Spectroscopic and Voltammetric Study of the Deceptively Simple Solution Chemistry of the $[Cr(CO)_2(Ph_2PCH_2CH_2PPh_2)_2]^{+/0}$ System

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IR, ESR, and ^{31}P NMR spectroscopy, electrospray mass spectrometry, steady-state microelectrode voltammetry, and rotating-disk voltammetry have been used to characterize the solution chemistry of the deceptively simple $Cr(CO)_2(dpe)_2$ (dpe = $Ph_2PCH_2CH_2PPh_2$) system in benzene, toluene, chloroform, dichloromethane, acetone, and acetonitrile. These techniques show that while the expected *cis*-$Cr(CO)_2(dpe)_2$ (*cis*^{0}) and *trans*-$Cr(CO)_2(dpe)_2$ (*trans*^{0}) compounds are present, *trans*-$[Cr(CO)_2(dpe)_2]^+$ (*trans*$^+$) also is involved in the solution chemistry of the $Cr(CO)_2(dpe)_2$ system and that complex and rapid reactions may occur between these three compounds. The 17-electron cation *trans*$^+$, formed in the presence of oxygen, is the key compound in these reactions. Electrospray mass spectrometry and ESR spectroscopy confirm that *trans*$^+$ is present in solutions of $Cr(CO)_2(dpe)_2$. The formation of paramagnetic *trans*$^+$ modifies the apparent isomeric distribution of the *cis*^{0} and *trans*^{0} isomers determined by NMR methods because of line-broadening and relaxation effects. There is also an unfortunate coincidence of IR absorptions between the two carbonyl bands of *cis*^{0} and the single bands of both *trans*^{0} and *trans*$^+$; therefore, interpretation of data obtained from IR spectroscopy is also difficult in this system. However, steady-state microelectrode and rotating-disk voltammetric techniques generally are able to resolve the isomerization equilibrium reaction *trans*^{0} $\rightleftharpoons$ *cis*^{0} from the redox reactions involving formation of the *trans*$^+$ cation. Equilibrium constant calculations for the reaction *trans*^{0} $\rightleftharpoons$ *cis*^{0} demonstrate that while *cis*^{0} is slightly favored in nonpolar solvents such as benzene and toluene, it is moderately favored in more polar solvents. Equilibrium constants for *cis*$^+$ $\rightleftharpoons$ *trans*$^+$ and *trans*^{0} + *cis*$^+$ $\rightleftharpoons$ *cis*^{0} + *trans*$^+$ reactions also are calculated from the voltammetric data and their solvent dependences are considered.

Introduction

There are three notable papers concerned with the solution chemistry of the $Cr(CO)_2(dpe)_2$ system (dpe = $Ph_2PCH_2CH_2PPh_2$), but there are discrepancies between them. Chatt and Watson[1] described the syntheses of a number of $M(CO)_2(P{-}P)_2$ compounds (M = Cr, Mo, W; P–P = diphosphine), but $Cr(CO)_2(dpe)_2$ was found to be unique among the compounds studied by these workers in that both cis and trans isomers were formed, the proportions of which in solution were reported to vary with the solvent. However, some caution may need to be attached to this conclusion, since Chatt and Watson also noted an unidentified side reaction in the interconversion of the isomers. Significantly, yields of $Cr(CO)_2(dpe)_2$ were less than 100% and, curiously, IR data were given only for the two carbonyl absorptions assigned to the cis isomer. In contrast, although Crossing and Snow[2] also reported two IR absorptions for the product, they attributed them to *trans*-$Cr(CO)_2(dpe)_2$ (*trans*^{0}) and *trans*-$[Cr(CO)_2(dpe)_2]^+$ (*trans*$^+$). A subsequent electrochemical study in dichloromethane and acetone solutions by Wimmer, Snow, and Bond[3] seemed to indicate that the original suggestion of a mixture of *cis*- and *trans*-$Cr(CO)_2(dpe)_2$ is indeed correct, although *trans*-$[Cr(CO)_2(dpe)_2]^+$ was identified via voltammetric measurements in organic solvents and, importantly, it also was shown that in the presence of oxygen, $Cr(CO)_2(dpe)_2$ in solution is readily oxidized to *trans*$^+$.

The earlier investigations depended upon IR spectroscopy for compound characterization, and confusion arose because of a double-coincidental degeneracy of frequencies. In fact, both *trans*^{0} and *trans*$^+$, together with *cis*-$Cr(CO)_2(dpe)_2$ (*cis*^{0}), are involved in this system, but the single IR carbonyl stretches of each of the two trans isomers fall at frequencies similar to those of the two carbonyl stretches for *cis*^{0} (Table 1); therefore, IR spectroscopy is a poor technique for characterizing this particular system.

In principle, it would be expected that the equilibrium distribution of the *cis*^{0} and *trans*^{0} isomers (eq 1) could be measured by phosphorus-31 NMR spectroscopy[4,5] and the solvent dependence studied very easily. However,

$$\mathit{trans}^0 \overset{K_1}{\rightleftharpoons} \mathit{cis}^0 \qquad (1)$$

the presence of *trans*$^+$ renders the interpretation of the NMR data ambiguous because of an electron-transfer self-exchange reaction (see later). This reaction therefore precludes the NMR method being used in many

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Table 1. IR, ^{31}P NMR, and ESR Data at 22 °C

	cis^0	*trans*^{0}	*trans*$^+$
	Benzene		
IR (cm^{-1})	1847, 1786	1796	insol
^{31}P (ppm)	94.6, 70.2	96.5	
	Toluene		
IR (cm^{-1})	1848, 1790	1797	insol
^{31}P NMR (ppm)	92.3, 68.0	94.2	
ESR			$g = 2.012$, $A = 28.77$ G
	Chloroform		
IR (cm^{-1})	1841, 1776	1790	1850
^{31}P NMR (ppm)	91.5, 66.0	(br)[a]	
^{31}P NMR + $CoCp_2$ (ppm)	92.6, 66.3	94.4	
^{31}P NMR + $CoCp_2$ (−30 °C, ppm)		93.3	
ESR			$g = 2.012$, $A = 28.61$ G
	Dichloromethane		
IR (cm^{-1})	1838, 1774	1791	1850
^{31}P NMR (ppm)	91.2, 65.7	93 (v br)	
^{31}P NMR + $CoCp_2$ (ppm)	91.7, 66.0	94.0	
^{31}P NMR + $CoCp_2$ (−40 °C, ppm)		92.0	
ESR			$g = 2.012$, $A = 28.63$ G
	Acetone		
IR (cm^{-1})	1835, *b*	*b*	1851
^{31}P NMR (ppm)	91.7, 66.3[c]		
ESR			$g = 2.012$, $A = 28.58$ G
	Acetonitrile		
IR (cm^{-1})	1833, 1769	1780	1849
^{31}P NMR (ppm)	too insol		
ESR			$g = 2.012$, $A = 28.57$ G

