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# FT-IR and 2-D NOE Phosphorus-31 NMR Spectroscopic Studies on Stereochemically Nonrigid, Octahedral Organochromium(0) Complexes

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The results of an FT-IR and 2-D NOE $^{31}$P NMR study of the isomerization processes in the stereochemically nonrigid octahedral $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = O, S, Se) complexes are reported. These complexes rearrange intramolecularly, and in the case of the thio- and selenocarbonyl derivatives, the lowest energy path for the rearrangement is via trigonal-prismatic (Bailar) intermediates rather than bicapped-tetrahedral ones. This is the first time that it has been possible to demonstrate the favored mechanism of isomerization of such octahedral complexes. The activation parameters for the isomerization reactions ($\Delta H^* =$ 15.5–18.0 kcal mol$^{-1}$; $\Delta S^* = -20$ to $-28$ cal mol$^{-1}$ deg$^{-1}$) and the spin-lattice relaxation times ($T_1 =$ 1.75–3.18 s) for the phosphorus nuclei in the $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = O, S, Se) isomers are also reported.

## Introduction

The arene displacement reactions of ($\eta$-arene)$Cr(CO)_2(CX)$ (X = S, Se) complexes by tertiary phosphite [L = $(RO)_3P$; R = Me, Et, *n*-Bu, Ph] and tridentate tertiary phospine ligands {L-L-L = triphos-U [$(MeC(CH_2P(Ph)_2)_3$], triphos [$(Ph_2PCH_2CH_2)_2PhP$]}[1,2] have recently been investigated. The stereochemistries of the isomeric $Cr(CO)_2(CX)L_3$ and (L-L-L)$Cr(CO)_2(CX)$ reaction products were established by FT-IR [$\nu$(CO) region] and $^{31}$P NMR spectroscopy. For the $Cr(CO)_2(CX)L_3$ complexes, the major products are the *mer*-I, not the *fac* isomers, as was the case for the triene displacement reactions of ($\eta$-$C_7H_8$)$M(CO)_3$ and the arene displacement reactions of ($\eta$-arene)$M(CO)_3$ (M = Cr, Mo, W).[3] The formation of the *mer*-I isomers may result from isomerization of the *fac* intermediates during the reactions. However, there have recently been several reports of *intramolecular* isomerization of group 6 metal[10] carbonyl complexes.[4-9,11-14]

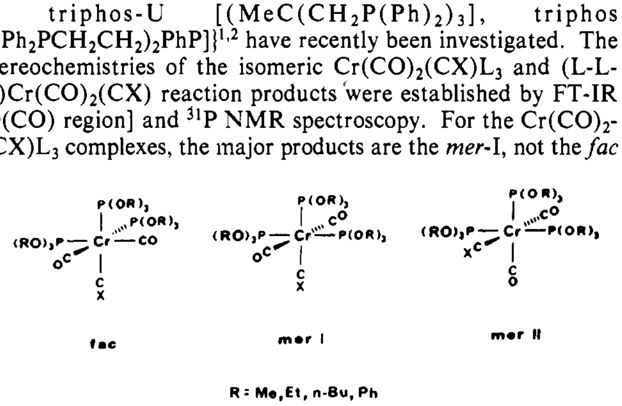

**Table I.** Activation Parameters Reported for Intramolecular Isomerizations of Group 6 Metal Carbonyl Complexes

| complex | process | $\Delta H^*$, kcal mol$^{-1}$ | $\Delta S^*$, cal mol$^{-1}$ deg$^{-1}$ | ref |
|---|---|---|---|---|
| $Cr(CO)_4$-[C(OMe)Me]($Et_3P$) | cis → trans | 21.2 ± 0.5 | −6.5 ± 1.5 | 4, 5 |
| | trans → cis | 22.5 ± 0.5 | −3.5 ± 1.5 | |
| $Cr(CO)_4(^{13}CO)(Et_3P)$ | cis → trans | 26.6 ± 4.3 | 1.8 ± 13.1 | 11 |
| $Mo(CO)_4(n\text{-}Bu_3P)_2$ | cis → trans | 24.5 ± 1.6 | −5.6 ± 4.8 | 7 |
| | trans → cis | 24.2 ± 1.3 | −9.8 ± 4.0 | |
| $W(CO)_4(^{13}CO)(Et_3P)$ | cis → trans | 9.2 ± 3.7 | −54.9 ± 11.4 | 11 |
| $W(CO)_4(^{13}CO)(CS)$ | trans → cis | 31.5 ± 1.9 | 9.1 ± 5 | 6 |

Intramolecular rearrangements of octahedral complexes have long been thought to proceed through either trigonal-prismatic (Bailar)[15] or bicapped-tetrahedral[16] intermediates (or transition states) (see Figure 1). One of the first examples of intramolecular rearrangement in group 6 metal complexes reported was the isomerization of $Cr(CO)_4[C(OMe)Me](Et_3P)$.[4,5] Shortly afterward, *trans*-$W(CO)_4(^{13}CO)(CS)$ was also shown to undergo isomerization through a nondissociative mechanism.[6] Since then, several other complexes such as $M(CO)_{6-n}(R_3P)_n$ (M = Cr, Mo; W, *n* = 1, 2; R = Me, Et, *i*-Pr, *n*-Bu, OMe, OEt) are considered to isomerize by nondissociative pathways,[7-9] with the rate of rearrangement decreasing in the order Cr > W > Mo.[9,11] Similarly, intramolecular isomerization of $M(CO)_4(PF_3)_2$ (M = Cr, Mo, W) has been reported.[12] Activation parameters have been determined for several of the complexes mentioned (Table I). In the case of *trans*-$Cr(CO)_4(^{13}CO)(Et_3P)$[11] and *trans*-$W(CO)_4(^{13}CO)(CS)$,[6] large positive enthalpies of activation and positive entropies of activation were obtained for isomerization to the cis isomers. On the basis of the large enthalpies of activation, significant bond lenghening in the activated states was postulated to occur. For *trans*-$W(CO)_4(^{13}CO)(Et_3P)$,[11] the isomerization process involved a small enthalpy and a large negative entropy, supportive of a trigonal-prismatic twist mechanism.

