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# Intramolecular Isomerization of an Octahedral Complex: Bis(tri-*n*-butylphosphine)molybdenum Tetracarbonyl

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The cis $\rightleftharpoons$ trans isomerization reaction of $Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ has been studied kinetically. The trans isomer was found to be slightly more stable than the cis isomer ($\Delta G \approx -1$ kcal) due to enhanced steric interactions in the cis isomeric form. This isomerization reaction is described as an *intramolecular, nondissociative process* on the basis of the lack of $^{13}CO$ incorporation into either *cis*- or *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ or formation of $Mo(CO)_4(^{13}CO)P\text{-}n\text{-}Bu_3$ during the rearrangement. A trigonal rotation mechanism is used to account for these observations. The activation energy for the cis → trans reaction was found to be ~5 kcal less than that observed for dissociative phosphine loss in closely related *cis*-$Mo(CO)_4L_2$ derivatives containing sterically more demanding phosphine ligands. Analogous observations were also made on the bis(triethylphosphine)molybdenum tetracarbonyl derivatives.

## Introduction

Disubstituted molybdenum tetracarbonyl octahedral complexes exhibit both cis and trans stereochemistries. For many of the monoligated phosphine species the trans derivative has been shown to be the thermodynamically more stable isomeric form; i.e., the equilibrium (eq 1) lies toward the right.[1-6]

$$cis\text{-}Mo(CO)_4L_2 \rightleftharpoons trans\text{-}Mo(CO)_4L_2 \qquad (1)$$

When L = $PPh_3$ we have found that the cis isomer thermally rearranges completely to the trans isomer via a dissociative process involving Mo–P bond cleavage.[5,6] However, photochemically at ambient temperature, *trans*-$Mo(CO)_4(PPh_3)_2$ isomerizes to *cis*-$Mo(CO)_4(PPh_3)_2$.[4] These results are explained employing a ground-state geometry for the five-coordinate intermediate $Mo(CO)_4PPh_3$ where $PPh_3$ preferentially occupies an equatorial position in the square-pyramidal structure.[7] It would be anticipated that the reaction described in eq 1 would be dependent on both the steric and electronic properties of the ligand L.

Stereochemical nonrigidity occurring by a non-bond-breaking mechanism is uncommon in octahedral complexes containing monodentate ligands, and the barrier to intramolecular rearrangement in most octahedral complexes is expected to be quite large.[8,9] The dihydrido complexes $H_2ML_4$ (M = Fe or Ru; L = phosphine or phosphite) have, however, been shown to undergo such rearrangements.[10] Also, Pomeroy and Graham[11] have observed that the cis → trans isomerization reactions of $Ru(CO)_4(SiCl_3)_2$ and $Os(CO)_4(SiMe_3)_2$ occur with no bond cleavage. Analogous processes of octahedral complexes of zerovalent $d^6$ metals, i.e., $d^6$ metals complexed entirely by neutral ligands, have not been *unambiguously* established until now. During recent studies of phosphine and phosphite dissociative processes in *cis*-$Mo(CO)_4L_2$ derivatives, we noted that *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ isomerized thermally to a cis–trans mixture, dominant in the *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ form, with no apparent ligand dissociation. Definitive experiments which establish this unusual intramolecular isomerization (eq 2) are herein reported.

$$cis\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \rightleftharpoons trans\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \qquad (2)$$

## Experimental Section

**Materials.** Molybdenum hexacarbonyl was the generous gift of Climax Molybdenum Corp. Tri-*n*-butylphosphine, tri-*o*-tolyl phosphite, and triethylphosphine were purchased from Aldrich Chemical Co., Strem Chemicals, and PCR Research Chemicals, Inc., respectively. Heptane was reagent grade material obtained from Matheson, Coleman, and Bell. Carbon monoxide (>90% $^{13}C$) was acquired from Prochem, B.O.C. Ltd., London. *cis*-$Mo(CO)_4(NHC_5H_{10})_2$ was prepared from $Mo(CO)_6$ and excess piperidine in refluxing heptane.[5]