[a] Position about δ 92−94, varying in different experiments depending upon relative proportions of *trans*$^+$ and *trans*^{0}. [b] Cannot be observed in acetone. [c] Very insoluble, many acquisitions required.

solvents, and the system cannot be adequately characterized by any of the commonly used spectroscopic methods.

In view of the discrepancies in the literature[1−3] concerning the equilibrium position of eq 1 and the complications introduced by the combination of isomerization and redox reactivity, we have reexamined the solution chemistry of the $Cr(CO)_2(dpe)_2$ system in a range of solvents (benzene, toluene, chloroform, dichloromethane, acetone, and acetonitrile) of varying dielectric constant. The complications and ambiguities introduced by the presence of *trans*$^+$ have been examined by a range of spectroscopic techniques, including ^{31}P NMR, ESR, and IR as well as electrospray mass spectrometry. However, only steady-state microelectrode and rotating-disk voltammetric methods are able to provide quantitative data which unambiguously elucidate the solvent-dependent chemistry of the $Cr(CO)_2(dpe)_2$ system.

Experimental Section

Materials and Methods. All solvents used were of analytical or HPLC reagent grade. The solvents were purified by passage through an alumina column. They were then stored over alumina, except for acetonitrile, which was stored over 4-Å molecular sieves. $Cr(CO)_6$ and dpe were purchased from Strem and used as supplied.

$Cr(CO)_2(dpe)_2$ was prepared by refluxing a solution of $Cr(CO)_6$ and 2 mol equiv of dpe in decane for about 65 h. After this mixture was cooled, the crude product containing red and yellow crystals was collected by filtration and then washed with a small amount of dichloromethane, which dissolved the yellow solid to leave red crystals of *trans*-$Cr(CO)_2(dpe)_2$. Addition of methanol to a dichloromethane solution of *trans*-$Cr(CO)_2(dpe)_2$ caused the yellow *cis*-$Cr(CO)_2(dpe)_2$ to separate from the solution, as reported in the literature.[1] The product was collected by filtration. Unless stated otherwise, all experiments were carried out using a pure isomer rather than a mixture of isomers.

trans-$[Cr(CO)_2(dpe)_2]PF_6$ was prepared by the slow addition of 1 mol of KPF_6 in methanol to a solution of either *cis*- or *trans*-$Cr(CO)_2(dpe)_2$ in dichloromethane exposed to the air.[2] The solvent was removed under reduced pressure until crystallization of the orange solid commenced. The solution was then cooled and the product collected by filtration.

^{31}P (proton-decoupled) NMR spectra were recorded on a Bruker AM 300 spectrometer at 121.5 MHz. Chemical shifts were referenced against external 85% H_3PO_4, and the high frequency positive sign convention is used. Due to the effects of paramagnetic *trans*$^+$ present in some solutions, the relaxation rates for *cis*^{0} and *trans*^{0} are very different because of rapid relaxation of *trans*^{0}. In order to achieve the correct values of K_1 (in agreement with those obtained by electrochemical means), it was necessary to add the paramagnetic relaxant $Cr(acac)_3$ to the solutions and to use a long delay time (1 s) between acquisitions. Under these conditions the *cis*^{0} isomer also relaxed completely.

ESR spectra were recorded in solution at room temperature using a Bruker ECS106 spectrometer. IR spectra in the carbonyl region were recorded in solution on a Perkin-Elmer FT-IR 1720 X spectrophotometer. The electrospray mass spectrum of *trans*-$[Cr(CO)_2(dpe)_2]^+$ was recorded on a VG Bio-Q (VG Bio Tech, Altrincham, U.K.) electrospray mass spectrometer. A 2 mM solution of the compound in chloroform or dichloromethane was diluted 1:10 with either dichloromethane or methanol and injected directly into the mass spectrometer via a Rheodyne Model 7125 injector equipped with a 10-μL loop. A Carlo Erba Phoenix 20 micro LC syringe pump was used to deliver the solution to the vaporization nozzle of the electrospray ion source of the mass spectrometer at a flow rate of 3 $\mu L\ min^{-1}$.

All voltammograms were acquired in the dark using a Cypress Systems Model CS-1090 computer-controlled electroanalytical system in the cyclic staircase mode. Rotating disk electrode experiments were undertaken at a rotation rate of 2000 revolutions/min using a Metrohm rotating disk electrode assembly driven by a Metrohm 628-10 power unit. Samples were always at 5.0×10^{-4} M concentration and supporting electrolytes at 0.1 M concentration. Supporting electrolytes were $(Hex)_4NPF_6$ in benzene, $(Hex)_4NClO_4$ in toluene, and Bu_4NPF_6 in the other solvents.

A single-compartment cell with a conventional three-electrode arrangement was used, the working electrode being a 12.5- or 25-μm-radius Pt-disk microelectrode or a 1.5-mm-radius glassy-carbon rotating-disk electrode. A Pt-wire pseudoreference electrode or a Ag/AgCl (saturated LiCl) reference electrode was used. Solutions were purged with nitrogen for at least 5 min prior to electrochemical measurements, and solutions were kept under a nitrogen atmosphere throughout the measurements. The reversible ferrocene oxidation (Fc^+/Fc) was recorded with the same experimental setup, and all potentials are quoted against this reference.

