational spectral analysis, i.e., both ligands are involved in  $\sigma$  and  $\pi$  bonding with the metal.



**Figure 1.** Low-energy absorptions in the room temperature electronic spectra in THF (concn  $10^{-4}$  M in 1.0-cm cell) of —,  $\text{Mo}(\text{CO})_5\text{PPh}_3$ ; - - -, *cis*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$ ; and — · —, *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$ .

Therefore, LF excitations in these derivatives would be expected to labilize dissociation of metal-carbonyl as well as metal-phosphorus bonds.

**$\nu(\text{CO})$  Infrared Analysis.** In order to determine the stereochemical position of an incoming  $^{13}\text{CO}$  ligand in  $\text{Mo}(\text{CO})_5\text{PPh}_3$  species prepared photochemically via dissociative loss of  $^{12}\text{CO}$  or  $\text{PPh}_3$  (eq 6), it was necessary to analyze the



$\nu(\text{CO})$  infrared region with a great deal of care. Figure 2 illustrates the approximate deconvoluted spectra expected for  $^{13}\text{CO}$ -enriched species of  $\text{Mo}(\text{CO})_5\text{PPh}_3$ . Because we are only interested in low-enrichment photochemical processes, the anticipated spectra of tri- and higher substituted  $^{13}\text{CO}$  species are omitted from consideration. Figure 3 depicts the observed

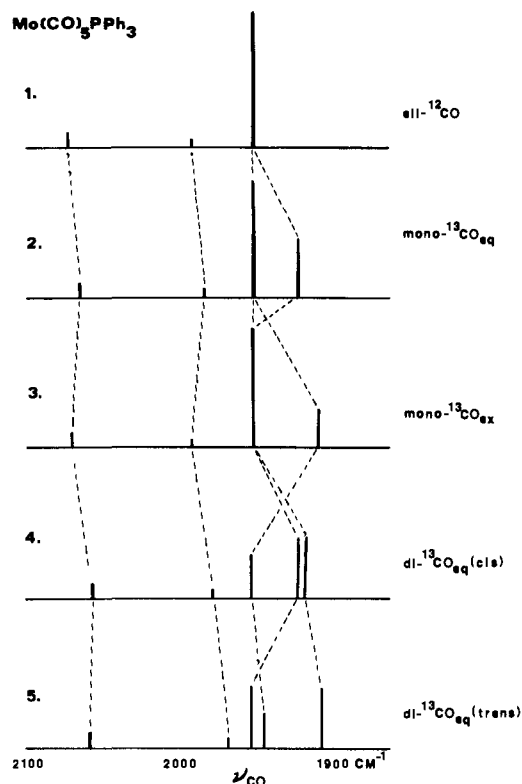
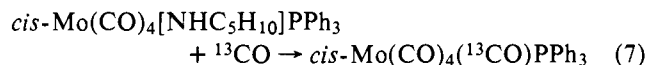


Figure 2. Line drawing of the deconvoluted  $\nu(\text{CO})$  spectra of the various  $^{13}\text{CO}$ -enriched  $\text{Mo}(\text{CO})_5\text{PPh}_3$  species.

natural abundance  $^{13}\text{CO}$  spectrum of  $\text{Mo}(\text{CO})_5\text{PPh}_3$  (providing the ratio of intensities of the two low-frequency absorptions in statistically  $^{13}\text{CO}$  monosubstituted species), along with a stereospecifically labeled mono- $^{13}\text{CO}$  derivative, *cis*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{PPh}_3$ , which was prepared employing the reaction



This latter species is believed to be greater than 95% stereochemically pure.<sup>23</sup> This conclusion is based on the lack of a significant shoulder on the low-energy side of the  $1921\text{-cm}^{-1}$  band at around  $1909\text{ cm}^{-1}$  which is assigned to *trans*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{PPh}_3$  (see Table I).