**Compound Preparations. (a) *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$.** This complex was prepared in its isomerically pure form by the published procedure.[5] Two grams of *cis*-$Mo(CO)_4(NHC_5H_{10})_2$ was stirred under reflux in dichloromethane with 2 mL of tri-*n*-butylphosphine for 15 min. The reaction mixture was filtered through Celite, and the filtrate was reduced in volume followed by the addition of methanol. Upon cooling of the solution below 0 °C, *white* crystals formed and were isolated by filtration. Purification was accomplished by two recrystallizations from cold methanol and vacuum-drying (mp 31.5 °C). Anal. Calcd for $Mo(CO)_4(P(C_4H_9)_3)_2$: C, 54.89; H, 8.89. Found: C, 55.46; H, 8.92.

**(b) *cis*-$Mo(CO)_4(PEt_3)_2$.** This complex was prepared in an identical manner as that described above for the tri-*n*-butylphosphine derivative. The compound was purified by recrystallization from cold methanol and vacuum-dried to afford *white* crystals, mp 70.5–71.5 °C (lit.[2] mp 73 °C).

**(c) *fac*-$Mo(CO)_3(^{13}CO)(P\text{-}n\text{-}Bu_3)_2$.** $Mo(CO)_3(^{13}CO)$(triene)[12,13] (triene = bicyclo[6.1.0]nona-2,4,6-triene) and $P\text{-}n\text{-}Bu_3$ were reacted at room temperature in chloroform for 2 h. The reaction solution was filtered through Celite, and the solvent was removed under vacuum. Methanol was added to the light yellow, oily residue, and the solution was stored below 0 °C to afford *white* crystals of the bis(tri-*n*-butylphosphine) derivative.

**(d) *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$.** Two grams of *cis*-$Mo(CO)_4(NHC_5H_{10})_2$ was stirred under reflux in heptane with 2 mL of tri-*n*-butylphosphine for 4 h. The solvent was removed under reduced pressure to yield a yellow oil. Methanol was added to the oil, and the mixture was cooled to below 0 °C at which time *yellow* crystals formed. Further purification was achieved by washing the crystalline product repeatedly with small volumes of methanol and finally by recrystallization from cold methanol followed by vacuum-drying (mp 41.5–42 °C). Anal. Calcd for $Mo(CO)_4(P(C_4H_9)_3)_2$: C, 54.89; H, 8.89. Found: C, 55.19; H, 8.46.

**Kinetic Measurements.** The isomerization reactions of $Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ were carried out in Schlenk storage tubes (25-mL capacity) under an atmosphere of carbon monoxide in heptane solvent. The tubes were fitted with septum caps secured by copper wire. The reaction flasks were placed in a constant-temperature bath, and samples were withdrawn at regular time intervals with a hypodermic syringe for infrared spectral analysis. The rates of *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ → *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ were followed by observing the decrease in the $A_1^{(1)}$ band (1913.7 $cm^{-1}$) of the cis isomer with time. Figure 1 illustrates the changes in $\nu$(CO) absorptions which take place as the cis–trans equilibrium is established (the $A_1^{(1)}$ band used in monitoring the kinetics is indicated by an asterisk). Rate constants ($k_1 + k_{-1}$) were calculated by use of a linear least-squares computer program for the first-order rate plots of ln ($A_t - A_e$) vs. time, where $A_t$ is the absorbance at time $t$ and $A_e$ is the absorbance at equilibrium. Similarly, the rates of *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ → *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ were determined by following the increase in the $A_1^{(1)}$ band of the cis isomer with time. The equilibrium constant for the cis $\rightleftharpoons$ trans isomerization was determined spectroscopically employing the $B_1$ band (1898.5 $cm^{-1}$) of the cis isomer and the $E_u$ band (1885.4 $cm^{-1}$) of the trans isomer.

