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Kinetics of the Cis–Trans Isomerization of $PhMn(CO)_4P(OPh)_3$

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The complex $PhMn(CO)_4P(OPh)_3$ has been shown to exist as a separable mixture of cis and trans isomers. The kinetics of isomerization of *trans*-$PhMn(CO)_4P(OPh)_3$ to a cis–trans equilibrium mixture have been studied over a temperature range of 30–55 °C in *n*-heptane solution. The isomerization is first order with respect to complex. Free $P(OPh)_3$ or CO at 1 atm was observed to have no effect on the rate of isomerization. Since exchange with free $P(OPh)_3$-d_{15} does not occur during isomerization, phosphite dissociation cannot play a role in the isomerization process. The kinetic results are consistent with an intramolecular mechanism.

Introduction

Reactions involving $RCOMn(CO)_4L$ and $RMn(CO)_4L$ complexes (R = alkyl, aryl) have been the subject of numerous mechanistic investigations.[1–22] Interest in these systems is due in large part to their relevance to synthetically useful stoichiometric[23–25] and catalytic[2,24,25] processes which are less amenable to direct study. Considerable mechanistic information has been inferred from the stereochemical changes which accompany various reactions of the manganese complexes.[1–10] Clearly, such mechanistic implications are necessarily dependent on a firm understanding of the configurational stability of $RCOMn(CO)_4L$ or $RMn(CO)_4L$ with respect to cis–trans isomerization.

Known $RCOMn(CO)_4L$ complexes have been shown to exist either as mixtures of cis and trans isomers or as exclusively cis isomers.[1–8,22,26–29] The stereochemistry is clearly dependent on the nature of the R and L groups[6,8] and, in some cases, on the method of preparation.[8] For those complexes where both isomers exist, qualitative studies of the isomerization reaction have been carried out.[6] In addition, a kinetic study[5] of the cis–trans isomerization of $MeCOMn(CO)_4PPh_3$ has shown that isomerization occurs by a first-order process which involves PPh_3 dissociation as the rate-determining step.

The variable stereochemistry of many $RCOMn(CO)_4L$ complexes is in distinct contrast to observations on the corresponding $RMn(CO)_4L$ derivatives. With one exception, decarbonylation reactions of *cis*- and *cis*- and *trans*-$RCOMn(CO)_4L$ complexes are reported to afford exclusively *cis*-$RMn(CO)_4L$ derivatives.[1,2,5–7,27–29] The existence of $PhMn(CO)_4P(OCH_2)_3CEt$ as a mixture of cis and trans isomers has been claimed on the basis of dipole moment and ^1H NMR measurements,[7] but further investigation of this complex has not been reported.

In the course of previous work[30] involving $PhMn(CO)_4P(OPh)_3$, we found this previously reported[7] cis complex to be in fact a separable mixture of cis and trans isomers. This result has provided the first opportunity of studying the cis–trans isomerization of a $RMn(CO)_4L$ complex. Accordingly, we have investigated the kinetics and mechanism of the isomerization of $PhMn(CO)_4P(OPh)_3$.

Experimental Section

General Procedures and Materials. All operations, including the purification of solvents, were carried out under an atmosphere of dry nitrogen. All solvents (reagent grade) were dried by appropriate methods and were freshly distilled prior to use. The *n*-heptane used in the kinetic and equilibrium studies was washed with concentrated H_2SO_4 and distilled water, passed through a silica gel column, and distilled from sodium wire. The distillate was stored over sodium wire and was freshly redistilled just prior to use. Triphenyl phosphite was distilled in vacuo and stored under nitrogen before use in the kinetic experiments. CP grade CO (99.3%) was used as received from Air Products and Chemicals, Inc. Phenol-d_6 (98% D) was purchased from Merck and Co., Inc.

The complex $PhMn(CO)_5$ was synthesized according to the literature method.[31] Triphenyl-d_{15} phosphite, $P(OC_6D_5)_3$, was prepared from PCl_3 and C_6D_5OD by a modification of the procedure given by Walsh[32] for the undeuterated analogue. The deuterium content of the $P(OC_6D_5)_3$ was determined as 98 ± 2% D by ^1H NMR methods using a weighed amount of CH_3CN as an internal integration standard. Microanalyses were carried out by Galbraith Laboratories, Knoxville, TN.

Spectra. Infrared spectra were obtained on a Perkin-Elmer 180 spectrophotometer which was calibrated in the $\nu(CO)$ region with CO. Solution spectra were run in NaCl cells by using *n*-heptane as solvent. Infrared spectral measurements during kinetic studies were obtained on a Perkin-Elmer 237 spectrophotometer equipped with a Moseley Model 7101A external recorder.

Proton and $^{31}P\{^1H\}$ NMR spectra were recorded at 90.00 and 36.43 MHz, respectively, on a Bruker WH-90DS spectrometer operating in the FT mode. Routine spectra were obtained in $CDCl_3$ solution. ^{31}P chemical shifts are referenced to an external sample of 85% H_3PO_4; positive chemical shifts are *downfield* from H_3PO_4.

