Organometallic Conformational Equilibria. XI. *cis–trans* Isomerism and Stereochemical Nonrigidity in Cyclopentadienylmolybdenum Complexes[1,2]

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Abstract: Kinetic and thermodynamic parameters for the *cis–trans* interconversion of compounds having the general formula $\pi\text{-}C_5H_5Mo(CO)_2LR$, where L = PPh_3, $P(n\text{-but})_3$, PMe_2Ph, $P(OMe)_3$, $P(OPh)_3$; R = H, D, Me, $PhCH_2$, Cl, Br, I, have been evaluated using a combination of pmr techniques. The equilibrium constants, [*cis*]/[*trans*], were generally found to increase in the order R = $PhCH_2 < Me < H, D < I < Br < Cl$; L = $PMe_2Ph \sim PPh_3 \sim P(but)_3 < P(OMe)_3 < P(OPh)_3$, with greater effects observed upon changing R. Although the *trans* → *cis* barrier, ΔF^*_{25}, is only slightly dependent on the nature of L, it is strongly dependent on the nature of R and tends to increase in the order H, D (12–14 kcal/mol) < Me, $PhCH_2$, (19–23 kcal/mol) < Cl, Br, I (22–26 kcal/mol). A model incorporating square pyramid–trigonal bipyramid–square pyramid interconversion has been proposed, and the possible conformational interchanges have been considered from a topological viewpoint. The lowest energy pathway appears to involve an intermediate approximating a trigonal bipyramid with the cyclopentadienyl ring occupying one apical position and either R or L occupying the other.

Compounds having the general formula of $\pi\text{-}C_5H_5\text{-}Mo(CO)_2LR$ may be formally regarded as seven-coordinate complexes of molybdenum with the cyclopentadienyl ring occupying three coordination positions. Sufficient crystallographic data are now available to assure that the idealized lowest energy configuration would involve the remaining ligands located approximately at the corners of a square, such that a structure similar to a square pyramid would result.[3] This square-pyramidal geometry suggests the possibility of the existence of two geometric isomers (see Figure 1). Although the majority of these compounds are present in solution predominantly as one isomer, in favorable cases appreciable concentrations of both isomers have been found. An equilibrium between these isomers has now been observed where L = a phosphine or phosphite and R = H, D, Me, $PhCH_2$, CH_3OCH_2, CH_3SCH_2, Cl, Br, or I.

Our studies of the rearrangement mechanism responsible for the stereochemical nonrigidity of π-allyl complexes of molybdenum and tungsten[18] led us to investigate the nature of the rearrangement process in these analogous $\pi\text{-}C_5H_5Mo(CO)_2LR$ compounds. In this paper we provide further verification of the assignments of *cis* and *trans* isomers, demonstrate that the rearrangement process which interconverts isomers is intramolecular, and report thermodynamic parameters obtained from the temperature dependence of the equilibrium constants and activation parameters obtained from fitting of the temperature dependence of the rates to the Arrhenius and Eyring equations. Since rates have been obtained in many cases over a temperature range in excess of 100°, these barriers to rearrangement are believed to be some of the most accurate yet measured for intramolecular processes in organometallic molecules.

Experimental Section

Infrared spectra of cyclohexane solutions of all compounds were measured where solubility permitted. A Perkin-Elmer 421 grating instrument was used with calibration from polystyrene film. Car-

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[3] An irregular structure may often be interpreted as a distorted form of a number of different more regular structural arrangements. The choice of a particular idealized structure is somewhat arbitrary, and although it might be argued that another structure is more appropriate, it is convenient here to consider these particular compounds as being derived from a 3:4 type of coordination geometry or from a square-base–trigonal-cap coordination geometry. Obviously, the steric interactions between the ligands, particularly since some have vastly different steric requirements than carbonyls, will cause distortions from the idealized coordination geometry. Nevertheless, it is apparent from the solid-state structures that the 3:4 structure is more appropriate than the 3:3:1 or monocapped-octahedral one. If the four ligands besides the π-cyclopentadienyl moiety are identical, pseudo-C_{4v} symmetry is observed, *e.g.*, $\pi\text{-}C_5H_5V(CO)_4$[4] or $\pi\text{-}C_5H_5Nb(CO)_4$.[5] Despite distortions the following examples provide convenient models for these idealized "square-pyramidal" structures: $\pi\text{-}C_5H_5Mo(CO)_3\text{-}C_2H_5$,[6] $\pi\text{-}C_5H_5Mo(CO)_3Cl$,[7] $\pi\text{-}C_5H_5Mo(CO)_3CH_2CO_2H$,[8] $\pi\text{-}C_5H_5Mo\text{-}(CO)_3C_3F_7$,[9] $[\pi\text{-}C_5H_5Mo(CO)_3]_2$,[10] $\pi\text{-}C_5H_5Mo(CO)_3\text{–}Sn[\pi\text{-}C_5H_5Fe(CO)_2]_2\text{-}Cl$,[11] $[\pi\text{-}C_5H_5Mo(CO)_2]_2\text{-}\mu\text{-}P(CH_3)_2\text{-}\mu\text{-}H$,[4] $\pi\text{-}C_5H_5Mo(CO)_2(PPh_3)CO\text{-}CH_3$,[12] $[\pi\text{-}C_5H_5W(CO)_3]_2$,[13] $\pi\text{-}C_6H_5W(CO)_3Au(PPh_3)$,[14] $[\pi\text{-}C_{10}H_8Mo\text{-}(CO)_3CH_3]_2$,[15] $\pi\text{-}C_{10}H_8Mo_2(CO)_6$,[16] $\pi\text{-}C_{14}H_{15}Mo_2(CO)_6$,[16] and $\pi\text{-}C_5H_5\text{-}Mo(CO)_2(CH_2C_6H_4CH_3)$.[17] In each of these cases, an approximately square projection is obtained if the atoms which are directly attached to the metal are projected onto the plane of the π-cyclopentadienyl ring.

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bonyl stretching frequencies are accurate to ±1 cm^{-1}. Nmr spectra were measured on Varian Associates A60 and HA100 spectrometers with variable-temperature probes. The temperature was measured with a copper–constantan thermocouple in an nmr tube with the junction at the level of the receiver coil.

Preparation of Compounds. Although at the initiation of our studies preparative procedures for these compounds were not readily available, synthetic methods for most of the compounds have now been reported. Hence, the syntheses which we devised are presented only when improved yields or purity were realized. Purity is at a premium in these preparations because the distinction between an isomeric form of the complex and an impurity is often a difficult task; therefore comments are included on the relative purity of samples prepared by different methods.

Halide Derivatives. Halides were prepared in good yield by procedures now present in the literature.[19,20] Treatment of the molybdenum dimer, $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with *equimolar* quantities of iodine or bromine in benzene led to rapid formation of $\pi\text{-}C_5H_5Mo(CO)_3R$ in good yield. Refluxing a benzene solution of the halide derivative for several hours in the presence of a slight excess of phosphine or phosphite gave $\pi\text{-}C_5H_5Mo(CO)_2LR$. Addition of iodine, bromine, or N-bromosuccinimide to a solution of $[\pi\text{-}C_5H_5Mo(CO)_2L]_2Hg$[20] in ether resulted in complete reaction within a few hours at room temperature. This procedure, however, leads to the formation of substantial quantities of the halomercury derivative, which cannot always be easily separated from the desired product. Chlorides were formed in quantitative yield by addition of carbon tetrachloride to the appropriate hydride.[21]

Purification of the halide derivatives was generally accomplished by removal of the solvent at reduced pressure and subsequent chromatography on deactivated alumina by elution with benzene and dichloromethane. Crystallization from methylcyclohexane–dichloromethane mixtures gave $\pi\text{-}C_5H_5Mo(CO)_2P(OMe)_3I$ as the pure *trans* isomer (mp 75°), whereas repeated crystallizations gave $\pi\text{-}C_5H_5Mo(CO)_2P(OMe)_3Br$ and $\pi\text{-}C_5H_5Mo(CO)_2P(OMe)_3Cl$ as the *cis* isomers (mp 96, 107°). Generally the chlorides and bromides crystallize as the *cis* isomer; however, iodides sometimes crystallize as mixtures of the *cis* and *trans* isomers (*e.g.*, L = PPh_3). The halides vary in color from light orange (R = Cl) to dark maroon (R = I) and are stable in air for several hours, even in solution.

