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Investigation of Isomerization Rates and Mechanism of Some 17- and 18-Electron Substituted Carbonyl Complexes of Chromium, Molybdenum, and Tungsten Using Double Potential Step Chronoamperometry

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Chemical and electrochemical oxidation and reduction of a series of $[M(CO)_2(P\text{-}P)_2]^{0,+}$ complexes (M = Cr, Mo, or W and P-P = DPM [bis(diphenylphosphino)methane], DPE [1,2-bis(diphenylphosphino)ethane], and DPP [1,3-bis(diphenylphosphino)propane]) have shown that cis and trans isomers occur in both the 18- and 17-electron configurations. Using the reaction scheme

$$\begin{array}{ccc} \textit{cis}\text{-}M(CO)_2(P\text{-}P)_2 & \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} & \textit{cis}\text{-}[M(CO)_2(P\text{-}P)_2]^+ \\ \uparrow k_2 & & \downarrow k_1 \\ \textit{trans}\text{-}M(CO)_2(P\text{-}P)_2 & \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} & \textit{trans}\text{-}[M(CO)_2(P\text{-}P)_2]^+ \end{array}$$

and a computerized version of double potential step chronoamperometry permits the measurement of k_1 and k_2 over a wide temperature range and in a variety of solvents and the calculation of the activation parameters ΔH^* and ΔS^*. The results indicate that the rate of isomerization depends on the electronic configuration of the metal and the size of the bidentate ligand but not on the solvent. Isomerization in both the 18-electron *trans*-$M(CO)_2(P\text{-}P)_2$ and 17-electron *cis*-$M(CO)_2(P\text{-}P_2)^+$ complexes is believed to occur via a twist mechanism.

Introduction

Chemical and electrochemical studies[2-8] on a series of $[M(CO)_2(P\text{-}P)_2]^{0,+,2+}$ complexes (M = Cr, Mo, or W and P-P = a bidentate phosphorus ligand) have shown that either cis or trans configurations can be adopted depending on the formal oxidation state. In the synthesis of the 18-electron $M(CO)_2(P\text{-}P)_2$ complexes (oxidation state zero) cis complexes are generally isolated except for $Cr(CO)_2(DPE)_2$ [DPE = 1,2-bis(diphenylphosphino)ethane ($Ph_2PCH_2CH_2PPH_2$)] where some of the trans isomer is also produced.[2] In contrast, only trans isomers are isolated with the 17-electron (formally oxidation state I) complexes, $[M(CO)_2(P\text{-}P)_2]^+$.[3,6,8] The $[M(CO)_2(P\text{-}P)_2]^{2+}$ complexes have not been isolated but only observed at low temperatures on the electrochemical time scale for chromium.[6,7] In view of the fact that both 18- and 17-electron systems can be isolated as stable complexes, the electrochemical reaction scheme shown below can be investigated quantitatively.

$$\begin{array}{ccc} \textit{cis}\text{-}M(CO)_2(P\text{-}P)_2 & \underset{}{\overset{E_1^\circ}{\rightleftharpoons}} & \textit{cis}\text{-}[M(CO)_2(P\text{-}P)_2]^+ \\ k_2 \uparrow & & \downarrow k_1 \\ \textit{trans}\text{-}M(CO)_2(P\text{-}P)_2 & \underset{}{\overset{E_2^\circ}{\rightleftharpoons}} & \textit{trans}\text{-}[M(CO)_2(P\text{-}P)_2]^+ \end{array}$$

Figure 1 shows a typical cyclic voltammogram for *cis*-$M(CO)_2(P\text{-}P)_2$. Previous studies on the DPE complexes in acetone, nitromethane, and dichloromethane[6] have shown that the differences in the thermodynamic parameters E_1° and E_2° (standard redox potentials) for a given metal are not very solvent dependent, although the values depend quite markedly on the nature of the phosphorus bidentate ligand.[6,7] However, very little quantitative data are available on the isomerization rates k_1 and k_2. In a brief report, Elson[9] has tabulated values of k_2 for the isomerization of *trans*-$Mo(CO)_2(DPE)_2$ to *cis*-$Mo(CO)_2(DPE)_2$ under a range of conditions and concluded that the isomerization occurs via a dissociative mechanism. In investigations from these laboratories[6,7] it was concluded that the rate of cis–trans isomerization, k_1, for the $[M(CO)_2(P\text{-}P)_2]^+$ complexes was considerably faster than k_2, but no quantitative data were obtained nor have mechanistic conclusions been drawn for isomerization in either the 18- or 17-electron configurations.