In view of the current interest in isomerization processes of octahedral complexes, we decided it would be worthwhile investigating the possibility that the *mer*-I-$Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = S, Se) complexes isolated in our previous work might be formed by intramolecular isomerization of the corresponding *fac* isomers. The results of an FT-IR and 2-D NOE $^{31}$P NMR investigation of these isomerizations are reported in this paper. Not only have we been able to demonstrate that these complexes do undergo rearrangement intramolecularly, but we have also managed to show, for the first time, that a trigonal-prismatic twist

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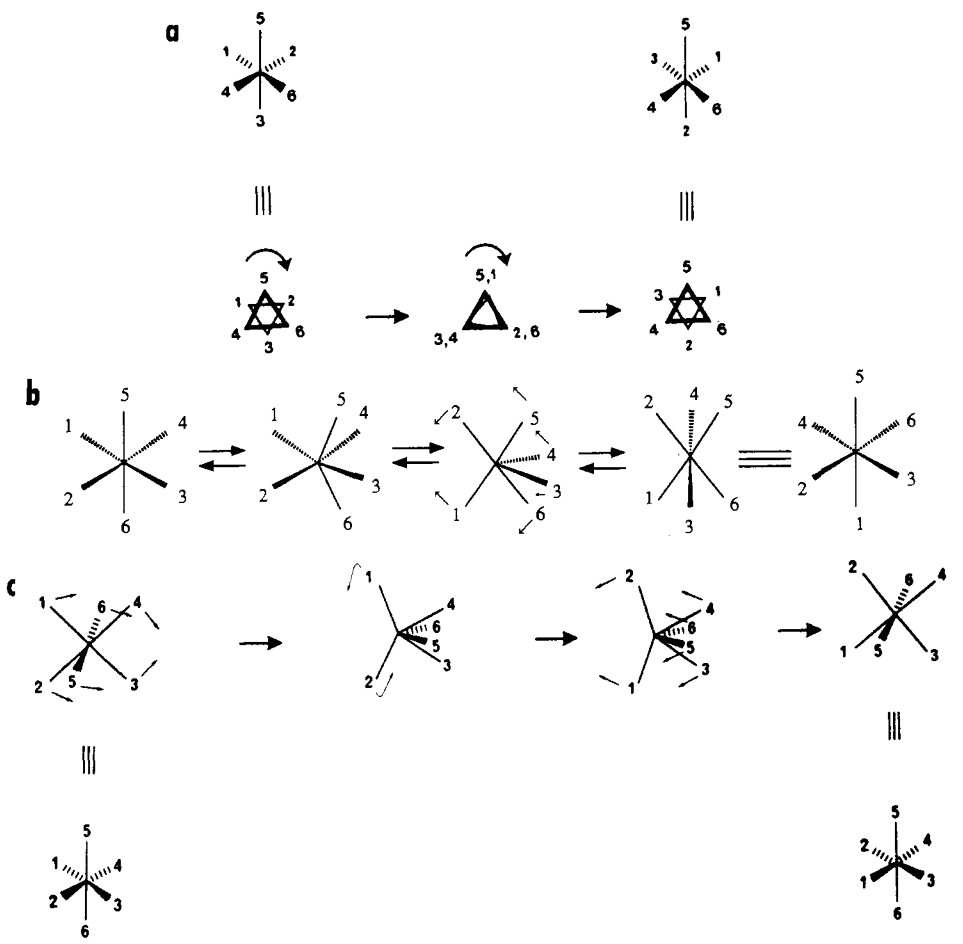

**Figure 1.** Proposed rearrangement pathways available to octahedral complexes: (a) through a trigonal-prismatic intermediate; (b) through a bicapped-tetrahedral intermediate with a 90° rotation of the tetrahedral edge; (c) through a bicapped-tetrahedral intermediate with a 180° rotation of the tetrahedral edge.

is the lowest energy pathway for such rearrangements.

## Experimental Section

The $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = S, Se) complexes were prepared from ($\eta$-arene)$Cr(CO)_2(CX)$ complexes by the synthetic procedures described in our earlier papers.[2,3]

**Synthesis of $Cr(CO)_2(^{13}CO)_3(CS)$.** In a typical experiment, ($\eta$-$PhCO_2Me$)$Cr(CO)_2(CS)$ (10 mg) was dissolved in THF (10 mL) and the solution transferred under $N_2$ to a specially constructed, high-pressure stainless-steel reaction vessel, lined with Teflon jacket (12 mL) and connected to a second stainless-steel chamber containing a measured amount (transferred on a vacuum line through a manometer) of $^{13}CO$ adsorbed on charcoal. The solution was degassed by three freeze–thaw cycles, and $^{13}CO$ was then admitted into the solution chamber to give 20-atm pressure. The valve to the $^{13}CO$ storage chamber was then closed. The solution was heated at 65 °C by an oil bath for periods of 8 h. Unreacted $^{13}CO$ was then readsorbed on the charcoal in the stainless-steel storage chamber upon opening the valve between the two chambers, while both chambers were kept submerged in liquid $N_2$. The product was isolated by careful evaporation of the solvent under reduced pressure at 15 °C due to the volatility of $Cr(CO)_2(^{13}CO)_3(CS)$.[17] $^{13}C$ NMR (10 scans) (relative to TMS): 212.1 (d, $J$ = 5 Hz, cis CO), 209.2 ppm (t, $J$ = 5 Hz, trans CO). FT-IR (Nicolet 6000 spectrometer, resolution 1 $cm^{-1}$; in $CS_2$ solution): $\nu$(CO) 2066 m, 2056 w, 2008 m, 1988 m, 1978 s, 1958 vs, 1956 vs, 1945 m $cm^{-1}$. The high-resolution mass spectrum of the product was obtained with a Du Pont 21-492B spectrometer interfaced to a Hewlett Packard computer. Mol wt: calcd for $^{13}C_3C_3O_5SCr$, 238.987; found, 238.984.