Hydride Derivatives. Sodium amalgam reduction of $[\pi\text{-}C_5H_5Mo(CO)_2L]_2Hg$ in THF gave the $[\pi\text{-}C_5H_5Mo(CO)_2L]^-$ anion, from which the hydride was prepared by addition of glacial acetic acid. Removal of the solvent at reduced pressure (15 mm) and extraction of the residue with benzene was followed by chromatographic purification of the extracts on deactivated alumina. Petroleum ether eluted the desired compounds in colorless solutions. Since the hydrides react with chloroform and methylene chloride, as well as with carbon tetrachloride, to form the corresponding chlorides, they were recrystallized from methylcyclohexane or a mixture of methylcyclohexane and ether.

The deuterated complex, $\pi\text{-}C_5H_5Mo(CO)_2(PPh_3)D$, was prepared by addition of D_3PO_4 to a solution of $Na[\pi\text{-}C_5H_5Mo(CO)_2PPh_3]$.

Pure hydride compounds are colorless or cream colored. When pure, some of the solids may be handled in air for several minutes without extensive decomposition. All, however, decompose within a few minutes if a solution is exposed to the air.

Alkyl Derivatives. Although sodium amalgam reduction of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ followed by addition of alkyl halide, isolation of $\pi\text{-}C_5H_5Mo(CO)_3R$, and subsequent treatment with L in refluxing benzene gave good yields of $\pi\text{-}C_5H_5Mo(CO)_2LR$ compounds;[22] this method in our hands gave appreciable quantities of impurities which were extremely difficult to remove by crystallization or chromatography. On the other hand, reduction of $[\pi\text{-}C_5H_5\text{-}Mo(CO)_2\text{-}L]_2Hg$ and addition of the alkyl halide gave exclusively the desired product.

Very pure products were generally obtained by removal of the solvent under reduced pressure and extraction of the residue with benzene followed by chromatography on deactivated neutral alumina. Elution with a mixture of petroleum ether and benzene gave products which were crystallized from methylcyclohexane and dried under vacuum. The complexes, $\pi\text{-}C_5H_5Mo(CO)_2[P(OPh)_3]CH_2Ph$, $\pi\text{-}C_5H_5Mo(CO)_2[P(OMe)_3]Me$, and $\pi\text{-}C_5H_5Mo(CO)_2(PPh_3)Me$, all of which exist as both *cis* and *trans* isomers in solution were obtained in the solid as pure *trans* isomers (mp 115, 67, 155° dec).

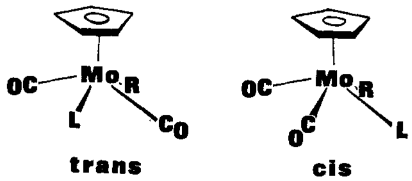

Figure 1. The isomers of a $\pi\text{-}C_5H_5Mo(CO)_2LR$ complex.

The alkyl derivatives vary in color from light to dark yellow and although stable in air as a solid for some time, they are noticeably less stable than halides.

Thermodynamics. Equilibrium constants were determined at several temperatures by integration or by weighing traces of the resonances. The percentages of the isomers obtained by these methods are believed to be correct within 1%. For the hydride compounds at high temperatures, equilibrium constants were computed from $J_{P\text{-}H}$ observed in the averaged nmr spectrum (*vide infra*). A least-squares fit of ln K, where K = [*cis*]/[*trans*], *vs.* $1/T$ gave ΔH between isomers. These values for the enthalpy difference are not extremely accurate; however, they are quite adequate for reproducing an accurate value of K at any desired temperature.

We have generally observed that even though chemical shifts are quite dependent on solvent and temperature, $^{13}C\text{-}H$ and $^{31}P\text{-}H$ coupling constants are virtually independent of solvent or temperature. For instance, in $\pi\text{-}C_5H_5Mo(CO)_2(PMe_2Ph)H$ the two coupling constants, $J_{PH_{cis}} = 65.7 \pm 0.2$ and $J_{PH_{trans}} = 23.4 \pm 0.2$ Hz remain constant from −30 to −98° in a 1:1 mixture of toluene and dichlorofluoromethane. These values are also the same in deuteriochloroform and in carbon disulfide. Hence, we feel justified in determining the equilibrium constant at higher temperatures from the observed average coupling constant, from the expression (where x = mole fraction of *cis* isomer)

$$J_{av} = xJ_{cis} + (1 - x)J_{trans}$$

Kinetics. When only one isomer was isolated in the solid, the rate of appearance of the other isomer was followed by nmr. Rate constants in the range 10^{-3}–10^{-6} sec^{-1} were calculated using the standard expression $\ln [m/(m - x)] = (k_{tc} + k_{ct})t$ for first-order kinetics, with

$$trans \underset{k_{ct}}{\overset{k_{tc}}{\rightleftarrows}} cis$$

When exchange began to cause line broadening in the nmr, the Kubo–Sack matrix method[23] was used to compute the line shape and the "rate" ($k_{tc} + k_{ct}$) determined by matching computed with experimental spectra. Since the chemical shifts of the resonances are quite sensitive to solvent properties, plots of the relative chemical shifts *vs.* temperature were made and extrapolated into the temperature range where chemical exchange is observed on the nmr time scale. Resonance line positions thus obtained were used in the matrix, as well as the populations determined from the equilibrium constant, and these values changed for each temperature. Such a correction is important in the cases of the halide and alkyl compounds, where rates were determined from the cyclopentadienyl peaks which are 5–10 Hz apart at 60 MHz. In the hydride compounds, however, for which the hydride resonances might be separated by as much as 100 Hz, the correction is negligible.

The rate data which were obtained are listed below with the temperature, k_{ct}, and k_{tc}.

$\pi\text{-}C_5H_5Mo(CO)_2P(OPh)_3H$ in deuteriochloroform: −56.0, 0.169, 19.9; −45.7, 0.625, 59.4; −36.0, 2.20, 173.; −27.0, 5.88, 394.; −18.3, 16.7, 983.

$\pi\text{-}C_5H_5Mo(CO)_2P(OMe)_3H$ in deuteriochloroform: −26.3, 9.06, 80.9; −18.4, 20.7, 169; −15.0, 30.5, 240; −11.1, 43.4, 327; −2.5, 102, 698; 12.5, 384, 2266; 31.0, 1660, 8340.

$\pi\text{-}C_5H_5Mo(CO)_2PPh_3H$ in deuteriochloroform: −29.5, 15.0, 22.9; −26.5, 19.8, 30.3; −5.6, 146, 235; −2.0, 210, 340; 1.7,

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Table I

π-C$_5$H$_5$Mo(CO)$_2$LR R	 L	*trans* π-C$_5$H$_5$ δ (J_{PH})[a]	*cis* π-C$_5$H$_5$ δ	*trans* R δ (J_{PR})	*cis* R δ (J_{PR})
H	P(OPh)$_3$	4.54 (1.0)	4.84	−6.30 (29.0)	−6.62 (73.0)
H	P(OMe)$_3$	5.29 (1.0)	5.38	−6.19 (26.8)	−6.98 (68.7)
H	PPh$_3$	5.00 (1.0)	5.20	−6.14 (21.4)	−5.33 (64.0)
H	P(*n*-but)$_3$	5.15 (1.0)	5.31	−6.53 (22.4)	−6.60 (64.9)
H	PMe$_2$Ph	4.98 (1.0)	5.22	−6.06 (23.3)	−6.15 (65.6)
Cl	P(OPh)$_3$		4.96		
I	P(OPh)$_3$		5.03		
Cl	P(OMe)$_3$	5.35 (2.3)	5.51		
Br	P(OMe)$_3$	5.40 (2.2)	5.55		
I	P(OMe)$_3$	5.38 (2.1)	5.53		
Cl	PPh$_3$		5.39		
Br	PPh$_3$	5.05 (2.0)	5.36		
I	PPh$_3$	5.13 (1.9)	5.43		
Cl	P(*n*-but)$_3$		5.36		
I	P(*n*-but)$_3$	5.21 (1.8)	5.37		
I	PMe$_2$Ph	4.62 (2.3)	4.73		
I	SbPh$_3$	5.24	5.44		
MeOCH$_2$	P(OPh)$_3$	4.62 (1.2)	4.78	4.60 (3.6)[b,c]	*f*
MeSCH$_2$[h]	P(OPh)$_3$	4.93 (1.4)	4.95	2.79 (4.1)[b,d]	3.02 (8.6) 2.91 (11.5) (8.2)[b]
Me	P(OPh)$_3$	4.53 (1.2)	4.72	0.29 (2.6)	0.27 (10.3)
PhCH$_2$	P(OPh)$_3$	4.45 (1.3)	4.63	2.76 (2.7)[b]	2.96 (10.2) 2.60 (11.0) (10.3)[b]
Me	P(OMe)$_3$	5.04 (1.2)	5.19	0.31 (3.2)	−0.01 (9.7)
Me	PPh$_3$	4.70 (1.4)	5.03	0.58 (2.3)	−0.08 (11.0)
PhCH$_2$	PPh$_3$	4.68 (1.4)[g]		2.19 (2.0)[b,g]	
Me	*P*(*n*-but)$_3$	4.83 (1.3)	5.15	0.24 (2.4)	0.02 (9.3)
MeOCH$_3$	PPh$_3$	4.84 (1.2)		4.74 (3.6)[b,e]	

