and benefited by a grant (to D.K.) by the Minerva Foundation. We thank Douglas Bond for considerable assistance and interest.

Registry No. $H_2C{=}BH$, 56125-75-8; $H_2C{=}NH$, 2053-29-4; $H_2C{=}AlH$, 79435-76-0; $H_2C{=}SiH_2$, 51067-84-6; $H_2C{=}PH$, 61183-53-7; $H_2C{=}S$, 865-36-1; $H_2Si{=}BH$, 98976-97-7; $H_2Si{=}NH$, 32520-13-1; $H_2Si{=}O$, 22755-01-7; $H_2Si{=}AlH$, 111771-61-0; $H_2Si{=}SiH_2$, 15435-77-5; $H_2Si{=}PH$, 98360-04-4; $H_2Si{=}S$, 69639-29-8; BH_2, 14452-64-3; CH_3, 2229-07-4; NH_2, 13770-40-6; OH, 3352-57-6; AlH_2, 14457-65-9; SiH_3, 13765-44-1; PH_2, 13765-43-0; SH, 13940-21-1; C, 7440-44-0; Si, 7440-21-3.

Supplementary Material Available: Absolute energies and geometries of all species calculated here in GAUSSIAN 82 archive format (3 pages). Ordering information is given on any current masthead page.

An Electrochemical Study of the Substitution and Decomposition Reactions of (Arene)tricarbonylchromium Radical Cations

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Abstract: Voltammetry with conventional electrodes and microelectrodes establishes that (arene)$Cr(CO)_3$ (arene = benzene, mesitylene) is oxidized by a chemically and electrochemically reversible one-electron step when the solvent is dichloromethane or benzene and the supporting electrolyte is tetrabutylammonium hexafluorophosphate or tetrahexylammonium hexafluorophosphate, respectively. With a more nucleophilic solvent (e.g., acetone or acetonitrile) or electrolyte (e.g., tetrabutylammonium perchlorate or tetrahexylammonium perchlorate), a two-electron oxidation obtains for $(C_6H_6)Cr(CO)_3$, corresponding to an ECE process where the chemical step is associative attack by the nucleophile on the radical cation to produce free benzene and a Cr(I) species which is rapidly oxidized. The rate constant for the reaction of $(C_6H_6)Cr(CO)_3^+$ in CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate was found to be 30 ± 10 s^{-1} at 20 °C. In the presence of tertiary phosphine and phosphite nucleophiles, (arene)$Cr(CO)_3^+$ undergoes rapid CO substitution in competition with decomposition. $P(OBu)_3$ substitution for CO in (mesitylene)$Cr(CO)_3^+$ is quantitative in propylene carbonate. While only monosubstitution occurs with $P(OBu)_3$ and PBu_3, the caged phosphite $P(OCH_2)_3CMe$ gives disubstitution at slow scan rates and monosubstitution at fast scan rates. Voltammetry with (mesitylene)$W(CO)_3$ shows that it is oxidized via a two-electron process in acetonitrile and dichloromethane, most likely to give an 18-electron W(II) species. The data are in conflict with recently published work on $(C_6Me_6)W(CO)_3$.

Over the past few years there has been an increasing appreciation of the importance of 17-electron organometallic radicals in stoichiometric and catalytic transformations. One of the primary reasons for this interest is the large increase in reactivity that frequently accompanies the oxidation or reduction of 18-electron complexes.[1] Truly amazing electrocatalytic syntheses and rate accelerations are known. The first organometallic example of ligand substitution initiated and catalyzed by electron addition was reported in 1981.[2] It was then demonstrated that electron-transfer-catalyzed nucleophilic substitution in polynuclear metal carbonyls is a rather general reaction and can lead to striking results.[3] Ligand substitution can also be initiated by oxidation, and examples of very rapid and efficient reactions are known.[4] Whether the reaction is initiated by oxidation or reduction, it is likely that the electroactivated substitutions proceed via 17-electron radical intermediates and that the mechanism is associative.[1] Carbon monoxide insertion reactions are also known to be subject to electroactivation. For example,[5] CO insertion into the Fe–Me bond in $CpFe(CO)(PPh_3)Me$ does not progress detectably after 5 days at 0 °C and 1 atm of CO; the addition of a few mole percent of Ag^+ causes complete conversion to $CpFe(CO)(PPh_3)COMe$ within 2 min. Interestingly, catalytic CO insertion may also be induced by reduction.[6] The application of electrochemistry to the synthesis of organometallics and the study of organometallic reaction mechanisms is an extremely promising field that has yet to be exploited in depth. Reactions like those listed above illustrate the chemistry waiting to be discovered and guarantee that organometallic electrochemistry will enjoy increasing popularity (and importance) in the years ahead.[7]

The recent development[8] of platinum and graphite disk microelectrodes with diameters ≤10 μm should prove to be particularly useful in organometallic chemistry. Microelectrodes offer several advantages over conventional electrodes in linear sweep voltammetric experiments. Of special interest in this paper is the steady-state response that is shown by microelectrodes at low sweep rates due to the predominance of spherical diffusion under these conditions. While the theory of steady-state response at microelectrodes is yet to be fully developed, it is already known[9] that

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Chart I. Complexes Discussed in This Study