Preparation of $PhMn(CO)_4P(OPh)_3$. A solution of $PhMn(CO)_5$ (5.11 g, 18.8 mmol) and $P(OPh)_3$ (5.91 g, 19.1 mmol) in 150 mL of THF was heated under reflux for 2.5 h. Solvent was removed on a rotary evaporator, and the residue was dissolved in hexane. The resulting solution was chromatographed on a 4 × 45 cm Florisil column with hexane as eluent. The chromatographic separation was monitored by infrared analysis of the eluate. The first chromatographic fraction (band A) contained primarily the cis isomer, but a complete separation of the pure cis isomer could not be achieved. The second fraction (band B) was eluted with a 9:1 mixture of hexane/dichloromethane. Band B contained the pure trans isomer and was collected at 0 °C to prevent isomerization during the slow elution process. Both chromatographic fractions were concentrated on the rotary evaporator before further workup procedures were carried out.

a. Isolation of Pure *trans*-$PhMn(CO)_4P(OPh)_3$. The band A solution was cooled at −20 °C to give a colorless crystalline solid which was separated by filtration. Workup of the colorless filtrate is described below in b. Recrystallization from hexane at −78 °C afforded 1.24 g of pure *trans*-$PhMn(CO)_4P(OPh)_3$. An additional 1.27 g of pure trans isomer was similarly isolated after cooling band B at −78 °C; total yield 2.51 g (24%). Anal. Calcd for $C_{28}H_{20}O_7PMn$: C, 60.66; H, 3.64; P, 5.59; Mn, 9.91. Found: C, 60.99; H, 3.87; P, 5.41; Mn, 9.01. IR spectrum (*n*-heptane): $\nu(CO)$ 2081 (vw), 2024 (vw), 1989 (s) cm^{-1}. ^{31}P NMR spectrum ($CDCl_3$): +173.0 ppm.

b. Isolation of the *cis*- and *trans*-$PhMn(CO)_4P(OPh)_3$ Mixture. The filtrate from the −20 °C solution of band A (see section a above) was concentrated on the rotary evaporator and cooled at −78 °C to produce a colorless crystalline solid. Filtration afforded 6.00 g (58% yield) of a mixture of *cis*- and *trans*-$PhMn(CO)_4P(OPh)_3$. Anal. Calcd for $C_{28}H_{20}O_7PMn$: C, 60.66; H, 3.64; P, 5.59; Mn, 9.91. Found: C, 60.88; H, 3.47; P, 5.49; Mn, 8.90. IR spectrum (*n*-heptane): $\nu(CO)$ 2078 (m), 2012 (m), 1990 (s), 1972 (m) cm^{-1}; $\nu(^{13}CO)$ 2067 (vw), 1932 (vw) cm^{-1}. ^{31}P NMR spectrum ($CDCl_3$): +158.0 (strong), +173.0 (weak) ppm.

Equilibrium Studies. The equilibrium constant K_{eq} for the isomerization reaction

$$trans\text{-}PhMn(CO)_4P(OPh)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} cis\text{-}PhMn(CO)_4P(OPh)_3$$

can be defined as

$$K_{eq} = [cis]/[trans] = k_1/k_{-1}$$

where [cis] and [trans] represent the equilibrium concentrations in

Table I. Equilibrium Constants for the Isomerization of $PhMn(CO)_4P(OPh)_3$ (Eq 1)

T, °C	K_{eq}[a]	T, °C	K_{eq}[a]
30.0	$2.7_9 \pm 0.0_5$	50.3	$2.8_9 \pm 0.0_8$
40.0	$3.0_2 \pm 0.0_6$	55.0	$3.3_2 \pm 0.0_7$
46.9	$3.3_2 \pm 0.0_6$	mean	$3.0_7 \pm 0.2_4$

[a] The indicated uncertainty represents one standard deviation.

M of the cis and trans isomers, respectively. Values of K_{eq} can thus be determined by measuring a spectroscopic property which is proportional to the ratio of the equilibrium concentrations of the two isomers. In practice, this was accomplished by measuring the relative areas of the ^{31}P NMR peaks due to the cis and trans isomers.[33] Since the broad ($\Delta\nu_{1/2} > 100$ Hz) resonances were not fully separated from one another, it was impossible to obtain reliable peak areas by instrumental integration. Thus, the $^{31}P\{^1H\}$ NMR spectrum was first resolved into its two component peaks by using a subroutine of the nonlinear least-squares program[34,35] FIT70. Lorentzian band shapes were assumed. Peak areas were computed directly by numerical integration of the individual resolved peaks. In general, 100–130 data points (intensity–frequency readings) were used to fit each spectrum in the region of interest. This corresponds to a frequency interval of about 25 Hz between successive data points. The standard deviation of the fit in general resulted in an uncertainty of ~2% in K_{eq}. Realistically, however, the error in K_{eq} is on the order of 10% in view of the difficulties associated with phasing such broad signals over a large sweep width. Equilibrium constant data are tabulated in Table I.

The equilibrium measurements were carried out as follows. A 0.26 M solution of *cis*- and *trans*-$PhMn(CO)_4P(OPh)_3$ in *n*-heptane was prepared in a nitrogen-filled 8-mm NMR tube. The tube was sealed under nitrogen or in vacuo and placed coaxially in a 10-mm NMR tube. The outer tube contained D_2O which served as an external lock. The two-tube assembly was placed in a constant-temperature bath until chemical equilibrium was attained before transfer to the NMR spectrometer. Temperatures were controlled to ±1 °C during NMR measurements by a Bruker BVT-1000 variable-temperature unit. This unit was previously calibrated with a copper–constantan thermocouple placed directly in the probe. The $^{31}P\{^1H\}$ NMR spectra were obtained under the following conditions: ~45° pulse angle, 8K data points, 5-kHz sweep width, and an exponential line-broadening function corresponding to 1 Hz broadening. The number of scans necessary to obtain an optimum signal/noise ratio was typically about 20K.