As noted in Table I and Figure 2, in order to detect the axially mono- $^{13}\text{CO}$  species it is necessary to avoid substantial production of equatorially disubstituted  $^{13}\text{CO}$  species, in particular  $\text{Mo}(\text{CO})_3(^{13}\text{CO})_2\text{PPh}_3$  where the  $^{13}\text{C}$ -carbonyl ligands are mutually *trans*.<sup>24</sup> This is illustrated in the  $\nu(\text{CO})$  spectrum of a more highly enriched sample of  $\text{Mo}(\text{CO})_5\text{PPh}_3$  shown in Figure 4. In addition, the *cis*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  derivative, which has some solubility in hydrocarbon solvents (under which conditions the *trans* analogue is essentially insoluble), has strong  $\nu(\text{CO})$  absorptions in the  $1930\text{--}1890\text{-cm}^{-1}$  region. Therefore, it was necessary to carefully chromatograph  $^{13}\text{CO}$ -enriched samples, as well as to minimize  $^{13}\text{CO}$  disubstitution, in order to accurately assess the relative extent of  $^{13}\text{CO}$  incorporation into equatorial and axial positions employing the  $\nu(\text{CO})$  absorptions at  $1921$  and  $1909\text{ cm}^{-1}$ .<sup>25,26</sup>

**Ligand Photosubstitution Reactions.** Irradiation of  $\text{Mo}(\text{CO})_5\text{PPh}_3$  at  $366$  and  $313\text{ nm}$  in tetrahydrofuran solvent in the presence of  $\text{PPh}_3$  resulted in substantial  $\text{CO}$  photodissociation with a concomitant production of both *cis*- and *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  products:

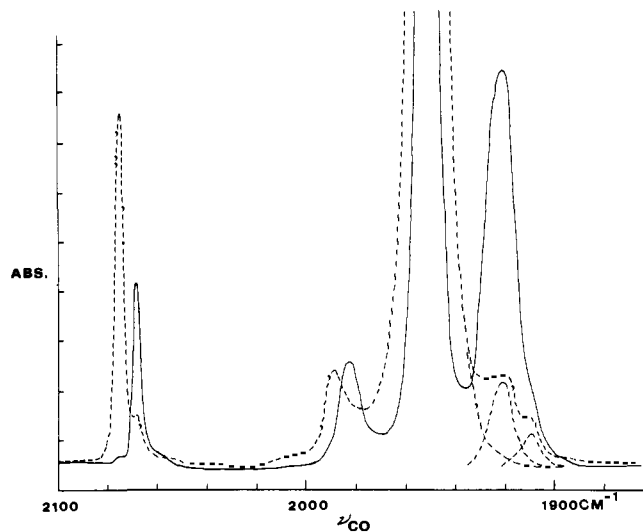
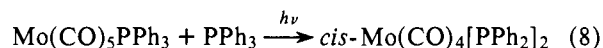


Figure 3. Observed spectra in the  $\nu(\text{CO})$  region in hydrocarbon solvent of - - -, natural abundance  $^{13}\text{CO}$   $\text{Mo}(\text{CO})_5\text{PPh}_3$ ; and —, *cis*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{PPh}_3$  prepared from *cis*- $\text{Mo}(\text{CO})_4[\text{NHC}_5\text{H}_{10}]\text{PPh}_3$  and  $^{13}\text{CO}$  at  $22^\circ\text{C}$ .

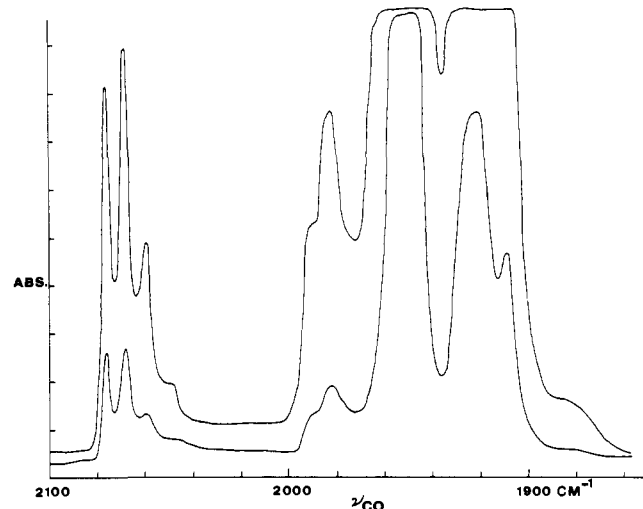
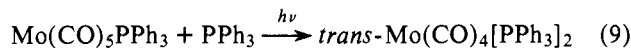


Figure 4. Observed spectra in the  $\nu(\text{CO})$  region in hydrocarbon solvent of highly  $^{13}\text{CO}$ -enriched  $\text{Mo}(\text{CO})_5\text{PPh}_3$  resulting from prolonged photolysis of  $\text{Mo}(\text{CO})_5\text{PPh}_3$  in the presence of  $^{13}\text{CO}$ .