(arene)$Cr(CO)_3$	(benzene)$Cr(CO)_3$	(mesitylene)$Cr(CO)_3$
1	**2**	**3**
$(C_6Me_6)Cr(CO)_3$	$(C_6Me_6)W(CO)_3$	(mesitylene)$W(CO)_3$
4	**5**	**6**

heterogeneous rate constants and transfer coefficients are conveniently measured in this way with an accuracy that exceeds that available with conventional cyclic voltammetry (which invariably is affected by *iR* distortion when organic solvents are utilized). It has also been shown[10] that microelectrodes can be used at low temperatures (ca. −80 °C) in relatively nonpolar solvents (e.g., CH_2Cl_2), so that the usual advantages of low temperatures in simplifying complex mechanisms can be realized.[11,12] An equally important application is the study of thermally unstable complexes that can be synthesized and characterized only at low temperatures.

Herein we describe an experimental and theoretical study of the oxidative electrochemistry of (arene)$Cr(CO)_3$ complexes (arene = benzene, mesitylene). Some related work with (mesitylene)$W(CO)_3$ is also presented. The chemistry of (arene)$Cr(CO)_3$ complexes (**1**) has been extensively studied and significant applications to organic synthesis have been found.[13] With $(C_6H_6)Cr(CO)_3$ (**2**), oxidation in MeCN or DMF results in an overall 2-electron or 3-electron process in which the initially formed $\mathbf{2}^+$ radical cation rapidly decomposes to liberate CO, C_6H_6, and a Cr(II) or Cr(III) species.[14-16] Oxidation of **2** in CH_2Cl_2 with tetrabutylammonium perchlorate (TBAP) as the electrolyte is also chemically irreversible at 20 °C, but it becomes reversible below ca. −50 °C.[12] It has recently been reported[12] that the use of $TBAPF_6$ instead of TBAP reduces the rate of decomposition of $\mathbf{2}^+$ in CH_2Cl_2 to the point where the $\mathbf{2}/\mathbf{2}^+$ couple is chemically reversible at room temperature on the cyclic voltammetry (CV) time scale. In general, $\mathbf{1}^+$ cations are more stable when the arene is alkylated or metalated and the solvent is nonnucleophilic (e.g., dichloromethane, propylene carbonate (PC), trifluoroacetic acid (TFAA)).[17] Available evidence suggests[14-16] that $\mathbf{1}^+$ decompose via nucleophilic attack by solvent or electrolyte anion, resulting in an intermediate Cr(I) species that is then oxidized to a Cr(II) or Cr(III) complex, depending on the solvent in use. In agreement with this, the use of sterically congested arenes in **1** generally leads to an increase in the stability of $\mathbf{1}^+$.[17,18] It would be more useful if nucleophilic attack on $\mathbf{1}^+$ led to stable organometallic species rather than to decomposition. There is one report[19] showing that the oxidation of (mesitylene)$Cr(CO)_3$ in MeCN in the presence of $P(OEt)_3$ leads to some CO substitution; upon subsequent reduction the combined yield of (mesitylene)$Cr(CO)_n[P(OEt)_3]_{3-n}$ (n = 1, 2) was 26%.

The present study was undertaken (1) to test the general applicability of microelectrodes, under both steady-state and transient-response conditions, to an important organometallic system, (2) to assess the feasibility of obtaining quality voltammetric data in benzene as the solvent, and (3) to determine the conditions favoring ligand substitution instead of decomposition. We show below that microelectrodes are very useful for investigating organometallic reactions, especially ones in fairly nonpolar solvents such as dichloromethane and benzene. The experimental data for the decomposition and substitution reactions of $\mathbf{1}^+$ suggest associative mechanisms and are shown to agree closely with theoretical considerations for steady-state and transient-response conditions; the current response for the relevant mechanistic schemes was determined by digital, numerical, and analytical solutions. Carbon monoxide substitution by phosphines and phosphites in $\mathbf{1}^+$ is extemely rapid and, under suitable conditions, mixed phosphite complexes, (arene)Cr(CO)LL′, can be readily identified.

The oxidative electrochemistry of $(C_6Me_6)W(CO)_3$ in MeCN was recently examined[18] and it was suggested that the complex undergoes a 1-electron oxidation to give a radical cation that rapidly coordinates with solvent to yield an expanded coordination sphere radical, which is persistent enough to allow subsequent reduction to be observed ca. 0.5 V negative of the initial oxidation. Herein we report studies with (mesitylene)$W(CO)_3$ showing that its electrochemical behavior is very similar to that observed with $(C_6Me_6)W(CO)_3$ and that the former complex is oxidized via a *2-electron* process in MeCN and CH_2Cl_2. It is likely that the previously reported mechanistic conclusions dealing with the oxidation of $(C_6Me_6)W(CO)_3$ in MeCN are incorrect.

