Spectroscopic and Microelectrode Techniques Applied to the Oxidation of Equilibrium and Nonequilibrium Mixtures of *cis*- and *trans*-Tetracarbonylbis(trimethyl phosphite)chromium(0): Deceptively Simple Electrochemical Responses

Alan M. Bond,*[1] Ray Colton,[2] and Terence F. Mann[1]

Division of Chemical and Physical Sciences, Deakin University, Waurn Ponds, Victoria 3217, Australia, and Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia

Received April 21, 1988

Microdisk electrodes of radii 0.5–25 μm have been used to study the voltammetric oxidation of *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ in dichloromethane and acetonitrile solutions. Both slow scan rate (steady-state) experiments and fast scan rate voltammetry (scan rates up to 50 000 V s^{-1}) on equilibrium and nonequilibrium mixtures result in the unexpectedly simple observation of a single apparently Nernstian redox couple over a wide time domain and temperature range. Calculations derived from spectroscopic measurements demonstrate that a standard redox potential difference of at least 65 mV exists for the redox couples *cis*-$[Cr(CO)_4(P\{OMe\}_3)_2]^+ + e^- \rightleftharpoons$ *cis*-$Cr(CO)_4(P\{OMe\}_3)_2$ and *trans*-$[Cr(CO)_4(P\{OMe\}_3)_2]^+ + e^- \rightleftharpoons$ *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ and demonstrate slow kinetics for the reaction *cis*-$Cr(CO)_4(P\{OMe\}_3)_2 \rightleftharpoons$ *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ so that observation of two processes, or at least a single broadened response, might have been expected. Spectroscopic evidence (^{31}P NMR and infrared) is provided for redox catalysis of the *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ to *cis*-$Cr(CO)_4(P\{OMe\}_3)_2$ isomerization in the presence of a very small amount of oxidized carbonyl compound via the equilibrium *cis*-$[Cr(CO)_4(P\{OMe\}_3)_2]^+ \rightleftharpoons$ *trans*-$[Cr(CO)_4(P\{OMe\}_3)_2]^+$ and the cross redox reaction *trans*-$[Cr(CO)_4(P\{OMe\}_3)_2]^+ +$ *cis*-$Cr(CO)_4(P\{OMe\}_3)_2 \rightleftharpoons$ *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ + *cis*-$[Cr(CO)_4(P\{OMe\}_3)_2]^+$. The deceptively simple voltammetry can be explained by assuming that the isomerization reaction in the 17-electron configuration and the cross redox reaction accompanying electron transfer are sufficiently fast so that oxidation of both the cis and trans isomers occurs at the reversible oxidation potential of the trans isomer.

Introduction

The electrochemical oxidation and reduction of compounds existing in two isomeric forms may be accompanied by conversion from one structural form to another. The early misconception in the literature that such structural changes will lead to the observation of slow electron transfer has now been widely disproved. In fact, a reversible wave may be observed if both the charge-transfer step and any structural change accompanying electron transfer are rapid with respect to the time scale of the experiment or where the thermodynamics and kinetics are in specified regimes.[3-5] Alternatively, provided the redox potentials between the isostructural pairs are not identical, then individual voltammetric processes associated with the redox properties of each isomer may be observed.[3-5]

For cyclic voltammetry, probably the most widely used electrochemical technique for studying redox reaction mechanisms, the time scale of the experiment is limited by the available potential scan rate. For electrodes of conventional size and using organic solvents, the upper limit is about 50 V s^{-1}, since at higher scan rates Ohmic iR drop leads to severe distortion of the voltammograms.

Disk-shaped microelectrodes with radii in the micrometer to submicrometer range have several advantages that make them suitable for mechanistic studies under both steady-state (slow scan rate, hemispherical diffusion) and fast scan rate (planar diffusion) conditions. Perhaps the most important features are the greatly reduced currents that are generated and the modified diffusion mode. These factors minimize iR drop effects under steady-state conditions.[6-9] The smaller currents also enable scan rates of 100 000 V s^{-1} or more to be achieved under appropriate conditions[10,11] with minimal problems due to iR drop, so that a very wide voltammetric time domain is now available for electrode kinetic investigations.