Kinetic Studies. a. Kinetics of Isomerization of *trans*-$PhMn(CO)_4P(OPh)_3$. The isomerization reaction of pure *trans*-$PhMn(CO)_4P(OPh)_3$ was followed by monitoring the appearance of the 2078 cm^{-1} $\nu(CO)$ band of the cis isomer as a function of time. Preliminary experiments established that solutions of the equilibrium cis–trans mixture obeyed Beer's law over the concentration range studied in the kinetic measurements (3.5×10^{-3}–2.0×10^{-2} M). Solutions of the trans isomer were prepared under nitrogen in 5- or 10-mL reaction flasks which were placed in a bath at constant temperature (±0.05 °C). Appropriate time was allowed for the solution to attain thermal equilibrium. Aliquots were withdrawn for infrared analysis at suitable time intervals. Between 20 and 40 readings were taken over a period of at least 3 half-lives. Light was excluded from the reaction flask for the duration of the kinetic run. The equilibrium absorbance value, A_∞, was determined from the mean absorbance of at least six different aliquots withdrawn after 10 half-lives of the reaction. The standard deviation of the mean was typically less than 1%.

Analysis of the kinetic data was carried out by using the nonlinear least-squares program[34] FIT70 to solve the first-order equation[36]

$$A_t = A_\infty - (A_\infty - A_0)e^{-k_{obsd}t}$$

where $k_{obsd} = (k_1 + k_{-1})$. Input data consisted of A_0, A_∞, and absorbance–time readings through at least 3 half-lives of the reaction. Unit weights were used in all cases. The standard deviation of the fit was typically 0.5–0.7% of k_{obsd}. Rate constants for the forward (k_1) and reverse (k_{-1}) reactions were determined from k_{obsd} by using the mean value of the equilibrium constant ($K_{eq} = 3.1$) from Table I. A subroutine of the FIT70 program[34] was used to calculate activation parameters from the k_1 and k_{-1} values at various temperatures. For these fits, $1/k^2$ weights were used in order to minimize the percent error between the observed and fitted values of the dependent variable. Appropriate kinetic results are shown in Table II.

Table II. First-Order Rate Constants for the Isomerization of $PhMn(CO)_4P(OPh)_3$ (Eq 1)

10^3 [trans], M[a]	T, °C	10^5k_{obsd}, s^{-1} [b]	10^5k_1, s^{-1} [c]	10^5k_{-1}, s^{-1} [c]
3.43	29.5	1.23 ± 0.01	0.93_0	0.30_0
4.94	35.0	2.53 ± 0.01	1.9_1	0.61_7
4.91	40.0	5.00 ± 0.03	3.7_8	1.2_2
4.76	45.0	9.36 ± 0.03	7.0_8	2.2_8
3.43	50.0	16.3 ± 0.1	$12._3$	3.9_6
4.28		16.4 ± 0.1		
9.93		16.2 ± 0.1		
20.1		16.1 ± 0.1		
4.86	55.0	27.7 ± 0.2	$20._9$	6.7_6
20.1[d]	50.0	16.1 ± 0.1		
4.28[e]	50.0	16.5 ± 0.1		
20.0[e]	50.0	16.5 ± 0.1		

[a] Initial concentration of *trans*-$PhMn(CO)_4P(OPh)_3$. [b] The indicated uncertainty represents one standard deviation. [c] Calculated from k_{obsd} by assuming $K_{eq} = 3.1$; see text. [d] In presence of free $P(OPh)_3$; $[P(OPh)_3] = 2.05 \times 10^{-2}$ M. [e] In presence of CO at ambient pressure; $[CO] = 9.0 \times 10^{-3}$ M.

b. Effect of Free $P(OPh)_3$. The effect of free $P(OPh)_3$ on the rate of isomerization was examined at 50.0 °C for a solution containing approximately equimolar amounts of *trans*-$PhMn(CO)_4P(OPh)_3$ (2.01×10^{-2} M) and $P(OPh)_3$ (2.05×10^{-2} M). Infrared analysis of the reaction mixture showed that isomerization was accompanied by the slow growth of $\nu(CO)$ bands at 2041, 1961, and 1953 cm^{-1} which were not observed in the absence of $P(OPh)_3$. These bands are assigned to the CO substitution product[7] $PhMn(CO)_3[P(OPh)_3]_2$ (and, perhaps, $PhCOMn(CO)_3[P(OPh)_3]_2$) by comparison with an authentic sample. The white crystalline complex $PhMn(CO)_3[P(OPh)_3]_2$ could be isolated from the reaction mixture at the end of the reaction. Although the rate of CO substitution is significantly slower than the rate of isomerization (see part c), the effect of the competitive reaction becomes appreciable after several half-lives of the isomerization reaction. Thus, A_∞ had to be determined from a kinetic study carried out in the absence of $P(OPh)_3$ under otherwise identical conditions. In order to minimize interference from the substitution reaction, absorbance–time data used in the kinetic analysis was limited to the first 2 half-lives of the isomerization reaction.

c. Kinetics of CO Substitution of *cis*- and *trans*-$PhMn(CO)_4P(OPh)_3$ by $P(OPh)_3$. The rate of CO substitution of the *cis*- and *trans*-$PhMn(CO)_4P(OPh)_3$ mixture by $P(OPh)_3$ was studied at 50.0 °C under pseudo-first-order conditions. Initial concentrations of the *cis*- and *trans*-$PhMn(CO)_4P(OPh)_3$ mixture and $P(OPh)_3$ were 1.00×10^{-2} and 4.28×10^{-1} M, respectively. The CO substitution reaction was followed by monitoring the disappearance of the 2078 cm^{-1} $\nu(CO)$ band of the cis isomer as a function of time. Other procedures were carried out as described in part a. The absorbance–time readings used in the kinetic analysis were those recorded after a time period corresponding to 5 half-lives of the much faster isomerization reaction. This procedure was necessary because the *initial* cis–trans mixture contains more cis isomer than an *equilibrium* mixture at 50.0 °C. Thus, the decrease in absorbance during the initial stages of the reaction is primarily due to the establishment of an equilibrium cis–trans mixture via cis → trans isomerization. The calculated rate constant, k_{obsd}, for the substitution reaction was $(7.30 \pm 0.04) \times 10^{-6}$ s^{-1}.

