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Electrochemical Investigations of Compounds Having Isomeric Forms with Similar Standard Redox Potentials: Oxidation of Bis(tri-*n*-butylphosphine)molybdenum Tetracarbonyl and Related Complexes

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Abstract: The electrochemical oxidation or reduction of compounds existing in isomeric forms can be accompanied by conversions from one structural form to another. If the isomeric forms have similar standard redox potentials, structural rearrangements can be difficult to detect. Thus, the electrochemistry of compounds having isomeric forms, while frequently appearing to be deceptively simple, can be extremely complicated. $Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ can exist in cis and trans isomeric forms and the $trans^+/trans^0$ and cis^+/cis^0 standard redox potentials are similar. This and related systems such as $Mo(CO)_4(PEt_3)_2$ and $Mo(CO)_4(PPh_3)_2$ are therefore used to provide examples which illustrate the interactions that may need to be considered. Importantly, it is demonstrated that structural rearrangements of these kind occurring via an intramolecular mechanism do not lead to the observation of slow electron transfer.

Cyclic voltammetry, polarography, and other electrochemical techniques have been employed widely to calculate reversible half-wave potentials, $E_{1/2}^{r}$. This parameter is particularly useful because frequently it can be equated to an excellent approximation with the thermodynamically significant standard redox potential, $E°$, more classically obtained from potentiometry.

In the case of compound A being electrochemically reduced by one electron to compound $[A]^-$ and unrelated compound B being reduced by one electron to compound $[B]^-$, the electrode reactions can be written as in eq 1 and 2, where k_s^n, α_n, $E_n°$ and

$$A + e^- \underset{}{\overset{k_s^1,\ \alpha_1}{\rightleftharpoons}} [A]^- \quad (E_1° \text{ or } E_{1/2}^{r_1}\ \text{V vs. reference electrode}) \tag{1}$$

$$B + e^- \underset{}{\overset{k_s^2,\ \alpha_2}{\rightleftharpoons}} [B]^- \quad (E_2° \text{ or } E_{1/2}^{r_2} V \text{ vs. reference electrode}) \tag{2}$$

$E_{1/2}^{r_n}$ (n = 1, 2) are the heterogeneous charge-transfer rate constant, charge-transfer coefficient, standard redox and reversible half-wave potential, respectively, associated with electrode process n. (For simplicity, α will be omitted in future equations).

If E_2^0 is more negative than E_1^0, then when $[B]^-$ is mixed with A, thermodynamically, the second-order reaction (3) can occur,

$$A + [B]^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} [A]^- + B \tag{3}$$

where k_f and k_b are the forward and reverse homogeneous chemical rate constants with $k_f > k_b$. At an electrode, under conditions of cyclic voltammetry or polarography etc., it is usually assumed that cyclic voltammograms or polarograms describing the reduction of A and B either in separate solutions or in mixture can be treated simply by the theory applicable to eq 1 and 2. However, clearly if the second-order chemical cross redox reaction represented by eq 3 is sufficiently fast (k_f rapid with respect to the time scale of electrochemical experiment), the electrode process 2 need not be the same in the presence of A as in the absence of A. That is the theory required to treat the current–voltage (i–E) or related curve would be

$$B + e^- \overset{k_s^2}{\rightleftharpoons} [B]^- + A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B + A^-$$

For example, Yamaoka[3] has demonstrated that the irreversible reduction step (4) is modified (enhanced currents) under conditions of AC polarography by the presence of the more easily reduced Fe(III). This was interpreted as being caused by the cross redox reaction.

$$Cr(III) + e^- \overset{k_s}{\rightleftharpoons} Cr(II) \tag{4}$$

$$Cr(II) + Fe(III) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Cr(III) + Fe(II)$$

Smith and co-workers[4–7] have subsequently examined the theory for this class of electrode process and computed values of k_f and k_b which agree very well with data obtained from stopped-flow experiments. A substantial number of workers have also considered the influence of reactions related to a second-order cross redox reaction in other situations as ref 8–10 indicate.

In the field of organometallic chemistry, many compounds can have a range of structural isomers which may be represented by the symbol I_j. Typically electrochemical measurements treat such systems in the manner illustrated in eq 5, and in most cases this

$$\begin{array}{ll}
I_1 + e^- \rightleftharpoons [I_1]^- & (E_{1/2}^{r_1}) \\
I_2 + e^- \rightleftharpoons [I_2]^- & (E_{1/2}^{r_2}) \\
\cdot & \cdot \\
\cdot & \cdot \\
\cdot & \cdot \\
I_j + e^- \rightleftharpoons [I_j]^- & (E_{1/2}^{r_j})
\end{array} \tag{5}$$

may be justified. However, in several instances where the $E_{1/2}^{r}$ values of I_1, I_2, ... I_j are well separated, it has been possible to clearly demonstrate that isomerization reactions occur. For example the oxidation of *cis*-$M(CO)_2$(bidentate phosphine)$_2$ [M = Cr, Mo, W][11,12] can be represented by the reaction scheme given in eq 6. Similar interactions occur on oxidation of *fac*-Mn-

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(1) Deakin University.