When the above reaction was performed by using less than 1-atm $^{13}CO$ pressure, partial decomposition of the starting material was observed. With octane in place of THF as the solvent and under conditions identical with those described above, no reaction occurred and the starting material was recovered unchanged.

**Kinetic Investigation of the Isomerization of the $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = O, S, Se) Complexes.** The *fac* $\rightleftharpoons$ *mer*-I isomerization reacions of the three complexes were monitored by FT-IR spectroscopy in the $\nu$(CO) region. Solutions of the complexes were prepared in dichloroethane (DCE) and transferred under $N_2$ to a thermostated IR cell (0.1-mm path length, NaCl windows) constructed in-house according to a design published earlier.[18] The thermostated-cell assembly was placed in the IR beam, and spectra were acquired at known time intervals. The rate of *fac* → *mer* isomerization of the tricarbonyl complex was followed by monitoring the decrease in intensity of the $a_1$ peak of the *fac* isomer, while the rates of *mer*-I → *fac* isomerization of the thio- and selenocarbonyl derivatives were monitored by the growth of the a′ peak of the *fac* isomers. Rate constants ($k_1 + k_{-1}$) were calculated from the first-order rate plots of ln $[A_e/(A_e - A_t)]$ vs time, where $A_t$ is the absorbance at time $t$ and $A_e$ is the absorbance at equilibrium, by using a linear least-squares program (Poltrax 2 from Engineering-Science Inc., Atlanta, GA). The rate constants for the forward and reverse reactions were obtained by solving eq 1 and 2, where $k_c$ is the calculated rate constant

$$k_c = k_1 + k_{-1} \qquad (1)$$

$$K_{eq} = k_1/k_{-1} \qquad (2)$$

and $K_{eq}$ was determined from the integrated areas of the resonances of the isomers in the $^{31}P$ NMR spectra recorded on a Varian XL-300 NMR spectrometer. The activation parameters were calculated from the rate constants at three different temperatures. The errors reported for the activation parameters correspond to one standard deviation.

**Monitoring the Stereochemical Nonridigity of $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = O, S, Se) Complexes by $^{31}P$ NMR Spectroscopy.** Two-dimensional NOE $^{31}P$ NMR measurements were performed on a Varian XL-300 spectrometer equipped with a 5-mm broad-band probe. $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = O, S, Se) was dissolved under $N_2$ in deuteriotoluene and the solution heated in the probe at temperatures ranging from 30 to 80 °C. Usually 4–32 transients were coadded to achieve a good S/N ratio. A total of 128–256 FIDs were acquired, and

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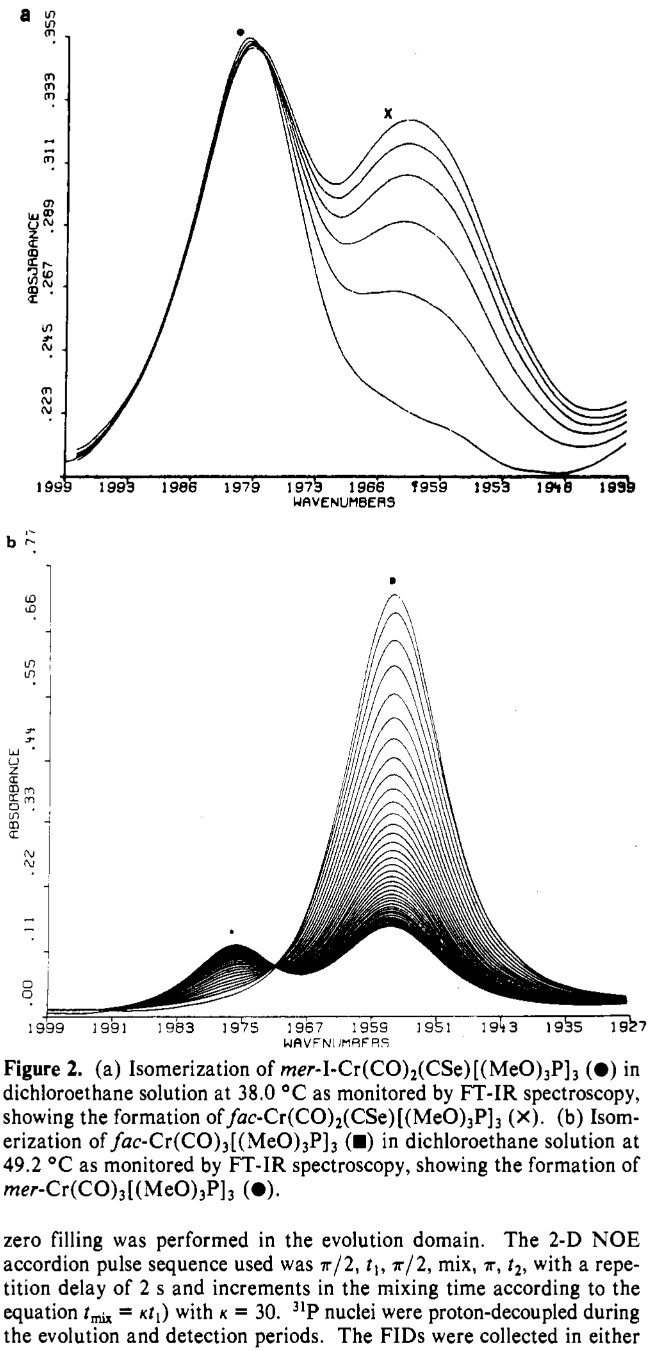

Figure 2. (a) Isomerization of *mer*-I-$Cr(CO)_2(CSe)[(MeO)_3P]_3$ (●) in dichloroethane solution at 38.0 °C as monitored by FT-IR spectroscopy, showing the formation of *fac*-$Cr(CO)_2(CSe)[(MeO)_3P]_3$ (×). (b) Isomerization of *fac*-$Cr(CO)_3[(MeO)_3P]_3$ (■) in dichloroethane solution at 49.2 °C as monitored by FT-IR spectroscopy, showing the formation of *mer*-$Cr(CO)_3[(MeO)_3P]_3$ (●).