**Infrared Measurements and Vibrational Analysis.** The infrared spectra were recorded on either a Perkin-Elmer 521 or 283 spectrophotometer, both equipped with a linear absorbance potentiometer.

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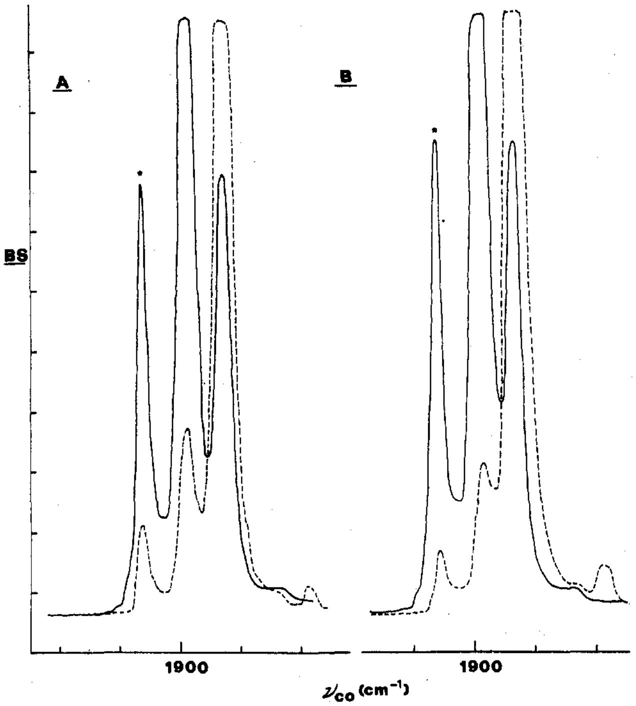

**Figure 1.** Changes in $\nu$(CO) absorptions as cis–trans equilibrium is established starting from the pure cis isomer: —, pure cis isomer; - - -, near-equilibrium mixture; A, $Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ derivative; B, $Mo(CO)_4(PEt_3)_2$ derivative. The peak labeled with an asterisk denotes the band employed in monitoring the kinetics of the reaction.

The spectra were calibrated against a water vapor spectrum below 2000 cm$^{-1}$ and against a CO spectrum above 2000 cm$^{-1}$. Matched sodium chloride cells were used in the measurements.

Initial CO stretching force constant calculations for *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ were performed by use of only the $^{12}CO$ frequency data and a modified Cotton–Kraihanzel[14] approach refined by Jernigan, Brown, and Dobson[15] and by employment of a program developed in our laboratories.[16] Similarly, the C–K procedure was employed in calculating the initial CO stretching force field for *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$. The trial force constants were refined by use of the $^{13}CO$ frequency data and an iterative computer program[17] 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 trial force constants were refined to reproduce the observed $^{12}CO$ and $^{13}CO$ vibrations generally to within an average of <1.0 cm$^{-1}$.

**$^{13}C$ Nuclear Magnetic Resonance Measurements.** $^{13}C$ resonances were measured on a JEOL FX60 operated at 15.03 MHz with an internal deuterium lock. Samples were run in $CDCl_3$ solvent in 10-mm tubes. Chemical shifts are expressed in ppm relative to $Me_4Si$, with positive $\delta$(C) values being at lower field than $Me_4Si$.

## Results

Upon heating *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ in tetrachloroethylene or heptane at elevated temperatures (60–80 °C), we observed an isomerization to a cis–trans mixture (~85% trans). The reaction solution remained clear, changing from the colorless solution of the pure cis isomer to the slightly yellow solution of the trans isomer, during the rearrangement with no decomposition occurring (spectroscopically, 100% of the starting material is accounted for in the isomeric mixture). The identical distribution of *cis*- and *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ can be reached as well by thermolysis of the pure *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ derivative. The position of equilibrium was not very temperature dependent between 60 and 80 °C, with $K_{eq}$ determined to be 5.3 ± 0.3. The isomerization reaction (eq 2) was carried out in a >90% $^{13}CO$ atmosphere with *no* incorporation of the labeled carbon monoxide in the *cis*- or *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ complexes and no formation of $Mo(CO)_4(^{13}CO)P\text{-}n\text{-}Bu_3$.[18] Additional confirmation that the reaction was proceeding without the production of an unsaturated intermediate (i.e., a non-bond-breaking process) was demonstrated when the reaction was performed in the presence of $P(O\text{-}o\text{-}tolyl)_3$ where no phosphine exchange was noted.