[a] All chemical shifts are given in parts per million downfield from TMS and coupling constants are given in hertz. Nmr spectra were determined at 100 MHz in deuteriochloroform except for the species L = P(OPh)$_3$, R = CH$_2$SCH$_3$, which were determined in benzene, and L = PPh$_3$, R = Me, which was determined in *o*-dichlorobenzene. Hydride spectra were determined at 50°; all others were determined at +38°. [b] Only methylene resonances are reported for R = substituted methyl. [c] The methyl resonances appear at δ 3.56 in the *trans* isomer and δ 3.31 in the *cis* isomer. [d] The methyl resonances appear at δ 2.35 in the *trans* isomer and δ 2.49, J = 0.5 Hz, in the *cis* isomer. [e] Only the methyl resonance (δ 3.38) of the *trans* isomer is observed. [f] Methylene protons of the *cis* isomer are obscured by the π-cyclopentadienyl resonances of both the *trans* and *cis* isomers and by the methylene proton resonances of the *trans* isomer. [g] This compound was reported by P. J. Craig and M. Green, *J. Chem. Soc. A*, 157 (1969), to arise from decarbonylation of the phenylacetyl derivative; however, the physical properties which they report are not consistent with our data. [h] The rearrangement of this complex has not been studied in detail due to the elimination reaction which yields π-C$_5$H$_5$Mo(CO)$_2$–π-CH$_2$SCH$_3$, which will be discussed elsewhere.

266, 434; 7.4, 378, 622; 12.4, 564, 936; 17.0, 972, 1630; 22.3, 1300, 2200; 29.7, 2210, 3790; 40.5, 4390, 7620.

π-C$_5$H$_5$Mo(CO)$_2$P(*n*-but)$_3$H in deuteriochloroform: −25.0, 6.97, 13.0; −21.0, 9.47, 17.9; −18.4, 11.7, 22.3; −12.8, 20.5, 39.5; −2.5, 50.5, 99.5; +3.8, 83.4, 167; 18.0, 263, 538; 32.9, 709, 1490.

π-C$_5$H$_5$Mo(CO)$_2$P(*n*-but)$_3$H in carbon disulfide: −25.0, 5.78, 9.22; −21.0, 8.04, 13.0; −12.8, 20.4, 33.6; 3.8, 84.7, 145; 18.0, 289, 511; 32.9, 892, 1610.

π-C$_5$H$_5$Mo(CO)$_2$P(*n*-but)$_3$H in toluene: −25.0, 5.58, 10.4; −21.0, 8.30, 15.7; −12.8, 18.8, 36.3; +3.8, 83.4, 167; 18.0, 296, 605; 32.9, 806, 1690; 38.0, 1280, 2720.

π-C$_5$H$_5$Mo(CO)$_2$P(Me)$_2$PhH in deuteriochloroform: −26.3, 7.91, 6.09; −18.4, 19.5, 15.5; −15.0, 24.9, 20.1; −9.5, 41.2, 33.8; −6.3, 60.1, 49.9; −2.5, 76.2, 63.8; +7.8, 187, 163; 18.8, 399, 361; 31.0, 983, 917; 40.5, 1530, 1470.

π-C$_5$H$_5$Mo(CO)$_2$P(Me)$_2$PhH in carbon disulfide: −25.0, 9.47, 7.53; −12.9, 30.4, 24.6; −11.5, 33.1, 26.9; −6.3, 54.6, 45.4; +7.8, 198, 172; 18.8, 447, 403; 38.0, 1800, 1710.

π-C$_5$H$_5$Mo(CO)$_2$P(OMe)$_3$Cl in *o*-dichlorobenzene: 6.0, 1.16×10^{-6}, 1.34×10^{-5}, 13.2, 2.72×10^{-6}, 3.80×10^{-5}; 115.0, 0.236, 1.65; 123.2, 0.449, 3.02.

π-C$_5$H$_5$Mo(CO)$_2$P(OMe)$_3$Br in *o*-dichlorobenzene: 6.0, 3.33×10^{-6}, 7.43×10^{-6}; 6.0, 2.84×10^{-6}, 6.32×10^{-6}, 115.0; 0.388, 1.10; 126.0, 0.944, 2.74; 153.6, 5.98, 18.0.

π-C$_5$H$_5$Mo(CO)$_2$P(OMe)$_3$I in *o*-dichlorobenzene: 6.0, 7.64×10^{-6}, 2.36×10^{-6}; 13.2, 2.36×10^{-5}, 7.90×10^{-6}; 118.8, 0.785, 0.456; 137.5, 3.08, 1.93; 142.3, 4.28, 2.72; 153.6, 9.00, 6.00.

π-C$_5$H$_5$Mo(CO)$_2$PPh$_3$I in *o*-dichlorobenzene: 153.6, 0.941, 1.05; 162.5, 1.79, 1.96; 172.9, 3.14, 3.58; 182.3, 6.28, 7.21; 186.7, 8.71, 9.61.

π-C$_5$H$_5$Mo(CO)$_2$P(Me)$_2$PhI in *o*-dichlorobenzene: 132.5, 0.234, 0.785; 142.3, 0.466, 1.57; 153.5, 0.942, 3.23; 172.9, 3.34, 11.7; 183.8; 6.20, 21.8.

π-C$_5$H$_5$Mo(CO)$_2$P(OPh)$_3$Me in toluene: 65.2, 2.20, 1.33; 70.2, 3.62, 2.21; 70.7, 3.93, 2.40; 75.6, 5.59, 3.41; 79.6, 7.48, 4.52; 80.5, 7.47, 4.53; 84.6, 10.6, 6.40; 90.2, 15.0, 9.05; 94.4, 20.0, 12.0, 99.0, 28.1, 16.9; 104.0, 40.6, 24.4; 108.8, 56.3, 33.7.

π-C$_5$H$_5$Mo(CO)$_2$P(OPh)$_3$CH$_2$Ph in toluene: −13.2, 3.77×10^{-4}, 4.10×10^{-5}; −5.5, 1.11×10^{-3}, 1.30×10^{-4}; 60.9, 1.89, 0.326; 70.7, 4.24, 0.762; 80.5, 7.67, 1.41.

π-C$_5$H$_5$(CO)$_2$P(OMe)$_3$Me in toluene: −13.2, 8.78×10^{-5}, 1.05×10^{-5}; −5.5, 4.38×10^{-4}, 5.50×10^{-5}; 70.7, 1.57, 0.270; 80.5, 3.14, 0.560; 90.2, 8.14, 1.51.

π-C$_5$H$_5$Mo(CO)$_2$PPh$_3$Me in *o*-dichlorobenzene: 90.2, 1.89, 0.178; 99.0, 3.93, 0.395; 115.0, 13.5, 1.49; 120.2, 19.7, 2.23; 132.5, 44.6, 5.38; 142.3, 79.9, 10.1.