In a previous study,[12] cyclic and differential pulse voltammetry of the equilibrium mixture of *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ using conventional sized electrodes gave only a single Nernstian process rather than two responses corresponding to the oxidation of the bulk concentration of each isomer. Reducing the time scale of the electrochemical experiment, lowering the temperature, or reducing the size of the microelectrode in steady-state experiments should, in principle, decrease the influence of chemical reactions following charge transfer and allow the observation of both redox couples and the determination of the thermodynamic and kinetic parameters associated with the redox chemistry, as has been the case in other studies.[6,13] The aim of this work was to apply microelectrode techniques, both slow scan (steady state) and fast scan experiments, to the $[Cr(CO)_4(P\{OMe\}_3)_2]^{+/0}$ redox couple to determine if voltammetric evidence could be obtained for the presence of chemical reactions accompanying the charge-transfer step. At the same time spectroscopic evidence to characterize the redox processes

---

[1] Deakin University.

[2] University of Melbourne.

[3] Bond, A. M.; Oldham, K. B. *J. Phys. Chem.* **1983**, *87*, 2492; **1985**, *89*, 3739 and references therein.

[4] Evans, D. H.; O'Connell, K. M. *Electroanal. Chem.* **1986**, *14*, 113 and references therein.

[5] Geiger, W. E. *Prog. Inorg. Chem.* **1985**, *33*, 275 and references therein.

[6] Fleischmann, M.; Pons, S.; Rolison, D. R.; Schmidt, P. P. *Ultramicroelectrodes*; Datatech Systems: Morganton, NC, 1987 and references therein.

[7] Bond, A. M.; Fleischmann, M.; Robinson, J. *J. Electroanal. Chem.* **1984**, *172*, 11.

[8] Wightman, R. M. *Anal. Chem.* **1981**, *53*, 1125A.

[9] Howell, J. O.; Wightman, R. M. *Anal. Chem.* **1984**, *56*, 524.

[10] Howell, J. O.; Wightman, R. M. *J. Phys. Chem.* **1984**, *88*, 3915.

[11] Amatore, C. A.; Jutand, A.; Pfluger, F. *J. Electroanal. Chem.* **1987**, *218*, 361.

[12] Bond, A. M.; Colton, R.; Kevekordes, J. E. *Inorg. Chem.* **1986**, *25*, 749.

[13] Bond, A. M.; Darensburg, D. J.; Mocellin, E.; Stewart, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 6827.

0276-7333/88/2307-2224$01.50/0

from thermodynamic and kinetic viewpoints was obtained to provide a rationalization and understanding of the deceptively simple voltammetric process previously reported.[12]

Experimental Section

All solvents were of AR grade and used as received. Supporting electrolytes, tetrabutylammonium perchlorate (TBAP) and tetraethylammonium perchlorate (TEAP), were obtained from G. Frederick Smith and dried under vacuum over P_2O_5, before use. *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ was prepared by the literature method.[14]

A range of platinum wire microelectrodes were constructed by sealing wires of various radii (0.5–25 μm) into soda glass.[15] Before each experiment, the electrodes were polished with 0.05 μm alumina/water slurries on a micropolishing cloth.

All microelectrode electrochemical experiments were performed with a two-electrode cell arrangement as the low currents generated mean that potentiostatic control is not required.[15] For steady-state experiments a Ag/AgCl (CH_2Cl_2 saturated LiCl, 0.1 M TBAP) reference electrode was used, separated from the test solution by a salt bridge containing 0.1 M TBAP in CH_2Cl_2. A platinum wire pseudoreference electrode was used for fast scan experiments as the internal resistance of a conventional reference electrode leads to distortion of the voltammograms.

A PAR Model 175 function generator was used to provide wave forms up to 10 000 V s^{-1}. For faster scan rates a Wavetek Model 20 function generator was used. For steady-state experiments the current was measured with a Keithley Model 480 picoammeter and voltammograms recorded on a Houston 100 X-Y recorder. For fast scan experiments the picoammeter was replaced with a current follower based on an OP-37 operational amplifier with a 1 M ohm resistor in the feedback loop. The voltage signal was then sent to a Gould Model 4035 digital storage oscilloscope which could then be transferred to an X-Y recorder or IBM personal computer via an IEEE 488 general purpose interface bus.