Experimental Section

Materials. (Arene)$Cr(CO)_3$ (arene = benzene, mesitylene) were purchased from Aldrich and (mesitylene)$W(CO)_3$ from Strem. Tri-*n*-butylphosphine and tri-*n*-butyl phosphite were distilled under argon at reduced pressure. The caged phosphite $P(OCH_2)_3CCH_3$ was synthesized by a published procedure.[20] TBAP was both purchased and synthesized by metathesis of TBABr and $HClO_4$. All TBAP was recrystallized from ethyl acetate/pentane and dried over P_2O_5 in vacuo. $TBAPF_6$ was made from TBABr and HPF_6, recrystallized from 95% ethanol, and dried over P_2O_5 in vacuo. Tetrahexylammonium perchlorate (THAP) was purchased and $THAPF_6$ was made by metathesis of $(C_6H_{13})_4NI$ and HPF_6 and recrystallized from 95% ethanol. Nitromethane was fractionally distilled under nitrogen and stored refrigerated under nitrogen. Dichloromethane and acetonitrile were freshly distilled under nitrogen from calcium hydride. Propylene carbonate was fractionally distilled twice at 1 Torr and stored refrigerated; it is colorless when pure.

Instrumentation and Procedures. All electrochemical experiments were done under a blanket of nitrogen or argon that was saturated with the solvent in use. Glassware was cleaned and stored in drying ovens prior to use. Work at low temperatures utilized a FTS Multi-Cool bath containing methanol. An Omega type T thermocouple probe was inserted directly into the electrochemical cell in order to monitor the temperature.

Bulk electrolysis was done with an EG&G 173 potentiostat and a 179 digital coulometer. The working electrode was a platinum basket, the counter electrode was a platinum mesh, and the reference electrode was Ag/AgCl (vide infra). The counter electrode was separated from the working electrode by a salt bridge containing the supporting electrolyte. Infrared spectra were recorded with a Mattson FTIR. HPLC examination of the electrolyzed solutions employed a reverse phase C18 column with a mobile phase consisting of 55/45 methanol/water. UV detection at 254 nm was used to monitor the benzene liberated from electrolysis of (benzene)$Cr(CO)_3$.

All of the voltammetric experiments utilized a platinum wire counter electrode. The reference was generally a Metrohm Ag/AgCl electrode filled with CH_2Cl_2/0.1 M TBAP and saturated with LiCl; this was separated from the test solution by a salt bridge containing CH_2Cl_2 and the electrolyte in use. For some experiments a platinum pseudoreference electrode was used. The working electrode was either a conventional BAS platinum (1.6 mm diameter) or glassy carbon (3.0 mm diameter), or a microelectrode. Platinum microelectrodes were fabricated by sealing the microwire (from Goodfellow or Omega) in an evacuated glass tube with a hot flame. Electrical contact was made to a copper wire via silver epoxy. The electrodes were ground with wet/dry paper (P500–P1200) and polished with alumina (5 to 0.05 μm). A scanning electron micrograph of a 10-μm Pt electrode showed a good seal between the metal and the glass.

Experiments with conventional electrodes utilized the usual 3-electrode arrangement. A variety of potentiostats were used: EG&G 173, 362,

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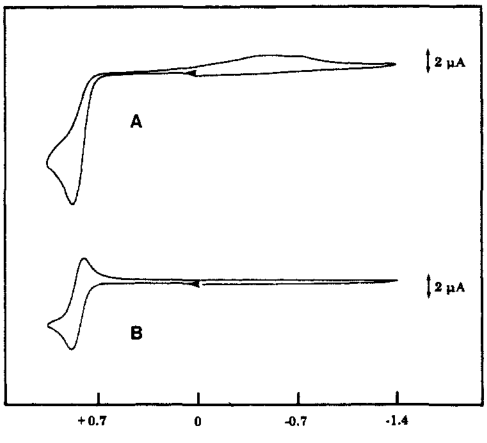

Figure 1. Cyclic voltammograms of 5 × 10^{-4} M $(C_6H_6)Cr(CO)_3$ (**2**) at 0.20 V/s in dichloromethane at 20 °C. The working electrode was a 1.6 mm platinum disk and the supporting electrolyte was 0.1 M TBAP for A and 0.1 M $TBAPF_6$ for B.

363, BAS CV27, and Amel 551. The voltage ramp was either generated internally or fed in from an EG&G 175 programmer. Steady-state experiments with microelectrodes were performed with a 2-electrode system with an EG&G 175 programmer and either a Keithley 480 picoammeter or a Keithley 427 current amplifier. Fast scan voltammetry with microelectrodes was done with both 2- and 3-electrode arrangements. For work in CH_2Cl_2 it was found that the reproducibility was improved by cleaning the microelectrodes by pulsing between ±3 V for several seconds prior to the experiment. For all experiments the output was fed to an X–Y recorder or to a digital oscilloscope (Nicolet 3091 or Gould 4035) and then transferred to an X–Y recorder.