Results and Discussion

The solution chemistry of the $Cr(CO)_2(dpe)_2$ system, rather than only involving *trans*^{0} $\rightleftharpoons$ *cis*^{0} isomerization (eq 1), is in fact quite complicated; therefore, a series of observations will be described before a general explanation is given. It will emerge from these studies that the factor determining the apparent stability of the *cis*^{0} and

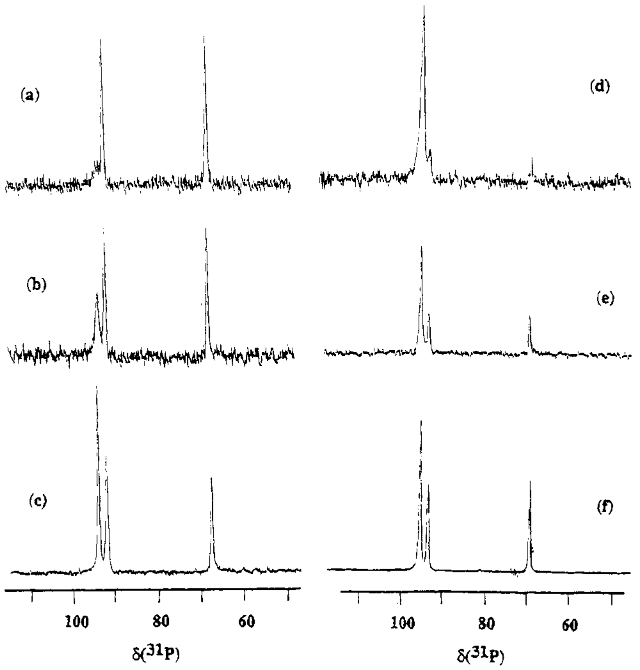

Figure 1. ^{31}P NMR spectra as a function of time for benzene solutions of initially *cis*^{0} (a) 2 min, (b) 8 min, and (c) several days after dissolution and initially *trans*^{0} (d) 2 min, (e) 8 min, and (f) several days after dissolution.

trans^0 isomers in the $Cr(CO)_2(dpe)_2$ system in some solvents is associated with the presence of *trans*$^+$ and some complex reactions associated with the presence of this moiety. In particular, the presence of *trans*$^+$ produces a modified distribution of carbonyl complexes which needs to be corrected for when the equilibrium constant (K_1) associated with eq 1 is calculated.

Solvent Dependence of Spectroscopic Data. (a) Toluene and Benzene. A freshly prepared solution of the red crystals of *trans*^{0} in toluene shows a strong carbonyl IR absorption at 1797 cm^{-1} consistent with the formulation of *trans*^{0} and similar to the value reported by Crossing and Snow,[2] but an additional weak band is always apparent at 1848 cm^{-1} which rapidly increases in relative intensity until after about 1 h two strong bands of approximately equal intensity are observed at 1848 and 1795 cm^{-1}. A freshly prepared solution of *cis*^{0} in the same solvent initially gave two strong carbonyl IR stretches of approximately equal intensity at 1848 and 1790 cm^{-1}. However, continuous monitoring of the IR spectrum over a period of several minutes showed that the peak at lower frequency rapidly shifted to about 1795 cm^{-1} so that the IR spectrum is finally the same irrespective of whether the initial isomer was *trans*^{0} or *cis*^{0}. Thus, the IR data suggest an equilibrium exists between the *trans*^{0} and *cis*^{0} isomers in toluene, but separate spectra for the two isomers cannot be observed because of the accidental degeneracy of the frequency of the carbonyl stretch for the *trans*^{0} isomer with one of the carbonyl stretches for the *cis*^{0} isomer. Very similar spectra were observed in benzene solution (Table 1).

Table 2. Equilibrium Constants for the *cis*^{0} $\rightleftharpoons$ *trans*^{0} Reaction in Toluene and Benzene As Determined by ^{31}P NMR Measurements at 22 °C

solvent	isomer initially in soln[a]	*cis*^{0}:*trans*^{0} ratio (K_1)
toluene	*cis*^{0}	1.0 ± 0.1
toluene	*trans*^{0}	1.0 ± 0.1
benzene	*cis*^{0}	1.2 ± 0.1
benzene	*trans*^{0}	1.2 ± 0.1

[a] To achieve equilibria, solutions were maintained at 22 °C for several days.

Figure 1 shows the ^{31}P NMR spectra of both *cis*- and *trans*-$Cr(CO)_2(dpe)_2$ in benzene as a function of time. Figure 1a shows the NMR spectrum of a solution initially containing only *cis*^{0} acquired as soon as possible after dissolving the solid. The two strong sharp resonances at δ 94.6 and 70.2 are due to *cis*^{0}, and a small signal due to *trans*^{0} is observed at about δ 96.5. After about 8 min (Figure 1b) the resonance due to *trans*^{0} is now quite intense. After several days the spectrum (Figure 1c) shows the equilibrium position which slightly favors *cis*^{0}. Figure 1d shows the NMR spectrum of a solution which initially contained only *trans*^{0}, acquired as soon as possible after dissolution of the solid. A resonance due to the *trans*^{0} isomer is apparent, and two weak, but sharp, signals due to *cis*^{0} also can be seen. After about 8 min the spectrum (Figure 1e) shows the peaks due to *cis*^{0} are now well developed, and finally Figure 1f shows the NMR spectrum after several days, which is similar to that shown in Figure 1c. Thus, the same equilibrium position is established in benzene irrespective of whether the *cis*^{0} or *trans*^{0} form is used as the starting material.

Very similar ^{31}P NMR spectra are observed in toluene solution, except that the signal due to *trans*^{0} is slightly broadened relative to the signal in benzene and also relative to the signals due to *cis*^{0} in toluene, especially when *trans*^{0} is present at relatively high concentrations. It is thought that the broadening of the *trans*^{0} signal is due to a slight solubility of *trans*$^+$ in this solvent, but not in benzene, which allows an electron self-exchange reaction to occur between *trans*^{0} and *trans*$^+$ (see next section for more details), leading to line broadening. No additional ^{31}P NMR resonances were observed in toluene or benzene over the period of several days the solutions were kept to ensure that equilibrium has been achieved.