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$$\begin{tikzcd}[column sep=large]
\textit{cis}\text{-M(CO)}_2\text{(bidentate phosphone)}_2 \arrow[r, shift left, "{k_s{}^1,\ E_{1/2}{}^{r_1}}"] \arrow[d, shift left, "k_{-1}"] & \textit{cis}\text{-[M(CO)}_2\text{(bidentate phosphine)}_2]^+ + e^- \arrow[l, shift left] \arrow[d, shift left, "k_{-2}"] \\
\textit{trans}\text{-M(CO)}_2\text{(bidentate phosphine)}_2 \arrow[r, shift left, "{k_s{}^2,\ E_{1/2}{}^{r_2}}"] \arrow[u, shift left, "k_1"] & \textit{trans}\text{-[M(CO)}_2\text{(bidentate phosphine)}_2]^+ + e^- \arrow[l, shift left] \arrow[u, shift left, "k_2"]
\end{tikzcd} \qquad (6)$$

$$\begin{tikzcd}[column sep=large]
\textit{cis}\text{-Mo(CO)}_4\text{(dicarbene)}_2 \arrow[r, shift left, "{k_s{}^1,\ E_{1/2}{}^{r_1}}"] & \textit{cis}\text{-[Mo(CO)}_4\text{(dicarbene)}_2]^+ + e^- \arrow[l, shift left] \\
\textit{trans}\text{-Mo(CO)}_4\text{(dicarbene)}_2 \arrow[r, shift left, "{k_s{}^2,\ E_{1/2}{}^{r_2}}"] \arrow[u, "k_1"'] & \textit{trans}\text{-[Mo(CO)}_4\text{(dicarbene)}_2]^+ + e^- \arrow[l, shift left] \arrow[u, "k_2"']
\end{tikzcd} \qquad (7)$$

(CO)$_3$(bidentate phosphorous)X [X = Cl, Br][13,14] involving the species *fac*-Mn(CO)$_3$(bidentate phosphorous)X, *fac*-[Mn(CO)$_3$(bidentate phosphorous)X]$^+$, *mer*-[Mn(CO)$_3$(bidentate phosphorous)X]$^+$, and *mer*-Mn(CO)$_3$(bidentate phosphorus)X. In the case of structurally more complex binuclear complexes, the probability of isomerization reactions increases. Rearrangement involving α and β forms of the ruthenium dithiocarbamate (dtc$^-$ = dithiocarbamate) [Ru$_2$(dtc)$_5$]$^{+/0/-}$ series have also been reported for example[15]. In the organic field of electrochemistry, cis–trans isomerization has been also considered in detail[16,17] as has the influence of conformational changes.[18]

In the case of electrochemical oxidation of dicarbene metal complexes,[19] Mo(CO)$_4$(dicarbene)$_2$, both trans and cis isomers can be prepared and a reaction scheme given in eq 7 is required to explain the observed electrochemistry. In this example $E_{1/2}{}^{r_2}$ is again more negative than $E_{1/2}{}^{r_1}$ as is the case in eq 6 so the above process can be identified unambiguously. However, the kinetics are such that k_1 occurs in the reverse direction to that in eq 6, and this has many extremely interesting consequences. For example, electrochemical oxidation of *trans*-Mo(CO)$_4$(dicarbene)$_2$ can lead to isomerization via an electrochemical reaction with essentially no net current flow. That is, the sequence of events that occurs on electrochemical oxidation is a follows. As the potential is scanned in the positive direction toward the $E_{1/2}{}^{r_2}$ value for the redox couple *trans*-[Mo(CO)$_4$(dicarbene)$_2$]$^+$/trans-Mo(CO)$_4$(dicarbene)$_2$, the *trans*-Mo(CO)$_4$(dicarbene)$_2$ complex is oxidized to the trans cation, which rapidly isomerizes to the cis cation. Since the potential at this point is much more negative than the reduction potential of the cis cation, the cis cation is immediately reduced to neutral *cis*-Mo(CO)$_4$(dicarbene)$_2$. If the isomerization rate of the trans$^+$ (k_1) → cis$^+$ step is extremely high, then no net current flow will be observed for the oxidation of trans Mo(CO)$_4$(dicarbene)$_2$ at $E_{1/2}{}^{r_2}$ because the oxidation current will approximately equal the reduction current. It is also of course possible that the cross redox reaction (8) can contribute to the

$$\begin{aligned}&\textit{trans}\text{-Mo(CO)}/_4\text{(dicarbene)}_2 + \\ &\qquad \textit{cis}\text{-[Mo(CO)}_4\text{(dicarbene)}_2]^+ \xrightarrow{k_3} \\ &[\textit{trans}\text{-Mo(CO)}_4\text{(dicarbene)}_2]^+ + \textit{cis}\text{-Mo(CO)}_4\text{(dicarbene)}_2\end{aligned} \qquad (8)$$

isomerization with no net current flow. In the above situation, the magnitude of the current observed at $E_{1/2}{}^{r_2}$ is governed by the rate of isomerization of the trans cation to the cis cation and the rate of the homogeneous cross redox reaction (eq 8). If these rate constants are fast, then the oxidative electrochemistry of *trans*-M(CO)$_4$(dicarbene)$_2$ will occur at the potential $E_{1/2}{}^{r_1}$ for oxidation of *cis*-Mo(CO)$_4$(dicarbene)$_2$, and both complexes could erroneously appear to have the same $E_{1/2}{}^{r_n}$ values.