Phosphorus-31 NMR spectra were recorded on a JEOL FX 100 spectrometer at 40.32 MHz, and chemical shifts were referenced against external 85% H_3PO_4, high-frequency positive convention being used. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer and calibrated against polystyrene (1601 cm^{-1}).

Results

cis- and *trans*-$Cr(CO)_4(P(OMe)_3)_2$ can clearly be distinguished by either infrared spectra in the carbonyl region or by phosphorus-31 NMR spectra.[14,16] NMR monitoring of an equilibrium mixture in dichloromethane over the temperature range 30 to −50 °C showed that the trans form is slightly favored with an almost temperature-independent equilibrium constant for the trans to cis concentration ratio of 1.9 ± 0.1. A value of 1.86 ± 0.01 has been reported previously[12] at 25 °C.

Steady-state voltammograms at a range of platinum microdisk electrodes were undertaken in dichloromethane (0.1 M TBAP) on equilibrium mixtures of *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ and on *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$, which slowly isomerizes to the cis form with a half-life of about half an hour. Results obtained at 15 °C at different concentrations are summarized in Table I. A simple reversible system should give a linear plot of E versus log $i/(i_d - i)$ with a slope of 57 mV at 15 °C (where E = potential, i = current, i_d = diffusion-controlled limiting current). The present system gives this ideal Nernstian-type behavior under both equilibrium and nonequilibrium conditions for electrodes of all radii and for all concentrations studied. At temperatures close to −78 °C there is a small departure from Nernstian slope of the wave, but there is no indication of a second wave being present under any conditions examined, despite spectroscopic evidence that both *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ are present in the bulk solution at voltammetrically detectable concentrations.

Table I. Electrochemical Data at 15 °C in Dichloromethane for Oxidation of Different Concentrations of an Equilibrium Mixture of *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ at Platinum Microelectrodes of Different Radii under Steady-State Conditions

	concn			
	5 × 10^{-4} M		5 × 10^{-5} M	
electrode radius (μm)	$E_{1/2}$ (V)[a]	slope[b] (mV)	$E_{1/2}$ (V)[a]	slope[b] (mV)
0.5	0.900	58	0.905	59
1.0	0.895	58	0.900	57
5.5	0.895	58	0.900	57
5.0	0.890	58	0.900	55
12.5	0.895	58	0.895	56

[a] V vs Ag/AgCl. [b] Slope of plot of E vs log $i/(i_d - i)$.

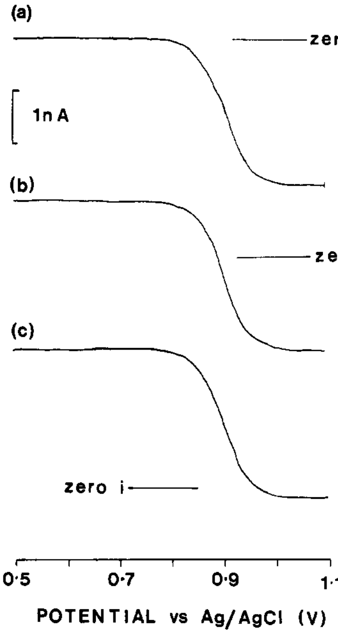


Figure 1. The effect of added $NOPF_6$ on the position of zero current for the oxidation of an equilibrium mixture of 5 × 10^{-4} *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ in dichloromethane (0.1 M TBAP) at 15 °C using a 5-μm radius platinum microelectrode: (a) no added $NOPF_6$; (b) less than 1:1 stoichiometric addition of $NOPF_6$; (c) 1:1 stoichiometric addition.

If the chemical oxidants $NOPF_6$ or $AgClO_4$ are added in stoichiometric (or greater) quantities to the equilibrium mixture of *cis* and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$, the effect on the steady-state voltammogram is only to shift the zero current position (Figure 1a–c). A plot of E versus log $i/(i_d - i)$ is still linear with a slope consistent with Nernstian behavior, and there is no change in the position of the half-wave potential, $E_{1/2}$. That is, over a wide concentration range, temperature range, and equilibrium or nonequilibrium conditions, the same apparently reversible one-electron oxidation process is observed. Infrared monitoring of the solutions in Figures 1a–c show, respectively, the presence of the mixture of *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$, a mixture of these species and *trans*-$[Cr(CO)_4(P\{OMe\}_3)_2]^+$, and finally only *trans*-$[Cr(CO)_4(P\{OMe\}_3)_2]^+$, clearly showing that the electrochemical response is independent of the exact composition of the solution, apart from the sign of the current that reflects the relative concentrations of oxidized and reduced forms

---

(14) Dixon, D. T.; Kola, J. C.; Howell, A. S. *J. Chem. Soc., Dalton Trans.* **1984**, 1307.