Results and Discussion

Non-Steady-State Voltammetry. The oxidation of $(C_6H_6)Cr(CO)_3$ (**2**) was studied in a variety of solvents. On the cyclic voltammetry (CV) time scale the chemical reversibility of the oxidation is very dependent on the solvent and electrolyte. In acetone, acetonitrile, and nitromethane (with 0.1 M TBAP) at room temperature we found no chemical reversibility up to the largest scan rate used (10 V/s). In propylene carbonate (PC) the $\mathbf{2}/\mathbf{2}^+$ couple is chemically reversible at 10 V/s. Much of the work reported herein refers to dichloromethane and the behavior in this solvent will be discussed in some detail. In a preliminary communication[12] we reported that using $TBAPF_6$ instead of TBAP greatly increased the half-life of the $\mathbf{2}^+$ radical cation. Figure 1 illustrates this effect, which is probably due to PF_6^- having a much lower nucleophilicity than ClO_4^- for attack on $\mathbf{2}^+$ as the initial step in its decomposition. Reversibility of the $\mathbf{2}/\mathbf{2}^+$ couple in CH_2Cl_2/0.1 M TBAP could only be observed by lowering the temperature below -50 °C[12] or by increasing the scan rate at room temperature to above 20 V/s; at 200 V/s the couple is completely reversible. Figure 2 shows the CV's of **2** with the positive limit extending to +1.6 V. With TBAP (Figure 2A) there is a hint of a second oxidation ca. 0.25 V positive of the first wave. The prominence of this second wave was highly irreproducible, sometimes being quite substantial. Since $\mathbf{2}^+$ decomposes rapidly in CH_2Cl_2/0.1 M TBAP, it is likely that the second oxidation is due to a decomposition product and may be also associated with electrode coating. The return scan in Figure 2A shows clear evidence for a desorption wave, the magnitude of which was found to vary widely among experiments. Figure 1A shows that a desorption wave may appear even if the anodic scan is stopped at +1.05 V. Steady-state experiments described below confirm that adsorption of the products of oxidation occurred.

With $TBAPF_6$ (Figure 2B) a second oxidation ca. 0.6–0.8 V positive of the $\mathbf{2}/\mathbf{2}^+$ oxidation wave is observed. By going to faster scan rates with microelectrodes it was established that this second wave appears whenever the $\mathbf{2}/\mathbf{2}^+$ couple is chemically reversible; thus at 100 V/s the $\mathbf{2}/\mathbf{2}^+$ couple is reversible with both TBAP and $TBAPF_6$ and the second wave appears with both electrolytes. It therefore is reasonable to assign the second wave to the oxidation of $\mathbf{2}^+$ to $\mathbf{2}^{2+}$. Given the sensitivity of the $\mathbf{2}^+$ radical to perchlorate and other nucleophiles (vide infra) it is not surprising to find that the $\mathbf{2}^+/\mathbf{2}^{2+}$ couple is chemically irreversible, even at 10 000 V/s at a 10 μm diameter platinum disk microelectrode.

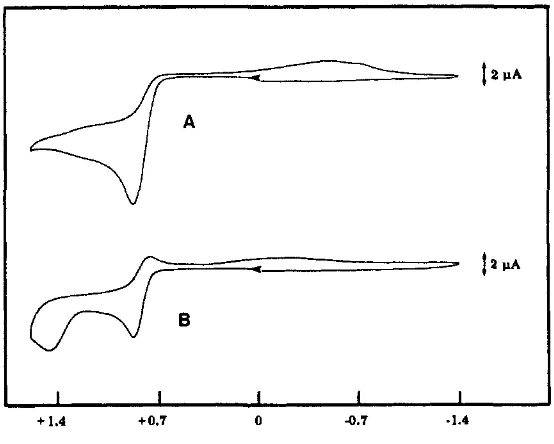

Figure 2. Cyclic voltammograms of $(C_6H_6)Cr(CO)_3$ (**2**) extending into the second oxidation range. The experimental conditions are the same as in Figure 1. The electrolyte was (A) 0.1 M TBAP and (B) 0.1 M $TBAPF_6$.

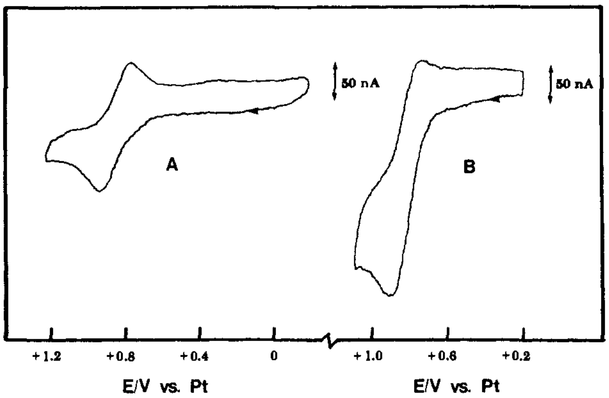

Figure 3. Cyclic voltammograms of 2 × 10^{-3} M $(C_6H_6)Cr(CO)_3$ (**2**) at 10 V/s and 20 °C in benzene. The working electrode was a 100 μm diameter platinum disk and the supporting electrolyte was 0.5 M $THAPF_6$ for A and 0.5 M THAP for B.

By using a 100 μm platinum disk electrode, high-quality CV's of **2** in benzene were obtained with 0.5 M $THAPF_6$ (Figure 3A) and THAP (Figure 3B). In analogy to the results in CH_2Cl_2, the CV with THAP shows only slight chemical reversibility at 10 V/s while $THAPF_6$ gives a reversible $\mathbf{2}/\mathbf{2}^+$ couple. The chemically irreversible oxidation of $\mathbf{2}^+$ was observed (with $THAPF_6$ at 10 V/s) at ca. 0.6 V positive of the first oxidation. The ability to obtain voltammetric data in benzene (without large *iR* distortions) is clearly beneficial when dealing with compounds unstable in more polar solvents. There are several previous reports[21-23] demonstrating the feasibility of voltammetry in benzene with use of microelectrodes.