The above examples cited are examples of geometric isomers where the $E°$ values are well separated and electrochemistry has been well studied and understood. In general terms the redox processes between two isomers I$_1$ and I$_2$ can be written as in eq 9, where the cross symbol represents the chemical cross redox

$$\begin{tikzcd}[column sep=huge]
\mathrm{I}_1 + e^- \arrow[r, shift left, "{\alpha_1,\ k_s{}^1,\ E_{1/2}{}^{r_1}}"] \arrow[d, shift left, "k_{-2}"] \arrow[dr, leftrightarrow] & {[\mathrm{I}_1]^-} \arrow[l, shift left] \arrow[d, shift left, "k_{-1}"] \arrow[dl, leftrightarrow] \\
\mathrm{I}_2 + e^- \arrow[r, shift left, "{\alpha_2,\ k_s{}^2,\ E_{1/2}{}^{r_2}}"] \arrow[u, shift left, "k_2"] & {[\mathrm{I}_2]^-} \arrow[l, shift left] \arrow[u, shift left, "k_1"]
\end{tikzcd} \qquad (9)$$

reaction I$_2$ + [I$_1$]$^-$ (k_3) ⇌ I$_1$ + [I$_2$]$^-$ (k_{-3}) and k_n and k_{-n} (n = 1–3) represent chemical rate constants for forward and reverse reactions. In essence, this is closely related to the "square" scheme and others that have been considered theoretically.[4,20,21]

In organometallic chemistry, the most probable result is that $E_{1/2}{}^{r_1}$ and $E_{1/2}{}^{r_2}$ are similar in magnitude, and under these circumstances, while a cyclic voltammogram may have the apparent appearance of a simple electron-transfer reaction, eq 10, this may

$$\mathrm{I} + e^- \xrightleftharpoons{k_s{}^1,\ E_{1/2}{}^{r_1}} [\mathrm{I}]^- \qquad (10)$$

only be a deceptively simple result. Similarly the observation of an apparently reversible couple need not mean that the $E_{1/2}$ value for the first observed electrode process is that of $E_{1/2}{}^{r_1}$, but is could be that for $E_{1/2}{}^{r_2}$, depending on the values of $E_{1/2}{}^{r_1}$, $E_{1/2}{}^{r_2}$, and chemical rate constants.

In summary, the above survey is presented to demonstrate how easily misleading information may result when structural isomers having different standard redox potentials exist and their electrochemistry is not considered in great detail.

As a further point of confusion it is frequently noted in papers correlating rate of electron transfer with structural change that fast electron-transfer rates (reversible or almost reversible responses) are associated with lack of drastic structural change.[22,23] Conversely, slow electron-transfer rates have been associated with structural change.[23,24] However, data cited seem to be in conflict in this area in the sense that isomerization steps represent a considerable structural change, but both electron-transfer steps may still be rapid because the "square scheme" assumes a finite existence of each isomer and requires that isomerization occurs in a homogeneous reaction which can be distinguished from the electron-transfer step. A mechanistic question which needs to be

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addressed is whether the isomerization occurs concomitantly or separately to the electron-transfer step. Moraczewski and Geiger[23] briefly considered both possibilities but their data was not sufficient to give an unequivocal answer as to exactly when the isomerization occurs. If generally correct, the "square" results must have considerable importance to the validity of equating rate of electron transfer with structural change.

This paper presents results on the electrochemical oxidation of some Mo(CO)$_4$(monodentatephosphine)$_2$ complexes to demonstrate the extreme care required in the interpretation of data. Disubstituted molybdenum tetracarbonyl octahedral complexes obviously can exhibit both cis and trans stereochemistries. For many of the monodentate phosphine ligands, the trans derivative has been shown to be the thermodynamically more stable isomeric form. That is the equilibrium given in eq 11 lies to the right (see

$$cis\text{-Mo(CO)}_4\text{(monodentate phosphine)}_2 \rightleftharpoons trans\text{-Mo(CO)}_4\text{(monodentate phosphine)}_2 \quad (11)$$

ref 25–30, for example). In many instances both cis and trans isomers can be synthesized. When the monodentate phosphorous ligand is triphenylphosphine, PPh$_3$, the cis isomer thermally rearranges to the trans isomer.[29] However, photochemically at ambient temperature, *trans*-Mo(CO)$_4$(PPh$_3$)$_2$ isomerizes to *cis*-Mo(CO)$_4$(PPh$_3$)$_2$.[28] With PPh$_3$ the conversion mechanism is thought to be dissociative. However, when the monodentate ligand is tri-*n*-butylphosphine, P-*n*-Bu$_3$, isomerization reactions occur via a non-bond-breaking intramolecular mechanism[30] as is believed to be the case with the Mo(CO)(bidentatephosphine)$_2$[13,31] and Mo(CO)$_4$(dicarbene)$_2$[19,32] complexes. The electrochemistry of Mo(CO)$_4$(P-*n*-Bu$_3$)$_2$ unlike that of the other mentioned compounds, has not been examined. On the other hand many complexes of the type M(CO)$_4$L$_2$(M = Cr, Mo, W) or related species have been briefly examined electrochemically with only cyclic voltammetric data provided (see ref 33, for example). From the above discussion much interesting chemistry could be anticipated from a detailed examination of the electrochemistry of Mo(CO)$_4$(P-*n*-Bu$_3$)$_2$ and related species.