zero filling was performed in the evolution domain. The 2-D NOE accordion pulse sequence used was $\pi/2$, $t_1$, $\pi/2$, mix, $\pi$, $t_2$, with a repetition delay of 2 s and increments in the mixing time according to the equation $t_{mix} = \kappa t_1$) with $\kappa = 30$. $^{31}P$ nuclei were proton-decoupled during the evolution and detection periods. The FIDs were collected in either a [512 × 512] or [1024 × 1024] matrix. The data matrices were Fourier transformed in two dimensions and plotted by a contour-plot program. The digital resolution in the evolution domain is $(sw)_2/NI$, where $(sw)_2$ is the spectral width in the evolution domain and NI is the number of increments or FIDs. The digital resolution in the detection domain is equal to 1/AT (AT = acquisition time) and was approximately 8 Hz.

## Results and Discussion

**Intramolecular Isomerization of $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = O, S, Se).** The isomerization of $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = S, Se) in solution at room temperature was established by monitoring the changes with time in the CO stretching region of the IR spectrum of the pure *mer*-I isomer. The *mer*-I to *fac* interconversion is illustrated in Figure 2a for the case of the selenocarbonyl derivative, displaying the decrease of the $\nu(CO)$ peak of the *mer*-I isomer at 1980 $cm^{-1}$ accompanied by the growth of the $\nu(CO)$ peak at 1962 $cm^{-1}$ characteristic of the *fac* isomer.[3]

The study was also extended to the analogous *fac*-$Cr(CO)_3[(MeO)_3P]_3$ complex. The higher energy $\nu(CO)$ mode in the FT-IR spectrum of this complex in solution at room temperature was observed to decrease with time, accompanied by the growth of a new peak at 1977 $cm^{-1}$ (Figure 2b) attributable to *mer*-$Cr(CO)_3[(MeO)_3P]_3$.[3] The intensity of the second $\nu(CO)$ mode of the *fac* isomer increased with time due to its coincidence with the intense lower energy $\nu(CO)$ mode of the *mer* isomer at 1875 $cm^{-1}$.[3] Thus, *fac*-$Cr(CO)_3[(MeO)_3P]_3$ also appears to undergo rearrangement in solution at room temperature. Recently, electrochemical oxidation has been reported to induce intramolecular isomerization of *fac*-$M(CO)_3[(MeO)_3P]_3$ (M = Cr, Mo).[13] This process occurs through the generation of *fac*-$\{M(CO)_3[(MeO)_3P]_3\}^+$, which undergoes rapid conversion to *mer*-$\{M(CO)_3[(MeO)_3P]_3\}^+$. Addition of one electron to the cationic *mer* isomer generates neutral *mer*-$M(CO)_3[(MeO)_3P]_3$. It was reported that the neutral complex exhibits intramolecular isomerization, but at a much slower rate than the cation.

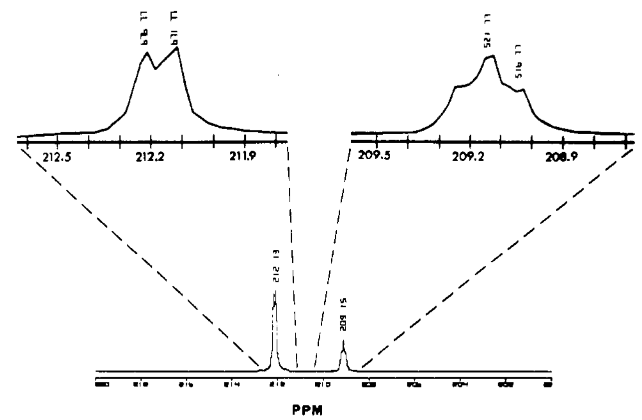

Figure 3. $^{13}C$ NMR spectrum of $Cr(CO)_2(^{13}CO)_3(CS)$ in $CD_2Cl_2$. Conditions: obtained on a Varian XL-200 FT spectrometer operating at 50.31 MHz; sweep width = 20 000 Hz; offset = 5000 Hz; flip angle = 30°; repetition time = 0.6 s; number of scans = 10.

In order to establish that the isomerization of $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = S, Se) proceeds through a nondissociative mechanism, the isomerization of the *mer*-I isomers was followed in solution in the presence of excess $(PhO)_3P$ at 60 °C by using FT-IR spectroscopy. No incorporation of $(PhO)_3P$ into the complexes was observed, as evidenced by the lack of any peaks in the FT-IR difference spectra of the equilibrium mixtures obtained in the presence and absence of $(PhO)_3P$. Furthermore, there was no shift in the position of the isosbestic point obtained for the isomerization process. The above evidence indicates that the isomerization occurs through a nondissociative pathway.

In another experiment, arene displacement from $(\eta\text{-}PhCO_2Me)Cr(CO)_2(CS)$ was effected in the presence of $^{13}CO$ at 60 °C for 6 h in THF to yield $Cr(CO)_2(^{13}CO)_3(CS)$. The $^{13}C$ NMR spectrum of this product (Figure 3) reveals that only three labeled carbonyl groups are present in this product, while a fourth $^{13}CO$ ligand would have been incorporated if isomerization occurred by a dissociative mechanism subsequent to product formation. The two $^{13}CO$ resonances observed were identified on the basis of the previous assignment of the $^{13}C$ NMR spectrum of $Cr(CO)_5(CS)$.[17] The higher field resonance (209.2 ppm) is attributed to $^{13}CO$ trans to the CS ligand and is split into a triplet, while the lower field resonance (212.1 ppm) due to $^{13}CO$ in the equatorial plane is split into a doublet. This splitting pattern is consistent with both the *fac* and *mer*-I configurations of $Cr(CO)_2(CS)L_3$ (L = $^{13}CO$), whereas the *mer*-II isomer, having three $^{13}CO$ ligands in the equatorial plane, would give rise to a singlet that may be hidden under the doublet. While the number of isomers of $Cr(CO)_2(^{13}CO)_3(CS)$ in the sample cannot be established from the $^{13}C$ NMR spectrum, the abundance of peaks in the carbonyl region of the IR spectrum (Table II) indicates that more than a single isomer is present. The comparison of the observed $\nu(CO)$ frequencies with the frequencies calculated in the energy-factored force field approximation on the basis of force constants reported for $Cr(CO)_5(CS)$[19] reveals that *fac*-$Cr(CO)_2(^{13}CO)_3(CS)$ is present together with some amount of either the *mer*-I or the *mer*-II isomer or both. These results do not