Results and Discussion

Although the different π-C$_5$H$_5$Mo(CO)$_2$LR isomers almost invariably show superimposed carbonyl stretching bands in the infrared spectrum, the isomers may be readily distinguished by the characteristic π-cyclopentadienyl resonances in the pmr spectrum. Generally a doublet with a splitting of from 0.9 to 2.3 Hz appears approximately 0.2 ppm to high field of a singlet ($J_P \leq 0.4$ Hz) in derivatives with phosphine or phosphite L groups (Table I). Assignment of these resonances to the appropriate isomer is readily accomplished by considering the effect of the presence of a plane of symmetry in the *trans* isomer and the lack of symmetry of the *cis* isomer. Even though rapidly rotating about the metal–carbon bond, the protons of a methylene group in an alkyl substituent are nonequivalent if the environment about the metal is asymmetric. Consequently, the methylene fragment gives rise to eight resonances, *i.e.*, the AB protion of an ABX spectrum (X = phosphorus), in a *cis* benzyl[24] or CH_3SCH_2 complex (see Figure 2). Similarly, when L = PMe_2Ph, the methyl groups are nonequivalent in the *cis* isomer but equivalent in the *trans* isomer. In each case the cyclopentadienyl resonance at higher field and having the larger splitting correlates with the *trans* isomer as determined by the method above.[25] Furthermore, the pmr spectrum of π-$C_5H_5Mo(CO)_2P(Ph)_3COMe$, which has the *trans* structure in the solid state,[12] indicates the presence of essentially only one isomer in solution, and the cyclopentadienyl resonance is a doublet in agreement with previous conclusions.

Thermodynamic Considerations. The energy differences between the isomers observed here are fairly small, so that one cannot really expect to be able to attribute relative stabilities to a single dominant factor. Nevertheless, the assessment of the relative importance of factors which contribute to thermodynamic stability should be useful in prediction of conformational preference. Consideration of the thermodynamic data in Table II shows that in some cases the equilibrium between isomers depends markedly on the solvent as well as on the substituents L and R. While changes in K are less than 20% when R = H, CH_3, or CH_2Ph; when R = I, Br, or Cl, changes of as much as 100% may occur if the polarity of the solvent is drastically changed. Presumably, such shifts in equilibrium constant tend to reflect changes in solvation of the two isomers, as indicated by changes in entropy differences. Of particular interest here, however, are the inherent enthalpy differences between isomers. Comparisons of the isomer ratios in a given solvent reveal the same trends in free energy and enthalpy differences, regardless of solvent. In attempting to understand these stability differences, an explanation involving the effect of steric interactions on the enthalpy of formation of each isomer might appear attractive. Thus one might expect a greater interaction between a halide and the L group in a *cis* complex in comparison to the interaction in a *trans* complex. Hence, the *trans* configuration should be favored for the iodide more than for the chloride, and indeed, one observes that within a series of halides containing the same L group the percentage of *cis* isomer decreases in the order Cl > Br > I. Likewise, one would expect that the greater steric interaction of the hydride or alkyl group with the L group in the *cis* complex would tend to favor the *trans* configuration for complexes containing a benzyl group when compared to those containing a hydride ligand. Again, within a series of halides containing the same L group, the percentage of *cis* isomer decreases in the order H > CH_3 > $C_6H_5CH_2$. Unfortunately, this approach fails to explain the observation that, for a given ligand L, the relative stability of the *trans* isomer of the hydride is often comparable to that of the iodide, *e.g.*, when L = $P(n\text{-but})_3$ or PPh_3. In addition, one might anticipate that a greater steric interaction might result in an increase in *trans* concentration on substituting triphenylantimony for triphenylphosphine; yet, this results in a more than 25-fold increase in *cis–trans* ratio. (Care must be exercised in arguments of this nature because an increase in metal–L bond length often offsets on increase in van der Waals radius.) Suffice it to say that steric effects are an important contributing factor in determining the equilibrium ratio of isomers, but they do not always dominate in the control of conformational preference. It thus appears that electronic factors must also be responsible in large measure for the isomer ratios which are observed.

Table II

π-$C_5H_5Mo(CO)_2LR$		ν_{CO}, cm^{-1}	[*cis*]/[*trans*]	ΔH,
R	L	C_6H_{12}	$CDCl_3$, 25° [d]	kcal/mol[e]
H	$P(OPh)_3$	1978, 1908	33	−2.1
H	$P(OMe)_3$	1964, 1893	5.3	−1.5
H	$P(Ph)_3$	1953, 1878	1.7	0.29
H	$P(n\text{-but})_3$	1945, 1866	2.1	0.30
H	$P(Me)_2Ph$	1941 1865 1951	0.92	0.51
Cl	$P(OPh)_3$	1995, 1913	>50	
I	$P(OPh)_3$	1986, 1916	>50	
Cl	$P(OMe)_3$	1989, 1905	9.2 (8.5[b])	−0.39[b]
Br	$P(OMe)_3$	1988, 1905	2.9 (2.4[b])	0.48[b]
I	$P(OMe)_3$	1984, 1913	0.30 (0.34)[b]	1.3[b]
Cl	$P(Ph)_3$	1975, 1886[a]	>50	
Br	$P(Ph)_3$	1974, 1886[a]	24	
I	$P(Ph)_3$	1971, 1892[a]	0.86[b]	0.50[b]
Cl	$P(n\text{-but})_3$	1975, 1883	>50	
I	$P(n\text{-but})_3$	1969, 1884	7.6	
I	$P(Me)_2Ph$	1976, 1889	2.8[b]	0.39[b]
Me	$P(OPh)_3$	1967, 1894	0.59 (0,63)[c]	−0.14
$PhCH_2$	$P(OPh)_3$	1962, 1889	0.18 (0.15)[c]	0.83[c]
Me	$P(OMe)_3$	1955, 1874	0.17 (0.15[c])	0.77[c]
Me	$P(Ph)_3$	1947, 1871	0.08[c] [0.06)[b]	1.6
$PhCH_2$	$P(Ph)_3$	1943, 1868	<0.02	
Me	$P(n\text{-but})_3$	1944, 1869	0.14	
I	$Sb(Ph)_3$	1970, 1885[a]	26.0	

[a] In $CHCl_3$. [b] In *o*-dichlorobenzene. [c] In toluene. [d] Maximum error, 3%. [e] Standard errors vary from 5% (with hydrides) to maximum of 15%.

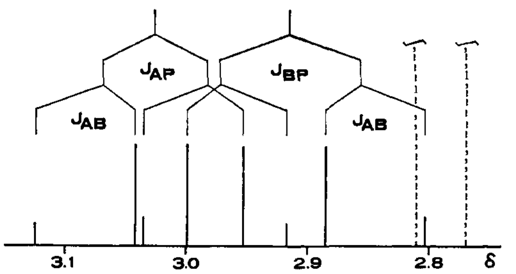

Figure 2. Methylene region of the 100-MHz pmr spectrum of π-$C_5H_5Mo(CO)_2P(OPh)_3$-CH_2SCH_3 in benzene at 30° showing the eight-line pattern for the *cis* isomer and the doublet for the *trans* isomer (broken lines).

Although these molybdenum systems may represent a rather large departure from a model system based on Pt(II) complexes, the classic work of Chatt and Wilkins on *cis–trans* equilibria in the platinum systems[26] provides some quidelines for correlating thermo-

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[24] A preliminary report of the use of this technique to distinguish these isomers has been published: J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **91**, 1550 (1969).

[25] We also note that the highest frequency carbonyl stretching mode in the infrared spectrum is more intense in the *cis* isomer than in the *trans* isomer, as expected on the basis of the angles between the carbonyl groups. The difference in intensities has been noted and discussed by other workers, particularly with respect to halide derivatives.[9,20]

[26] J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, **273**, 4300 (1952); 70 (1953); 525 (1956). Both infrared[27,28] and nmr [29–32] studies have

dynamic properties of these molybdenum complexes.[33] Correlation of thermodynamic, as well as kinetic, phenomena in the Pt(II) systems leads to a decreasing *trans effect* order as follows: CO $>$ PR_3 $\sim$ H^- $\sim$ CH_3^- $>$ I^- $>$ Br^- $>$ Cl^- and $PR_3 > SbR_3 > P(OR)_3 > AsR_3$. The major result of thermodynamic importance is that ligands which are high in the *trans effect series* tend to avoid occupying positions which are *trans* to one another. Although some minor rearrangements in order might be anticipated in the molybdenum systems, the trends would generally be expected to be the same. Regardless, consideration of the empirical relationship, *in the absence of severe steric interactions, strong trans effect ligands tend to be cis*, allows for the anticipation of some of the anomalies in correlations based on steric effects and prediction of most of the observed trends.