(15) Method used provides an all glass seal and was adapted from: Bixler, J. W.; Bond, A. M.; Lay, P. A.; Thormann, W.; Van den Bosch, P. A.; Fleischmann, M.; Pons, B. S. *Anal. Chim. Acta* **1986**, *187*, 67.

(16) Bond, A. M.; Carr, S. W.; Colton, R. *Inorg. Chem.* **1984**, *23*, 2343.

of $Cr(CO)_4(P\{OMe\}_3)_2$ but does not depend upon the isomeric distribution.

If a sample of the pure *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$, as obtained from the synthetic procedure used in this work, is dissolved in dichloromethane and the infrared spectrum recorded immediately, a single carbonyl stretch is observed at 1908 cm^{-1}. A peak[12] due to *cis*-$Cr(CO)_4(P\{OMe\}_3)_2$ (2030 cm^{-1}) is observed to grow in over a period of approximately 40 min until the equilibrium mixture is obtained. However, if a trace amount of a chemical oxidant such as $NOPF_6$ is added to the freshly prepared solution of *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ and the spectrum recorded immediately, it is found that the equilibrium mixture has already been attained. The identical result is obtained electrochemically if a solution of the trans isomer is subjected to a very small amount of oxidative-controlled potential electrolysis. Thus, small quantities of *trans*-$[Cr(CO)_4(P\{OMe\}_3)_2]^+$ catalyze the isomerization of *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ to *cis*-$Cr(CO)_4(P\{OMe\}_3)_2$. This greatly increased rate of isomerization can be explained by a rapid equilibrium between *trans*-$[Cr(CO)_4(P\{OMe\}_3)_2]^+$ (trans$^+$) and *cis*-$Cr(CO)_4(P\{OMe\}_3)_2]^+$ (cis$^+$) followed by the cross redox reaction with cis$^+$ being the catalyst.

$$\text{trans}^0 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \text{trans}^+ \rightleftharpoons \text{cis}^+$$

$$\text{cis}^+ + \text{trans}^0 \rightarrow \text{cis}^0 + \text{trans}^+ \rightleftharpoons \text{cis}^+ \text{ etc} \quad (1)$$

Examples of redox catalyzed isomerizations have been reported for other carbonyl systems.[5,12,16-18]

Further spectroscopic evidence for the existence of the cross redox reaction and the trans$^+$ to cis$^+$ isomerization reaction is provided by the following NMR experiment. If a very small amount of $NOPF_6$ is added to the equilibrium mixture of *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ in dichloromethane (or alternatively a small amount of electrochemical oxidation is undertaken), the two sharp resonances in the phosphorus-31 NMR spectrum corresponding to the cis and trans isomers (Figure 2a) are immediately replaced by a single broad resonance (Figure 2b) and a further small addition of $NOPF_6$ causes the resonance to broaden still further (Figure 2c). Addition of some $LiAlH_4$ to the solution resolves the resonance as shown in Figure 2d, and addition of excess $LiAlH_4$ restores the original spectrum as shown in Figure 2e. Similar broadening of the spectrum occurs on the addition of small quantities of $[NH(C_6H_4Br)_3][SbCl_6]$ to the mixture of tetracarbonyls.

The broad exchange average resonance is consistent with a rapid exchange between *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$. The amount of trans$^+$ (and cis$^+$) species is very low and insufficient to cause a significant contact shift by electron exchange between the paramagnetic and diamagnetic species.[16] However, it is important to note that there is no detectable change in the infrared spectrum of the solution. It is believed that the cis$^+$ species is involved in the equilibria and the following reaction scheme is consistent with the data.