The fate of $\mathbf{2}^+$ in CH_2Cl_2 was examined in some detail. Bulk electrolysis of **2** in CH_2Cl_2 at a potential ≤150 mV positive of the peak potential gave 2.0 ± 0.2 for the number of electrons involved in the oxidation of **2** in either 0.1 M TBAP or $TBAPF_6$. In order to get reproducible results care had to be taken to properly clean the Pt basket working electrode; this was best accomplished by treatment with 1:1 H_2SO_4/HNO_3, washing, and holding at -1.2 V for ca. 10 min in CH_2Cl_2 with electrolyte present. In addition the electrolysis potential had to be kept well negative of the second oxidation process (see Figure 2) or rapid fouling

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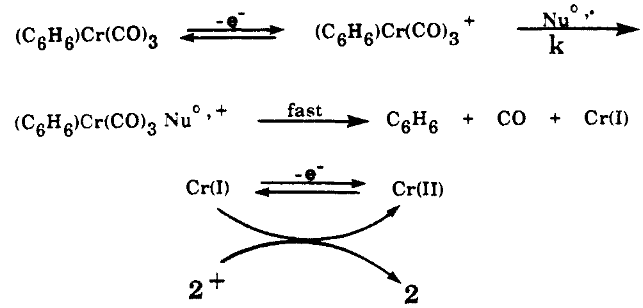
Scheme I



(coating) of the electrode occurred with attendant incomplete electrolysis. After electrolysis, the solutions were colorless and contained no ν_{CO} bands in the IR. HPLC analysis indicated the quantitative formation of free benzene. Electrolyses performed in a CO atmosphere gave results identical with that obtained with a N_2 atmosphere.

Experiments on a shorter time scale than electrolysis also provided useful information concerning the fate of the $\mathbf{2}^+$ radical cation. Rotating disk voltammetry in CH_2Cl_2 at a platinum electrode indicated that the oxidation of **2** is a 2-electron process with 0.1 M TBAP and a 1-electron process with 0.1 M $TBAPF_6$. The electron count was determined by reference to ferrocene standards. It was independently determined via steady-state microelectrode experiments (vide infra) that the diffusion coefficient of **2** is about 0.9 times that of ferrocene. The diffusion coefficient of ferrocene was found to be the same in 0.1 M TBAP and 0.1 M $TBAPF_6$; this would be expected to be true for **2** as well. Cyclic voltammetric data confirmed the RDE results. Thus in Figures 1 and 2 the anodic peak current with TBAP is about twice that with $TBAPF_6$. However, as the scan rate is increased so that the $\mathbf{2}/\mathbf{2}^+$ couple becomes reversible with TBAP, the peak currents become nearly equal. Quite analogous results obtain in benzene as shown, e.g., in Figure 3, in which the peak current is much greater with THAP than with $THAPF_6$ because of the lack of chemical reversibility with the former. Several experiments were done to test the effect of MeCN, MeOH, and water on the reversibility of the $\mathbf{2}/\mathbf{2}^+$ couple in $CH_2Cl_2/TBAPF_6$. In all three cases very small amounts (ca. 0.1 M) destroyed the reversibility and gave peak current increases consistent with a change to an overall 2-electron process.

The decomposition of $\mathbf{2}^+$ and related cation radicals in MeCN has been studied previously.[14,15] It was found that the oxidation of **2** is a 2-electron process and an ECE_h mechanism was proposed in which E_h is a homogeneous redox reaction between $\mathbf{2}^+$ and a Cr(I) species produced in the chemical step. It was estimated that in neat MeCN $\mathbf{2}^+$ decomposes with a rate constant of 2500 s^{-1} at 25 °C. The decomposition of $\mathbf{2}^+$ has also been studied in DMF, in which an overall 3-electron process occurs.[15,16] It was suggested that attack by solvent is the initial step in the decomposition and that the reaction is much faster in DMF than in MeCN due to the former being a generally better nucleophile.

We have analyzed our data in CH_2Cl_2 and benzene assuming the $\bar{E}C\bar{E}$ mechanism given in Scheme I. The reversible 1-electron oxidation of **2** is followed by rate-determining attack by nucleophile $Nu^{0,-}$ to give a Cr(I) species and free benzene. A Cr(I) species would be rapidly oxidized by $\mathbf{2}^+$, or, at a potential near that of the first oxidation wave, at the electrode surface.[24] We shall ignore a role for $\mathbf{2}^{2+}$ by considering only those experiments with potentials well negative of that required to generate $\mathbf{2}^{2+}$. Pseudo-first-order rate constants for the chemical step in Scheme I were obtained by comparison of experimental CV's with computer-simulated[25] CV's for an $\bar{E}C\bar{E}$ mechanism or with CV's based on numerical expressions given by Nicholson and Shain.[26] The error function calculations required for the latter method utilized the algorithm reported by Oldham.[27] Good fits to experimental data were obtained without the need to explicitly include the homogeneous electron-transfer reaction. In the computations it was assumed that the oxidation $\mathbf{2}/\mathbf{2}^+$ is 0.5 V positive of that for Cr(I)/Cr(II) (see Scheme I); however, this potential difference may be more than 0.5 V without significantly affecting the results. The digital simulation and numerical solutions gave the same results. In the calculations the relevant kinetic parameter is $\psi = kRT/Fv$, where k is the rate constant in Scheme I and v is the scan rate. When $\psi = 0$ the response is, of course, just the reversible $\mathbf{2}/\mathbf{2}^+$ couple. As the chemical reaction rate becomes significant the anodic peak current increases until in the limit it is 2.2 times the reversible ($\psi = 0$) peak current. As expected, this $\psi \rightarrow \infty$ limit was found to be twice that for a system involving an irreversible chemical step following charge transfer (EC).[28]