d. Effect of CO. Two experiments were carried out at 50.0 °C to determine the effect of CO on the rate of isomerization. In each case the solution of *trans*-$PhMn(CO)_4P(OPh)_3$ was prepared under a CO atmosphere by using *n*-heptane which had been thoroughly saturated with CO. The concentration of CO in a saturated *n*-heptane solution at 50.0 °C can be estimated as 9.0×10^{-3} M from the reported solubility[37] and the known[38] vapor pressure of *n*-heptane, assuming Henry's law is obeyed. In one experiment, the initial concentration of complex (2.01×10^{-2} M) was greater than the concentration of CO; in the other experiment, the initial concentration of complex (4.28×10^{-3} M) was less than the CO concentration. These initial concentrations of *trans*-$PhMn(CO)_4P(OPh)_3$ were identical with those used in previous kinetic runs carried out in the absence of CO.

Infrared monitoring of the solutions showed that isomerization was accompanied by the slow growth of $\nu(CO)$ bands at 2114 and 2020

cm^{-1}. These bands were not observed in the absence of CO and are attributable to $PhMn(CO)_5$ by comparison with an authentic sample.[39,40] The intensities of these bands were negligible prior to at least 2 half-lives of the isomerization reaction, indicating that the rate of substitution of $P(OPh)_3$ by CO is significantly slower than the rate of isomerization. Analysis of the kinetic data followed the procedure described in part a. A quantitative study of the substitution reaction was not carried out.

Investigation of $P(OPh)_3$ Exchange during Isomerization of *trans*-$PhMn(CO)_4P(OPh)_3$. A solution of *trans*-$PhMn(CO)_4P(OPh)_3$ (0.530 g, 0.957 mmol) and $P(OC_6D_5)_3$ (0.336 g, 1.04 mmol) in 75 mL of *n*-heptane was placed in a constant-temperature bath at 50.0 °C. All procedures were identical with those used in the kinetic studies described previously. After a time period corresponding to 3 half-lives of the isomerization reaction (~3.5 h), the solution was quenched at 0 °C. Solvent was removed in vacuo at room temperature. The residue was treated as described previously except that no attempt was made to separate the trans isomer during the chromatography step. The colorless crystalline product was identified as a cis–trans mixture by infrared spectroscopy.

The extent of incorporation of $P(OC_6D_5)_3$ in the recovered complex was investigated by ^1H NMR spectroscopy using a CD_2Cl_2 solution of the complex (32.8 mg, 0.059 mmol). Acetonitrile (17.7 mg, 0.431 mmol) was added as an internal integration standard. The mean value of the (methyl proton/phenyl proton) area ratio was 1.04 ± 0.03 for 16 integrations. Based upon the amounts of $PhMn(CO)_4P(OPh)_3$ and CH_3CN present, the expected value for this ratio is 1.09 assuming *no* incorporation of $P(OC_6D_5)_3$. Statistical distribution of $P(OC_6D_5)_3$ after 3 half-lives would give a value of 1.70 for this ratio.

Results and Discussion

The reaction of equimolar amounts of $PhMn(CO)_5$ and $P(OPh)_3$ at 60 °C in tetrahydrofuran afforded a mixture of *cis*- and *trans*-$PhMn(CO)_4P(OPh)_3$. It was possible to separate the isomeric mixture by using a combination of chromatography and fractional crystallization. This procedure yielded isomerically pure samples of *trans*-$PhMn(CO)_4P(OPh)_3$, but *cis*-$PhMn(CO)_4P(OPh)_3$ could not be obtained completely free of the trans isomer. An infrared study of the chromatographic separation indicated that *cis*-$PhMn(CO)_4P(OPh)_3$ is eluted before the trans isomer. This result is consistent with the elution order observed for chromatographic separations of *cis*- and *trans*-$XMn(CO)_4PPh_3$ complexes (X = Br,[41] MeCO[5]).

The $\nu(CO)$ infrared spectra of the two isomers (Figure 1) are consistent with the expected C_{4v} (trans) and C_s (cis) local symmetry at the metal atom. For the trans isomer, the very weak band at 2081 cm^{-1} and the strong band at 1989 cm^{-1} are readily assigned to the A_1 and E modes, respectively.[42] A second weak band at 2024 cm^{-1} is assigned[42] to the normally only Raman-active B_1 mode which has gained a slight infrared intensity in the reduction of symmetry from strict C_{4v}. Bands attributable to the cis isomer were observed to appear when solutions of the trans isomer were allowed to remain in the infrared beam for moderate time periods (~30 min).

For the cis isomer, the highest energy band (2078 cm^{-1}) can be assigned to the A′ mode which involves primarily the symmetric stretch of the pair of mutually trans CO groups.[43] The strong band at 1990 cm^{-1} corresponds to the asymmetric stretch (A″ mode) of the same two CO groups.[43] Unambiguous assignment of the two remaining $\nu(CO)$ bands at 2012 and 1972 cm^{-1} is less straightforward.[43] Two additional very weak absorptions at 2067 and 1932 cm^{-1} are assigned to $\nu(^{13}CO)$ modes. As in the case of a variety of related tetracarbonylmetal complexes,[5,6,8,43-47] two of the $\nu(CO)$ bands of *cis*-$PhMn(CO)_4P(OPh)_3$ are essentially coincident with the A_1 and E modes of the trans isomer. Thus, infrared spectroscopy cannot distinguish between the presence of a pure cis isomer and a cis–trans mixture.