Table I. First-Order Rate Constants for the Isomerization Reactions of *cis*- and *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ in Heptane

| obsd process | temp, °C | rate constants × $10^4$, s$^{-1}$ | | |
|---|---|---|---|---|
| | | $k_1 + k_{-1}$ [a] | $k_1$ [b] | $k_{-1}$ [b] |
| cis → trans | 64.8 | 1.99 ± 0.05 | 1.67 | 0.32 |
| trans → cis | 64.8 | 1.85 ± 0.01 | 1.55 | 0.30 |
| cis → trans | 70.2 | 3.59 ± 0.08 | 3.02 | 0.57 |
| cis → trans | 74.1 | 5.11 ± 0.06 | 4.29 | 0.82 |
| cis → trans | 79.2 | 8.96 ± 0.59 | 7.54 | 1.42 |

[a] Error limits for rate constant data represent 90% confidence limits. [b] Individual rate constants calculated employing a $K_{eq}$ value of 5.3.

Table II. Activation Parameters for Isomerization Reaction of $Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ in Heptane

| process | $\Delta H^*$, kcal/mol [a] | $\Delta S^*$, eu [a] |
|---|---|---|
| cis → trans | 24.5 ± 1.6 | −5.6 ± 4.8 |
| trans → cis | 24.2 ± 1.3 | −9.8 ± 4.0 |

[a] Error limits for activation parameters represent 90% confidence limits.

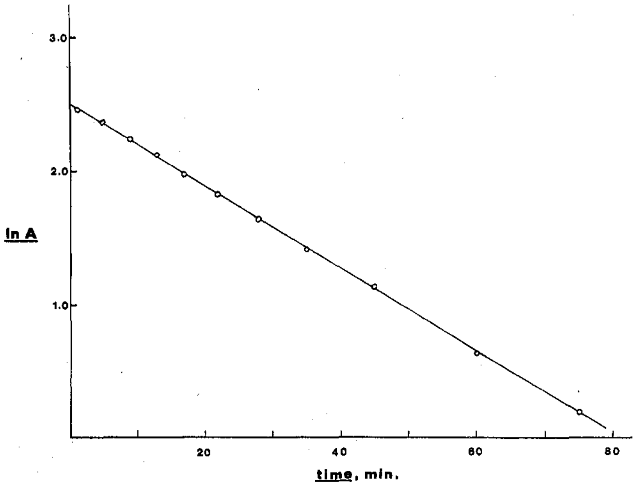

**Figure 2.** First-order rate plot for the isomerization reaction of $Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ in heptane at 74.1 °C starting from pure *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$. *A* represents the absorbance values in arbitrary units of mm.

The rates of isomerization were analyzed as opposing first-order reactions (eq 3) where $K_{eq} = k_1/k_{-1} = [trans\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]_{eq}/[cis\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]_{eq}$.

$$cis\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \quad (3)$$

Since $K_{eq}$ is much less than 100, $k_1$ being approximately $5k_{-1}$, both reactions must be considered. Values of the composite rate constants ($k_1 + k_{-1}$) determined for reaction 3 approached from either direction starting with the respective pure complex are given in Table I for several temperatures. Also included in Table I are the individual rate constants, $k_1$ and $k_{-1}$, obtained from $k_1 + k_{-1}$ values and the spectroscopically determined equilibrium constant. Figure 2 illustrates a typical linear first-order rate plot obtained over 3.5 half-lives. Although both isomeric forms of $Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ are thermally stable under the reaction conditions, the reactions were carried out in a CO atmosphere in order to be able to detect any formation of $Mo(CO)_5P\text{-}n\text{-}Bu_3$ during the isomerization process. The rates of isomerization were the same