$$\text{cis}^0 + {}^*\text{cis}^+ \rightleftharpoons \text{cis}^+ + {}^*\text{cis}^0 \quad (2)$$

$$\text{trans}^0 + {}^*\text{trans}^+ \rightleftharpoons \text{trans}^+ + {}^*\text{trans}^0 \quad (3)$$

$$\text{cis}^0 + \text{trans}^+ \rightleftharpoons \text{cis}^+ + \text{trans}^0 \quad (4)$$

$$\text{trans}^+ \rightleftharpoons \text{cis}^+ \quad (5)$$

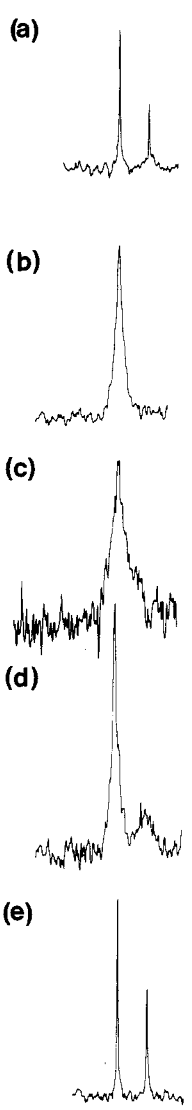


Figure 2. Phosphorus-31 NMR spectra in dichloromethane at 25 °C for (a) the equilibrium mixture of *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$, (b) the same solution with a trace amount of $NOPF_6$ added, (c) the same solution after a small amount of $NOPF_6$ added, (d) the same solution after addition of a small amount of $LiAlH_4$, and (e) the same solution after addition of excess $LiAlH_4$.

Fast scan rate cyclic voltammetry of both equilibrium and nonequilibrium mixtures of *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ in dichloromethane (1.0 M TBAP) also results in only a single chemically reversible couple being observed with scan rates up to 50 000 V s^{-1}. Figure 3 shows some examples of fast scan rate experiments, and the high quality of the data even in this high resistance solvent can be appreciated. The very high electrolyte concentration was used to minimize Ohmic *iR* drop. Nevertheless, some features attributable to iR drop are discernible in the data given in Table II, for example, the increase in the separation of the forward and reverse peaks at very fast scan rates and the dependence on the electrode radius. Experiments in acetonitrile (0.5 M TEAP) give similar results to those in dichloromethane, except that the effects of *iR* drop are less pronounced in this more conducting solvent.

Discussion

In previous studies,[12,14] spectroscopic measurements proved that the 18-electron species $Cr(CO)_4(P\{OMe\}_3)_2$ exists as an equilibrium mixture of cis and trans isomers in solution. The equilibrium is slowly established over

---

(17) Rieke, R. D.; Kojima, H.; Ofele, K. *J. Am. Chem. Soc.* **1976**, *98*, 6735.

(18) Connelly, N. G.; Raven, S. J.; Corriedo, G. A.; Riera, V. *J. Chem. Soc., Chem. Commun.* **1986**, 992.

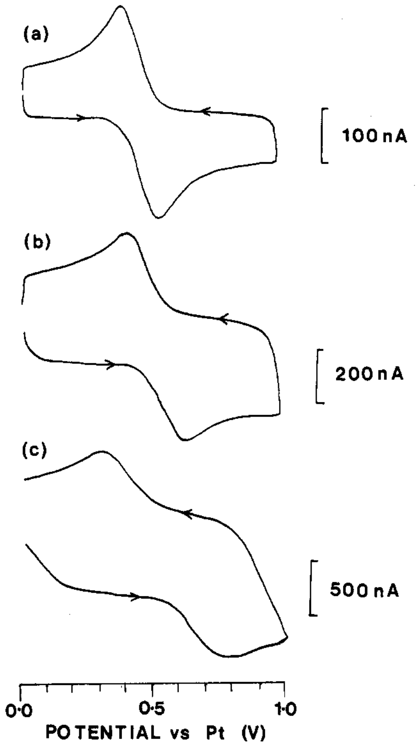


Figure 3. Fast scan rate cyclic voltammograms at a 5-μm radius platinum microelectrode for the oxidation of an equilibrium mixture of 1 × 10^{-2} M *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ in dichloromethane (1.0 M TBAP) at 15 °C. Scan rates are (a) 3000 V s^{-1}, (b) 10 000 V s^{-1}, and (c) 50 000 V s^{-1}.