Proton NMR spectroscopy was also of no use in this regard. The ^1H NMR spectra of both isomers exhibited a complex pattern due to overlap of resonances from the $P(OPh)_3$ ligand and the manganese-bound phenyl group. Fortunately, ^{31}P NMR spectroscopy proved to be of more value as a stereochemical probe. The $^{31}P\{^1H\}$ NMR spectrum of repeatedly purified "*cis*-$PhMn(CO)_4P(OPh)_3$" consisted of *two* broad ($\Delta\nu_{1/2} > 100$ Hz) resonances at +173.0 and +158.0 ppm.[48] The former (weaker) signal was unambiguously assigned to the trans isomer by comparison with the spectrum of an authentic, isomerically pure sample. Assignment of the more intense, high-field signal to the cis isomer necessarily follows.[49] The ^{31}P NMR technique thus provides direct spectroscopic evidence for the simultaneous presence of the trans isomer in samples of *cis*-$PhMn(CO)_4P(OPh)_3$.

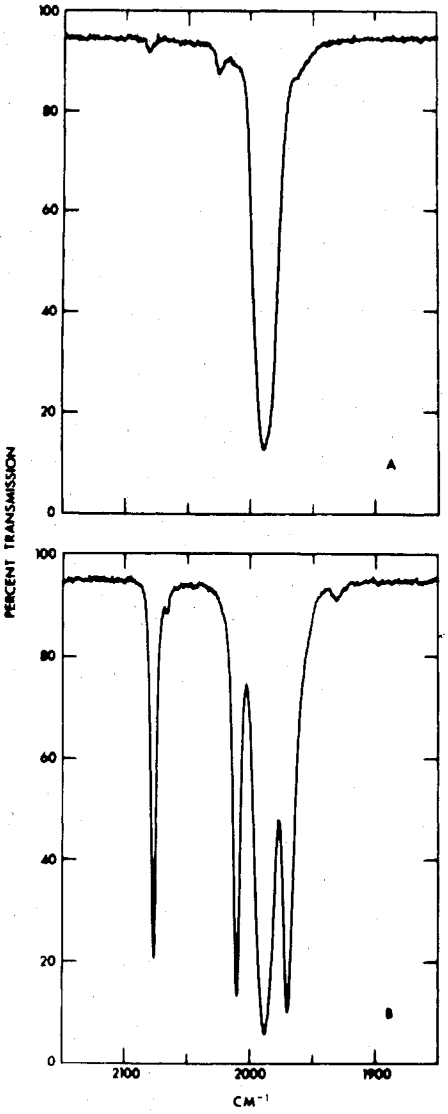


Figure 1. (A) Infrared spectrum in *n*-heptane of *trans*-$PhMn(CO)_4P(OPh_3)$. (B) Infrared spectrum in *n*-heptane of the *cis*- and *trans*-$PhMn(CO)_4P(OPh)_3$ mixture.

In view of the difficulties associated with distinguishing between a pure cis isomer and a cis–trans mixture, it is not surprising that *trans*-$PhMn(CO)_4P(OPh)_3$ was not identified by previous[7] workers. In fact, it is quite likely that *other* $RMn(CO)_4L$ complexes also exist as cis–trans mixtures since stereochemical assignment of these molecules has often been based on $\nu(CO)$ infrared spectra alone. It is interesting to note the difference in stereochemistry between $PhMn(CO)_4P(OPh)_3$ and the closely related complexes $MeMn(CO)_4P(OPh)_3$ and $PhCH_2Mn(CO)_4P(OPh)_3$. The latter two complexes are reported[6,8] to exist exclusively as cis isomers from ^1H NMR studies in the methyl or methylene proton region. The origin of this stereochemical difference is presumably steric,[6,8] but further work on related $RMn(CO)_4L$ systems is clearly necessary.

Equilibrium Studies. The equilibrium constant (K_{eq}) for the isomerization of $PhMn(CO)_4P(OPh)_3$ (eq 1) was determined

$$trans\text{-}PhMn(CO)_4P(OPh)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} cis\text{-}PhMn(CO)_4P(OPh)_3 \quad (1)$$

by measuring the relative areas of the ^{31}P peaks of the two isomers in equilibrated *n*-heptane solutions. Measurements were carried out over a temperature range of 30–55 °C, and the results are shown in Table I. Since the equilibrium constant for reaction 1 is essentially insensitive to temperature change within the experimental error (~10%) of the measurements, we feel that the calculation of numerical values of $\Delta H°$ and $\Delta S°$ is unwarranted. The approximate temperature independence and magnitude of K_{eq} necessarily imply, however, that $\Delta H°$ and $\Delta S°$ for the isomerization process are small. Similar conclusions have been reached for the isomerization of related $M(CO)_4XY$ molecules such as $Os(CO)_4(SiMe_3)_2$[44] and $Cr(CO)_4[C(OMe)Me](PR_3)$.[50]

It is interesting to note that the magnitude of K_{eq} (3.1 ± 0.2) is slightly smaller than the statistical value of 4.0. Although this could be rationalized on the basis of purely steric effects, it is possible that electronic effects are also of importance. For example, Angelici and co-workers[51] have shown that the equilibrium constants for a series of $W(CO)_4(CS)L$ complexes correlate with the π-acceptor ability of L. In all cases,[51] the equilibrium constant was observed to be less than the statistical value of 4.0, ranging from 0.7 when L = $P(C_6H_4Me)_3$ to 2.6 when L = $P(OMe)_3$.