A sample of *trans*-$[Cr(CO)_2(dpe)_2]PF_6$ was too insoluble to allow observation of an IR spectrum in benzene or toluene, but *trans*$^+$ is sufficiently soluble in toluene, although not in benzene, for a weak ESR signal to be observed (Table 1). It will emerge that it is this insolubility of *trans*$^+$ which greatly simplifies the chemistry in these solvents relative to others, and under these circumstances an accurate estimate of K_1 can be made by NMR methods. Table 2 provides a summary of the equilibrium constants calculated from the ^{31}P NMR data in benzene and toluene, and it can be seen that the *cis*^{0} isomer is slightly favored in benzene with almost equal amounts of each isomer in toluene.

(b) Chloroform. In chloroform solution a freshly prepared solution of the red crystals of *trans*^{0} shows a strong carbonyl stretch at 1790 cm^{-1}, corresponding to that observed for toluene and benzene solutions, but after a few minutes a rather broad new absorption appears at 1850 cm^{-1} and with successive scans this peak sharpens and increases in intensity until it is of approximately the same intensity as the band at around 1790 cm^{-1}, which has in turn broadened slightly. If the chloroform solution is allowed to stand for several days, only the absorption at 1850 cm^{-1} remains, but it is now sharp and symmetrical. This is the peak assigned by Crossing and Snow[2] to the carbonyl stretch of *trans*$^+$.

The IR spectrum of a freshly prepared solution of *cis*^{0} in chloroform shows two strong bands at 1841 and 1776 cm^{-1}. However, after a few minutes the band at lower frequency begins to broaden (but no resolution of peaks is observed) and gradually reduces in intensity relative to the peak at higher frequency. Concomitantly, this peak gradually shifts from 1841 to 1850 cm^{-1}, being slightly broadened in the process, but eventually it becomes sharp again. After several days only the sharp symmetrical absorption at 1850 cm^{-1} remains.

The IR spectrum of *trans*-[Cr(CO)$_2$(dpe)$_2$]PF$_6$ in chloroform solution gives a single strong stretch at 1850 cm^{-1} whose position does not change with time.

It will become apparent, on the basis of further evidence presented in this paper, that in chloroform solution there is not only the equilibrium between *trans*^{0} and *cis*^{0} but also easy formation of *trans*$^+$ by oxidation of *trans*^{0}. However, there is now a double-coincidental degeneracy of carbonyl stretching frequencies, since that for *trans*$^+$ is very similar to that of the higher frequency band for *cis*^{0} while the stretch for *trans*^{0} almost coincides with the lower frequency band of *cis*^{0}.

The ^{31}P NMR spectrum of a freshly prepared solution of *trans*^{0} in chloroform at room temperature is very broad, unlike the case in benzene. However, if *trans*^{0} is dissolved in chloroform in the presence of cobaltocene (CoCp$_2$), then at −30 °C an extremely sharp ^{31}P NMR resonance is observed at δ 93.3 due to *trans*^{0}. This result can be rationalized by the fact that cobaltocene reduces *trans*$^+$ to *trans*^{0}, via the reaction

$$trans\text{-}[\mathrm{Cr(CO)_2(dpe)_2}]^+ + \mathrm{CoCp_2} \rightarrow trans\text{-}\mathrm{Cr(CO)_2(dpe)_2} + [\mathrm{CoCp_2}]^+ \quad (2)$$

and removal of the *trans*$^+$ moiety leads to a sharp NMR signal for *trans*^{0}. Since, in the absence of CoCp$_2$, *trans*$^+$ in the solution of *trans*^{0} leads to substantial line broadening, it suggests that the self-exchange reaction

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

is fast on the NMR time scale. When the above solution is warmed to room temperature, the sharp *trans*^{0} signal broadens and decays rapidly and the very sharp resonances due to *cis*^{0} appear and their intensities increase rapidly, but on the longer time scale all ^{31}P NMR signals disappear for chloroform solutions due to the quantitative formation of paramagnetic *trans*$^+$ (see later).

It is not easy to estimate K_1 at room temperature in chloroform by ^{31}P NMR spectroscopy because of the self-exchange reaction. In contrast, in benzene and toluene, where *trans*$^+$ is almost insoluble, relatively sharp ^{31}P NMR spectra were observed for *trans*^{0}, although in the case of toluene some broadening of the signal was apparent due to the presence of trace concentrations of *trans*$^+$. Nevertheless, the NMR spectrum (unlike IR) does unambiguously show the presence of *cis*^{0} in chloroform solutions originally containing only *trans*^{0}.

The ^{31}P NMR spectrum of a freshly prepared chloroform solution of *cis*^{0} consists of two sharp signals of equal intensity at δ 91.5 and 66.0, together with a weak broad resonance assigned to *trans*^{0} undergoing fast electron exchange with *trans*$^+$, which is rapidly formed in this solution by aerial oxidation. Confirmation of the facile oxidation of *trans*^{0} is provided by the ESR spectrum of a freshly prepared chloroform solution of the red crystals of *trans*^{0}, which gives the expected[6] five-line spectrum (A = 28.61 G) of *trans*-[Cr(CO)$_2$(dpe)$_2$]$^+$ and whose intensity increases with time.

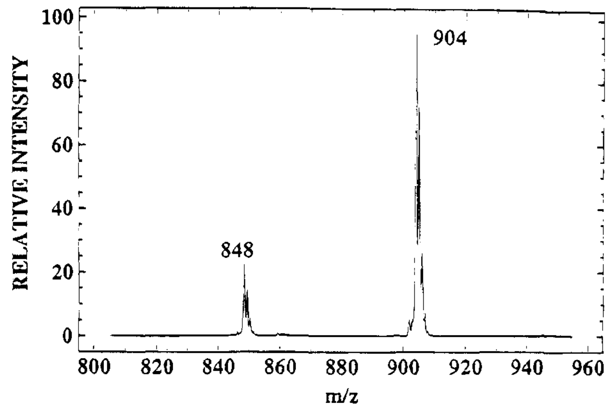

Figure 2. Positive ion electrospray mass spectrum of a chloroform solution of *trans*$^+$.