Table II. Fast Scan Rate Cyclic Voltammetric Data Obtained at a 5-μm Radius Platinum Electrode Data for the Oxidation of Equlibrium Mixtures of 1 × 10^{-2} M *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ in Dichloromethane and Acetonitrile at 15 °C

	ΔE_p, mV	
scan rate, V s^{-1}	CH_2Cl_2 (1.0 M TBAP)	CH_3CN (0.5 M TEAP)
200	84	74
500	84	84
1000	107	91
2000	113	105
5000	144	137
10000	215	175
20000	273	115[a]
50000	475	170[a]

[a] 1-μm radius microelectrode.

some 40 min following dissolution of *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$. The equilibrium constant ($K_1 = k_1/k_{-1}$) for the reaction

$$cis\text{-}Cr(CO)_4(P\{OMe\}_3)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-}Cr(CO)_4(P\{OMe\}_3)_2 \quad (6)$$

was found to be 1.86 ± 0.01 at 25 °C in dichloromethane.[12] The values of k_1 and k_{-1} are known to be 10.5 × 10^{-4} s^{-1} and 2.19 × 10^{-4} s^{-1} in toluene, respectively.[14] In dichloromethane, exact values of the rate constants are unknown, but data obtained in this work confirm that they are of the same order of magnitude as those in toluene. The rate of interconversion between *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ is dramatically increased by a factor of about 10^7 by the introduction of a very small amount of the oxidized form $[Cr(CO)_4(P\{OMe\}_3)_2]^+$ since the exchange becomes moderately rapid on the NMR time scale. The infrared spectrum of the rapidly exchanging solution shows the equilibrium proportions of *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ and shows no indication of the presence of *trans*-$[Cr(CO)_4(P\{OMe\}_3)_2]^+$, thus confirming the proportion of oxidized species is very low. On addition of excess reductant, the exchange again becomes slow on the NMR time scale and the two isomers of $Cr(CO)_4(P\{OMe\}_3)_2$ are seen in the equilibrium proportions.

The result of a single electrochemical response could be explained by assuming that the standard redox potentials ($E°$ values) for the processes

$$cis\text{-}[Cr(CO)_4(P\{OMe\}_3)_2]^+ + e^- \overset{E°_1}{\rightleftharpoons} cis\text{-}Cr(CO)_4(P\{OMe\}_3)_2 \quad (7)$$

$$trans\text{-}[Cr(CO)_4(P\{OMe\}_3)_2]^+ + e^- \overset{E°_2}{\rightleftharpoons} trans\text{-}Cr(CO)_4(P\{OMe\}_3)_2 \quad (8)$$

are identical (or very similar) as predicted from ligand substitution theory.[19] Such a result would imply that the equilibrium constants K_1 and K_2 in the square reaction scheme

$$\begin{tikzcd} \text{cis}^+ + e^- \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, shift left, "K_2"] & \text{cis} \arrow[d, shift left, "K_1"] \\ \text{trans}^+ + e^- \arrow[r, phantom, "\rightleftharpoons"] \arrow[u, shift left] & \text{trans} \arrow[u, shift left] \end{tikzcd} \quad (9)$$

must be identical. This follows from the necessity for the data to comply with the thermodynamic relationship $\Delta E° = RT \ln K_3/nF$ where $K_3 = K_2/K_1$ and is the equilibrium constant for the cross redox reaction between the two redox couples given in eq 7 and 8. However, this cannot be the case since controlled potential electrolysis or chemical oxidation of an equilibrium mixture of *cis*- and *trans*-$Cr(CO)_4(P\{OMe\}_3)_2$ results in only the $trans^+$ isomer[12] being detected in the infrared spectrum of the oxidized solution. Assuming the carbonyl oscillator strengths in the 17-electron compounds are similar to those in the 18-electron systems, in which both isomers are readily detected in the presence of each other, this leads to a conservative estimate of a lower limit for K_2 of 25 in the equation

$$cis\text{-}[Cr(CO)_4(P\{OMe\}_3)_2]^+ \overset{K_2}{\rightleftharpoons} trans\text{-}[Cr(CO)_4(P\{OMe\}_3)_2]^+ \quad (10)$$