The *cis* product was afforded in much higher yield than its *trans* analogue, *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  comprising only 14% of the total disubstituted material produced. As detailed in the Experimental Section we were indeed able to isolate the *trans* isomer produced in this photochemical process. This was felt necessary since the two disubstituted derivatives have grossly overlapping  $\nu(\text{CO})$  spectra, and the *trans* isomer, when present to a small extent, contributes only subtly to the normal *cis*  $\nu(\text{CO})$  band pattern. Product quantum yields are listed in Table II. A slight decrease (<15%) in photochemical reactivity was noted upon going to shorter wavelengths.

Similarly, photolysis of  $\text{Mo}(\text{CO})_5\text{PPh}_3$  in the presence of  $^{13}\text{CO}$  afforded initially both *cis*- and *trans*- $\text{Mo}(\text{CO})_2(^{13}\text{CO})\text{PPh}_3$  with about the same quantum efficiency as that for bistrisphenylphosphine production, along with a small quantity of  $^{13}\text{CO}$ -enriched  $\text{Mo}(\text{CO})_6$ . The percentage of *trans*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{PPh}_3$  formed varied slightly (generally >20%) in several experiments since its production is dependent

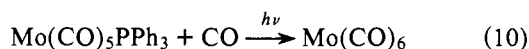
Table II. Photosubstitution Quantum Yields for Triphenylphosphine Derivatives of Molybdenum<sup>a</sup>

Complex	Entering <sup>b</sup> ligand	Wavelength of irradiation, nm	Product	Quantum yield
Mo(CO) <sub>5</sub> PPh <sub>3</sub>	PPh <sub>3</sub>	366	<i>cis</i> -Mo(CO) <sub>4</sub> [PPh <sub>3</sub> ] <sub>2</sub>	0.50
Mo(CO) <sub>5</sub> PPh <sub>3</sub>	PPh <sub>3</sub>	313	<i>cis</i> -Mo(CO) <sub>4</sub> [PPh <sub>3</sub> ] <sub>2</sub>	0.43
Mo(CO) <sub>5</sub> PPh <sub>3</sub>	PPh <sub>3</sub>	366	<i>trans</i> -Mo(CO) <sub>4</sub> [PPh <sub>3</sub> ] <sub>2</sub>	0.08
Mo(CO) <sub>5</sub> PPh <sub>3</sub>	PPh <sub>3</sub>	313	<i>trans</i> -Mo(CO) <sub>4</sub> [PPh <sub>3</sub> ] <sub>2</sub>	0.07
Mo(CO) <sub>5</sub> PPh <sub>3</sub>	CO	366	Mo(CO) <sub>6</sub>	0.11
Mo(CO) <sub>5</sub> PPh <sub>3</sub>	CO	313	Mo(CO) <sub>6</sub>	0.07
<i>trans</i> -Mo(CO) <sub>4</sub> [PPh <sub>3</sub> ] <sub>2</sub>	PPh <sub>3</sub>	366	<i>cis</i> -Mo(CO) <sub>4</sub> [PPh <sub>3</sub> ] <sub>2</sub>	0.33
<i>trans</i> -Mo(CO) <sub>4</sub> [PPh <sub>3</sub> ] <sub>2</sub>	PPh <sub>3</sub>	313	<i>cis</i> -Mo(CO) <sub>4</sub> [PPh <sub>3</sub> ] <sub>2</sub>	0.16
<i>trans</i> -Mo(CO) <sub>4</sub> [PPh <sub>3</sub> ] <sub>2</sub>	CO	366	Mo(CO) <sub>5</sub> PPh <sub>3</sub>	0.30
<i>trans</i> -Mo(CO) <sub>4</sub> [PPh <sub>3</sub> ] <sub>2</sub>	CO	313	Mo(CO) <sub>5</sub> PPh <sub>3</sub>	0.20
<i>cis</i> -Mo(CO) <sub>4</sub> [PPh <sub>3</sub> ] <sub>2</sub>	CO	366	Mo(CO) <sub>5</sub> PPh <sub>3</sub>	0.31
<i>cis</i> -Mo(CO) <sub>4</sub> [PPh <sub>3</sub> ] <sub>2</sub>	CO	313	Mo(CO) <sub>5</sub> PPh <sub>3</sub>	0.33