The purpose of the present work was to quantitatively study the rates of isomerization of k_1 and k_2 in a range of solvents and at various temperatures in an endeavor to see if the mechanism for the

$$\text{trans}^0 \xrightarrow{k_2} \text{cis}^0$$

and

$$\text{cis}^+ \xrightarrow{k_1} \text{trans}^+$$

isomerizations is the same and to critically evaluate the observed differences in rates obtained when varying the metal and/or bidentate ligand. To achieve internal consistency in the measurements it was believed to be desirable that the same technique be used to measure all values of k_1 and k_2. Because k_1 and k_2 vary over a wide range this was found to be a nontrivial problem. However, by developing a completely on-line computerized version of double potential step chronoamperometry to provide variable pulse times and correction for charging current this could be achieved provided the measurement method was coupled with a careful choice of temperature range to give a rate constant appropriate to the measurement time scale (pulse width). The instrumentation and methodology have been briefly described elsewhere.[10] However, because the technique forms an extremely important facet of the reported data it is described in detail in the present communication.

Experimental Section

The *cis*-$M(CO)_2(DPE)_2$ and *cis*-$M(CO)_2(DPM)_2$ complexes [DPE = 1,2-bis(diphenylphosphino)ethane; DPM = bis(diphenylphosphino)methane] were prepared by literature methods.[7] The complex $Mo(CO)_2(DPP)_2$ [DPP = 1,3-bis(diphenylphosphino)propane] was prepared by refluxing stoichiometric amounts of $Mo(CO)_6$ and DPP under nitrogen for 3 days. This complex does not appear to have been reported previously. All the complexes were recrystallized from dichloromethane/hexane and characterized by their infrared carbonyl bands and cyclic voltammetry.

The *trans*-$[M(CO)_2(P\text{-}P)_2]^+$ complexes were prepared by exhaustive controlled-potential electrolysis under nitrogen at a platinum gauze electrode in the solvent and supporting electrolyte under study. For unstable species such as *trans*-$[Mo(CO)_2(DPM)_2]^+$ and *trans*-$[W(CO)_2(DPM)_2]^+$ all subsequent measurements were performed in the coulometric cell.

All the complexes were characterized by cyclic voltammetry prior to performing the double potential step chronoamperometry experiment. Solutions were degassed with nitrogen for 5 min and

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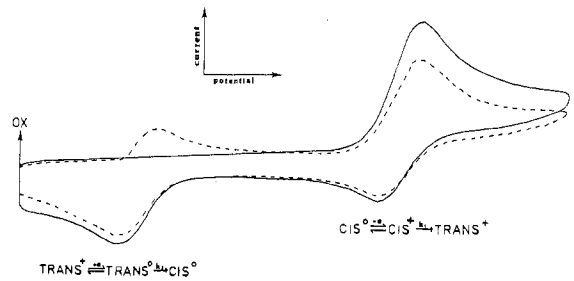

Figure 1. A typical cyclic voltammogram of *cis*-$M(CO)_2(P\text{-}P)_2$ showing the isomerizations of these systems. The solid line indicates the first scan.

maintained under this inert atmosphere during each experiment. All measurements were made immediately after the preparation of each solution.

The supporting electrolyte used was 0.1 M Et_4NClO_4 in acetone and acetonitrile and 0.07 M Et_4NClO_4 in dichloromethane.

Apparatus

All cyclic voltammograms and double potential step chronoamperograms were obtained with a PAR Model 174 polarographic analyzer. The working electrode in both cases was a fixed length of platinum wire exposed to the solution. The working electrode was rinsed in 6 M nitric acid, washed in distilled water and then solvent, and wiped before each use. The reference electrode in acetone and acetonitrile was Ag|AgCl (saturated LiCl in acetone), separated from the test solution by a salt bridge containing acetone (0.1 M Et_4NClO_4). The reference electrode in dichloromethane was Ag|AgCl (saturated LiCl in dichloromethane), separated from the test solution by a salt bridge containing 0.07 M Et_4NClO_4 in dichloromethane.

Controlled-potential electrolysis experiments were performed at a platinum gauze working electrode with a PAR Model 173 potentiostat in conjunction with a PAR Model 179 digital coulometer and a PAR Model 9600 coulometry cell system. A three-electrode system was used as for the voltammetry and chronoamperometry, except that platinum gauze was used as the auxiliary electrode. This electrode was filled with supporting electrolyte solution and separated from the test solution by a salt bridge containing a porous Vycor sinter. All controlled potential electrolyses were done at potentials determined by the cyclic voltammograms and the working electrode was cleaned in 6 M nitric acid and rinsed before each use.