That is, in the 17-electron configuration, the $trans^+$ isomer is heavily favored, whereas the $trans^0$ isomer is only slightly favored in the eighteen configuration. This enhanced preference for the $trans^+$ isomer in the 17-electron configuration is consistent with theoretical calculations[20] and experimental data on related systems.[5,12,13,16,21–24] If K_2 = 25, then calculations show an expected $E°$ difference for the two couples of 65 mV, and higher values of K_2 would increase this separation. Digital simulation of the theory for this situation shows that two processes, or a broad unresolved response, should be observed for kinetically inert systems with the $trans^0$ being easier to oxidize than the cis^0 complex. Since k_1 and k_{-1} are both slow, then the concept that the entire system is in equilibrium cannot be

---

(19) Burston, B. E. *J. Am. Chem. Soc.* **1982**, *104*, 1299.

(20) Mingos, D. M. P. *J. Organomet. Chem.* **1979**, *179*, C29.

(21) Kotz, J. C. *Topics in Organic Electrochemistry*; Fry, A. J., Britton, W. E., Eds.; Plenum: New York, 1986; pp 81–176.

(22) Bond, A. M.; Colton, R.; Jackowski, J. J. *Inorg. Chem.* **1975**, *14*, 2526 and references therein.

(23) Connor, K. A.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 4422 and references therein.

(24) Vallat, A.; Person, M.; Rouiller, L.; Laviron, F. *Inorg. Chem.* **1987**, *26*, 332 and references therein.

supported, and the unusual concept that an apparently reversible process is observed when nonequilibrium conditions apply must be invoked. The observed single wave Nernstian response for oxidation of the mixture of isomers must therefore be a consequence of the rapid isomerization of the oxidized cis^+ species. Alternatively, or in addition, a rapid cross redox reaction represented by the equation

$$\mathrm{cis}^+ + \mathrm{trans} \overset{K_3}{\rightleftharpoons} \mathrm{trans}^+ + \mathrm{cis} \qquad (11)$$

would lead to the same observation where $K_3 = K_2/K_1$. Spectroscopic evidence indicates that both these reactions are fast.

The voltammetric results are deceptively simple because oxidation and reduction of both equilibrium and nonequilibrium mixtures of *cis*- and *trans*-$\mathrm{Cr(CO)_4(P\{OMe\}_3)_2}$ occurs at the oxidation potential for the $\mathrm{trans}^+/\mathrm{trans}^0$ couple. However, the $\mathrm{cis}^+/\mathrm{cis}^0$ couple, unperturbed by chemical reactions, really occurs at a considerably more positive potentials than the $\mathrm{trans}^+/\mathrm{trans}^0$ couple. If chemical reactions following the charge-transfer step are fast as in eq 12, the cis oxidation process would be shifted

$$\begin{array}{lcl} \mathit{cis}\text{-}\mathrm{Cr(CO)_4(P\{OMe\}_3)_2} & \rightleftharpoons & \mathit{cis}\text{-}\mathrm{[Cr(CO)_4(P\{OMe\}_3)_2]^+} + e^- \\ & & \quad \Big\downarrow \text{fast} \\ & & \mathit{trans}\text{-}\mathrm{[Cr(CO)_4(P\{OMe\}_3)_2]^+} \end{array} \qquad (12)$$

toward the potential for the trans oxidation process. However, the limit of the shift in potential of the cis^0 oxidation process (which generates trans^+) cannot be shifted beyond that for the trans^0 oxidation. This limit applies because the trans^+ isomer cannot exist at less positive potentials than the $E°$ value for the $\mathrm{trans}^+/\mathrm{trans}^0$ couple. At such potentials trans^+ is reduced to trans^0 at the diffusion-controlled rate. The cross redox reaction similarly constrains the position of the chemically perturbed cis^0 oxidation. Since only one response is observed under all conditions, it can be concluded that this limit has been reached and that redox responses are always observed at the $\mathrm{trans}^+/\mathrm{trans}^0$ redox potential, irrespective of whether equilibrium or nonequilibrium mixtures of the cis and trans isomers are present in the bulk solution. This study emphasizes that deceptively simple reversible electrochemical responses can be observed that involve substantial structural changes of an isomeric kind or large changes in bond lengths.[25]

Acknowledgment. We thank Dr. D. Dakternieks for obtaining some of the phosphorus-31 NMR spectra. T. F.M. thanks the Commonwealth Government for a postgraduate research scholarship.