At this time we feel that it would be premature to engage in extensive discourse concerning the origin of the *trans effect* phenomenon in these molybdenum complexes;[34] nevertheless, some preliminary comments are probably in order. Despite the differences in bonding (the bond angles between *trans* ligands are expected to be in the range of 100–120° and between *cis* ligands in the range of 70–80°) compared to the Pt(II) systems, the argument which compares the relative degree of d-orbital charge delocalization between two π acceptors sharing the same d orbital to that in which two different d orbitals are utilized might be expected to apply. This approach, however, encounters difficulties in the following cases: (1) when R = hydride, too much *trans* isomer is observed; (2) for the series with constant R (*e.g.*, R = H), the *cis–trans* ratio does not decrease with increasing π-acceptor ability of L;[35] and (3) the carbonyl stretching frequencies are nearly identical for both isomers. Carbonyl stretching frequencies have generally been considered to be a fairly reliable indicator of the state of affairs electronically in the vicinity of the metal atom. It is therefore unusual that the stretching vibrations for the *cis* and *trans* isomers invariably give rise to absorptions at nearly identical infrared frequencies, particularly if π-acceptor considerations are important in determining stabilities. Nevertheless, the occurance of identical stretching frequencies does not necessarily imply identical degrees of π bonding. For instance, within the Cotton–Kraihanzel approximations,[37–40] the magnitudes of the carbon–oxygen stretching force constants reflect the strengths of the CO bonds, and in the *trans* isomer these force constants must be equal by symmetry. The difference between symmetric and antisymmetric stretching frequencies arises from the magnitude of aninteraction constant. In the *cis* isomer, on the other hand, the force constant for each of the carbonyls can be different so that a smaller interaction constant might account for the difference in frequencies. This, in fact, is the situation in these compounds; nevertheless, the differences in carbonyl force constants are smaller than would be anticipated.[41] Hence, it appears that σ-*trans* effects, *i.e.*, weakenings of the bond *trans* to a given ligand transmitted through a σ orbital,[42] should be fairly important in the molybdenum systems. That is, in terms of thermodynamic stability, aside from possible advantages from greater electron delocalization, one does not gain as much as might be anticipated from π bonding. This follows from the generally accepted description of metal–carbonyl bonding and the bond order arguments of Cotton;[39] *i.e.*, an increase in back-bonding from the metal to the carbonyl increases the metal–carbon bond order, but causes a concomitant decrease in the carbon–oxygen bond order. Hence the increase in stability arising from increased metal–carbon bonding is significantly offset by the decrease in stability resulting from the lowering of the carbon–oxygen bond order. However, further application of this approach requires a more detailed knowledge of the σ bonding in these complexes than is available at this time.[34] Suffice it to say that in all of the π-$C_5H_5Mo(CO)_2LR$ compounds a delicate balance between steric and electronic effects exist. It is surprising that consideration of *trans* effects and steric effects allows some predictive capability for the isomer ratios; nevertheless, exceptions are to be expected when dealing with energy differences on the order of 1 kcal.

Kinetic Considerations. The rates of *trans–cis* interconversion for a series of these molybdenum complexes have been measured over a fairly wide temperature range using several nmr techniques, and the results are summarized in Table III. Typically, the compound will

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allowed the extension of the *trans* effect series, particularly with respect to thermodynamic properties, and in some cases the determination of the relative importance of σ-donor and π-acceptor ability.[31,32]

(27) D. M. Adams, J. Chatt, J. Garrett, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

(28) J. M. Jenkins and B. L. Shaw, *ibid.*, 6789 (1965).

(29) J. Powell and B. L. Shaw, *ibid.*, 3879 (1965).

(30) A. Pidcock, R. E. Richards, and L. M. Venanzi, *Proc. Chem. Soc. London*, 184 (1962).

(31) G. W. Parshall, *J. Amer. Chem. Soc.*, **86**, 5367 (1964).

(32) R. V. Lindsey, G. W. Parshall, and U. G. Stolberg, *ibid.*, **87**, 658 (1965).

(33) Thermodynamic effects and bond length comparisons reflect the *trans effect* order as a *trans*-bond-weakening ability in six-coordinate as well as four-coordinate complexes: L. Aslanov, R. Mason, A. G. Wheeler, and P. O. Whimp, *Chem. Commun.*, 30 (1970), and references therein.

(34) We are currently carrying out a detailed investigation of the bonding in these molybdenum and the analogous tungsten complexes.

(35) As the π-acceptor ability of the ligand L becomes comparable to that of carbonyl, the tendency of the carbonyls to be *cis* to each other should be reduced. The relative π-acceptor abilities of the L ligands can be noted in the order of the carbonyl stretching frequencies for variations of L within a series of constant R. That is, the greater the π-acceptor ability of L, the lesser will be the degree of delocalization into the carbonyl antibonding orbitals, and the higher will be the carbonyl stretching frequencies. For example, with R = H the order of decreasing carbonyl frequencies $P(OPh)_3 > P(OMe)_3 > PPh_3 > P(n\text{-but})_3$ correlates with the decreasing π-acceptor ability of L and agrees with the π-acceptor order suggested by the spectrochemical series of Horrocks and Taylor.[36]

(36) W. D. Horrocks, Jr., and R. C. Taylor, *Inorg. Chem.*, **2**, 723 (1963).

(37) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc*, **84**, 4432 (1962).

(38) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

(39) F. A. Cotton, *ibid.*, **3**, 702 (1964).

(40) F. A. Cotton and R. M. Wing, *ibid.*, **4**, 314 (1965).

(41) Both the *cis* and *trans* isomer of π-$C_5H_5Mo(^{12}CO)_2(P(OMe)_3Cl$ show carbonyl stretching modes at 1989 and 1905 cm^{-1}. For *cis* π-$C_5H_5Mo(^{12}CO)(^{13}CO)P(OMe)_3Cl$, three of the four expected carbonyl bands are observed and they occur at 1965, 1882, and 1868 cm^{-1}. Using the 1965-cm^{-1} band for the ^{13}C compound along with 1989- and 1905-cm^{-1} bands, one obtains values for the force constants of k_1 = 15.54, k_2 = 15.09, and k_i = 0.62 mdyn/Å for the *cis* isomer. The values for the *trans* isomer are k_1 = 15.32 and k_i = 0.66 mdyn/Å. The apparent inconsistency of having a weaker π acceptor "*trans*" to a carbonyl and giving rise to a larger force constant (15.54 as compared to 15.32 for a *trans* carbonyl) can be attributed in large measure to the bond angles expected for these compounds (~110° for *trans* ligands and ~80° for *cis* ligands compared to 180 and 90° in octahedral compounds).

(42) This designation is a bastardization of the term used by C. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1966.