Applying the above criteria to $CH_2Cl_2/0.1$ M TBAP solutions gave $k = 40 \pm 10\ s^{-1}$ at 20 °C at a platinum electrode. By varying the concentration of TBAP from 5×10^{-4} to 3×10^{-3} M in a solution of **2** containing 0.1 M $TBAPF_6$ it was established that k is linearly dependent on the TBAP concentration. Interestingly, **2** in benzene with 0.5 M THAP gave CV's consistent with $k = 40\ s^{-1}$ in this solvent; Figure 3B shows one CV used for these determinations. Hence, it may be concluded that the rate of decomposition of $\mathbf{2}^+$ in the presence of R_4NClO_4 is similar in CH_2Cl_2 and benzene. A quantitative comparison of the two solvents is difficult, however, since the extent of ion pairing of the electrolyte salts differs in the two systems. Data obtained at −30 °C in $CH_2Cl_2/0.1$ M TBAP yielded $k = 1.0 \pm 0.3\ s^{-1}$. The values of k at 20 °C and −30 °C give a rough estimate of the activation parameters for $\mathbf{2}^+$ decomposition in $CH_2Cl_2/0.1$ M TBAP: $\Delta H^* \approx 42$ kJ mol^{-1}; $\Delta S^* \approx -73$ J mol^{-1} K^{-1}. By running CV's in an atmosphere of CO it was shown that free CO has no effect on the rate constant. The results in benzene suggest that free benzene also has little or no effect on the rate of decomposition of $\mathbf{2}^+$. These observations along with the dependence of k on the TBAP concentration suggest that $\mathbf{2}^+$ decomposes via an associative mechanism. Consistent with this are the much greater rates found in MeCN and DMF.[14-16] That the 17-electron $\mathbf{2}^+$ should react via initial nucleophilic attack rather than via rate-determining CO or arene dissociation is no suprise since almost all 17-electron organometallic complexes studied to date react by associative pathways.[1]

In contrast to the behavior of **2**, the radical cation of (mesitylene)$Cr(CO)_3$ (**3**) is stable enough to give a chemically reversible 1-electron oxidation at 0.2 V/s in CH_2Cl_2, $MeNO_2$, and PC (all 0.1 M TBAP). In agreement with previous work,[14,15] **3** was found to be irreversibly oxidized via a 2-electron process at 0.2 V/s in MeCN/0.1 M TBAP or $TBAPF_6$ (vide infra). The greater stability of $\mathbf{3}^+$ compared to $\mathbf{2}^+$ is not surprising since the former offers greater steric hindrance to nucleophilic attack and a less electrophilic metal center.

Steady-State Voltammetry at Microelectrodes. Due to edge effects, a steady-state current response is expected for slow scan rates at very small electrodes. At fast scan rates the more familiar planar diffusion dominates and the usual transient response seen at conventional electrodes is observed. Figure 4 gives the steady-state CV's for **2** in $CH_2Cl_2/0.1$ M TBAP. Figure 4A shows that a reduction wave appears after the positive scan and Figure 4B that this reduction wave increases in magnitude the more positive the switching potential. Since $\mathbf{2}^+$ rapidly decomposes in 0.1 M TBAP (vide supra), it is probable that electrode coating occurs, thus accounting for the reduction wave as well as the poor quality of the CV in Figure 4B. In fact, the steady-state nature of the CV in Figure 4A means that the reduction wave cannot be due to a substance in solution and, therefore, must correspond to adsorption on the electrode. Results obtained for the oxidation of **2** in $CH_2Cl_2/0.1$ M $TBAPF_6$ were similar except that, as expected, adsorption effects were less obvious for scans not ex-

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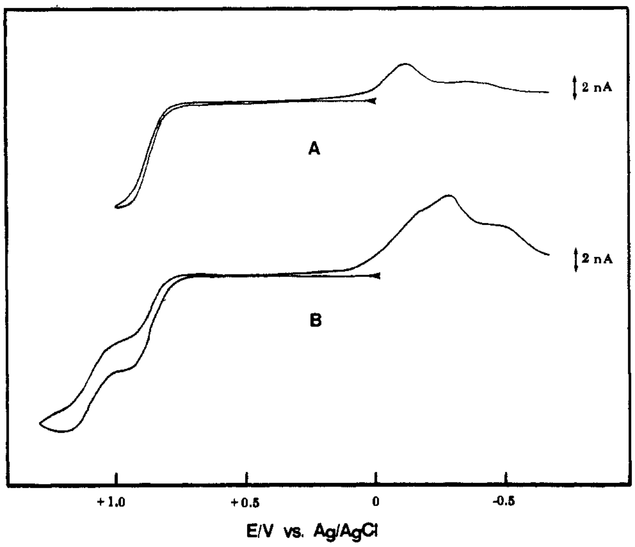

Figure 4. Steady-state cyclic voltammograms of 1 × 10^{-3} M (C_6H_6)-$Cr(CO)_3$ (**2**) at 50 mV/s and 20 °C in dichloromethane with 0.1 M TBAP. The working electrode was a 25 μm diameter platinum disk.