Experimental Section

Materials. All chemicals used were of analytical reagent grade purity unless otherwise specified.

Compound Preparations. All compounds examined were prepared by methods described or referred to in ref 30. Infrared spectra recorded on a Perkin-Elmer either 521 or 283 spectrophotometer were used to verify the purity of the compounds and monitor any possible isomerization reaction is the dichloromethane or acetone media used in the electrochemical investigations.

Electrochemical Instrumentation. Cyclic voltammograms were obtained by using a Princeton Applied Research Corp., PAR, Model 174 polarographic analyzer. The working electrode was a platinum wire or a platinum disk, the reference electrode was Ag/AgCl (acetone; saturated LiCl) separated from the test solution via a salt bridge containing the solvent/supporting electrolyte, and the auxiliary electrode was platinum wire. All solutions were thoroughly degassed with nitrogen prior to recording cyclic voltammograms. When acetone was the solvent, 0.1 M Et$_4$NClO$_4$ was the supporting electrolyte, whereas in dichloromethane, 0.1 M Bu$_4$NClO$_4$ was used instead of the tetraethylammonium salt, because of its higher solubility.

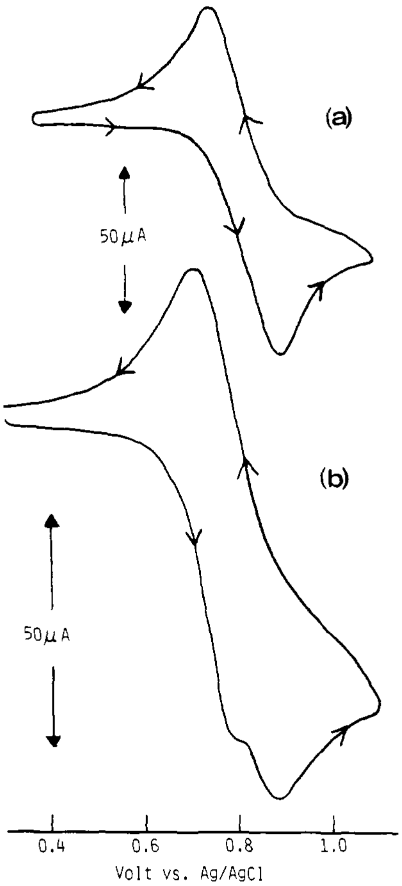

Figure 1. Cyclic voltammogram for oxidation of 5 × 10^{-4} M (a) *cis*-Mo(CO)$_4$(P-*n*-Bu$_3$)$_2$ and (b) trans-Mo(CO)$_4$(P-*n*-Bu$_3$)$_2$ at a Pt electrode in acetone (0.1 M Et$_4$NClO$_4$) at 20 °C and with a scan rate of 200 mV/s.

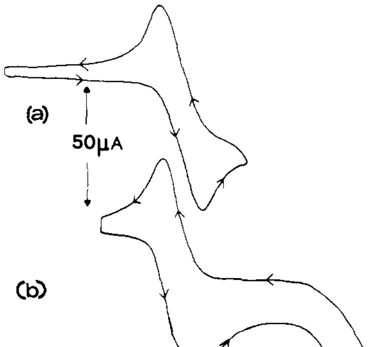

Figure 2. Cyclic voltammograms for oxidation of 5 × 10^{-4} M (a) *cis*-Mo(CO)$_4$(P-*nBu*$_3$)$_2$ and (b,c) *trans*-Mo(CO)$_4$(P-*n*-Bu$_3$)$_2$ at a Pt electrode in dichloromethane (0.1 M Bu$_4$NClO$_4$) at 20 °C and with a scan rate of 200 mV/s.

For controlled potential electrolysis experiments, a PAR Model 173 potentiostat/galvanostat was used with a large platinum gauze working

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electrode. The reference electrode was the same as for the voltammetry. The auxiliary electrode was a platinum coil placed in a salt bridge containing solvent/supporting electrolyte, and it was separated from the test solution by porous Vycor. A PAR Model 179 digital coulometer was used in conjunction with the PAR Model 173 potentiostat to calculate the coulombs consumbed in the controlled potential electrolysis experiments.

Positive feedback circuitry was used to minimize uncompensated resistance. For low-temperature studies, various slush baths were prepared; e.g., dry ice/acetone was used for studies at −78 °C. The reference electrode was maintained at ambient temperatures in the low-temperature work.