Registry No. TBAP, 1923-70-2; TEAP, 2567-83-1; *cis*-$\mathrm{[Cr(CO)_4(P\{OMe\}_3)_2]^+}$, 115888-45-4; *trans*-$\mathrm{[Cr(CO)_4(P\{OMe\}_3)_2]^+}$, 100165-44-4; *cis*-$\mathrm{Cr(CO)_4(P\{OMe\}_3)_2}$, 16027-43-3; *trans*-$\mathrm{Cr(CO)_4(P\{OMe\}_3)_2}$, 21370-42-3; Pt, 7440-06-4; P, 7723-14-0; NOPFe, 16921-91-8; $\mathrm{AgClO_4}$, 7783-93-9; $\mathrm{[NH(C_6H_4Br)_3]SbCl_6}$, 40927-19-3; $\mathrm{LiAlH_4}$, 16853-85-3; dichloromethane, 75-09-2; acetonitrile, 75-05-8.

---

[25] Gennett, T.; Geiger, W. E.; Willett, B.; Anson, F. C. *J. Electroanal. Chem.* 1987, *222*, 151.

Communications

Stoichiometric Hydroformylation of Coordinated Acetone

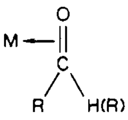
Stephen A. Matchett, Jack R. Norton,* and Oren P. Anderson

Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523

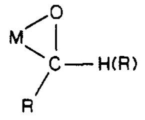
Received April 26, 1988

Summary: The bridging acetone in $\mathrm{Cp_2Zr[(\mu\text{-}OC)Mo(CO)_2Cp][(\mu\text{-}\eta^2,\eta^1\text{-}CMe_2O)Zr(Me)Cp_2]}$ (**1**) undergoes CO insertion into its Zr–C bond, with the oxygen of the new η^2-acyl ligand displacing the acetone oxygen from one Zr. Acidification of the η^2-acyl complex **2** gives α-hydroxyisobutyraldehyde, the product of the formal hydroformylation of the coordinated acetone.

While the hydroformylation of formaldehyde has been effected stoichiometrically with $\mathrm{HCo(CO)_4}$[1] and has been catalyzed by a number of other reagents,[2] the hydroformylation of higher aldehydes and ketones has not been reported.[3] The difficulty of inserting carbon monoxide into bonds between metals and oxygen-bearing carbons[4] makes such reactions uncommon. One approach to them involves the aldehyde and ketone complexes (I) of the early transition metals—complexes which are better described as metallaoxiranes (II) with metal–carbon σ bonds.[5] Most



I



II

such complexes have proven unreactive toward carbon monoxide, but we have been able to carbonylate the Zr–C

---

[1] Roth, J. A.; Orchin, M. *J. Organomet. Chem.* 1979, *172*, C27.

[2] (a) Spencer, A. *J. Organomet. Chem.* 1980, *194*, 113. (b) Okano, T.; Makino, M.; Konishi, H.; Kiji, J. *Chem. Lett.* 1985, 1793. (c) Jacobson, S. E. *J. Mol. Catal.* 1987, *41*, 163. (d) Marchionna, M.; Longoni, G. *J. Chem. Soc. Chem. Commun.* 1987, 1097 and references therein.

[3] The cobalt-catalyzed addition of CO and $\mathrm{R_3Si{-}H}$ to aldehydes has been reported: Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. *Angew. Chem., Int. Ed. Engl.* 1979, *18*, 3393. The cobalt-catalyzed addition of CO and $\mathrm{R_3Si{-}H}$ to cyclobutanone has also been reported: Chatani, N.; Furukawa, H.; Kato, T.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* 1984, *106*, 430.

[4] Examples of such insertions, and discussions of the general problem, can be found in: (a) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* 1981, *219*, 353. (b) Selover, J. C.; Vaughn, G. D.; Strouse, C. E.; Gladysz, J. A. *J. Am. Chem. Soc.* 1986, *108*, 1462 and references therein. (c) Tso, C. C.; Cutler, A. R.; Kullnig, R. K. *J. Am. Chem. Soc.* 1987, *109*, 5844 and references therein.

[5] Erker, G.; Rosenfeldt, F. *J. Organomet. Chem.* 1982, *224*, 29.

0276-7333/88/2307-2228$01.50/0