Kinetic Studies. Kinetic studies of the trans → cis isomerization of $PhMn(CO)_4P(OPh)_3$ (eq 1) were carried out over a temperature range of 30–55 °C in *n*-heptane solution. Infrared monitoring of the reaction mixture indicated the absence of detectable amounts of other carbonyl-containing species through 10 half-lives. The isomerization reaction was observed to be first order with respect to complex. Appropriate rate data are shown in Table II, where $k_{obsd} = (k_1 + k_{-1})$. Values for k_1 and k_{-1} were determined from k_{obsd} by using the mean value of the equilibrium constant ($K_{eq} = 3.1$) from Table I. Activation parameters for the forward reaction ($\Delta H_1^\ddagger$ = 23.6 ± 0.3 kcal/mol, $\Delta S_1^\ddagger$ = −3.5 ± 1.1 eu) and reverse reaction ($\Delta H_{-1}^\ddagger$ = 23.6 ± 0.3 kcal/mol, $\Delta S_{-1}^\ddagger$ = −5.8 ± 1.0 eu) were calculated from the rate constants k_1 and k_{-1} in Table II.

The rate of isomerization of $PhMn(CO)_4P(OPh)_3$ at 50 °C was found to be unaffected by the presence of an equimolar amount of free $P(OPh)_3$. Although substitution of CO by $P(OPh)_3$ was evidenced by the slow growth of ν(CO) bands attributable to $PhMn(CO)_3[P(OPh)_3]_2$, the qualitative rate of this competitive process was significantly slower than the rate of isomerization. By analogy with closely related systems,[1,2,16] the $PhMn(CO)_3[P(OPh)_3]_2$ product is presumably formed in the two-step sequence depicted in eq 2. However,

$$PhMn(CO)_4P(OPh)_3 + P(OPh)_3 \xrightarrow{a} PhCOMn(CO)_3[P(OPh)_3]_2 \xrightarrow{b} PhMn(CO)_3[P(OPh)_3]_2 + CO \quad (2)$$

direct evidence for the known[7] acyl complex $PhCOMn(CO)_3[P(OPh)_3]_2$ is lacking since the infrared spectra of $PhCOMn(CO)_3[P(OPh)_3]_2$ and $PhMn(CO)_3[P(OPh)_3]_2$ are virtually superimposable in the terminal ν(CO) region.[7] In addition, the acyl ν(CO) band of $PhCOMn(CO)_3[P(OPh)_3]_2$ (reported[7] at 1560 cm^{-1}) would be masked by a strong band of $P(OPh)_3$ at ~1590 cm^{-1}. The observation that only $PhMn(CO)_3[P(OPh)_3]_2$ is isolated from the final reaction mixture indicates that decarbonylation of $PhCOMn(CO)_3[P(OPh)_3]_2$ is facile under the conditions used.

Table III. Rate Constants for the Formation of the $RCOMn(CO)_4$ Intermediate from $RMn(CO)_5$ (Eq 7)

R	solvent	*T*, °C	k_1, s^{-1}	ref
Me	$MeNO_2$	25.5	1.66×10^{-3}	13
	THF	25.5	9.63×10^{-4}	13
	$(EtOCH_2CH_2)_2O$	25.5	3.69×10^{-4}	13
		30.0	8.0×10^{-4}	2
	mesitylene	25.5	2.18×10^{-6}	13
Ph	$MeNO_2$	25.0	3.45×10^{-4}	16
		30.0	7.68×10^{-4}	16
	THF	25.0	1.95×10^{-4}	16
	$(EtOCH_2CH_2)_2O$	30.0	1.0×10^{-4}	2
	$CHCl_3$	25.0	8.0×10^{-6}	16

An independent kinetic investigation of the CO substitution reaction was carried out at 50 °C in the presence of a 40-fold excess of free $P(OPh)_3$. Under these pseudo-first-order conditions, the rate constant[52] for substitution of CO in $PhMn(CO)_4P(OPh)_3$ by $P(OPh)_3$ was measured as 7.30×10^{-6} s^{-1}. Thus even in the presence of a *large excess* of $P(OPh)_3$, the rate of CO substitution is at least 20 times slower than the rate of isomerization.

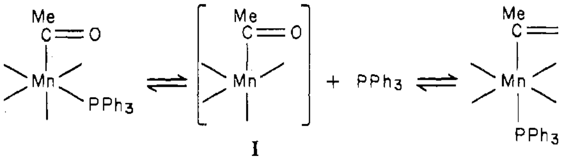
In a separate experiment at 50 °C, the isomerization of *trans*-$PhMn(CO)_4P(OPh)_3$ was carried out in the presence of an approximately equimolar amount of $P(OPh)_3$-d_{15}. The reaction was quenched after 3 half-lives to prevent appreciable interference from reaction 2. A ^1H NMR study of the recovered $PhMn(CO)_4P(OPh)_3$ isomeric mixture showed no incorporation of deuterium within the experimental error (±3%) of the measurement. This observation indicates that isomerization of $PhMn(CO)_4P(OPh)_3$ is not accompanied by $P(OPh)_3$ dissociation.

The kinetics of isomerization of *trans*-$PhMn(CO)_4P(OPh)_3$ were also investigated at 50 °C under ambient pressure of CO. In two separate experiments which involved CO/$PhMn(CO)_4P(OPh)_3$ concentration ratios of 0.45 and 2.10, the rate of isomerization was found to be unaffected by CO. The slow growth of ν(CO) bands attributable to $PhMn(CO)_5$ in these reaction mixtures indicated that the substitution of $P(OPh)_3$ in $PhMn(CO)_4P(OPh)_3$ by CO (eq 3) occurs under relatively

$$PhMn(CO)_4P(OPh)_3 + CO \rightarrow PhMn(CO)_5 + P(OPh)_3 \quad (3)$$

mild conditions. Although not measured quantitatively, the rate of reaction 3 was *qualitatively* observed to be appreciably slower than the rate of isomerization. The related carbonylation of $PhMn(CO)_4PPh_3$ to $PhCOMn(CO)_5$ has been reported.[27] In view of the conditions employed in this latter study[27] (250 atm CO, 25 °C), it is not surprising that an *acyl* complex is the ultimate product. Further carbonylation of $PhMn(CO)_5$ to $PhCOMn(CO)_5$ is apparently precluded in our system by the use of relatively low CO pressure and higher temperature.