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**Table II.** Observed and Calculated Frequencies (cm$^{-1}$) for $\nu$(CO) Modes of Cr(CO)$_2$($^{13}$CO)$_3$(CS) in CS$_2$

| obsd | calcd$^a$ *fac* | *mer*-I | *mer*-II |
|---|---|---|---|
| 2066 | 2067 | 2069 | 2066 |
| 2056 | | | |
| 2008 | 2007 | | 2014 |
| 1988 | | 1991 | 1986 |
| | | 1989 | |
| 1978 | 1978 | | |
| | | 1972 | |
| 1958 | 1959 | | |
| 1956 | 1955 | | 1957 |
| 1945 | | 1945 | 1945 |

$^a$Calculated from energy-factored anharmonic force constants reported in ref 19 for Cr(CO)$_5$(CS) in CS$_2$ solution: $k_{\rm CO}$(ax) = 16.63, $k_{\rm CO}$(eq) = 16.46, $k_{\rm CO,CO}$(ax,eq) = 0.22, $k_{\rm CO,CO(cis)}$(eq,eq) = 0.24, $k_{\rm CO,CO(trans)}$(eq,eq) = 0.47 mdyn Å$^{-1}$.

demonstrate definitively that Cr(CO)$_2$($^{13}$CO)$_3$(CS) also undergoes intramolecular isomerization, since the observation of at least two isomers of this complex may be the result of a rearrangement process during the course of the arene displacement reaction. However, they do establish that if Cr(CO)$_2$($^{13}$CO)$_3$(CS) does isomerize, it does so by a nondissociative mechanism, as does W(CO)$_4$($^{13}$CO)(CS).[6]

The rate constants for *fac* → *mer* and *mer* → *fac* isomerization of Cr(CO)$_2$(CX)[(MeO)$_3$P]$_3$ (X = S, Se; *mer* = *mer*-I) and Cr(CO)$_3$[(MeO)$_3$P]$_3$ were calculated from the opposing first-order reactions

$$\textit{fac}\text{-Cr(CO)}_2\text{(CX)[(MeO)}_3\text{P]}_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{mer}\text{-Cr(CO)}_2\text{(CX)[(MeO)}_3\text{P]}_3 \quad (3)$$

$$\text{X} = \text{O, S, Se}$$

by using eq 4 and 5, where $A_t$ is the absorbance at time $t$ and $A_e$

$$K_{\rm eq} = \frac{k_1}{k_{-1}} = \frac{[\textit{mer}\text{-Cr(CO)}_2\text{(CX)[(MeO)}_3\text{P]}_3]}{[\textit{fac}\text{-Cr(CO)}_2\text{(CX)[(MeO)}_3\text{P]}_3]} \quad (4)$$

$$k_1 + k_{-1} = t^{-1} \ln [A_e/(A_e - A_t)] \quad (5)$$

is the absorbance at equilibrium of a $\nu$(CO) mode in the FT-IR spectrum.

In order to determine the rates of the forward and reverse reactions, it was necessary to measure the distribution of the isomers at equilibrium. $^{31}$P FT-NMR spectroscopy was the technique chosen. The relative intensities of the peaks in a $^{31}$P NMR spectrum are a reliable measure of relative concentration, providing the nuclei are given sufficient time to relax between pulses. Consequently, the spin–lattice relaxation times, $T_1$, were determined for the isomers under investigation and the values obtained are shown in Table III. When gated decoupling was used, with an interval between pulses approximately 10 times longer than $T_1$, thereby allowing the nuclei sufficient time to relax, the relative ratios of the isomers present were obtained. The equilibrium constants were not found to be temperature dependent in the 20–80 °C range. For all three complexes, the *mer* isomer (*mer*-I in the case of the CS and CSe complexes) is predominant and the equilibrium *mer*/*fac* ratio is approximately the same ($K_{\rm eq}$ = 5.0).