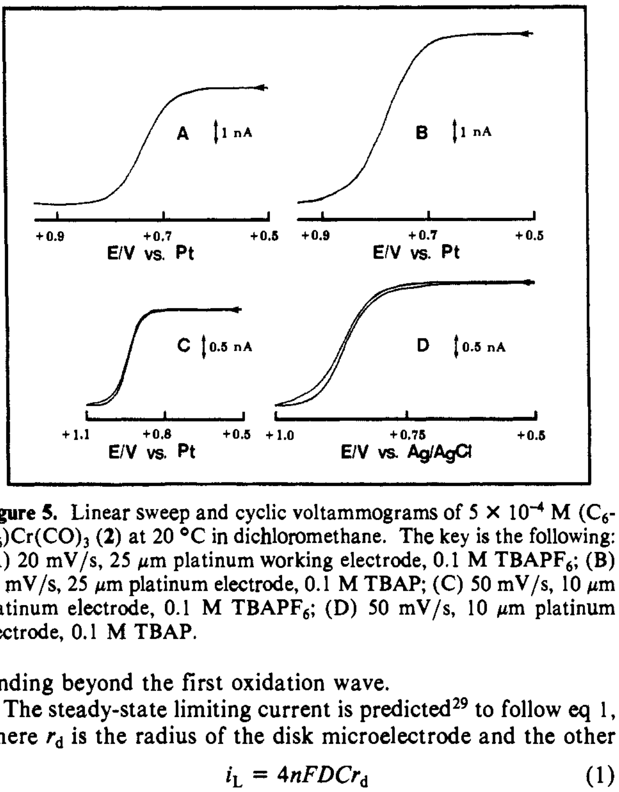

Figure 5. Linear sweep and cyclic voltammograms of 5 × 10^{-4} M (C_6H_6)$Cr(CO)_3$ (**2**) at 20 °C in dichloromethane. The key is the following: (A) 20 mV/s, 25 μm platinum working electrode, 0.1 M $TBAPF_6$; (B) 20 mV/s, 25 μm platinum electrode, 0.1 M TBAP; (C) 50 mV/s, 10 μm platinum electrode, 0.1 M $TBAPF_6$; (D) 50 mV/s, 10 μm platinum electrode, 0.1 M TBAP.

tending beyond the first oxidation wave.

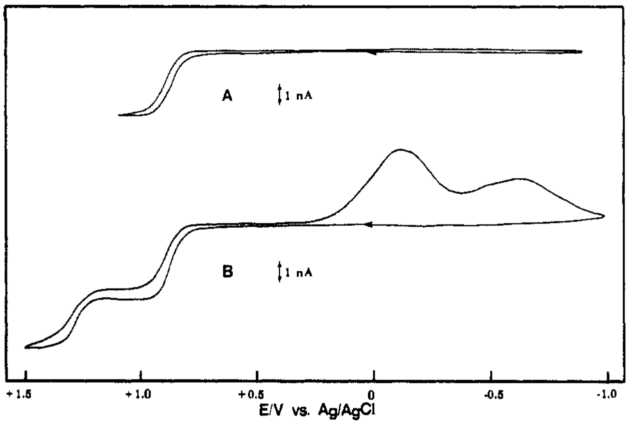

Figure 6. Steady-state cyclic voltammograms of 1 × 10^{-3} M (C_6H_6)-$Cr(CO)_3$ (**2**) at 50 mV/s and 20 °C in benzene with 0.5 M $THAPF_6$. The working electrode was a 25 μm diameter platinum disk.

The steady-state limiting current is predicted[29] to follow eq 1, where r_d is the radius of the disk microelectrode and the other

$$i_L = 4nFDCr_d \qquad (1)$$

symbols have their usual meanings. By comparisons to steady-state CV's of ferrocene, the diffusion coefficient of **2** was estimated as 0.9 times that of ferrocene, which is reported[9,30] as 2 × 10^{-5} cm^2/s in CH_2Cl_2/0.1 M TBAP. Equation 1 then predicts limiting diffusion currents of 4.3 and 1.7 nA at 25 and 10 μm diameter electrodes, respectively, for $n = 1$ and $C = 5 \times 10^{-7}$ mol/ml. As shown in Figure 5, the observed i_L values in CH_2Cl_2/0.1 M $TBAPF_6$, in which the **2**/**2**$^+$ couple is reversible, are 4.4 and 1.8 nA, respectively. In CH_2Cl_2/0.1 M TBAP the apparent n values (from Figure 5, B and D) are 1.5 at a 25 μm diameter electrode and 1.3 at a 10 μm electrode. By assuming[8,31-34] that the steady-state response at a disk microelectrode is equivalent to that at a spherical electrode, an analytical solution to the $\vec{E}_1C\vec{E}_2$ mechanism was derived for the case $E_1^0 - E_2^0 \geq 0.2$ V. (This is the case for the decomposition of **2**$^+$; see Scheme I.) The limiting current, and hence the apparent number of electrons (n_{app}), depends on the kinetic parameter $\lambda = r_s(k/D)^{1/2}$, in which k is the rate constant for the chemical step and r_s is taken[31] as $(2/\pi)r_d$ with r_d being the radius of the disk electrode. As discussed by Fleischmann et al.,[35] for any given rate constant k, the value of n_{app} will decrease from a value of 2 for large electrodes toward a value of 1 as the electrode is made smaller. The behavior is analogous to that at a rotating disk electrode with the mass transfer coefficient changing with electrode size rather than with the rotation rate. Assuming that deviations of n_{app} from the limits of one or two can be measured to within ca. 0.05, the accessible rate constants at a $r_d = 5$ μm electrode range from 1 to 10^4 s^{-1}. The steady-state microelectrode method is particularly convenient for measuring the rate constants since iR and charging current distortions are generally much smaller than that seen with conventional cyclic voltammetry and other transient response techniques. The n_{app} values quoted above for the decomposition of **2**$^+$ in CH_2Cl_2/0.1 M TBAP correspond to $k = 30$ s^{-1} for both the 10 and 25 μm diameter electrodes. This compares favorably with the value of 40 s^{-1} obtained by conventional cyclic voltammetry (vide supra).