Table III

π-$C_5H_5Mo(CO)_2LX$			E_a, kcal/mol	Log A	ΔH^*, kcal/mol	ΔS^*, eu	ΔF^* at 25°, kcal/mol
X	L						
H[a]	PPh_3	$c \rightarrow t$	12.3 ± 0.1	12.2 ± 0.1	11.8 ± 0.1	−4.3 ± 0.5	13.1
		$t \rightarrow c$	12.6 ± 0.1	12.7 ± 0.1	12.1 ± 0.1	−2.3 ± 0.5	12.8
H[a]	$P(CH_3)_2Ph$	$c \rightarrow t$	12.2 ± 0.2	11.7 ± 0.1	11.6 ± 0.2	−6.8 ± 0.6	13.6
		$t \rightarrow c$	12.7 ± 0.2	12.1 ± 0.1	12.1 ± 0.2	−5.3 ± 0.6	13.7
H[b]	$P(CH_3)_2Ph$	$c \rightarrow t$	12.9 ± 0.1	12.3 ± 0.1	12.3 ± 0.1	−4.2 ± 0.4	13.5
		$t \rightarrow c$	13.3 ± 0.1	12.6 ± 0.1	12.8 ± 0.1	−2.8 ± 0.5	13.6
H[a]	*P*(*n*-but)$_3$	$c \rightarrow t$	12.2 ± 0.1	11.6 ± 0.1	11.7 ± 0.1	−7.3 ± 0.4	13.9
		$t \rightarrow c$	12.5 ± 0.1	12.1 ± 0.1	12.0 ± 0.1	−4.9 ± 0.4	13.4
H[b]	P(*n*-but)$_3$	$c \rightarrow t$	13.2 ± 0.1	12.4 ± 0.1	12.6 ± 0.1	−3.8 ± 0.5	13.8
		$t \rightarrow c$	13.5 ± 0.1	12.8 ± 0.1	13.0 ± 0.1	−1.6 ± 0.5	13.4
H[c]	P(*n*-but)$_3$	$c \rightarrow t$	13.2 ± 0.1	12.3 ± 0.1	12.6 ± 0.1	−3.9 ± 0.4	13.8
		$t \rightarrow c$	13.5 ± 0.1	12.9 ± 0.1	12.9 ± 0.1	−1.4 ± 0.4	13.4
H[a]	$P(OCH_3)_3$	$c \rightarrow t$	13.6 ± 0.1	13.0 ± 0.1	13.0 ± 0.1	−1.0 ± 0.3	13.3
		$t \rightarrow c$	12.1 ± 0.1	12.6 ± 0.1	11.5 ± 0.1	−2.7 ± 0.3	12.3
H[a]	$P(OPh)_3$	$c \rightarrow t$	13.4 ± 0.2	12.7 ± 0.2	12.9 ± 0.2	−2.1 ± 0.9	13.5
		$t \rightarrow c$	11.3 ± 0.2	12.7 ± 0.2	10.9 ± 0.2	−2.1 ± 1.0	11.5
CH_3[c]	$P(OPh)_3$	$c \rightarrow t$	18.4 ± 0.3	12.3 ± 0.2	17.7 ± 0.3	−4.7 ± 0.7	19.1
		$t \rightarrow c$	18.3 ± 0.3	12.0 ± 0.2	17.6 ± 0.3	−5.9 ± 0.7	19.4
$PhCH_2$[c]	$P(OPh)_3$	$c \rightarrow t$	19.6 ± 0.2	13.1 ± 0.2	19.0 ± 0.2	−0.8 ± 0.7	19.2
		$t \rightarrow c$	20.6 ± 0.2	13.0 ± 0.2	20.0 ± 0.2	−1.2 ± 0.8	20.4
CH_3[c]	$P(OMe)_3$	$c \rightarrow t$	20.2 ± 0.4	13.0 ± 0.3	19.6 ± 0.4	−0.9 ± 1.3	19.9
		$t \rightarrow c$	21.0 ± 0.4	12.8 ± 0.3	20.4 ± 0.4	−2.1 ± 1.3	21.0
CH_3[d]	PPh_3	$c \rightarrow t$	21.6 ± 0.2	13.3 ± 0.1	20.9 ± 0.2	−0.2 ± 0.6	20.9
		$t \rightarrow c$	23.3 ± 0.2	13.3 ± 0.1	22.5 ± 0.2	−0.2 ± 0.6	22.6
Cl[d]	$P(OMe)_3$	$c \rightarrow t$	24.4 ± 0.2	13.1 ± 0.1	23.7 ± 0.2	−0.8 ± 0.5	24.0
		$t \rightarrow c$	23.1 ± 0.1	13.2 ± 0.1	22.5 ± 0.1	−0.2 ± 0.1	22.5
Br[d]	$P(OMe)_3$	$c \rightarrow t$	23 2 ± 0.1	12.7 ± 0.1	22.6 ± 0.1	−2.8 ± 0.3	23.4
		$t \rightarrow c$	23.7 ± 0.1	13.4 ± 0.1	23.1 ± 0.1	+0.6 ± 0.3	22.9
I[d]	$P(OMe)_3$	$c \rightarrow t$	22.3 ± 0.1	12.3 ± 0.1	21.6 ± 0.1	−4.4 ± 0.2	22.9
		$t \rightarrow c$	23.5 ± 0.1	12.8 ± 0.1	22.8 ± 0.1	−2.4 ± 0.3	23.5
I[d]	PPh_3	$c \rightarrow t$	25.8 ± 0.9	13.2 ± 0.4	24.9 ± 0.9	−1.1 ± 2.1	25.2
		$t \rightarrow c$	25.9 ± 0.7	13.3 ± 0.4	25.1 ± 0.7	−0.4 ± 1.7	25.2
I[d]	$P(CH_3)_2Ph$	$c \rightarrow t$	23.6 ± 0.2	12.1 ± 0.1	22.7 ± 0.2	−6.0 ± 0.5	24.5
		$t \rightarrow c$	24.0 ± 0.2	12.8 ± 0.1	23.1 ± 0.2	−2.7 ± 0.5	23.9

[a] $CDCl_3$. [b] CS_2. [c] Toluene. [d] *o*-Dichlorobenzene.

crystallize entirely as one isomeric form. If the crystals are dissolved at a sufficiently low temperature and the nmr spectrum determined after several time intervals, the isomerization can be detected by the decrease in intensity of the resonances associated with one isomer and the appearance and subsequent increase in the intensity of the other isomer. Quantitative measurements of the intensities as a function of time allows the determination of the rate constants for both the forward (k_{tc}) and the reverse reactions (k_{ct}). At higher temperatures the isomerization rate becomes sufficiently rapid that averaging of the nmr resonances occurs. This averaging is readily followed by observing the temperature dependence of the line shapes of the π-cyclopentadienyl resonances, as is shown in Figure 8 for a typical example. A survey of the results of these kinetics studies shows that even though there is only a slight dependence of k_{tc} on the nature of L, there is a strong dependence on R, such that there is a decrease in the order H, D > Me, CH_2Ph > Cl, Br, I.

Generally the rate constants are relatively insensitive to solvent effects (*e.g.*, for L = P(*n*-but)$_3$ and R = H, the rate constants vary less than 25% among several solvents); however, the ratio of the forward and reverse rate constants varies somewhat as evidenced by changes in the equilibrium constants. The isomerizations appear to be nondissociative unimolecular processes as suggested by: (1) the absence of any significant concentration effect on $1/\tau_c$ or $1/\tau_t$, which implies first-order kinetics; (2) the consistency of log A values and entropies of activation with unimolecular processes; (3) the retention of P^{31}–H coupling to the π-cyclopentadienyl ligand and the R group in averaged spectra; and (4) the retention of C^{13}–H coupling between carbonyl and hydride ligands in averaged spectra.[43] Absence of significant bond breaking in the transition state, at least with regard to the molybdenum–hydrogen bond, is suggested by the absence of a significant isotope effect (k_H/k_D = 1.00 ± 0.05) on the rearrangement rate of π-$C_5H_5Mo(CO)_2[P(Ph)_3]H$ compared with π-$C_5H_5Mo(CO)_2[P(Ph)_3]D$. Hence, we suggest that isomerization occurs principally *via* angle bending or *allogonal* processes. These types of rearrangements lend to be fairly complicated and several modes of rearrangement are possible. Therefore, we will direct our attention to the pathways which might contribute to isomerization.

The Mechanism of Rearrangement. These complexes have been considered as seven coordinate in the initial considerations of bonding and structure; however, in discussing the rearrangement mechanism we will find it convenient to consider them as pseudo-five-coordinate complexes, in which the π-cyclopentadienyl group is considered to take up one coordination position. The

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(43) Some of the details of these arguments have been considered previously.[25,44,45]

(44) J. W. Faller, A. S. Anderson, and C. C. Chen, *J. Organometal. Chem.*, 17, 7 (1969). Recent determinations of the isotope effects give values of k_H/k_D = 1.00 ± 0.05, rather than the value of 1.06 reported in this paper.

(45) J. W. Faller, A. S. Anderson, and C. C. Chen, *Chem. Commun.*, 719 (1969).

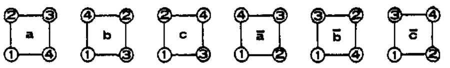

Figure 3. The isomers which arise from substitution of the pseudo-five-coordinate molybdenum complex. The π-cyclopentadienyl ring is assumed to be "remote"; *i.e.*, the four basal ligands are nearest the viewer.