**Table III.** Calculated and Observed CO Stretching Frequencies ($cm^{-1}$) in *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ Species[a]

| molecule | symmetry | obsd[b] | calcd |
|---|---|---|---|
| all $^{12}CO$ species | $A_1$ | *2012.4* | 2012.6 |
| | $A_1$ | *1913.7* | 1912.5 |
| | $B_1$ | *1898.5* | 1899.5 |
| | $B_2$ | *1886.7* | 1886.8 |
| mono-$^{13}CO$ axially substituted | $A'$ | *1999.6* | 1999.7 |
| | $A'$ | *1910.2* | 1910.5 |
| | $A'$ | *1869.9* | 1871.2 |
| | $A''$ | 1886.7 | 1886.8 |
| mono-$^{13}CO$ equatorially substituted | $A'$ | *2005.8* | 2008.2 |
| | $A'$ | 1906.0 | 1905.0 |
| | $A'$ | *c* | 1856.1 |
| | $A''$ | 1899.5 | 1899.5 |

[a] Frequencies were measured in heptane solution. [b] The eight frequencies in italics were used as input and were calculated with an average error of 0.8 $cm^{-1}$ or 0.043%. Force constants calculated were $k_1 = 14.78_1$, $k_2 = 15.25_1$, $k_c = 0.35_0$, $k_c' = 0.40_7$, and $k_t = 0.68_3$. [c] This frequency was buried beneath the more prominent band of *trans*-$Mo(CO)_3(^{13}CO)(P\text{-}n\text{-}Bu_3)_2$.

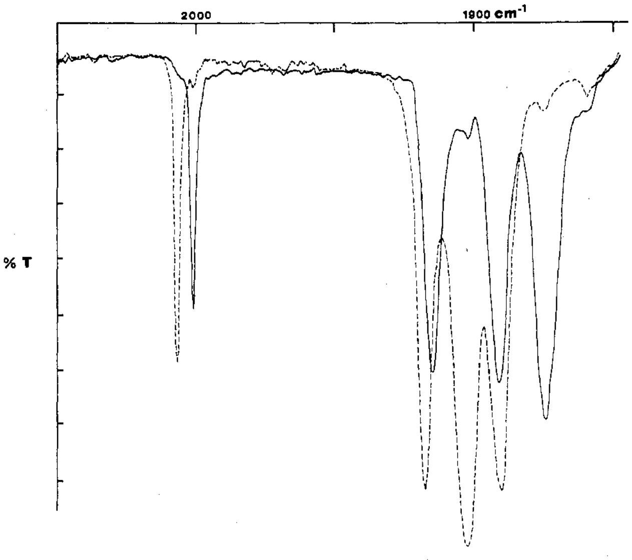

**Figure 3.** Infrared spectra in $\nu(CO)$ region of *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ in heptane: ---, natural-abundance $^{13}CO$ spectrum; —, axially mono-$^{13}CO$ *cis*-$Mo(CO)_3(^{13}CO)(P\text{-}n\text{-}Bu_3)_2$ spectrum.

in either a CO or $N_2$ atmosphere. The activation parameters for the isomerization processes are reported in Table II. The more negative entropy of activation for trans → cis accounts for the slightly greater stability of the trans isomer, $\Delta G$ being about −1 kcal for reaction 3.