Mechanism of Isomerization. The mechanism of isomerization of $PhMn(CO)_4P(OPh)_3$ is clearly quite different from the dissociative mechanism proposed[5] for the related *acyl* complex $MeCOMn(CO)_4PPh_3$ (eq 4). Unlike the latter case,

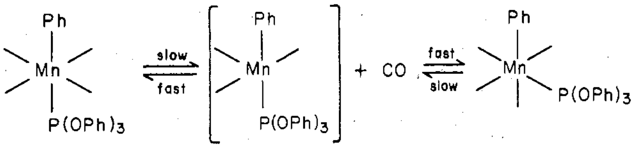


I

(4)

the isomerization of $PhMn(CO)_4P(OPh)_3$ cannot involve dissociation of the phosphorus ligand since exchange with free $P(OPh)_3$-d_{15} is not observed during isomerization. The difference in these two systems is perhaps a consequence of the different ligands involved. However, it seems likely that the major difference is the solvent—acetone in the case of $MeCOMn(CO)_4PPh_3$ and *n*-heptane in the present study. In contrast to the relatively inert solvent *n*-heptane, a coordinating solvent like acetone could enhance ligand dissociation by direct participation in a solvent-assisted process and/or by stabilization of the $MeCOMn(CO)_4$ intermediate (**1**) through coordination.[1,2,5,13]

An alternative dissociative mechanism for isomerization is shown in eq 5. The rate-determining step involves dissociative

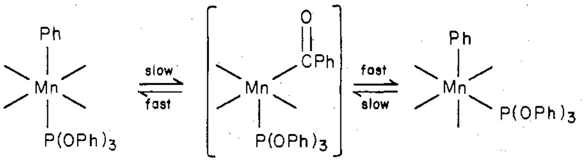


2

(5)

loss of CO to form a five-coordinate intermediate **2** which, upon rearrangement and recombination with CO, would lead to isomerization. An analogous mechanism involving CO dissociation as the rate-determining step has been proposed[53-56] for the CO substitution and exchange reactions of $XMn(CO)_4L$ complexes (X = Cl, Br, I; L = CO, group 5 donor ligand). However, it seems unlikely that such a mechanism could be operative for the isomerization of $PhMn(CO)_4P(OPh)_3$. Kinetic studies[53,54] of the CO substitution reactions of $XMn(CO)_4L$ complexes in noncoordinating solvents have shown that these reactions are characterized by a *large positive* entropy of activation ($\Delta S^\ddagger$ = 15–21 eu). Such a result is, of course, expected for a dissociative process but is in direct contrast to the *small negative* entropy of activation for reaction 1 ($\Delta S_1^\ddagger = -3.5$ eu, $\Delta S_{-1}^\ddagger = -5.8$ eu). Moreover, there exists a large amount of experimental evidence[55] which suggests that the five-coordinate $PhMn(CO)_3P(OPh)_3$ intermediate (**2**), once formed, should be readily captured by any available nucleophile. In particular, rapid conversion of **2** into $PhMn(CO)_3[P(OPh)_3]_2$ would be expected to occur in the presence of excess $P(OPh)_3$. In other words, if the mechanism of eq 5 is operative, the rate of isomerization and rate of CO substitution of $PhMn(CO)_4P(OPh)_3$ should be comparable, contrary to experimental result. These observations indicate that isomerization of $PhMn(CO)_4P(OPh)_3$ is not accompanied by CO dissociation and suggest that an *intramolecular* process is operative.

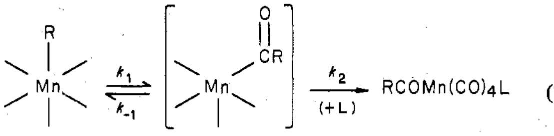
Conclusive evidence for intramolecular isomerizations of *nonchelate* octahedral complexes appears to be limited to the following five classes of complexes: (1) H_2ML_4 (M = Fe, Ru; L = phosphine, phosphite);[57] (2) $M(CO)_4(ER_3)_2$ (M = Fe, Ru, Os; E = Si, Ge, Sn, Pb; R = organic group, Cl);[44,58] (3) $Cr(CO)_4[C(OMe)Me]PR_3$ (R = Et, Cy);[50] (4) $W(CO)_4(^{13}CO)CS$;[59] (5) $Mo(CO)_4(PBu_3)_2$.[60] The two commonly invoked mechanisms for the intramolecular isomerization of nonchelate octahedral complexes are the trigonal twist[61] and the tetrahedral jump.[57] However, an additional mechanism would seem uniquely attractive for the intramolecular isomerization of $PhMn(CO)_4P(OPh)_3$ (eq 6). The rate-determining step of this mechanism involves migration of the phenyl group to coordinated CO with formation of a five-coordinate *acyl* intermediate **3**. This "alkyl migration" reaction is a particularly well-documented[1,2] process for $RMn(CO)_5$ systems. Rearrangement of the $PhCOMn(CO)_3P(OPh)_3$ intermediate (**3**), followed by reverse migration of the phenyl group, would result in isomerization. We note that a similar mechanism was proposed by Brown[62] in an early attempt to account for the intramolecular exchange of axial and equatorial CO groups in $XMn(CO)_5$ complexes (X = H, Cl, Br, I).