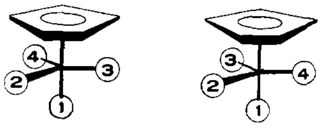

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Figure 4. Two of the eight possible intermediates, which are distinguished by the number of the ligand in the axial position and the chirality of the equatorial ligands (2, 3, 4 clockwise = **1**; 2, 3, 4 counterclockwise = $\bar{\mathbf{1}}$.

topological representation of steroisomerism proposed by Muetterties[46–48] is very effective in dealing with the multitude of possible rearrangement processes. In this technique each vertex of a polyhedron is assigned to represent a given isomer of the compound. Rearrangements are then considered as paths along edges of the polyhedron which allow the various vertices (isomers) to be traversed.

Previous workers have generally treated the rearrangements of the trigonal-bipyramidal polytope and a greater number of isomers than is necessary here. Actually there are 30 possible isomers for a square-pyramidal structure and 20 possible isomers for a trigonal-bipyramidal structure, which leads to rather unwieldy topological models. Nevertheless, a fairly tractable model can be obtained by consideration of the subset of six square pyramids with a π-cyclopentadienyl group at the apex and eight trigonal bipyramids with the π-cyclopentadienyl group in an axial position. This limitation of the number of isomers to be considered should not lead to any difficulties in this situation since the structural requirements of the π-cyclopentadienyl group virtually assure that it will occupy the apical position of the square pyramid in low-energy structures (*vide supra*).

The distortions due to steric interactions are sufficiently severe in these complexes that belaboring the issue of an idealized polytope to represent an intermediate or a transition state is unjustified. Furthermore, we wish to consider here only situations for which there is a reasonable likelihood that the rearrangement will be detectable. Hence, the proposed intermediate form should have some geometry which will allow for the observed conversions, but the most important prerequisite is the possibility of keeping track of the relative positions of the ligands. This appears to be most easily accomplished by considering the π-cyclopentadienylmolybdenum moiety as a reference point and following the interchange of other ligand positions relative to it. Hence, the essential features of the hypothetical intermediate become: (1) the ligand which assumes the position farthest away from the plane of the cyclopentadienyl ring and (2) the sense or chirality of the remaining three ligands about the metal atom. A trigonal bipyramid with the π-cyclopentadienyl ligand occupying an axial position incorporates all of these features. For the general case of four different ligands, the six different isomers of the square pyramid are considered to be labeled as in Figure 3. The eight intermediates are distinguished by the number of the ligand on the axial position and the chirality of the equatorial ligands (Figure 4).

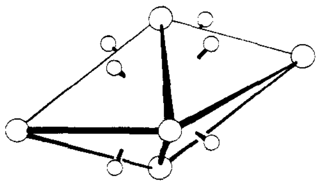

Figure 5. A stellated octahedron.

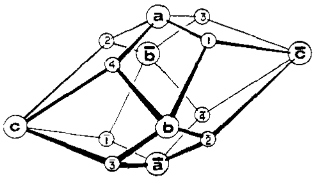

Figure 6. A topological model for rearrangements for a square pyramid assuming only basal ligands interchange positions.

A suitable topological representation for this system can be constructed using a stellated octahedron (see Figure 5). A closed system results if each vertex of the octahedron is assigned to one of the six square-pyramidal isomers and the vertices which cap the triangular faces of the octahedron are assigned to the eight trigonal bipyramidal intermediates. Connections from the corners of each triangular face to the vertex which caps the face provides a connectivity of four for the square-pyramidal set and a connectivity of three for the trigonal bipyramidal set (see Figure 6). Hence, a given intermediate can provide a pathway for conversion of one square-pyramidal isomer into only two (those sharing the triangular face of the octahedron which is capped by the vertex representing that intermediate) of the other five isomers. For instance, isomer a can only convert into b or c *via* intermediate **4**.

Within this approach to the mechanisms of rearrangement one notes that if a given isomer is converted into another, it can only occur *via* two of the eight possible intermediates. That is, a can only convert into b *via* intermediate **1** or **4**. Futhermore, one notes that an isomer of a given chirality cannot be converted into its enantiomer without invoking at least two different intermediates. In the situations we have at hand, however, one might be skeptical about the value of this model because two of the ligands are the same and consequently only two isomers are detected. Nevertheless, one can make some very definite statements within the framework of this model about the mechanisms. For instance, there is the possibility of following more than merely *cis–trans* rearrangement because the chirality of the *cis* species can be detected by the methylene protons in benzyl groups or the methyl protons of dimethylphenylphosphine ligands. At this point it is probably useful to consider a specific compound rather than an abstract

(46) E. L. Muetterties, *J. Amer. Chem. Soc.*, 91, 4115 (1969).
(47) E. L. Muetterties, *ibid.*, 91, 1636 (1969).
(48) See also P. C. Lauterbur and F. Ramirez, *ibid.*, 90, 6722 (1968).

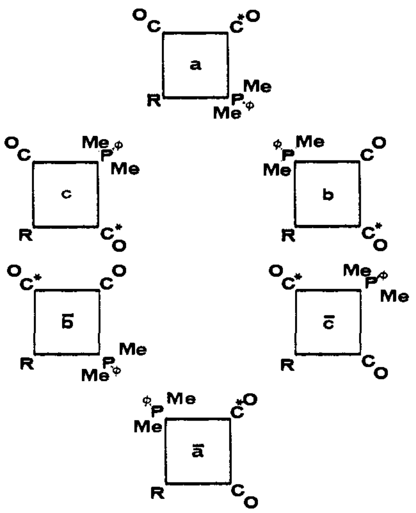

Figure 7. The isomers of a dimethylphenylphosphine derivative.

example. π-C$_5$H$_5$Mo(CO)$_2$[Me$_2$PPh]I is a particularly useful complex in this regard. For sake of comparison one of the carbonyls will be considered to be labeled (actually the mono-^{13}C carbonyl species can be observed in the pmr spectrum of the hydride complex). This leads to the six isomers shown in Figure 7, in which the following arbitrary ligand assignments have been made: ligand 1 = R; ligand 2 = CO; ligand 3 = C*O; and ligand 4 = Me$_2$PPh. Since the pmr spectrum does not allow the detection of enantiomers and since the carbonyls are in fact not labeled, the nmr spectrum actually only distinguished *cis* species, (a, b, $\bar{a}$, and $\bar{b}$) and *trans* species (c and $\bar{c}$). As shown in Figure 8, the *cis* isomers give rise to a single π-cyclopentadienyl resonance with a slight splitting at lower field than that of the *trans* isomer. The methyl region of the spectrum shows a doublet ($J = 9.1$ Hz) at δ 1.72 attributed to the equivalent methyl groups of the phosphine ligand in the *trans* isomer and two superposed doublets for the diastereotopic methyl groups in the *cis* isomer ($J = 8.7$ Hz, δ 1.90 and $J = 8.7$ Hz, δ 1.99). Although it is virtually impossible to assign a given methyl resonance in the *cis* isomer to a specific methyl group, it is important to note that the chemical shift of the *pro-R* methyl in a or $\bar{b}$ is the same as the *pro-S* methyl in $\bar{a}$ or b.[49] That is, if one assumes that the configuration of the phosphorus atom does not change during the rearrangement, the interconversion between a or b and $\bar{a}$ or $\bar{b}$ would average the diasteretopic proton resonances, owing to the effective averaging of the chirality of the molybdenum-containing moiety. On the other hand, interconversion between a and $\bar{b}$ or between b and $\bar{a}$ would not result in averaging.