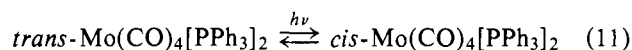
<sup>a</sup> All reactions were carried out in THF. Quantum yields are for appearance of product with an error estimated at  $\pm 10\%$ . <sup>b</sup> The PPh<sub>3</sub> concentration was generally  $5 \times 10^{-2}$  M. Its concentration, however, was varied from  $1 \times 10^{-3}$  to  $3 \times 10^{-1}$  M in some experiments with no variation in quantum yields noted outside of experimental error, consistent with dissociative substitution processes.

on the effectiveness of <sup>13</sup>CO trapping of the less favorable form of [Mo(CO)<sub>4</sub>PPh<sub>3</sub>] (square pyramidal with PPh<sub>3</sub> in the axial position). Therefore, rearrangement to the more stable form of the intermediate, PPh<sub>3</sub> in the equatorial plane, can occur prior to <sup>13</sup>CO incorporation. Thus, formation of *trans*-Mo(CO)<sub>4</sub>(<sup>13</sup>CO)PPh<sub>3</sub> is very dependent on the carbon monoxide concentration.<sup>27</sup>

The quantum yield for replacement of the unique ligand (eq 10) was found to be considerably less than that for CO replacement (Table II).



We have previously demonstrated that *trans*-Mo(CO)<sub>4</sub>[PPh<sub>3</sub>]<sub>2</sub> undergoes isomerization to *cis*-Mo(CO)<sub>4</sub>[PPh<sub>3</sub>]<sub>2</sub> upon photolysis:



It is, therefore, necessary to obtain the quantum yield for this process vs. the quantum yield for *cis*-Mo(CO)<sub>4</sub>[PPh<sub>3</sub>]<sub>2</sub> production from Mo(CO)<sub>5</sub>PPh<sub>3</sub> and PPh<sub>3</sub> in order to assert whether the *cis* derivative is a primary photoproduct or the result of a secondary photochemical isomerization process. As is seen in Table II, the quantum yield for *trans* → *cis* isomerization is less than that for formation of the *cis* derivative from Mo(CO)<sub>5</sub>PPh<sub>3</sub> and PPh<sub>3</sub>. This, therefore, rules out the possibility that *trans*-Mo(CO)<sub>4</sub>[PPh<sub>3</sub>]<sub>2</sub> is formed exclusively in the initial photochemical reaction followed by a rapid interconversion to the *cis* isomer. Indeed, if both of these processes are dissociative (loss of CO or PPh<sub>3</sub> from Mo(CO)<sub>5</sub>PPh<sub>3</sub> and *trans*-Mo(CO)<sub>4</sub>[PPh<sub>3</sub>]<sub>2</sub>, respectively) to afford a fluxional [Mo(CO)<sub>4</sub>PPh<sub>3</sub>] intermediate, this conclusion would be anticipated.

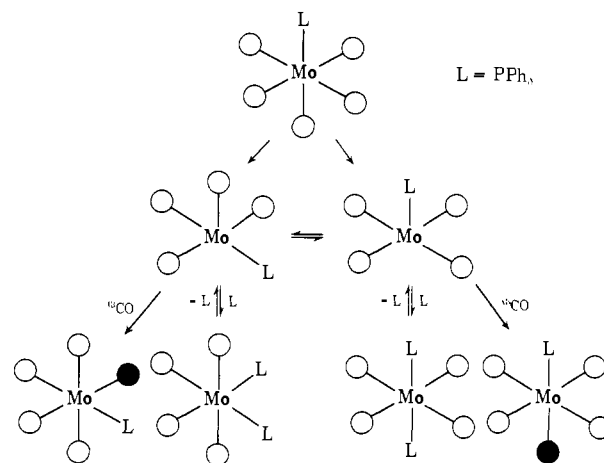
The photoisomerization process (eq 11) is in fact believed to proceed via dissociative loss of PPh<sub>3</sub> to afford [Mo(CO)<sub>4</sub>PPh<sub>3</sub>] (*C*<sub>4v</sub> isomer) with concomitant rearrangement to the *C*<sub>s</sub> form of the intermediate followed by a reentry of PPh<sub>3</sub> into the coordination sphere with formation of *cis*-Mo(CO)<sub>4</sub>[PPh<sub>3</sub>]<sub>2</sub>. As noted in Table II, the quantum yield for this reaction is independent of the nature of the incoming ligand (CO or PPh<sub>3</sub>), and the reaction displays a significant decline in quantum efficiency upon going to shorter wavelength. This wavelength dependency is probably indicative of longer wavelength irradiation preferentially labilizing ligands along the *z* axis, i.e., population of the *d*<sub>z<sup>2</sup></sub> σ\* level.