An on-line system for measuring the rate of isomerization following the charge-transfer step by double potential step chronoamperometry was built by interfacing the polarographic analyzer with a PDP 11/10 minicomputer (Digital Equipment Corp.) and using a CAPS-11 operating system.

A DR 11 general purpose interface for 16-bit parallel I/O transfers was used in conjunction with a module having two serial 8-bit (i.e., 16 bit wide) D/A converters to generate program-controlled potential pulses. The pulses were fed through an external input into the PAR 174 polarographic analyzer.

The pulse duration was program controlled using a programmable real time clock. Sampling of the current output from the polarographic analyzer was performed using an AR 11 real time analog sub-system which included a 16 channel, 10-bit A/D converter with sample and hold, a programmable real time clock with one external input, and a display control with two 10-bit D/A converters.

The current was sampled each 3 ms and the pulse duration was 100 ms or greater. Sampled data as well as any transformed data were displayed either on a Tektronix D 13 storage oscilloscope or on an X-Y recorder.

A program for generating potential pulses, acquiring data, evaluation, and display was written in BASIC language using system subroutines written in PAL 11 assembly language. Input parameters for the program were the following: potential for the first step, potential for the second step, optional blank subtraction, and step duration.

Theory and Method for Determining Rates of Isomerization

Schwarz and Shain[11] derived theoretical expressions for current–time behavior of electrode processes in which the product of an electron-transfer step undergoes further chemical reaction. Two potential steps are applied to the system which obeys the reaction scheme

$$O + ne \rightleftarrows R \xrightarrow{k} Z \tag{1}$$

The theory can also be applied to an oxidation in an analogous fashion, although only reduction is considered in the theory presented subsequently.

In this work, the oxidation

$$cis^0 \overset{E_1^\circ}{\rightleftarrows} cis^+ \xrightarrow{k_1} trans^+$$

leads to values of k_1 for the 17-electron isomerization, and the reduction

$$trans^+ \overset{E_2^\circ}{\rightleftarrows} trans^0 \xrightarrow{k_2} cis^0$$

gives k_2 for the 18-electron isomerization.

The electrolysis is performed in the first step at the potential where the rate of generation of R is controlled only by the diffusion of O to the electrode surface. The potential is switched back to the initial value after a pulse duration time, τ, and the resulting current decay is controlled by the diffusion of chemically unreacted R.

Assuming planar diffusion, modified by the appropriate chemical kinetic terms, Schwarz and Shain derived the current–time expressions for the cathodic current, i.e., at time $t < \tau$ (t = time, τ = pulse duration)

$$I_c = nFAC_0^*(D_0/\pi t)^{1/2} \tag{2}$$

where A = area of the electrode, C_0^* = the bulk concentration, and D_0 = the diffusion coefficient.

For the anodic current, i.e., at time $t > \tau$

$$I_a = nFAC_0^* D_0^{1/2}\left[\frac{\phi(k,t,\tau)}{(\pi(t-\tau))^{1/2}} - \frac{1}{(\pi t)^{1/2}}\right] \tag{3}$$

where $\phi(k,t,\tau)$ is a function of the first-order rate constant, k, time, t, and potential pulse duration, τ, and is defined as

$$\phi(k,t,\tau) = [e^{-kt}{}_1F_1(^1/_2,1,k\tau) + \sum_{n=1}^{\infty}\left(\frac{e^{-kt}[(t-\tau)k]^n}{n!}\right) \times {}_1F_1(n + {}^1/_2, n+1, k\tau)] \tag{4}$$

In eq 4 ${}_1F_1(a,b,x)$ is a confluent hypergeometric function[12] which can be evaluated as a series:

$${}_1F_1(a,b,x) = 1 + \frac{a}{b}x + \frac{a(a+1)}{b(b+1)2!}x^2 + \frac{a(a+1)(a+2)}{b(b+1)(b+2)3!}x^3 + \ldots \tag{5}$$

This series converges for all values of arguments a and b and variable x, except for $b = 0, -1, -2, \ldots$.

Since the current–time behavior for cathodic and anodic current is known, a further practical simplification can be made by dividing eq 3 by eq 2 which eliminates the dependence of the bulk concentration of electroactive species, the electrode area and the diffusion coefficient.