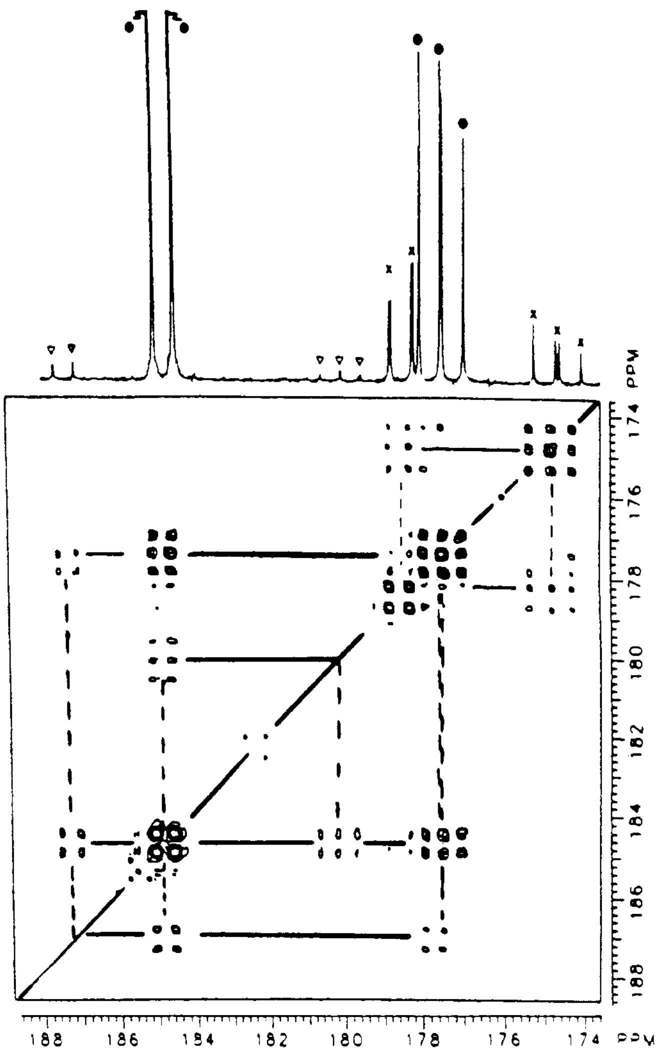

**Figure 4.** 2-D $^{31}$P contour map for Cr(CO)$_2$(CSe)[(MeO)$_3$P]$_3$ in deuteriotoluene at 61 °C on a Varian XL-300 spectrometer. An NOE accordion pulse sequence was employed with $\kappa$ = 30. All three isomers exhibit an AB$_2$ coupling pattern as follows (chemical shifts are relative to H$_3$PO$_4$ as external standard). *mer*-II (▽): P$_2$,P$_3$(d) 187.2 ppm, P$_1$(t) 180.3 ppm ($J$ = 63 Hz). *mer*-I (●): P$_1$,P$_2$(d) 184.9 ppm, P$_3$(t) 177.5 ppm ($J$ = 63 Hz). *fac* (×): P$_2$,P$_3$(d) 178.6 ppm, P$_1$(t) 174.7 ppm ($J$ = 72 Hz). The numbering pattern is in accordance with Figure 6.

Although the *mer*-II isomer of Cr(CO)$_2$(CX)[(MeO)$_3$P]$_3$ (X = S, Se) has not been observed spectroscopically by FT-IR or $^{13}$C NMR spectroscopy, the $^{31}$P NMR spectra of both the thiocarbonyl and the selenocarbonyl complexes provided some empirical evidence of a minor component (<5% of the *mer*-I isomer) with a splitting pattern and chemical shift consistent with the *mer*-II configuration. That is, the appearance of a doublet and a triplet with a coupling constant similar to that of the *mer*-I isomer suggests a structure in which two (MeO)$_3$P ligands are trans to each other and cis to a third (MeO)$_3$P ligand. Furthermore, the location of the triplet resonance downfield from the triplet of both *fac* and *mer*-I isomers is indicative of a phosphorus trans to CO rather than CX, while the upfield shift of the doublet resonance relative to that of *mer*-Cr(CO)$_3$[(MeO)$_3$P]$_3$ reveals a lower

**Table III.** Spin–Lattice Relaxation Times ($T_1$) for Phosphorus Nuclei in Cr(CO)$_2$(CX)[(MeO)$_3$P]$_3$ (X = O, S, Se)

| complex | $T_1$, s<br>P trans to P | P trans to CS/CSe | P trans to CO |
|---|---|---|---|
| *fac*-Cr(CO)$_3$[(MeO)$_3$P]$_3$ | | | 2.35 ± 0.03 |
| *mer*-Cr(CO)$_3$[(MeO)$_3$P]$_3$ | 1.84 ± 0.03 | | 2.37 ± 0.06 |
| *fac*-Cr(CO)$_2$(CS)[(MeO)$_3$P]$_3$ | | 2.40 ± 0.04 | 2.28 ± 0.03 |
| *mer*-I-Cr(CO)$_2$(CS)[(MeO)$_3$P]$_3$ | 1.76 ± 0.05 | 2.45 ± 0.02 | |
| *mer*-II-Cr(CO)$_2$(CS)[(MeO)$_3$P]$_3$ | 1.86 ± 0.05 | | 2.41 ± 0.10 |
| *fac*-Cr(CO)$_2$(CSe)[(MeO)$_3$P]$_3$ | | 3.17 ± 0.24 | 2.84 ± 0.22 |
| *mer*-I-Cr(CO)$_2$(CSe)[(MeO)$_3$P]$_3$ | 2.40 ± 0.14 | 3.18 ± 0.23 | |

**Table IV.** First-Order Rate Constants for the Isomerization Processes of $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = O, S, Se) in Dichloroethane

| | | | rate const × $10^4$, $s^{-1}$ | | |
|---|---|---|---|---|---|
| CX | obsd process | $T$, °C | $k_1 + k_{-1}$ | $k_1$ | $k_{-1}$ |
| CSe | *mer*-I → *fac* | 50.4 | 8.82 | 7.35 | 1.47 |
| | | 38.0 | 3.28 | 2.73 | 0.55 |
| | | 32.6 | 2.14 | 1.78 | 0.36 |
| CS | *fac* → *mer*-I | 61.8 | 15.28 | 12.73 | 2.55 |
| | | 45.3 | 3.88 | 3.23 | 0.65 |
| | | 23.4 | 0.60 | 0.50 | 0.10 |
| CO | *fac* → *mer* | 59.0 | 3.58 | 2.98 | 0.60 |
| | | 49.2 | 1.64 | 1.37 | 0.27 |
| | | 22.0 | 0.12 | 0.10 | 0.02 |