The photochemical reaction (eq 11) has been demonstrated to be reversible; however, the position of equilibrium lies extensively in favor of the *cis* isomer.<sup>28</sup> Nevertheless, the PPh<sub>3</sub>

ligand in *cis*-Mo(CO)<sub>4</sub>[PPh<sub>3</sub>]<sub>2</sub> is photosubstituted readily with CO with a quantum efficiency similar to that in the corresponding reaction of *trans*-Mo(CO)<sub>4</sub>[PPh<sub>3</sub>]<sub>2</sub> (see Table II). On the other hand, *cis*-Mo(CO)<sub>4</sub>[PPh<sub>3</sub>]<sub>2</sub> undergoes rearrangement to the *trans* isomer at elevated temperatures where the higher energy form of the intermediate, [Mo(CO)<sub>4</sub>PPh<sub>3</sub>] (*C*<sub>4v</sub>), is more accessible.<sup>17</sup> This thermal isomerization reaction (*cis* → *trans*) has been shown to proceed via dissociation of PPh<sub>3</sub> with rearrangement of the thus formed *C*<sub>s</sub> isomer of [Mo(CO)<sub>4</sub>PPh<sub>3</sub>] to the *C*<sub>4v</sub> isomer prior to reaction with an incoming PPh<sub>3</sub> ligand.<sup>29</sup> Therefore, the photochemical stationary state of reaction 11 lies in favor of the less thermodynamically stable isomeric form of Mo(CO)<sub>4</sub>[PPh<sub>3</sub>]<sub>2</sub>, *cis*-Mo(CO)<sub>4</sub>[PPh<sub>3</sub>]<sub>2</sub>; or in other words the photochemical stationary state of reaction 11 represents an example of a conrathermodynamic process.

Our observations on the photochemistry of triphenylphosphine substituted molybdenum carbonyl derivatives are summarized in Scheme I.

Scheme I



The fact that both types of carbonyl ligands are photochemically labile in Mo(CO)<sub>5</sub>PPh<sub>3</sub> has been demonstrated by the following observations: (1) *trans*-Mo(CO)<sub>4</sub>(<sup>13</sup>CO)PPh<sub>3</sub> was observed from photolysis of Mo(CO)<sub>5</sub>PPh<sub>3</sub> in the presence of <sup>13</sup>CO in quantities generally greater than 20%. Since the [Mo(CO)<sub>4</sub>PPh<sub>3</sub>] (*C*<sub>4v</sub>) intermediate is unstable with respect to its *C*<sub>s</sub> form, it follows that there was some loss of an axial carbonyl ligand with trapping of the *C*<sub>4v</sub> intermediate by <sup>13</sup>CO before rearrangement. (2) Photolysis of *cis*-Mo(CO)<sub>4</sub>(<sup>13</sup>CO)PPh<sub>3</sub>, prepared from *cis*-Mo(CO)<sub>4</sub>[NHC<sub>5</sub>H<sub>10</sub>]PPh<sub>3</sub>

and  $^{13}\text{CO}$  thermally, with  $^{12}\text{CO}$  afforded some of the all- $^{12}\text{CO}$   $\text{Mo}(\text{CO})_5\text{PPh}_3$  species.<sup>30</sup>

Unfortunately, in order to determine quantitatively the extent of loss of axial vs. equatorial CO groups, it will be necessary to prepare a relatively pure sample of *trans*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{PPh}_3$  and subject it to photolysis in the presence of  $^{12}\text{CO}$ . Thus far, we have not been able to devise a synthesis of this species, and indeed feel that its preparation will be a real challenge.<sup>31</sup>