The final expression is represented as

$$-I_a/I_c = \phi(k\tau,(t-\tau)/\tau) - \left(\frac{(t-\tau)/\tau}{1+(t-\tau)/\tau}\right)^{1/2} \tag{6}$$

After the current–time curves were stored in memory, the same experiment was performed with the electrolyte solution in order to obtain the charging current correction. To verify that the current–time behavior for the first potential step follows the theoretically predicted diffusion-controlled model,

Table I. Experimental Rate Constants for the Isomerization

$$cis\text{-}[M(CO)_2(P\text{-}P)_2]^+ \xrightarrow{k_1} trans\text{-}[M(CO)_2(P\text{-}P)_2]^+$$

at Various Temperatures in Acetone (0.1 M Et_4NClO_4)

Complex	Temp, °C	k, s^{-1}
cis-$[Cr(CO)_2(DPM)_2]^+$	23.0	1.1 ± 0.1
	19.0	1.0 ± 0.1
	1.0	0.5 ± 0.1
	−13.0	0.3 ± 0.1
cis-$[Mo(CO)_2(DPM)_2]^+$	1.0	13.6 ± 1.5
	−16.0	8.2 ± 1.0
	−30.0	6.8 ± 0.8
	−35.0	5.5 ± 0.7
cis-$[W(CO)_2(DPM)_2]^+$	1.0	19.3 ± 1.2
	−15.0	10.5 ± 1.4
	−35.0	7.8 ± 0.9
cis-$[Cr(CO)_2(DPE)_2]^+$	19.0	19.7 ± 0.7
	1.0	9.1 ± 1.7
	−12.0	3.1 ± 1.2
	−35.0	1.3 ± 0.5
cis-$[Mo(CO)_2(DPE)_2]^+$	1.0	13.0 ± 1.0
	−13.0	8.3 ± 0.6
	−35.0	2.6 ± 0.4
cis-$[W(CO)_2(DPE)_2]^+$	−12.0	18 ± 1
	−35.0	8.9 ± 1.4

a plot of I_c vs. $t^{-1/2}$ was calculated, evaluated by linear regression, and displayed.

The program then calculated and displayed the ratio of oxidation/reduction currents vs. $(t - \tau)/\tau$. Anodic current sampled at time t_1 was always coupled with cathodic current sampled at time $(t_1 - \tau)$. Then, according to eq 6, the theoretical curves of I_a/I_c vs. the dimensionless parameter $k\tau$ are calculated for every experimental value of $(t - \tau)/\tau$. The first 25 points of the curve were calculated for k = 0–25 s^{-1} and linear interpolation of experimental values of I_a/I_c was performed in order to determine the corresponding $k\tau$ value.

The $\phi[k\tau,(t - \tau)/\tau]$ function was calculated using five terms of both series in eq 4 and 5. To improve the interpolation the same curve was then calculated again but this time in the range from k = 0 to 1.5 times the value of k obtained in the first interpolation.

The final value of the rate constant was obtained by averaging the values obtained for the first 25 experimental $(t - \tau)/\tau$ points.

Results and Discussion

A temperature range of −35 to 40 °C was considered for evaluation of the rate constants. The rates of isomerization

$$cis^+ \xrightarrow{k_1} trans^+$$

were generally too fast to be measured conveniently at ambient temperatures and generally temperatures at the lower end of the range available were chosen to study this isomerization. Data in acetone for these complexes are presented in Table I.

For the

$$trans^0 \xrightarrow{k_2} cis^0$$

isomerization, the rates at low temperatures tended to be rather slower and higher temperatures were used to generate the data contained in Table II for the acetone (0.1 M Et_4NClO_4) solvent system. The instability of the *trans*-$[M(CO)_2(DPM)_2]^+$ (M = Mo, W) species precluded a wide range of data being obtained for the

$$trans^0 \xrightarrow{k_2} cis^0$$

isomerization. This result is consistent with our inability to isolate these $trans^+$ complexes in the solid state,[7] even though they can be prepared in solution under argon. The isomerization of *trans*-$Cr(CO)_2(DPE)_2$ to the cis isomer was too slow to be detected by double potential step chronoamperometry. Instead, this species was produced by controlled-potential electrolysis and its change in concentration monitored as a function of time by polarography. The other $trans^0$ complexes of DPE could also be prepared by rapid controlled-potential electrolysis, although isomerization occurred too fast to monitor concentrations conveniently by polarography. Approximate results obtained by this method were, however, in agreement with data obtained by double potential step chronoamperometry. The *trans*-$Cr(CO)_2(DPE)_2$ complex is stable in the solid state and its relative kinetic inertness explains its reported isolation along with the usually obtained cis form. These controlled-potential electrolysis experiments coupled with polarographic monitoring of concentrations proved that product conversions were 100% in all isomerizations and that no side reactions occurred.