Electrospray mass spectrometry (ESMS) is a new technique which allows ions in solution to be gently transferred to the gas phase and then examined by conventional mass spectrometric techniques.[7,8] We have recently shown that ESMS can be applied to organometallic systems, including carbonyl compounds.[9,10] Figure 2 shows the electrospray mass spectrum of a solution of Cr(CO)$_2$(dpe)$_2$ in chloroform which has been exposed to the air. The peak at *m/z* 904 is due to the intact ion [Cr(CO)$_2$(dpe)$_2$]$^+$, and it shows the expected isotopic mass distribution. There is another prominent peak at *m/z* 848 that corresponds to the ion [Cr(dpe)$_2$]$^+$ (loss of the carbonyl ligands) which is formed by collisional activation of the intact ions in the high-pressure region of the sampling orifice of the mass spectrometer since its intensity relative to that of *m/z* 904 increases with increasing collisional energy. Therefore, there can be no doubt on the basis of ESR and ESMS data that *trans*$^+$ is the product formed from oxidation of *trans*^{0}, so that solutions of Cr(CO)$_2$(dpe)$_2$ in chloroform evidently consist of mixtures of *cis*^{0}, *trans*^{0}, and *trans*$^+$. The formation of *trans*$^+$ in solution is due to the oxidation of *trans*^{0} by oxygen which may be acid-catalyzed,[3] and the distribution of the *cis*^{0}, *trans*^{0}, and *trans*$^+$ species is therefore dependent upon a complex combination of several reactions and not just eq 1.

The properties of the Cr(CO)$_2$(dpe)$_2$ system can be understood in terms of eq 4, in which the second equilibrium lies heavily in favor of *trans*$^+$. The evidence

$$cis\text{-}\mathrm{Cr(CO)_2(dpe)_2} \rightleftharpoons trans\text{-}\mathrm{Cr(CO)_2(dpe)_2} \xrightarrow{\mathrm{O_2}} trans\text{-}[\mathrm{Cr(CO)_2(dpe)_2}]^+ \rightleftharpoons cis\text{-}[\mathrm{Cr(CO)_2(dpe)_2}]^+ \quad (4)$$

for *cis*$^+$ is based on voltammetric data for dichloromethane solution presented in ref 3 and data for other

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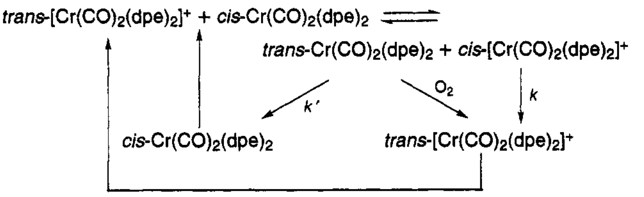
Scheme 1



solvents to be given later in this paper. Thus, in chloroform solution, *cis*^{0} may be in equilibrium with *trans*^{0} but the aerial oxidation of *trans*^{0} generates *trans*$^+$.

The equilibrium position of the cross redox reaction

$$trans\text{-}[Cr(CO)_2(dpe)_2]^+ + cis\text{-}Cr(CO)_2(dpe)_2 \rightleftharpoons trans\text{-}Cr(CO)_2(dpe)_2 + cis\text{-}[Cr(CO)_2(dpe)_2]^+ \quad (5)$$

lies heavily to the left, but because it is fast, it can combine with the equilibria in eq 4 to give a cyclic exchange process. Thus, *trans*^{0} generated in eq 5 partially isomerizes to *cis*^{0} and *cis*$^+$ isomerizes to *trans*$^+$ in accordance with eq 4. That is, the original reactants are re-formed. In addition, especially in chloroform, aerial oxidation of *trans*^{0} to *trans*$^+$ ensures that the final product is *trans*$^+$. The overall reaction in chloroform solution is shown in Scheme 1.

(c) Dichloromethane. A freshly prepared solution of the red crystals of *trans*^{0} in dichloromethane shows a single IR absorption at 1791 cm^{-1}. However, a repeat scan of the spectrum a few minutes later shows a decrease in the intensity of the 1791 cm^{-1} band and the development of three new bands at 1845 and 1838 cm^{-1} (barely resolved) and at 1774 cm^{-1} (barely resolved from the peak at 1791 cm^{-1}). Further monitoring of the solution spectrum showed that the peaks at 1838 and 1774 cm^{-1} gradually disappear and the peak at 1845 cm^{-1} gradually moves to 1850 cm^{-1} as the others decrease. When the solution stands for several days, the peak at 1850 cm^{-1}, which is assigned to *trans*$^+$, becomes dominant. A freshly prepared solution of an authentic sample of *cis*^{0} gave carbonyl absorptions at 1838 and 1774 cm^{-1}, thus strongly suggesting that some *cis*^{0} is present in solution at some stages during the overall oxidation to *trans*$^+$.

Figure 3a shows the ^{31}P NMR spectrum of a solution of *trans*^{0} in CH_2Cl_2 in the presence of $CoCp_2$ at −40 °C. The sharp signal is assigned to *trans*^{0}. When the solution is warmed to room temperature, the signal broadens as shown in Figure 3b and after about 7 min sharp signals due to *cis*^{0} are observed in addition to the broad peak for *trans*^{0} (Figure 3c). After about 2 h (Figure 3d) the spectrum is dominated by the resonances of *cis*^{0}. Thus, this NMR spectroscopic evidence shows, like the IR evidence, that in dichloromethane *trans*^{0} isomerizes to *cis*^{0}. However, on the longer time scale the final product is *trans*$^+$, which of course is not observed by NMR spectroscopy, but its presence was confirmed by both ESR and ESMS methods.

(d) Acetone and Acetonitrile. IR spectra in acetonitrile are generally similar to those in dichloromethane, but in acetone the absorption for *trans*^{0} and the lower frequency carbonyl band for *cis*^{0} cannot be observed due to absorption by the solvent. Both *cis*^{0} and *trans*^{0} are only very sparingly soluble in acetone, and the equilibrium between them favors *cis*^{0} (see electrochemistry later). As a result of the sparing solubility, the ^{31}P NMR spectra of *cis*^{0} could only be observed in acetone after many scans and *trans*^{0} could not be detected. No NMR spectra were detected in acetonitrile because of solubility problems.