**Table V.** Activation Parameters for Isomerization Processes of $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = O, S, Se)

| complex | process | $\Delta H^*$, kcal $mol^{-1}$ | $\Delta S^*$, cal $mol^{-1}$ $deg^{-1}$ |
|---|---|---|---|
| $Cr(CO)_2(CSe)[(MeO)_3P]_3$ | *fac* → *mer*-I | 15.6 ± 0.3 | −25 ± 1 |
| $Cr(CO)_2(CSe)[(MeO)_3P]_3$ | *mer*-I → *fac* | 15.5 ± 0.3 | −28 ± 1 |
| $Cr(CO)_2(CS)[(MeO)_3P]_3$ | *fac* → *mer*-I | 16.6 ± 0.4 | −22 ± 1 |
| $Cr(CO)_2(CS)[(MeO)_3P]_3$ | *mer*-I → *fac* | 16.6 ± 0.4 | −25 ± 1 |
| $Cr(CO)_3[(MeO)_3P]_3$ | *fac* → *mer* | 18.0 ± 0.3 | −20 ± 1 |
| $Cr(CO)_3[(MeO)_3P]_3$ | *mer* → *fac* | 18.0 ± 0.3 | −24 ± 1 |

electron density at the chromium atom, confirming the presence of the CX ligand. The low concentration of the *mer*-II isomer relative to that of the *fac* or *mer*-I isomer can be interpreted in terms of a site preference of the CX ligand. In studies of the trans → cis isomerization of a series of $W(CO)_4(CS)(L)$ complexes,[20] it was found that $K_{eq} = [cis]/[trans]$ decreased with an increase in the ratio of $\sigma$-donor/$\pi$-acceptor strength of the ligand L. Therefore, the thiocarbonyl ligand appears to exhibit a preference for a site trans to a strong $\sigma$-donor/weak $\pi$-acceptor. Consequently, the *fac* and *mer*-I isomers, in which the CS ligand is trans to $(MeO)_3P$, would be predicted to be favored with respect to the *mer*-II isomer, in which CS is trans to CO. While the site preference of the CSe ligand has not been investigated, it is expected to be the same as that of CS, due to the similarity in the bonding properties of these ligands.

The rate constants for the *fac* ↔ *mer* isomerization of $Cr(CO)_2(CX)[(MeO)_3P]_3$ (*mer*-I for X = S, Se) revealed that $k_1 > k_{-1}$ (Table IV) and that $k_1$ decreases in the order X = Se > S > O. The activation parameters for the forward and reverse process are given in Table V. The enthalpies of activation are large and positive, while the entropies of activation are negative. Moreover, for the three chalcocarbonyl complexes examined, the forward and reverse reactions differ mainly in the entropy value, indicating steric factors determine the equilibrium ratio. The greater stability of the *mer* and *mer*-I isomers most probably results from the decreased steric interactions between the tertiary phosphite ligands in these isomers compared to those in the *fac* isomers.

Large enthalpies of activation have been reported for the intramolecular isomerizations of other group 6 metal carbonyl complexes (Table I); these have been attributed to bond lengthening in the activated complexes prior to, or during, the rearrangements.[11] The enthalpies of activation for the selenocarbonyl and thiocarbonyl complexes are smaller than that for the tricarbonyl analogue. This observation is in line with the observed trans-labilizing effect of CS and CSe ligands in dissociative processes. The increasing negative entropy of activation in the order O < S < Se reflects the relative sizes of the chalcogen atoms (O < S < Se).

**2-D NOE $^{31}P$ Studies.** Two-dimensional NMR spectroscopy[21] has recently been employed in the study of chemical exchange processes of organometallic complexes.[22,23] In the present work, 2-D NOE NMR investigations established that dynamic intramolecular interconversion takes place between the *mer*-I and *mer*-II isomers of $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = S, Se) on the time scale of the NMR experiment at temperatures above 50 °C (Figure 4). The intramolecular nature of the process was demonstrated by the lack of correlation in 2-D spectra between resonances of the complexes and those of excess ligand present in solution. However, *fac* to *mer*-I or *fac* to *mer*-II interconversions were not observed at temperatures ranging up to 80 °C for either the selenocarbonyl or the thiocarbonyl complex. Temperatures higher than 80 °C resulted in decomposition of these complexes.

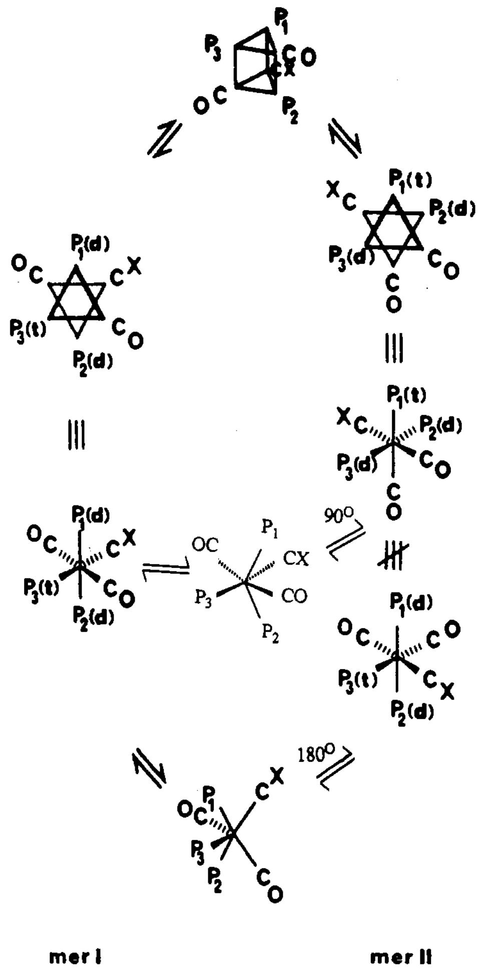

**Figure 5.** Schematic representation of possible pathways for the interconversion of the *mer*-I and *mer*-II isomers of $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = S, Se): (top) trigonal-prismatic intermediate; (bottom) bicapped-tetrahedral intermediates. For the sake of clarity, the $(MeO)_3P$ ligands have been represented by $P_1$, $P_2$, and $P_3$.

The 2-D NMR studies of the *mer*-I to *mer*-II isomerization of $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = S, Se) also provided valuable information on the possible nature of the intermediates involved. For both the trigonal-prismatic twist (Figure 1a) and the rearrangement via a bicapped-tetrahedral intermediate involving a 90° rotation of a pair of ligands (Figure 1b), the triplet of the *mer*-I isomer would correlate with the doublet of the *mer*-II isomer, while the doublet of the *mer*-II isomer would correlate with both the triplet and the doublet in the spectrum of the *mer*-II isomer (Figure 5). On the other hand, the mechanism involving a 180° rotation of a pair of ligands in the bicapped-tetrahedral intermediate (Figure 1c) would preserve the coupling pattern for each phosphorus nucleus in the two isomers.