Table II. Experimental Rate Constants for the Isomerization of *trans*-$M(CO)_2(P\text{-}P)_2$ to *cis*-$M(CO)_2(P\text{-}P)_2$ at Various Temperatures in Acetone (0.1 M Et_4NClO_4)

Complex	Temp, °C	k, s^{-1}
trans-$Cr(CO)_2(DPM)_2$	34.0	0.33 ± 0.02
	30.0	0.28 ± 0.03
	28.0	0.25 ± 0.04
	22.0	0.17 ± 0.03
	16.0	0.13 ± 0.01
trans-$Mo(CO)_2(DPM)_2$[a]	16.0	0.20 ± 0.02
trans-$W(CO)_2(DPM)_2$	16.0	0.83 ± 0.04
	9.0	0.67 ± 0.07
	3.0	0.49 ± 0.07
trans-$Cr(CO)_2(DPE)_2$[b]	16.0	2.0×10^{-3}
trans-$Mo(CO)_2(DPE)_2$	39.0	0.115 ± 0.007
	24.0	0.050 ± 0.006
	16.0	0.034 ± 0.002
	8.0	0.024 ± 0.003
	3.0	0.017 ± 0.004
trans-$W(CO)_2(DPE)_2$	23.0	0.094 ± 0.006
	22.0	0.092 ± 0.007
	17.0	0.081 ± 0.006
	10.0	0.055 ± 0.007
trans-$Mo(CO)_2(DPP)_2$	16.0	0.068 ± 0.013

[a] *trans*-$[Mo(CO)_2(DPM)_2]^+$ decomposes readily. [b] Determined polarographically.

Table III. Calculated Values of Rate Constants and Activation Parameters at 25 °C for the Isomerization of *cis*-$[M(CO)_2(P\text{-}P)_2]^+$ and *trans*-$M(CO)_2(P\text{-}P)_2$ in Acetone (0.1 M Et_4NClO_4)

Complex	$k_{25\,°C}$, s^{-1}	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, J/K mol
cis-$[Cr(CO)_2(DPM)_2]^+$	1.2	23.6 ± 0.7	−164 ± 3
cis-$[Mo(CO)_2(DPM)_2]^+$	20.5	12.8 ± 1.7	−177 ± 7
cis-$[W(CO)_2(DPM)_2]^+$	28.1	13.2 ± 4.1	−173 ± 16
cis-$[Cr(CO)_2(DPE)_2]^+$	23.4	29.8 ± 3.8	−119 ± 15
cis-$[Mo(CO)_2(DPE)_2]^+$	32.7	24.6 ± 2.1	−133 ± 8
cis-$[W(CO)_2(DPE)_2]^+$	44.5	16 ± 2	−160 ± 10
trans-$Cr(CO)_2(DPM)_2$	0.21	38.2 ± 2.9	−130 ± 10
trans-$W(CO)_2(DPM)_2$	1.20	27.3 ± 2.8	−152 ± 10
trans-$Mo(CO)_2(DPE)_2$	0.055	36.8 ± 1.3	−146 ± 5
trans-$W(CO)_2(DPE)_2$	0.10	28.7 ± 3.7	−167 ± 13

In all cases where data was obtained over a range of temperatures, linear log k vs. $1/T$ plots enabled calculation of rate constants at 25 °C. Enthalpies ($\Delta H^{\ddagger}$) and entropies ($\Delta S^{\ddagger}$) of activation can also be calculated from these Arrhenius plots. Kinetic and activation data from these calculations are summarized in Table III. Results from cyclic voltammetry indicated that rates of isomerization were not very solvent dependent. Some selected complexes were examined quantitatively by double potential step chronoamperometry in acetonitrile, acetone, and dichloromethane to give the data tabulated in Table IV. Confirming the cyclic voltammetric

Table IV. Rate of Isomerization of *cis*-$[M(CO)_2(P\text{-}P)_2]^+$ and *trans*-$M(CO)_2(P\text{-}P)_2$ in Various Solvents

Complex	Temp, °C	k, s^{-1} Acetonitrile (0.1 M Et_4NClO_4)	Acetone (0.1 M Et_4NClO_4)	Dichloromethane (0.07 M Et_4NClO_4)
cis-$[Cr(CO)_2(DPM)_2]^+$	12.0	1.2 ± 0.1	1.0 ± 0.1	2.5 ± 0.5
cis-$[Cr(CO)_2(DPE)_2]^+$	−35.0	*a*	1.3 ± 0.5	1.5 ± 0.5
trans-$Cr(CO)_2(DPM)_2$	16.0	0.128 ± 0.007	0.13 ± 0.01	0.15 ± 0.03
trans-$W(CO)_2(DPM)_2$	16.0	*b*	0.83 ± 0.04	0.8 ± 0.1
trans-$Mo(CO)_2(DPE)_2$	16.0	0.067 ± 0.006	0.034 ± 0.002	0.10 ± 0.02
trans-$W(CO)_2(DPE)_2$	16.0	0.046 ± 0.003	0.079 ± 0.006	0.08 ± 0.01