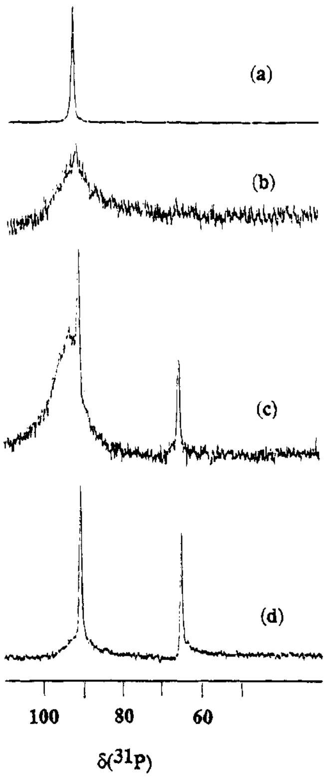


Figure 3. ^{31}P NMR spectra for a dichloromethane solution of initially *trans*^{0} (a) at −40 °C in the presence of $CoCp_2$, (b) on warming to room temperature, (c) after a further 7 min, and (d) after 2 h.

In summary, each of the spectroscopic methods used in the present study has limitations in the calculation of the equilibrium constants for eq 1 and the thermodynamics of the redox chemistry coupled to this reaction. Most of the problems can be traced to the formation of *trans*$^+$, and except in the cases of benzene and toluene, the determination of K_1 is not trivial using spectroscopic techniques. In addition, the accidental coincidence of the carbonyl IR absorption bands has contributed to confusion in this system.

Determination of K_1 by Steady-State Microelectrode and Rotating-Disk Voltammetry. In principle, steady-state voltammetric studies at microelectrodes or voltammetric studies at rotating-disk electrodes should be able to distinguish between both the isomeric form and oxidation state of the various components in the $Cr(CO)_2(dpe)_2$ system and, hence, lead to reliable values for the equilibrium constant K_1 (Table 3) in all solvents. Voltammetry at a rotating-disk electrode also is capable of distinguishing between the oxidative and reductive components of a redox process, but in this case the rising part of the voltammograms are distorted by uncompensated resistance. However, the limiting currents are independent of resistance; therefore, the equilibrium constants (K_1) derived from them are valid. The proportions of *cis*^{0} and *trans*^{0} present in various solvents measured using a rotating glassy carbon disk electrode (radius 1.5 mm) are given in Table 3 and

Table 3. Voltammetric Data in Different Solvents at 22 °C[a]

initial isomer (electrolyte)	voltammetric technique	$E_{1/2}$ (V vs Fc^+/Fc) $cis^{+/0}$	$E_{1/2}$ (V vs Fc^+/Fc) $trans^{+/0}$	$\Delta E_{1/2}$ (mV)	amt at equil (%) cis^0	amt at equil (%) $trans^0$	K_1
Benzene (Dielectric Constant 2.27)							
0.5 mM cis^0 (0.1 M $(THA)PF_6$)	25-μm Pt disk	−0.754	−1.086	332	55	45	1.2
0.5 mM $trans^0$ (0.1 M $(THA)PF_6$)	25-μm Pt disk				53	47	
Toluene (Dielectric Constant 2.38)							
0.5 mM cis^0 (0.1 M THAP)	12.5-μm Pt disk	−0.758	−1.082	324	51	49	1.1
0.5 mM $trans^0$ (0.1 M THAP)	25-μm Pt disk				53	47	
Chloroform (Dielectric Constant 4.81)							
0.5 mM cis^0 (0.1 M $(TBA)PF_6$)	12.5-μm Pt disk	−0.719	−1.059	340	66	34	2.1
0.5 mM $trans^0$ (0.1 M $(TBA)PF_6$)	1.5-μm GC RDE[b]				69	31	
Dichloromethane (Dielectric Constant 8.93)							
0.5 mM cis^0 (0.1 M $(TBA)PF_6$)	12.5-μm Pt disk	−0.705	−1.065	360	87	13	6.7
0.5 mM cis^0 (0.1 M $(TBA)PF_6$)	1.5-mm GC RDE[b]				88	12	
0.5 mM $trans^0$ (0.1 M $(TBA)PF_6$)	1.5-mm GC RDE[b]				86	14	
Acetone (Dielectric Constant 20.56)							
0.5 mM cis^0 (0.1 M $(TBA)PF_6$)	12.5-μm Pt disk	−0.667	−1.012	345	86	14	5.7
0.5 mM cis^0 (0.1 M $(TBA)PF_6$)	1.5-mm GC RDE[b]				85	15	
0.5 mM $trans^0$ (0.1 M $(TBA)PF_6$)	1.5-mm GC RDE[b]				84	16	
Acetonitrile (Dielectric Constant 35.94)							
0.5 mM cis^0 (0.1 M $(TBA)PF_6$)	12.5-μm Pt disk	−0.621	−0.995	374	93	7	11.5
0.5 mM cis^0 (0.1 M $(TBA)PF_6$)	1.5-mm GC RDE[b]				92	8	
0.5 mM $trans^0$ (0.1 M $(TBA)PF_6$)	1.5-mm GC RDE[b]				91	9	

[a] Dielectric constants at 20 °C except for chloroform, which is the value at 25 °C: Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: New York, 1988. $(THA)PF_6 = Hex_4NPF_6$, THAP = Hex_4NClO_4, and $(TBA)PF_6 = Bu_4NPF_6$. Other experimental parameters are the same as those given in the captions for Figures 4 and 5. [b] No actual values for $E^r_{1/2}$ reported because of distortions due to uncompensated resistance, but the equilibrium constants obtained from the limiting currents are independent of resistance and therefore valid.

confirm the values derived from the steady-state microelectrode measurements. Consequently, an electrochemical study of the system has been carried out in the same solvents used for spectroscopic studies.