The distinct symmetrical off-diagonal contours on the 2-D NMR exchange maps (Figure 4) illustrate both NOE and possible chemical exchange between the phosphorus nuclei of the same

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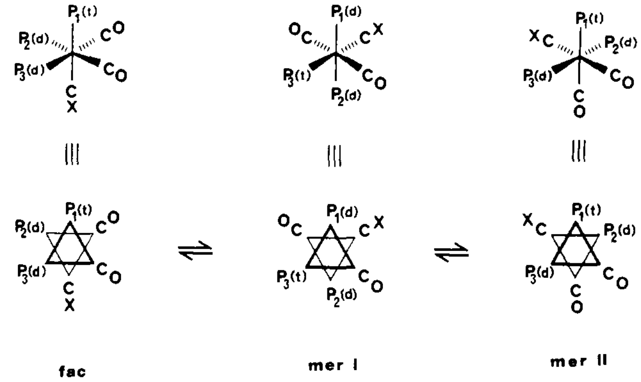

**Figure 6.** Schematic representation of the intramolecular isomerization of $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = S, Se) through trigonal-prismatic intermediates.

molecule. Moreover, the exchange between the *mer*-I and *mer*-II isomers indicates dynamic rearrangement via either a trigonal prism or a bicapped tetrahedron with 90° rotation of the ligands, as seen from the correlation of the off-diagonal peak of the doublet of the *mer*-II isomer (bottom left-hand side of the contour map) to the doublet and triplet of *mer*-I, while the triplet of *mer*-II is exchanging with the doublet of *mer*-I. The observed exchange pattern is not consistent with the third possible mechanism, involving the 180° rotation of a pair of ligands in a bicapped-tetrahedral intermediate.

The failure to observe the dynamic interconversion of the *fac* and *mer* isomers implies that the rearrangement is taking place at too slow a rate to be observed on the NMR time scale. This in turn indicates that the energy barrier for *mer*-I to *mer*-II isomerization is lower than that for *mer* to *fac* exchange. This result is inconsistent with rearrangement via a bicapped-tetrahedral intermediate, since, for such a mechanism, the energy of the transition state is expected to be approximately the same for *fac* ↔ *mer*-I, *fac* ↔ *mer*-II, and *mer*-I ↔ *mer*-II exchanges, leading to exchange correlations being observed between all these three isomers. On the other hand, it can be accounted for in terms of steric effects in the transition state of the trigonal-prismatic twist mechanism. Figure 6 shows the schematic representation of the rearrangement of the thio- or selenocarbonyl complex through a trigonal-prismatic twist. This mechanism should involve a large negative entropy for interconversion from *mer*-I to *fac* due to the steric hindrance resulting from the eclipsing of two phosphite ligands in the transition state. However, the *mer*-I to *mer*-II interconversion should take place with a smaller entropy of activation; in this case, the transition state would have the phosphite ligands eclipsing the CO and CX ligands, thus minimizing the steric effect. Therefore, the 2-D NMR evidence strongly suggests that the lowest energy path for the isomerization of $Cr(CO)_2(CX)[(MeO)_3P]_3$ is through a trigonal-prismatic twist.

The off-diagonal correlation observed between the doublet and triplet of the *fac* isomer in the 2-D NMR spectrum of $Cr(CO)_2(CX)[(MeO)_3P]_3$ (X = S, Se) can be attributed to chemical exchange between equivalent *fac* isomers. The energy barrier for such a rearrangement by a trigonal-prismatic mechanism would be expected to be comparable to that for *mer*-I to *mer*-II interconversion, since the activated state would involve the eclipsing of each phosphite by a CO or CX ligand, rather than by a second phosphite ligand. However, the possibility that the observed correlation is solely due to NOE cannot be ruled out at present.

## Conclusion

The $Cr(CO)_2(CX)[(MeO)P]_3$ (X = S, Se) complexes as compared to their tricarbonyl analogue have been found to exhibit enhanced rates of intramolecular isomerization. In view of the apparent involvement of bond lengthening in the intramolecular isomerization, this effect can be related to the trans-labilizing effect of the CS and CSe ligands in dissociative processes resulting from the stronger $\pi$-accepting properties of these ligands relative to those of CO. The lower symmetry of the $Cr(CO)_2(CX)[MeO]P]_3$ (X = S, Se) complexes has made possible the investigation of the mechanism of intramolecular isomerization by 2-D NOE $^{31}P$ NMR spectroscopy, providing evidence for the isomerization by trigonal-prismatic twist. Accordingly, series of $Cr(CO)_2(CX)L_3$ complexes containing a variety of ligands L may prove useful as probes of the effects of electronic and steric factors on the mechanism and rate of intramolecular isomerization of octahedral complexes.

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**Registry No.** ($\eta$-$PhCO_2Me$)$Cr(CO)_2(CS)$, 52140-27-9; *fac*-$Cr(CO)_3[(MeO)_3P]_3$, 17764-72-6; *fac*-$Cr(CO)_2(CS)[(MeO)_3P]_3$, 98168-89-9; *fac*-$Cr(CO)_2(CSe)[(MeO)_3P]_3$, 98168-91-3; $Cr(CO)_2(^{13}CO)_3(CS)$, 119071-29-3; *mer*-$Cr(CO)_3[(MeO)_3P]_3$, 30571-27-8; *mer*-I-$Cr(CO)_2(CS)[(MeO)_3P]_3$, 97279-46-4; *mer*-II-$Cr(CO)_2(CS)[(MeO)_3P]_3$, 98168-88-8; *mer*-I-$Cr(CO)_2(CSe)[(MeO)_3P]_3$, 98105-32-9.