[a] Acetonitrile freezes near this temperature. [b] *trans*-$[W(CO)_2(DPM)_2]^+$ is unstable in acetonitrile.

results, no systematic solvent dependence on the rate constants was found in progressing from the relatively coordinating acetonitrile solvent to the relatively inert dichloromethane solvent. The presence of the supporting electrolyte in our studies meant that ionic strengths are much more comparable than those of many studies using the solvent directly. Consequently, comparison of rate constants is probably realistic with respect to examining the influence of coordinating properties of the various solvents. The thermodynamic $E_1°$ and $E_2°$ values associated with the isomerization step, like the kinetic parameters, k_1 and k_2, are also essentially independent of the solvent and it would seem that neither kinetically or thermodynamically does the nature of the solvent exert an important influence at high ionic strength.

The rate of isomerization for both the 17- and 18-electron systems follows the order Cr < Mo < W, with chromium being the most inert kinetically. For the

$$cis^+ \xrightarrow{k_1} trans^+$$

reaction, isomerization of DPE complexes is considerably faster than for the DPM situation. Conversely for the 18-electron systems

$$trans^0 \xrightarrow{k_2} cis^0$$

the DPE complexes isomerize more slowly than their DPM counterparts. Rate constants for $Mo(CO)_2(DPP)_2^{0,+}$ were similar to the corresponding DPE complexes. In all cases, isomerization of the 17-electron system is faster than that for the 18-electron system and activation enthalpies follow the expected order associated with k_1 and k_2 values. However, $\Delta S^‡$ values for all complexes in each oxidation state are significantly negative and are of similar magnitude. The variations in rate constants when varying metal or ligand can therefore be attributed to the different activation energies and probably not to different mechanisms of isomerization.

The generally accepted pathway for isomerization is via either an intramolecular twist or bond rupture (dissociative) mechanism. The isomerization of *cis*-$Mn(CO)_3L_2Br_2$ (L = monodentate ligand)[13] is thought to occur via a bond rupture mechanism and the trans isomer is postulated to form via a trigonal-bipyramidal intermediate. In this case, the $\Delta S^‡$ values are always positive which is expected for a dissociative process.[14] Positive $\Delta S^‡$ values have also been oberved for substitution reactions with triethyl phosphite involving bond rupture mechanisms in complexes of the type $W(CO)_4$(bidentate)[15] and $Mo(CO)_4$(bidentate).[16,17]

Our studies demonstrate the isomerizations

$$cis^+ \xrightarrow{k_1} trans^+$$

and

$$trans^0 \xrightarrow{k_2} cis^0$$

for the $[M(CO)_2(P\text{-}P)_2]^{0,+}$ complexes occur with negative $\Delta S^‡$ values. The rates of isomerization are essentially independent of (P-P) concentration, CO concentration, and solvent so we conclude that the isomerization probably occurs via a twist mechanism.

It has been documented that terminal group exchange, i.e., rapid configurational rearrangement of terminal groups on the bidentate ligands between two nonequivalent sites of the isomer in $M(chel)_2X_2$ complexes[18] occurs with a negative value of $\Delta S^‡$ and the negative values of $\Delta S^‡$ for these exchanges are said to be consistent with a twist mechanism. One of the proposed mechanisms for terminal group exchange includes a pathway for cis–trans isomerization and a negative $\Delta S^‡$ value would therefore seem reasonable for a twist mechanism being operative in the complexes we have studied. Recently, a twist mechanism has also been proposed for rearrangements of (P-P) in complexes of the type $(\eta^3\text{-}C_3H_5)M(CO)_3(P\text{-}P)X$ where M = Mo or W and X = Cl or I.[19]