The stereospecifically, axially labeled $^{13}CO$ species *cis*-$Mo(CO)_3(^{13}CO)(P\text{-}n\text{-}Bu_3)_2$ (I) was prepared from $Mo(CO)_3(^{13}CO)$(triene) (triene = bicyclo [6.1.0]nona-2,4,6-triene) and P-*n*-$Bu_3$.[13] The position of the $^{13}CO$ in species I was determined by $\nu(CO)$ infrared spectroscopy coupled with restricted CO force field computations (see Table III and Figure 3) and by $^{13}C$ NMR spectroscopy (triplet centered at 211.5 ppm with $J(^{31}P-^{13}C)$ = 9.76 Hz). Species I was subjected to the isomerization reaction resulting in formation of $^{13}CO$-labeled *trans*-$Mo(CO)_3(^{13}CO)(P\text{-}n\text{-}Bu_3)_2$ ($\nu(CO)$ is shown in Table IV, and $^{13}C$ NMR was a triplet centered at 212.8 ppm with $J(^{31}P-^{13}C)$ = 8.79 Hz) and a mixture of axially and equatorially $^{13}CO$-labeled *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ (see Table III and Figure 4). No intramolecular carbon monoxide ligand exchange was observed in the stereospecifically labeled cis isomer prior to the establishment of the cis–trans equilibrium; i.e., there was no lower barrier process of CO ligand interchange other than formation of the *trans*-$Mo(CO)_3(^{13}CO)(P\text{-}n\text{-}Bu_3)_2$ species.

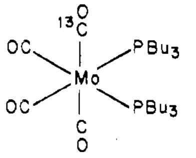

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**Table IV.** Calculated and Observed CO Stretching Frequencies ($cm^{-1}$) in *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ Species[a]

| molecule | symmetry | obsd[b] | calcd |
|---|---|---|---|
| all $^{12}CO$ species | $A_{1g}$ | | 2050.4 |
| | $B_{1g}$ | | 1933.9 |
| | $E_u$ | *1885.4* | 1886.1 |
| mono-$^{13}CO$ substituted | $A_1$ | | 2041.1 |
| | $A_1$ | *1925.5* | 1926.4 |
| | $A_1$ | *1857.9* | 1859.7 |
| | $B_1$ | 1885.4 | 1886.1 |

[a] Frequencies were measured in heptane solution. [b] The three frequencies in italics were used as input and were calculated with an average error of 1.1 $cm^{-1}$ or 0.059%. Force constants calculated were $k = 15.19_9$, $k_c = 0.46_9$, and $k_t = 0.83_7$.

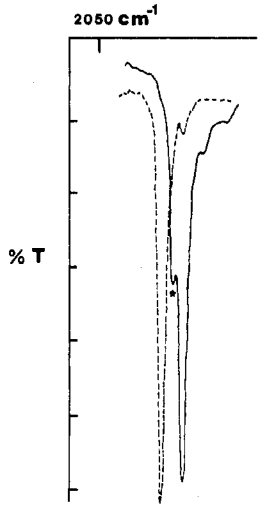
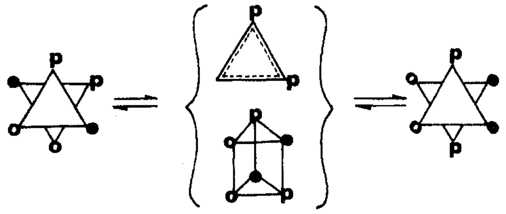


**Figure 4.** Spectra in high-frequency $\nu(CO)$ region for *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ species: —, stereospecially, axially $^{13}CO$-labeled derivative, with isomerization near completion, the peak denoted by an asterisk corresponding to that of the equatorially $^{13}CO$-labeled derivative (2005.8 $cm^{-1}$ in Table I); ---, natural-abundance $^{13}CO$ derivative.

Scheme I



## Discussion

On the basis of the lack of $^{13}CO$ incorporation and phosphine exchange during the rearrangement reaction of $Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$, it is concluded that a non-bond-breaking (Mo–C or Mo–P) process is the lowest energy mechanism for isomerization.[19] This most likely proceeds through a trigonal-prismatic intermediate or transition state (Scheme I, where ○ and ● represent equatorial and axial CO ligands, respectively). The mechanism described in Scheme I is commonly referred to as the "Bailar twist";[20] however no distinction is intended here between the face rotation and the other alternative rotation processes, e.g., the Rây–Dutt[21] or the Springer–Sievers[22] processes.