The temperature dependence of the methyl resonances allows one to deduce some unusual aspects of the interconversion pathways and the possible intermediates involved. Of specific importance is the observation that the nonequivalence of the diastereotopic methyl resonances of the *cis* isomer is almost completely averaged out before *cis–trans* isomerization occurs at an appreciable rate (Figure 9). Hence, as is shown in Figure 8, at 115° the π-cyclopentadienyl resonaces show no sign of *cis–trans* interchange and furthermore the *trans* methyl resonances are sharp (indicating the k_{tc} <0.5 sec^{-1}), whereas the methyl resonances of the *cis* isomer have coalesced (k_{cc} = 6.0 sec^{-1}). This implies that there is a rapid interconversion of the enantiomers of the *cis* isomer occuring before any appreciable interconversion of the *cis* and *trans* isomers. Rapid interconversion of the *cis* and *trans* isomers does occur at higher temperatures, as indicated by the averaging of both *cis* and *trans* methyl reso-

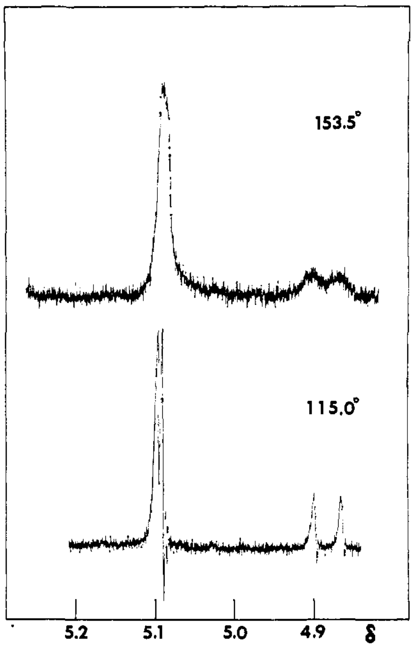

Figure 8. The pmr spectrum in the cyclopentadienyl region of π-C$_5$H$_5$Mo(CO)$_2$(PMe$_2$Ph)I in *o*-dichlorobenzene.

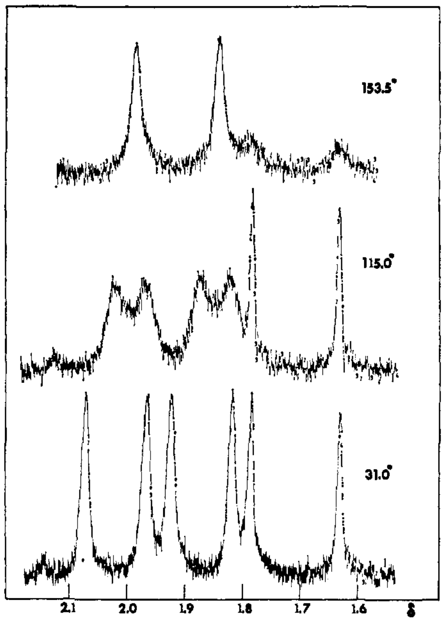

Figure 9. The pmr spectrum in the methyl region of π-C$_5$H$_5$Mo(CO)$_2$(PMe$_2$Ph)I in *o*-dichlorobenzene.

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(49) These designations correspond to the nomenclature suggested by Hanson.[50] The *pro-S* methyl group is the methyl nearest to the ligand R in the conformation shown in a, whereas it is the methyl farthest from R in b. Note also that these diastereotopic methyl groups are nonequivalent, even though there is rapid rotation about the metal–phosphorus bond on the nmr time scale, as discussed previously.[3]

(50) K. R. Hanson, *J. Amer. Chem. Soc.*, **88**, 2731 (1966).

nances. We tentatively assume that this corresponds to a rapid equilibrium between a and b as well as $\bar{a}$ and $\bar{b}$.[51] Reference to the topological model thus indicates that either intermediates **1** and $\bar{\mathbf{1}}$ or **4** and $\bar{\mathbf{4}}$ should be involved in the principal pathway for the process, but neither **2**, $\bar{\mathbf{2}}$, **3**, or $\bar{\mathbf{3}}$ is implicated. Hence, we conclude that this process does not involve a carbonyl ligand assuming an axial position in the intermediate or transition state. If one assumes further that the same intermediate is involved in *cis–trans* isomerism, then the barrier along the reaction coordinate leading to the *trans* isomer is significantly higher (in this case 3 kcal/mol higher) than that leading to the *cis* isomer.

As an example, of intermediate **4** were involved, a free-energy activation barrier of 21.2 kcal/mol would be encountered in a reaction path from a → **4** or b → **4**, whereas a barrier of 23.9 kcal/mol would be encountered for c → **4**. Since there is a free-energy difference between the *cis* and *trans* isomers of 0.6 kcal/mol, a barrier along **4** → a or **4** → b would be expected to be 2.9 kcal/mol lower than **4** → c.[52]

The increase in the barrier height with R appears to parallel the increase in van der Waals radius of R, which suggest that the barrier to interconversion of isomers is largely steric in nature. But as in the case of the equilibrium constants, van der Waals radii can be misleading because an increase in covalent radius usually accompanies an increase in van der Waals radius.[53] Although in hydride complexes one might expect that moving the hydrogen atom to an axial position (intermediate **1** and $\bar{\mathbf{1}}$) might be favorable on the basis of less steric interaction with the equatorial ligands, consideration of interactions of the equatorial ligands with the π-cyclopentadienyl ring suggests that the bulkiest ligand might preferably assume the axial position. Churchill and Fennessey[12] have noted that there is considerably steric interaction between the phosphine ligand and the ring in $\pi\text{-}C_5H_5Mo(CO)_2(PPh_3)COCH_3$ in the square-pyramidal structure found in the solid. Since moving any ligand to the axial position in the intermediate would require increased interaction of the remaining equatorial ligands with the ring, the interaction of the ring with the equatorial phosphine ligand could be so severe as to make that pathway energetically prohibitive. We are not in a position at this time to decide between the predominant intermediacy of **1** and $\bar{\mathbf{1}}$ or **4** and $\bar{\mathbf{4}}$. Since the *cis–cis* process seems to occur generally about 3 kcal/mol lower than the *cis–trans* process for different R groups (R = H and R = I are pertinent examples), a process common to all of the rearrangements would appear appropriate. Carbonyl ligands would be expected to have steric effects intermediate between those of iodide and hydride ligands; hence, one would expect that if the ligand which moved to the axial position were the smallest, then a change in mechanism would be anticipated upon substitution of iodide for hydride. This provides an additional implication that the most bulky ligand assums the axial position in the intermediate; *i.e.*, **4** and $\bar{\mathbf{4}}$ would be preferred over **1** and $\bar{\mathbf{1}}$. However, we feel that it is premature to speculate about the situations in which the most bulky ligand would occupy the axial position preferentially. Since there are undoubtedly electronic factors which significantly influence the barrier height and since this type of stereochemical nonrigidity is also observed in the tricarbonyl hydrides, suffice it to say that isomerization can probably occur *via* all of the intermediates; however, in these cases, the intermediates suspected in the lowest energy pathway do not involve carbonyl ligands in the axial position.[54]

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(51) Obviously, in the absence of a label a cannot be distinguished from b nor can $\bar{a}$ be distinguished from $\bar{b}$. However, in the hydrides, which undergo analogous rearrangements at lower temperatures, the ^{13}C–H coupling constants in the $(^{12}CO)(^{13}CO)$ compounds give specific information regarding this interchange. Studies are in progress with enriched samples to provide these data.

(52) It is obvious that a different transition state is involved in the *cis–cis* "enantiomeric" interconversion than in the *cis–trans* interconversion. It is not necessary to assume that an intermediate is present in low concentration; however, we feel that these transition states are similar to that of the intermediate suggested. Line-shape analysis of the methyl resonances provided the following data (temperature, k_{cc}, sec^{-1}): 99.0, 2.05; 115.0, 6.00; 126.0, 13.0; 132.5, 20.0; 142.3, 40.0. Least-squares analysis gave the following: $E_a = 21.0 \pm 0.5$; $\log A = 12.6 \pm 0.3$; $\Delta H^* = 20.2 \pm 0.5$; $\Delta S^* = 3.3 \pm 1.3$; $\Delta F^*_{25} = 21.2$.

(53) This compensation effect has been observed frequently in axial–equatorial equilibria in cyclohexane derivatives. For example, see J. A. Hinsch, *Top. Stereochem.*, **1**, 199 (1967).

(54) These studies do not preclude the possibility of a carbonyl assuming the apical position in an even lower energy barrier equilibrium, *e.g.*, a = $\bar{b}$ *via* **2** or **3**; or $\bar{a}$ = b *via* $\bar{\mathbf{2}}$ or $\bar{\mathbf{3}}$. It is unlikely, however, that the *trans* isomer might rearrange *via* a similar low-barrier equilibrium, since axial carbonyl ligands (**2**, **3**, $\bar{\mathbf{2}}$, $\bar{\mathbf{3}}$) would lead to intermediate formation of the *cis* isomer in an equilibrium between c and $\bar{c}$.