Elson[9] in his measurements of the rate of isomerization of *trans*-$Mo(CO)_2(DPE)_2$ in a 10:1 mixture of dichloromethane/methanol (0.1 M Et_4NBF_4) obtained a rate constant at 20 °C of 0.06 ± 0.01. A $\Delta H^‡$ value of 55.6 kJ/mol and $\Delta S^‡$ = −66.9 J/(K mol) were also obtained from the temperature-dependent behavior. All values are essentially consistent with our data. While noting that the negative $\Delta S^‡$ value was not expected for a dissociative process, Elson still postulated a dissociative mechanism. From an extremely small data set with very similar rate constants obtained in two different solvent mixtures, he concluded that a solvent dependence was observed as expected for a dissociative mechanism. We do not believe the interpretation placed on the small data set was statistically meaningful and, in light of all our additional data, the conclusion that his results also demonstrate results to be essentially independent of solvent can be reached. Finally, we believe his interpretation of the George and Siebold NMR data[5] is incorrect with respect to mechanistic conclusions. These NMR data, together with the rate constants measured recently by Wreford,[20] have been obtained in the absence of supporting electrolyte, and as a result, the rate of isomerization appears to be much slower. Apparently medium effects (ionic strength) are extremely critical and invalid comparisons of data have been made by Elson. At best, these data are ambiguous or irrelevant as a basis for distinguishing between twist and dissociative mechanisms. It is our contention that, because the rates of isomerization are independent of bidentate ligand and CO concentration, the $\Delta S^‡$ values are all similar and negative and both the kinetics and thermodynamics of isomerization are essentially independent of solvent at similar ionic strengths; the data are in agreement with a twist mechanism occurring in both the 18- and 17-electron configurations for the $[M(CO)_2(P\text{-}P)_2]^{0,+}$ complexes.

In a recent communication, Wreford[21] has advised us that results from chemical oxidation and reduction reactions coupled with NMR data are consistent with the 17-electron cis–trans isomerization proceeding by a trigonal twist mechanism. Furthermore, the authors of ref 20[21] feel that rate order data for their neutral 18-electron systems are also suggestive of a twist mechanism.

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Registry No. *cis*-$[Cr(CO)_2(DPM)_2]^+$, 66700-92-3; *cis*-$[Mo(CO)_2(DPM)_2]^+$, 66700-91-2; *cis*-$[W(CO)_2(DPM)_2]^+$, 66700-90-1; *cis*-$[Cr(CO)_2(DPE)_2]^+$, 37753-97-2; *cis*-$[Mo(CO)_2(DPE)_2]^+$, 37684-59-6; *cis*-$[W(CO)_2(DPE)_2]^+$, 37684-60-9; *trans*-$Cr(CO)_2(DPM)_2$, 66700-95-6; *trans*-$Mo(CO)_2(DPM)_2$, 26743-82-8; *trans*-$W(CO)_2(DPM)_2$, 66700-94-5; *trans*-$Cr(CO)_2(DPE)_2$, 31320-75-9; *trans*-$Mo(CO)_2(DPE)_2$, 40219-77-0; *trans*-$W(CO)_2(DPF)_2$, 51202-31-4; *trans*-$Mo(CO)_2(DPP)_2$, 66700-93-4; $Mo(CO)_2(DPP)_2$, 66633-00-9; $Mo(CO)_6$, 13939-06-5.

References and Notes

(1) On leave from the Department of Inorganic Chemistry, Faculty of Technology, University of Zagreb, Zagreb, Yugoslavia.
(2) J. Chatt and H. R. Watson, *J. Chem. Soc.*, 4980 (1961).
(3) J. Lewis and R. Whyman, *J. Chem. Soc.*, 5486 (1965).
(4) P. F. Crossing and M. R. Snow, *J. Chem. Soc.*, 610 (1971).
(5) T. A. George and C. D. Siebold, *Inorg. Chem.*, **12**, 2548 (1973).
(6) F. L. Wimmer, M. R. Snow, and A. M. Bond, *Inorg. Chem.*, **13**, 1617 (1974).
(7) A. M. Bond, R. Colton, and J. J. Jackowski, *Inorg. Chem.*, **14**, 274 (1975).
(8) A. M. Bond, R. Colton, and J. J. Jackowski, *Inorg. Chem.*, **14**, 2526 (1975).
(9) C. M. Elson, *Inorg. Chem.*, **15**, 469 (1976).
(10) A. M. Bond, B. S. Grabaric, and Z. Grabaric, *Inorg. Chem.*, **17**, 1013 (1978).
(11) W. M. Schwarz and I. Shain, *J. Phys. Chem.*, **69**, 30 (1965).
(12) L. J. Slater, "Confluent Hypergeometric Functions", Cambridge University Press, London, 1960.
(13) R. J. Angelici, F. Basolo, and A. J. Poe, *J. Am. Chem. Soc.*, **85**, 2215 (1963).
(14) F. Basolo and R. G. Pearson in "Mechanisms of Inorganic Reactions", 2nd ed, Wiley, New York, N.Y., 1967, pp 526–624.
(15) G. R. Dobson and G. C. Faber, *Inorg. Chim. Acta*, **4**, 87 (1970).
(16) G. R. Dobson and G. C. Faber, *Inorg. Chim. Acta*, **2**, 479 (1968).
(17) G. R. Dobson and A. J. Rettenmaier, *Inorg. Chim. Acta*, **6**, 507 (1972).
(18) N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, **17**, 391 (1972).
(19) J. W. Faller, D. A. Haitko, R. D. Adams, and D. F. Chodosh, *J. Am. Chem. Soc.*, **99**, 1654 (1977).
(20) S. Datta, T. J. McNeese, and S. S. Wreford, *Inorg. Chem.*, **16**, 2661 (1977).
(21) S. S. Wreford, Department of Chemistry, Harvard University, private communication, 1978.