A notable observation in this work is the lack of axial CO–equatorial CO exchange in *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ in advance of formation of the trans isomer, for the trigonal-prismatic intermediate or transition state afforded by means of a 60° clockwise rotation does not equilibrate axial and equatorial CO ligands. However, a 60° counterclockwise rotation of the two triangular octahedral faces, which is sterically quite hindered for bulky ligands, would equilibrate the CO groups. This type of process has been proposed to explain the axial–equatorial exchange of carbonyl ligands in disubstituted complexes containing bidentate ligands, namely, *cis*-$L_2Mo(CO)_4$ ($L_2$ = substituted diazabutadienes)[23a] and (1,3-butadiene)$Cr(CO)_4$.[23b]

The activation energy for the herein reported cis → trans isomerization reaction of $Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ is about 5 kcal lower in energy than that measured for the dissociative loss of phosphine ligands in *cis*-$Mo(CO)_4(PPh_3)_2$ and *cis*-$Mo(CO)_4(PCy_2Ph)_2$.[6] We have reexamined the cis ⇌ trans isomerization reaction of $Mo(CO)_4(PEt_3)_2$ previously described by Poilblanc and Bigorgne,[2] since triethylphosphine is electronically and sterically quite similar to tri-*n*-butylphosphine. This process was also found to be intramolecular, with only small differences in rates and $K_{eq}$ being noted for the two derivatives.[24] It therefore appears that for more bulky phosphines (cone angles:[25] $PEt_3$, 132°; P-*n*-$Bu_3$, 132°; $PPh_3$, 145°; $PCy_2Ph$, 162°) like $PPh_3$ and $PCy_2Ph$, Mo–P bond cleavage is a more favorable process for stereochemical rearrangements than transformation to a trigonal-prismatic intermediate or transition state where steric interactions are greatly enhanced.[26]

Other isomerization reactions of disubstituted group 6B metal carbonyls which are thought to be occurring by a nondissociative, intramolecular process have been published. These include isomerization reactions of $M(CO)_4(PR_3'')C(OR)R'$,[27] $W(CO)_4(^{13}CO)CS$,[28] and (Imid)$M(CO)_4$ (Imid = 1,3-dimethyl-4-imidazolin-2-ylidene).[29] Of interest is the observation that the thermal isomerization of the latter complex is greatly enhanced upon formation of the monocationic species.[30] The oxidation of the more highly substituted molybdenum derivatives *cis*-$Mo(CO)_2$(bidentate phosphine)$_2$ to the paramagnetic, 17-electron $[Mo(CO)_2(\text{bidentate phosphine})_2]^+$ species is also known to occur with a concomitant rapid cis → trans isomerization.[31,32] In the case of bidentate phosphine = 1-(dimethylphosphino)-2-(diphenylphosphino)ethane, this isomerization process has been observed to be consistent with a trigonal twist mechanism.[31] We have plans to carry out similar kinetic investigations of the oxidized form of the bis(phosphine) derivatives reported upon in this study. Further, it is possible that the number of cases of non-bond-breaking isomerization processes in octahedral metal carbonyl derivatives is less rare than previously suspected; thus a search for other examples of nonrigidity in bis(phosphine) complexes of the group 6B metals is in progress.[33]

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**Registry No.** *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$, 16244-54-5; *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$, 17652-79-8; *cis*-$Mo(CO)_4(PEt_3)_2$, 19217-80-2; *fac*-$Mo(CO)_3(^{13}CO)(P\text{-}n\text{-}Bu_3)_2$, 68122-37-2; *cis*-$Mo(CO)_4(NHC_5H_{10})_2$, 65337-26-0; $Mo(CO)_3(^{13}CO)$(triene), 67392-40-9.

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