Results and Discussion

Oxidation of *cis*- and *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$. Figure 1 shows a cyclic voltammogram for oxidation of 5×10^{-4} M *cis*- and *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ at a platinum electrode in acetone at 20 °C. Figure 2 shows equivalent scans in dichloromethane, except that one of the scans is extended to more positive potentials to reveal the existence of an additional irreversible electrode process near the solvent limit. The more positive process, presumably an irreversible $Mo(I) \rightarrow Mo(II) + e^-$ step, is not considered further in this paper. The electrode processes in both solvents are essentially the same, but some instability of the compounds was observed in acetone and the majority of the studies were therefore undertaken in dichloromethane. However, the observation of an essentially solvent-independent result is important in that it is a characteristic expected of an isomerization mechanism occurring via an intramolecular mechanism.[13,14]

Examination of the first oxidation process for the cis complex in Figure 1 and 2 could naively lead to the incorrect assignment of this as a drawn-out quasi-reversible one-electron oxidation electrode process (eq 12), as the cyclic voltammogram has the

$$\textit{cis}\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \rightleftharpoons \textit{cis}\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ + e^- \qquad (12)$$

required characteristics for this mechanism. However, the first oxidation process of the trans complex is associated with two waves on the first forward scan, the second having a similar oxidation potential as observed with the cis complex, and on the reverse scan the reduction peak observed for this electrode process corresponds to that found for the cis complex. These observations imply that eq 12 is incorrect and the rearrangements must be occurring in accordance with the square scheme presented in eq 9.

Infrared spectroscopic monitoring of the carbonyl bands over a period of 3 h demonstrated that under the electrochemical conditions prevailing, neither of the reactions represented by k_1 and k_{-1} in eq 13 occurs at a rate which would require their inclusion into the experiments associated with the relatively short time scale of the electrochemical experiment.

$$\textit{trans}\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{cis}\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \qquad (13)$$

After oxidation, 17 electron cations are usually far more kinetically labile than their 18 electron counterparts,[13,19,34] so that the

$$\textit{trans}\text{-}[Mo(CO)_4(P\text{-}\textit{nBu}_3)_2]^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \textit{cis}\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ \qquad (14)$$

step may need to be considered, as may the cross redox reaction necessarily incorporated into the square scheme (eq 9). Assuming that E° (cis$^+$/cis$^\circ$) is more positive than E° (trans$^+$/trans^0) implies that equilibrium in eq 15 lies to the right. However, the E° values

$$\textit{cis}\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ + \textit{trans}\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \textit{trans}\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ + \textit{cis}\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \qquad (15)$$

for the two couples are similar (see later discussion) so that both the forward and back directions of this reaction could be important.

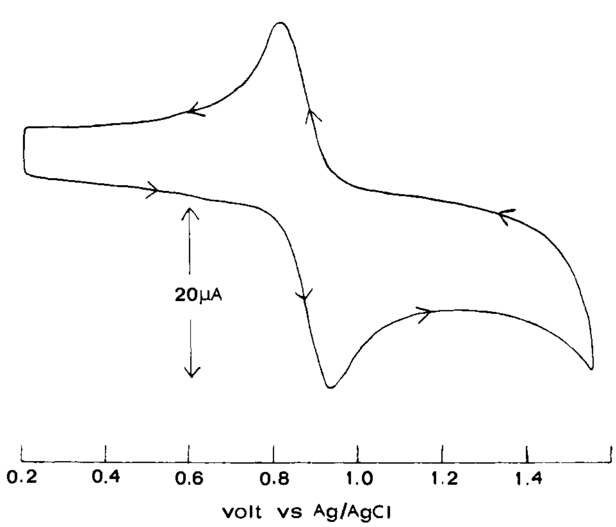

Figure 3. Cyclic voltammogram for oxidation approximately 2×10^{-4} M *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ at a platinum electrode in dichloromethane (0.1 M Bu_4NClO_4) at −78 °C and with a scan rate of 200 mV/s.

Considering the reactions in the above manner, the oxidation of the trans isomer can be written as in eq 16. Thus, as trans

$$\textit{trans}\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \rightleftharpoons \textit{trans}\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ + e^- \qquad (16a)$$

$$\textit{trans}\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \textit{cis}\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ \qquad (16b)$$

$$\textit{cis}\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ + e^- \rightleftharpoons \textit{cis}\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \qquad (16c)$$

$$\textit{trans}\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ + \textit{cis}\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \underset{k_3}{\overset{k_{-3}}{\rightleftharpoons}} \textit{cis}\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ + \textit{trans}\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \qquad (16d)$$

cations are generated at potentials near E° for the trans$^+$/trans^0 couple, they are immediately reduced to the cis species. However, the equilibrium constant, $K_1 = k_1/k_{-1}$, for the reaction trans^0 (k_1) $\rightleftharpoons$ cis^0 (k_{-1}) is approximately 0.2 (infrared data)[30] so that such a process cannot occur to anywhere near completion, even if k_2 is rapid, because the ratio cis^0/trans^0 has a thermodynamic restraint. Similarly, the cross redox reaction, being a function of the E^0 difference, is also thermodynamically limited in the extent to which it can occur as well as the potential range over which it can occur. The second oxidation step for the trans complex can therefore occur at potentials representing the oxidation of neutral, cis^0 to the cis$^+$ cation. At potentials more positive than E^0(cis$^+$/cis^0) where direct electrochemical reduction of the cis$^+$ cation ceases, the cross redox reaction represented by eq 15 can occur to generate the trans$^+$ cation, thereby leaving the trans$^+$ + e$^-$ $\rightleftharpoons$ trans^0 reduction process as the dominant reaction (only detectable one) observed on the reverse scan of the cyclic voltammogram describing the oxidation of *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ under the conditions of Figure 2.