(6)

3

Kinetic data for CO substitution reactions of $RMn(CO)_5$ complexes (R = Me, Ph) are consistent with the related mechanism depicted in eq 7. Rate constants (k_1 in eq 7) for



(7)

4

the formation of the five-coordinate $RCOMn(CO)_4$ intermediate (**4**) analogous to **3** have been measured in a variety of solvents.[2,13,16] Appropriate data from the literature are summarized in Table III. With these data, it is possible to obtain a reasonable estimate of the rate constant for formation of the $PhCOMn(CO)_3P(OPh)_3$ intermediate **3** in eq 6.

Although kinetic data for the formation of $PhCOMn(CO)_4$ in *nonpolar* solvents are not available, the rate constant[13] for formation of $MeCOMn(CO)_4$ in mesitylene at 25.5 °C is $2.18 \times 10^{-6}\ s^{-1}$. From Table III it is apparent that k_1 approximately doubles for a temperature increase from 25 to 30 °C. Moreover, k_1 for formation of $PhCOMn(CO)_4$ is 5–8 times *smaller* than k_1 for formation of $MeCOMn(CO)_4$ under the same conditions. Thus, a generous upper limit estimate for the rate constant for formation of $PhCOMn(CO)_4$ in the nonpolar solvent mesitylene at 30 °C is $\sim 8 \times 10^{-7}\ s^{-1}$.

The proposed $PhCOMn(CO)_3P(OPh)_3$ intermediate in eq 6 differs from $PhCOMn(CO)_4$ by $P(OPh)_3$ substitution of CO. Hence, the question naturally arises as to how this difference would alter the migratory aptitude of the phenyl group. Although there is no quantitative experimental evidence related to this question, it is appropriate to comment on the results of a recent theoretical study of this problem by Berke and Hoffmann.[63] Extended Hückel calculations[63] indicate that the activation energy for migration of the methyl group in *trans*-$MeMn(CO)_4PH_3$ is 4–5 kcal/mol *higher* than in $MeMn(CO)_5$. On this basis the rate constant for formation of the $PhCOMn(CO)_3P(OPh)_3$ intermediate **3** should be *significantly less* than the rate constant estimated above for formation of $PhCOMn(CO)_4$ ($\sim 8 \times 10^{-7}\ s^{-1}$ at 30 °C). Comparison with Table II suggests that the observed rate of isomerization of $PhMn(CO)_4P(OPh)_3$ ($k_1 = 9.30 \times 10^{-6}\ s^{-1}$ at 29.5 °C) is far too rapid to be accounted for by eq 6.

In conclusion, the present study indicates that the isomerization of $PhMn(CO)_4P(OPh)_3$ occurs by an intramolecular process. Although a mechanism involving phenyl migration (eq 6) can probably be ruled out, the experimental results afford no distinction between the alternative trigonal-twist and tetrahedral-jump mechanisms. It should be pointed out that the latter mechanism is apparently restricted to six-coordinate complexes which show an appreciable *ground-state* distortion from octahedral to bicapped-tetrahedral geometry.[57] Since there is no reason to expect that such is the case for $PhMn(CO)_4P(OPh)_3$, we tend to favor the trigonal-twist mechanism.

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Registry No. *cis*-$PhMn(CO)_4P(OPh)_3$, 22289-58-3; *trans*-$PhMn(CO)_4P(OPh)_3$, 70397-98-7; $PhMn(CO)_5$, 13985-77-8.

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Electronic Absorption Spectra of Metal Tetracarbonyls

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The electronic absorption spectra of approximately tetrahedral $M(CO)_4$ (M = Ni, Pd, Pt, Co, Rh, Ir) molecules have been measured. The closed-shell molecules (M = Ni, Pd, Pt) exhibit d → π^* CO bands in the ultraviolet region of the spectrum. The band at 36 630 cm^{-1} in the spectrum of $Ni(CO)_4$ is assigned to $t_2(d) \rightarrow t_2(\pi^*)$, and the broad system at 41 670 cm^{-1} probably represents several other d → π^* transitions. Similar bands are observed at slightly higher energies in the spectrum of $Pd(CO)_4$. The spectrum of $Pt(CO)_4$ shows a single band at 48 310 cm^{-1}, which is attributed to a d → p or d → π^* transition. Relatively low-energy $\sigma \rightarrow t_2(d)$ transitions are observed in the spectra of the open-shell molecules (28 190, 28 900, 31 720 cm^{-1} in $Co(CO)_4$; 29 850 cm^{-1} in $Rh(CO)_4$; 32 570 cm^{-1} in $Ir(CO)_4$). Transitions with d → π^* character are observed at 37 180, 39 060, and 44 840 cm^{-1} in $Co(CO)_4$, 41 670 and 46 510 cm^{-1} in $Rh(CO)_4$, and 40 650 and 48 080 cm^{-1} in $Ir(CO)_4$.

Introduction

It has been known for several years that metal carbonyl complexes possess relatively low-lying excited states of the metal-to-ligand charge-transfer (MLCT) type. The most extensive investigations of the electronic spectra have been performed on metal hexacarbonyls,[2,3] although other systems have been studied in a less detailed fashion.[4] The recent characterization of $M(CO)_4$ molecules in matrix-isolation experiments[5,6] has allowed us to probe the electronic energy levels of approximately tetrahedral closed-shell (M = Ni, Pd, Pt)[5] and open-shell (M = Co, Rh, Ir)[6] molecules. The electronic spectra of metal carbonyl molecules with open-shell ground states have turned out to be of special interest, as we have observed low-lying ligand-to-metal charge transitions (LMCT) in these cases.

Experimental Section

Monoatomic metal vapors of Ni, Co, and Rh were generated by directly heating thin ribbon filaments (0.010 in.) with an alternating current. For the other metals, Pd (0.005 in. foil), Pt (0.020 in. wire), and Ir (0.010 in. wire) were wound around a tungsten rod (0.030 in.

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