In order to further establish the reactivity patterns of the two geometries of the  $[\text{Mo}(\text{CO})_4\text{PPh}_3]$  intermediate with  $^{13}\text{CO}$  we have examined the photochemical reactions of *cis*- and *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  with  $^{13}\text{CO}$ . As indicated in Scheme I dissociation of  $\text{PPh}_3$  in the *cis* and *trans* derivatives initially leads exclusively to the  $C_s$  and  $C_{4v}$  forms of the  $[\text{Mo}(\text{CO})_4\text{PPh}_3]$  intermediate, respectively. When the *cis* derivative was photolyzed in the presence of  $^{13}\text{CO}$  mostly *cis*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{PPh}_3$  was formed with only a small quantity of *trans*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{PPh}_3$  being produced, thus indicating some slight equilibration of the  $C_s$  form with the  $C_{4v}$  isomeric form of the intermediate.<sup>32,33</sup> This result is in agreement with the fact that we observed a small degree of photoisomerization of *cis*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  to *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$ . A similar experiment employing the *trans* derivative resulted in production of sizable quantity of *cis*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{PPh}_3$  with around 20% *trans*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{PPh}_3$ , a significantly greater quantity than afforded from the reaction of *cis*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  with  $^{13}\text{CO}$ . This experiment again demonstrates the facile rearrangement of the  $C_{4v}$  structure of  $[\text{Mo}(\text{CO})_4\text{PPh}_3]$  to the  $C_s$  structure prior to  $^{13}\text{CO}$  incorporation.

Similar observations to those reported above for the photochemical reactions were noted as well in the thermal reactions of *cis*- and *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  with  $^{13}\text{CO}$ . That is, both *cis*- and *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  afforded mostly *cis*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{PPh}_3$  in thermal substitution reactions with  $^{13}\text{CO}$ . These findings would suggest that the equilibration of the 5-coordinate intermediates ( $C_{4v} \rightleftharpoons C_s$ ) in the photochemical process is not greatly affected by excess energy. However, the intermediates do not appear to be thermally equilibrated in either the thermal or photochemical processes prior to reacting with  $^{13}\text{CO}$  as evidenced by a difference in the relative quantities of axial and equatorial  $^{13}\text{CO}$ -labeled derivatives depending on whether one starts with *cis*- or *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$ . The details of the thermal substitution and isomerization reactions will be the subject of a future publication.

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- We have evidence that the intermediate involved in the preparation of this labeled derivative,  $[\text{Mo}(\text{CO})_4\text{PPh}_3]$  (square pyramidal with  $\text{PPh}_3$  in the equatorial plane), can undergo rearrangement to the axial  $\text{PPh}_3$  species to a small degree. This species could then react with  $^{13}\text{CO}$  to afford minute quantities of the *trans*- $\text{Mo}(\text{CO})_4(^{13}\text{CO})\text{PPh}_3$  isomer.
- Fortunately, this disubstituted species is expected to be present to only 50% the level of its *cis* analogue.
- In our previous publication (ref 26), we overestimated the degree of  $^{13}\text{CO}$  incorporation in  $\text{M}(\text{CO})_5\text{PPh}_3$  ( $\text{M} = \text{Mo}, \text{W}$ ) into an axial position because of our failure to correct for these effects.
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- It should also be noted that similar arguments can be put forth for the relative production of *cis* and *trans* isomers of  $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$ , although in this case the incoming ligand,  $\text{PPh}_3$ , can have a preference for one form of the intermediate.
- Photolysis of *cis*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  in the presence of  $\text{PPh}_3$  was found to result in the production of a small quantity of *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$ .
- D. J. Darensbourg, unpublished results.
- The all- $^{12}\text{CO}$  species was detected by an increase in the intensity of the highest frequency  $A_1 \nu(\text{CO})$  band at  $2072 \text{ cm}^{-1}$ .
- This preparation is severely hampered by the facile rearrangement of the  $[\text{Mo}(\text{CO})_4\text{PPh}_3]$  ( $C_{4v}$ ) intermediate. The directions we are currently exploring include low-temperature photolysis of *trans*- $\text{Mo}(\text{CO})_4[\text{PPh}_3]_2$  with  $^{13}\text{CO}$ , and oxygen exchange reactions with labeled hydroxide ion.
- That this equilibration occurs to only a slight extent has been further demonstrated in the thermal reactions of *fac*- $\text{Mo}(\text{CO})_3(^{13}\text{CO})(\text{triene})$  with  $\text{PPh}_3$  and diphos.<sup>33</sup> In these reactions the  $^{13}\text{CO}$  ligand in the bisphosphine derivatives has been shown to be primarily in an axial position, thereby indicating a barrier to scrambling of carbonyl ligands in the  $[\text{Mo}(\text{CO})_3(^{13}\text{CO})\text{PPh}_3]$  intermediate where the  $^{13}\text{CO}$  and  $\text{PPh}_3$  are both in the equatorial plane and *cis* to one another.
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