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Association Reactions and Equilibrium Constants in Tetracoordinate Iridium(I) Complexes

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Reversible association reactions of a neutral molecule to a potential catalyst d^8 tetracoordinate complex can be considered as a model of one of the steps involved in the catalytic process. Here are reported the reactions of triphenylphosphine addition to a number of isostructural and isoelectronic complexes of the type $Ir(NO)(cat)(PPh_3)$ (cat = catecholato) having different catecholato ring substituents to give the corresponding series of pentacoordinate $Ir(NO)(cat)(PPh_3)_2$ complexes. The equilibrium constants relative to the pentacoordinate species formation have been determined by IR measurements of the tetracoordinate nitrosyl band intensity at different equilibrium positions. The equilibrium constant values are discussed in terms of electron density of the central metal and electron-releasing or -withdrawing power of the catecholato ring substituents. The plot of log K_{eq} vs. ν(NO) for the tetracoordinate species gives a good linear dependence confirming that ν(NO) is a good test of the relative electronic situation on the metal in such classes of complexes. Moreover, it is pointed out that the plot of log K_{eq} vs. pK_a^I of the free, differently substituted catechols provides a useful tool to predict the electron density on the central metal and, consequently, its ability to associate neutral molecules of catalytic interest such as unsaturated hydrocarbons.

Introduction

Transition-metal complexes homogeneously catalyze numerous organic reactions. Catalysis is attributed to the ability of the metal complexes in solution to reversibly coordinate reacting molecules, orienting them in adjacent sites and thereby creating a low-energy pathway for bond making and bond breaking. In addition, the catalytic circles of many processes must be visualized as varying sequences of elementary organometallic reactions. These reaction steps include availability of a coordinatively unsaturated metal center (four-coordinate d^8 complexes figure prominently), coordination of an unsaturated molecule (e.g., an alkene) to the metal center, oxidative addition of a saturated molecule (e.g., hydrogen), combination of the ligands within the coordination sphere, and dissociation of the product. Several plausible mechanisms, specially in the case of homogeneous hydrogenation, have resulted from extensive studies. Two main pathways are generally operating in this case: (i) a hydride route in which the primary step is the formation of a hydrido species and (ii) an unsaturated route in which the primary step is the coordination of the unsaturated molecule. Generally it is assumed that both pathways are simultaneously operating in every catalytic cycle. The extensively studied chemistry of the iridium(I) Vaska's compound offers several good and appropriate examples of both pathway situations. In fact, it has been demonstrated that the stability trend of the iridium(III) dihydride derivative of Vaska's complex, $H_2IrX(CO)(PPh_3)_2$, reflects the electronegativity trend of the changed ligand X (more electronegative, less stable) and the basicity scale of the phosphine group[2] (more basic, more stable). When we turn to consider the unsaturate route, the synergic character of the metal–alkene bond must be taken into account. The relative importance of the σ and π components of the metal–alkene bond depends either on the metal electron density or on the substituents attached to the olefinic double bond,[3] both influencing the stability of the organometallic complex. Significant results on the role played by the metal have been obtained by Strohmaier, who measured the associative constants of reactions between dimethyl maleate and various $IrX(CO)(PPh_3)_2$ complexes, changing with X the electron density on the metal.[4] The found trend indicates increasing stability of the olefin complexes with decreasing electron density of the iridium atom. The olefinic ligands are characterized by the presence of sufficiently energetic low-lying unoccupied molecular orbitals. In addition to unsaturated hydrocarbons, ligands such as CO, NO, and CN^- together with tertiary phosphines, arsines, and stibines constitute the most important examples of this group of π-acid ligands. The above

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