(a) Toluene and Benzene. The use of most voltammetric methods has been considered impossible in high-resistance solvents such as benzene and toluene. However, recently it has been shown[11] that microelectrode voltammetry in these high-resistance solvents can lead to the theoretical responses when tetrahexylammonium salts, for example $(Hex)_4NClO_4$ (Hex = $n\text{-}C_6H_{13}$), are used as supporting electrolytes. The principles of the use of steady-state measurements at microdisk electrodes in high-resistance media have been reviewed recently by Heinze.[12] With microdisk electrodes and at slow scan rates, near-steady-state conditions can be achieved. Furthermore, the steady-state method, unlike conventional cyclic voltammetry, can be used to distinguish between *trans*^{0} and *trans*$^+$ species via the relative proportions of reduction (*trans*$^+$) and oxidation (*trans*^{0}) components of the total current for the process

$$trans^+ + e^- \rightleftharpoons trans^0 \qquad (6)$$

as well as that of the *cis*^{0} species via the reaction

$$cis^0 \rightleftharpoons e^- + cis^+ \ (\rightarrow trans^+) \qquad (7)$$

Fortunately, the potential for this latter process is well separated from the *trans*$^+$/*trans*^{0} redox potential and occurs at more positive potentials; therefore, it does not contribute to the current associated with the reaction in eq 6. Still more fortunately, on the time scale of steady-state measurements, the isomerization of *cis*$^+$ to *trans*$^+$ does not contribute to the voltammetric response, unlike the situation in conventional cyclic voltammetric experiments.[3]

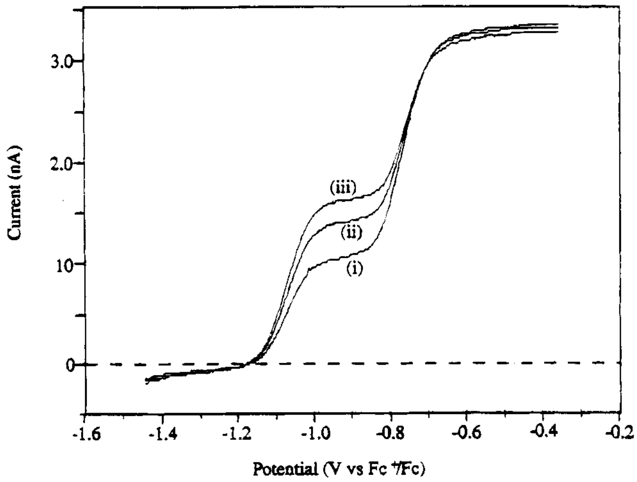


Figure 4. Voltammetry of 5×10^{-4} M *cis*^{0} in toluene (0.1 M $(Hex)_4NPF_6$) as a function of time: (i) 5 min; (ii) 10 min; (iii) 20 min. Experimental parameters: 25-μm-radius Pt-microdisk electrode; scan rate 10 mV s^{-1}; temperature 22 °C.

Figure 4 shows the steady-state voltammogram of the $Cr(CO)_2(dpe)_2$ system in toluene (0.1 M $(Hex)_4NClO_4$) at a platinum-disk microelectrode obtained as a function of time, starting with the *cis*^{0} isomer. The first scan, recorded approximately 5 min after dissolution of the solid, shows two well-separated, well-defined sigmoidal-shaped responses with $E^r_{1/2}$ ($E^r_{1/2}$ = reversible half-wave potential) values of −0.758 and −1.082 V vs Fc^+/Fc corresponding to the processes in eqs 7 and 6, respectively. With long periods of time, the total current slowly decreases but the $E^r_{1/2}$ values remain the same and the ratio of the oxidation currents for *cis*^{0} and *trans*^{0} becomes constant. The ratio of the oxidation currents for the two processes is a direct measurement of relative

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[11] Bond, A. M.; Mann, T. F. *Electrochim. Acta* **1987**, *32*, 863 and references cited therein.

[12] Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1269.

concentrations and therefore of the equilibrium constant, which in this case is close to unity (Table 3). This value is in agreement with that derived from NMR measurements. The very small reduction current (below the zero of current) is consistent with the presence of a very low concentration of *trans*$^+$ in the bulk solution, but this current does not increase significantly with time presumably because the concentration attained the value governed by its solubility limit. The overall decrease in total current with time is due to the slow formation of *trans*$^+$, most of which precipitates due to its low solubility in toluene, although traces of *trans*$^+$ can be detected in solution by ESR spectroscopy.

Similar voltammograms are obtained for benzene solutions, but there is no voltammetrically detectable reduction current for trans$^+$, which is consistent with our inability to observe an ESR signal due to *trans*$^+$ in this solvent. The value of K_1 in benzene is found by microelectrode voltammetry to be 1.2 irrespective of the isomeric form of the starting material, again in agreement with the NMR data.

(b) Chloroform. In chloroform *trans*$^+$ is rapidly generated by aerial oxidation and it is soluble in this solvent (cf IR results); this changes the characteristics of the electrochemical responses for the system. Figure 5a shows rotating-disk voltammograms of a solution initially containing *trans*^{0} in chloroform. Two responses are again observed, but the *trans*$^+$/*trans*^{0} couple now shows a large reduction component, confirming the presence of significant concentrations of *trans*$^+$ in solution. The reduction current for *trans*$^+$, and the oxidation currents for *trans*^{0} and *cis*^{0}, are proportional to their concentrations in the bulk solution.

In order to calculate the value of K_1 in chloroform, it is necessary only to observe the oxidative components of the two electrochemical responses; therefore, Figure 5b shows these as a function of time for a solution initially containing only *trans*^{0}. After a time, the ratio of the oxidation currents becomes constant as the *trans*^{0}/*cis*^{0} equilibrium is established and the value of K_1 is found to be 2.1 in chloroform. The total oxidation current decreases with time as more *trans*$^+$ is formed (cf. IR and ESR data). However, the isomerization reaction is faster than the formation of *trans*$^+$ under these conditions where oxygen is largely excluded (see Experimental Section), and the ratio of the concentrations of *cis*^{0} and *trans*^{0} (K_1) is independent of time once the equilibrium is established.

The same electrochemical responses are observed for a solution initially containing only the *cis*^{0} isomer, and after equilibrium is reached, the same value of K_1 is obtained.

(c) Dichloromethane. Figure 5c shows that the electrochemical responses in dichloromethane are similar to those in chloroform, but the equilibrium position (curve iii) favors *cis*^{0} to a greater extent, and the formation of *trans*$^+$ is slower. However, after 9 h the solution contains only *trans*$^+$.

(d) Acetone and Acetonitrile. Although both isomers of $Cr(CO)_2(dpe)_2$ are relatively insoluble in acetone and acetonitrile so that NMR measurements are difficult, they are sufficiently soluble for electrochemical studies. The electrochemical responses are generally similar to those in dichloromethane, and the values for K_1 in these solvents are given in Table 3.