Figure 3 shows the cyclic voltammogram for oxidation of *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ at −78 °C. In lowering the temperature, considerable apparent simplification of the cyclic voltammogram occurs. A simple chemically reversible redox process assignable to the process

$$\textit{trans}\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \rightleftharpoons \textit{trans}\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ + e^-$$

remains at −78 °C under conditions of Figure 3. This would be the case if reactions k_2 and k_3 are slowed down sufficiently so as to relatively unimportant on the electrochemical time scale at −78 °C.

The oxidation of *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ is of course governed by the same thermodynamic constraints as the oxidation of the

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(34) R. Davis and D. J. Darensbourg, *J. Organomet. Chem.*, **161**, C11 (1978).

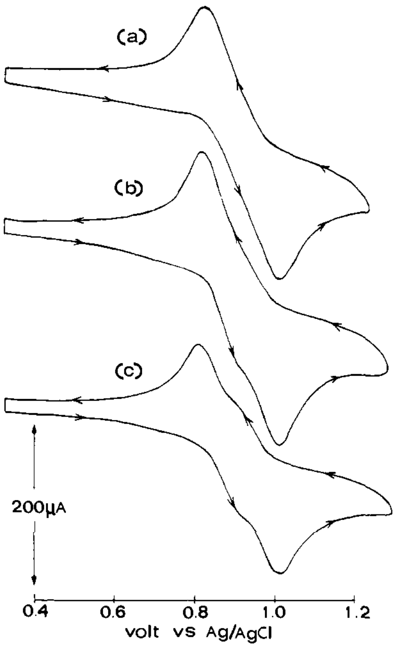

Figure 4. Cyclic voltammogram for oxidation of approximately 2×10^{-3} M *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ at a platinum electrode in dichloromethane (0.1 M Bu_4NClO_4) with a scan rate of 200 mV/s and at (a) 20 °C, (b) -40 °C, and (c) -78 °C.

trans isomer. That is K_1, K_2, and K_3 are all not greatly removed from unity and k_1 and k_{-1} can be neglected in accordance with IR data. However, since k_2 and k_3 were considered to be important in interpreting the electrochemistry for oxidation of *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$, it therefore follows that k_{-2} and k_{-3} cannot be neglected in the interpretation of the oxidation of the cis isomer. Interactions consistent with the values of K_1, K_2, and K_3 can therefore occur.

The apparently simple but drawn out wave for oxidation of *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ (Figure 2) is replaced by two apparently chemically reversible couples at -78 °C (Figure 4). The position of the less positive couple at -78 °C corresponds to that for the oxidation of *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ at -78 °C, and as previously presumed the more positive couple corresponds to that for the redox process *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \rightleftharpoons$ *cis*-$[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ + e^-$. The cyclic voltammograms for oxidation of *cis*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ confirm the necessity for introducing the "square" reaction scheme to provide a definitive explanation of the electrochemistry of complexes having the possibility of existing in different geometric configurations.

In its simplest form the oxidation of the cis isomer can be represented by the reaction scheme given in eq 17a–d. Presumably, k_{-2}, k_{-3}, and k_2 are significant on the electrochemical time scale at 20 °C, producing an unresolved current response at all potentials between the trans$^+$/trans^0 and cis$^+$/cis^0 couples. From data at lower temperatures on the trans compound, the rate constant k_2 appears to have relatively little influence on the cyclic voltammetry at -78 °C. However, reactions associated with k_{-2} and k_{-3} may still need to be considered, enabling responses ap-

$$cis\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \rightleftharpoons cis\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ + e^- \quad (17a)$$

$$cis\text{-}[Mo(CO)_4(P\text{-}nBu_3)_2]^+ \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} trans\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ \quad (17b)$$

$$trans\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2{}^+ + cis\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \underset{k_3}{\overset{k_{-3}}{\rightleftharpoons}} trans\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 + cis\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ \quad (17c)$$

$$trans\text{-}Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2 \rightleftharpoons trans\text{-}[Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2]^+ + e^- \quad (17d)$$

parently corresponding to the individual $E°$ values to be resolved at -78 °C. Importantly, electrode processes are kinetically rather than thermodynamically controlled under all conditions examined in this work.

Variable concentration studies and scan rate dependence are consistent with the presence of a second-order chemical reaction being important in the electrode process (the cross redox reaction).