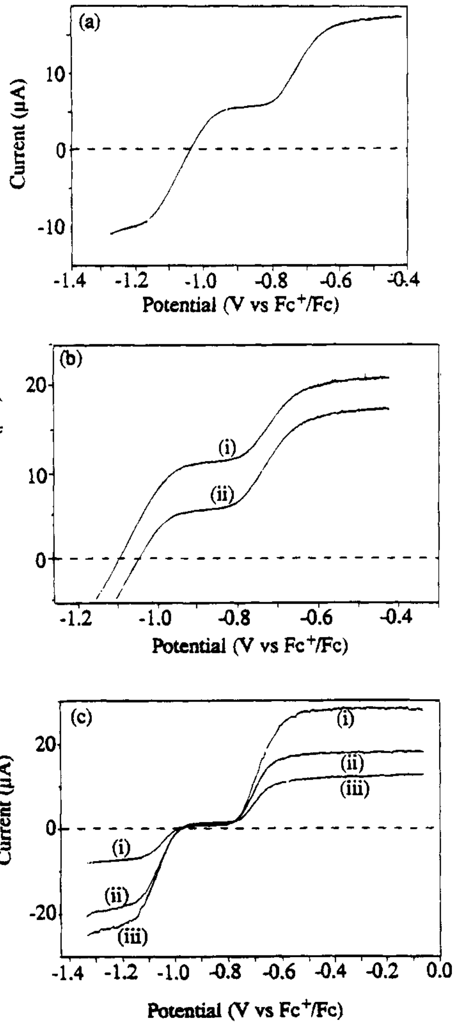

Figure 5. Voltammetry of the $Cr(CO)_2(dpe)_2$ system as a function of time at a rotated 1.5-mm-radius glassy-carbon-disk electrode: (a) 5×10^{-4} M *trans*^{0} in chloroform (0.1 M Bu_4NPF_6) after 15 min; (b) 5×10^{-4} M *trans*^{0} in chloroform (0.1 M Bu_4NPF_6) with expanded scale for the oxidation processes after (i) 5 min and (ii) 15 min; (c) 5×10^{-4} M *cis*^{0} in dichloromethane (0.1 M Bu_4NPF_6) after (i) 5 min, (ii) 15 min, and (iii) 50 min. Experimental parameters: scan rate 10 mV s^{-1}; rotation rate 2000 rpm; temperature 22 °C.

Calculation of Further Thermodynamic Data from Steady-State Microelectrode Voltammetry. The equilibrium constant (K_2) for the reaction

$$trans^0 + cis^+ \overset{K_2}{\rightleftharpoons} trans^+ + cis^0 \qquad (8)$$

may be calculated from the separate measurement of the reversible potentials for the

$$cis^+ + e^- \overset{E^r{}_{1/2}(1)}{\rightleftharpoons} cis^0 \qquad (9)$$

couple and eq 6, assuming that the $E^r{}_{1/2}$ value for the *cis*$^+$/*cis*^{0} couple measured under short time domain steady-state conditions does not contain a contribution from the *cis*$^+$ → *trans*$^+$ isomerization reaction and using the relationship

$$\Delta G° = -RT \ln K_2 = -F\Delta E^r{}_{1/2} \qquad (10)$$

Additionally the equilibrium constant for the reaction

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

may be calculated from the relationship $K_3 = K_2/K_1$.

The thermodynamic data obtained from the steady-state voltammetry of the $Cr(CO)_2(dpe)_2$ system are summarized in Table 4. Under conditions where extraneous reactions are eliminated from influencing the measurements, it is now found that in low-dielectric solvents such as toluene the *trans*^{0} and *cis*^{0} concentrations are essentially equal at equilibrium. However, as the dielectric constant of the solvent increases, the *cis*^{0} form generally becomes more favored by a factor of about 2:1 in chloroform, 7:1 in dichloromethane, 6:1 in acetone, and 12:1 in acetonitrile. The reversible potentials in the different solvents relative to the ferrocene redox potential (Fc^+/Fc) given in Table 3 are not strongly solvent dependent, ranging over less than 100 mV for each couple. The value of K_2 is very large (in the range 10^5-10^6) and indicates that in the redox sense *trans*$^+$ and *cis*^{0} are the favored components as previously deduced.[3] K_2 is only slightly dependent upon solvent, increasing slightly with dielectric constant with the single exception of acetone. In the higher oxidation state, the *trans*$^+$ isomer is very strongly favored over *cis*$^+$ (K_3) by a factor of about 10^5, which is consistent with earlier studies of other 17-electron systems.[13,14] Interestingly this equilibrium constant is almost independent of solvent. In previous studies it was shown that the kinetics of isomerization also were not very solvent dependent.[15]

Table 4. Equilibrium Constants K_1, K_2, and K_3 at 22 °C

	Equilibrium Constants		
solvent	K_1	K_2	K_3
benzene	1.2	4.7×10^5	4.0×10^5
toluene	1.1	3.6×10^5	3.3×10^5
chloroform	2.1	6.7×10^5	3.2×10^5
dichloromethane	6.7	1.5×10^6	2.2×10^5
acetone	5.7	8.2×10^5	1.4×10^5
acetonitrile	11.5	2.6×10^6	2.2×10^5

Conclusions

The present study demonstrates that the chemistry of the $Cr(CO)_2(dpe)_2$ system may be deceptively simple when examined by conventional spectroscopic techniques. Thus, the double-degeneracy of the frequencies of the carbonyl bands for *cis*^{0} with those of *trans*^{0} and *trans*$^+$ causes ambiguity in the interpretation of the IR spectra and the rapid electron exchange between *trans*^{0} and *trans*$^+$ causes analogous ambiguity in the interpretation of the ^{31}P NMR data. The problems with the system are dominated by the extreme ease of oxidation of *trans*^{0} to *trans*$^+$. However, voltammetric measurements may be reliably interpreted because both redox and isomer distributions may be evaluated separately. The steady-state microelectrode data lead to the conclusion that low-dielectric-constant solvents best favor the *trans*^{0} isomer. The formation of significant amounts of *trans*^{0} isomer by refluxing the hexacarbonyl species and dpe in the low dielectric constant decane (see Experimental Section) is consistent with this conclusion. In all solvents the amount of *cis*$^+$ is very small as determined by the electrochemical measurements and is below the detection limits of all the spectroscopic techniques used in this work.

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