A theoretical simulation of the problem for the technique of DC cyclic voltammetry was attempted by using the method of Feldberg.[35] Accurate simulation is difficult when the two $E°$ values are so close, since each of the variables $E_1°$, $E_2°$, k_s^1, k_s^2, α_1, α_2, k_1, k_{-1}, k_2, k_{-2}, k^3, and k_{-3} are required, and not of these parameters are amenable to direct and accurate independent experimental determination. When $E_1°$, and $E_2°$ are well separated, most of the parameters can be obtained, as indicated in other studies, because it is immediately clear which rate constants are unimportant and separate treatment of different aspects of the problem is sometimes possible.[8,9,12,13,18,36] The work of Nelsen et al.,[18] uncomplicated by the difficulty of similar $E°$ values, can be cited as an example to illustrate the difficulties confronting a complete interpretation of the theory. In the present case, the cross redox reaction is required in the simulation of the theory. The second-order reactions are extremely difficult to handle from the point of view of accuracy (computer time),[35] and in the particular case of the present system no reliable estimate of values could be obtained. This is consistent with Feldberg's observation.[8] Furthermore, the necessity of having experimental data obtained in the very high resistance solvent, dichloromethane, further decreased the confidence of obtaining an adequate result to apply to the theory.

Despite problems associated with the theoretical simulation, orders of magnitude may be placed on some parameters as follows: (i) $E°$ values of trans$^+$/trans^0 and cis$^+$/cis^0 couples differ by about 50 mV with the cis$^+$/cis^0 couple being the more positive; (ii) result (i) implies that the equilibrium constant for the reaction, trans^0 + cis$^+$ $\rightleftharpoons$ trans$^+$ + cis^0, has a value of approximately 7 at 20 °C; (iii) assuming the equilibrium constant for the trans° $\rightleftharpoons$ cis^0 isomerization is 0.2 (see previous discussion) coupled with information contained in i and ii implies that the trans$^+$ $\rightleftharpoons$ cis$^+$ isomerization has an equilibrium constant of approximately 0.03; (iv) k_s values for both the trans^0 $\rightleftharpoons$ trans$^+$ + e^- and cis^0 $\rightleftharpoons$ cis$^+$ + e step are fast and are $\geq 10^{-2}$ cm s^{-1} at 20 °C.

In summary, the square reaction scheme seems adequate to explain the data. In the particular example presented in this study there seems no doubt that all four isomers have a finite existence and that the electron-transfer and isomerization steps occur sequentially.

The thrust of our argument is that structural change is not concomitant with electron transfer but occurs before or after electron transfer. Rapid electron transfer under these circumstances is not excluded by an intramolecular structural change.

Controlled potential electrolysis at 20 °C of the *cis*- or *trans*-$Mo(CO)_4(P\text{-}n\text{-}Bu_3)_2$ complex at platinum gauze electrodes gave a coulometric n value of 2.1 ± 0.2 and produced non-carbonyl-containing species (IR evidence). The same experiments at -78 °C produced variable n values between 1.5 and 2.0, implying initial generation of the cation on the synthetic time scale at -78 °C followed by a slow chemical reaction leading to a molybdenum(II) species and loss of carbon monoxide. Unfortunately, the cations were insufficiently stable to characterize even at -78 °C. All of the above data suggest that a more definitive treatment of this class of electrode process requires the use of techniques other than cyclic voltammetry. Ring-disk electrodes could be superior,[17] but ultimately spectroscopic techniques probably need to be coupled to the electrolysis step in order to provide a quantitative account of the cross redox reactions. This was inferred in the work of Feldberg.[8] An extensive program of

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(35) S. W. Feldberg in "Electroanalytical Chemistry", Vol. 3, (A. J. Bard, Ed., Marcel Dekker, New York, 1969, pp 199–296.

(36) A. M. Bond, R. J. O'Halloran, I. Ruzic, and D. E. Smith, *J. Electroanal. Chem.*, in press.

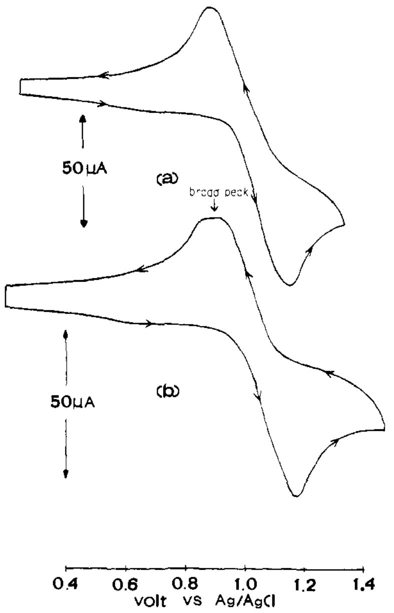

Figure 5. Cyclic voltammograms for oxidation of approximately 5 × 10^{-4} M *cis*-$Mo(CO)_4(PEt_3)_2$ in dichloromethane (0.1 M Bu_4NClO_4) at a platinum electrode at (a) 20 °C and (b) −78 °C and with scan rate of 200 mV/s. Note the broadening and splitting of the peak on the reverse scan at −78 °C.

research to investigate possible approaches in this direction is planned for the future.

Oxidation of *cis*-$Mo(CO)_4(PEt_3)_2$. Triethylphosphine is electronically and sterically quite similar to tri-*n*-butylphosphine.[30,37] It has the same cone angle of 132°[37] and a similar equilibrium constant for the $cis^0 \rightleftharpoons trans^0$ reaction.[30] Additionally, isomerization appears to occur also via an intramolecular mechanism. Electrochemical reactions could therefore also be expected to be similar. Figure 5 shows cyclic voltammograms for the first oxidation of the cis^0 isomer at two temperatures. An additional oxidation process near the solvent limit similar to that for $Mo(CO)_4(P\text{-}nBu_3)_2$ is not shown. Only by very close inspection of the curve at −78 °C can evidence be found for the "square" reaction scheme. At higher temperatures, the electrode process appears to be a single quasi-reversible oxidation

$$cis\text{-}Mo(CO)_4(PEt_3)_2 \rightleftharpoons cis\text{-}[Mo(CO)_4(PEt_3)_2]^+ + e^-$$

Presumably, the $E°$ values for the cis^+/cis^0 and $trans^+/trans^0$ complexes are even closer together than when the ligand is P-*n*-Bu_3. Alternatively, small variations in rate constants could also readily lead to difficulties in detecting any "anomalous" behavior associated with rearrangement reactions.

Oxidation of *cis*- and *trans*-$Mo(CO)_4(PPh_3)_2$. Figure 6 shows a cyclic voltammogram for oxidation of *cis*-$Mo(CO)_4(PPh_3)_2$ at 20 and at −78 °C. The electrode process is chemically irreversible at 20 °C but partially reversible in the chemical sense at −78 °C in acetone (reversible in dichloromethane). The trans isomer produced cyclic voltammograms which were indistinguishable from those of the cis isomer. In view of the inherently greater instability of the 17 electron cations, $[Mo(CO)_4(PPh_3)_2]^+$, coupled with the possiblity of almost identical $E°$ values for the cis^+/cis^0 and $trans^+/trans^0$ complexes, the need to incorporate a "square" reaction scheme into the interpretation of the electrode processes is uncertain. However, it can be noted that the interpretation of the above data in terms of usual reaction schemes (eq 18) or its trans analogue may be rather simplisitic and may erroneously omit the rearrangment processes of the kind known to occur with the previously discussed complexes.

$$\begin{array}{ccc} cis\text{-}Mo(CO)_4(PPh_3)_2 & \rightleftharpoons & cis\text{-}[Mo(CO)_4(PPh_3)_2]^+ \\ & & \text{unstable} \\ & & \downarrow \\ & & \text{product} \end{array} \tag{18}$$

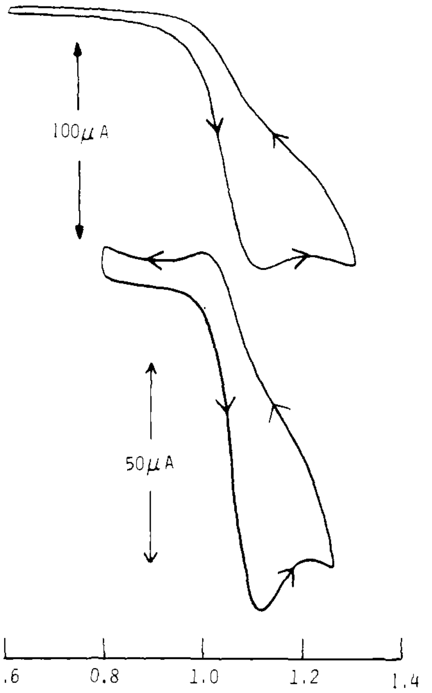

Figure 6. Cyclic voltammograms for oxidation of approximately 2 × 10^{-3} M *cis*-$Mo(CO)_4(PPh_3)_2$ in acetone (0.1 M Et_4NClO_4) at a platinum electrode at (a) 20 °C and (b) −78 °C and with a scan rate of 200 mV/s.

For the PPh_3 ligand, and unlike the case when the ligand is P-*n*-Bu_3 or PEt_3, the isomerization processes in the neutral 18-electron configuration occur via a dissociative process involving Mo–P bond cleavage.[29,38] The cone angle when the ligand is PPh_3 is 145°[37] and is greater than those for the other ligands considered in this work. Thus it appears that the more bulky ligands like PPh_3 may produce greater instability in the system toward loss of carbon monoxide and this effect is amplified in the kinetically labile 17 electron cations where the lifetime of $[Mo(CO)_4(PPh_3)_2]^+ << [Mo(CO)_4P\text{-}n\text{-}Bu_3)_2]^+$ or $[Mo(CO)_4(PEt_3)_2]^+$.

Conclusions

The above examples describing the electrochemical oxidation of some substituted carbonyl complexes, which can exist as cis or trans isomers having similar $E°$ values, demonstrate the difficulties involved in interpreting the current–voltage curves for this category of compound. The number of variables necessarily available when a "square" reaction scheme is operative or potentially operative provide the possibility for several reaction schemes involving first and higher order chemical kinetics which may be reversible or irreversible processes. Furthermore, these are coupled with heterogeneous electron-transfer steps which may also be reversible or irreversible. Further studies are in progress in these laboratories aimed at more ready identification and quantification of the processes involved in the electrochemistry of structurally related complexes.

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(37) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).

(38) D. J. Darensbourg and A. Graves, *Inorg. Chem.*, **18** 1257 (1979).