Significantly, it was possible to obtain good-quality steady-state CV's of **2** in benzene/0.5 M $THAPF_6$ with a microelectrode (Figure 6). As was observed in CH_2Cl_2, a desorption wave occurs on the reverse scan when the initial positive scan extends beyond the **2**/**2**$^+$ wave into the second oxidation wave. The results in Figure 6 nicely illustrate the utility of microelectrodes for obtaining voltammetric data in solvents of very low polarity such as benzene. It is known that microelectrodes may even be used with solvents as nonpolar as heptane. It is possible to show that the steady-state CV's in benzene are at most only very slightly distorted by iR drop. This follows from Figure 6A, in which the value of $E_{3/4} - E_{1/4}$ is 62 mV. This is only slightly greater than the theoretical 56 mV expected for an electrochemically reversible 1-electron transfer at 25 °C. It is likely that this small difference represents iR drop and is not due to the electron-transfer rate being small enough to affect $E_{3/4} - E_{1/4}$. Indeed, the steady-state CV's in CH_2Cl_2 have $E_{3/4} - E_{1/4}$ for the oxidation of **2** within error (±3 mV) equal to the Nernstian value of 56 mV. This fact can be used to place a lower limit on k_s, the heterogeneous rate constant at $E°$. Using the expression for the oxidation current at a spherical

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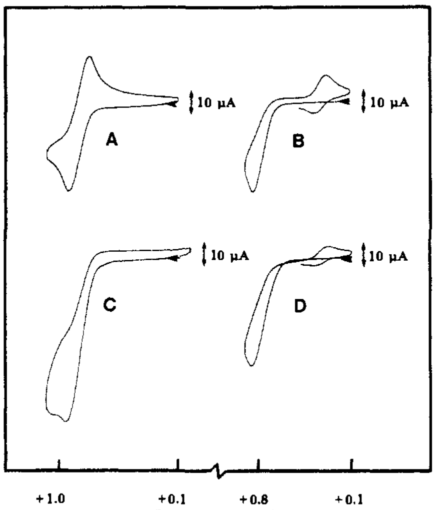

Figure 7. Cyclic voltammograms of 1 × 10^{-3} M $(C_6H_6)Cr(CO)_3$ (**2**) at 0.20 V/s and 20 °C in dichloromethane. The working electrode was a 3 mm glassy carbon disk. The key is the following: (A) no added nucleophile, 0.1 M $TBAPF_6$; (B) 4 × 10^{-3} M $P(OBu)_3$, 0.1 M $TBAPF_6$; (C) no added nucleophile, 0.1 M TBAP; (D) 4 × 10^{-3} M $P(OBu)_3$, 0.1 M TBAP.

microelectrode in a steady-state diffusion field[9] and the result that $E_{3/4} - E_{1/4}$ for the oxidation of **2** in CH_2Cl_2 is ≤60 mV at a 10 μm diameter electrode, one calculates that $k_s \geq 0.3$ cm/s at 25 °C. Microelectrodes are convenient for measuring k_s values due to the relative freedom from iR distortion and the ability to easily change the accessible range of rate constants by changing the electrode size,[36-38] which means that electron transfers that are reversible with DC experiments at conventional electrodes may be rendered irreversible (and hence easily characterized) by using microelectrodes of the appropriate size.

Induced-Ligand Substitution in (Arene)Cr(CO)$_3$. Nucleophiles such as MeCN, MeOH, H_2O, etc., induce the decomposition of 1^+ radical cations and lead to an overall 2-electron oxidation of **1**. An alternative pathway would be CO substitution. A previous report[19] suggests that this occurs to some extent when **3** is oxidized in MeCN in the presence of $P(OEt)_3$. It would seem feasible, therefore, to synthesize (arene)$Cr(CO)_2L$ complexes via electroactivation, provided the product radical cations persist long enough to permit reduction. Presently such complexes are prepared[39] by photolysis of (arene)$Cr(CO)_3$ in the presence of L; this is often a low-yield reaction, particularly with tertiary phosphites. We found that phosphine and phosphite nucleophiles can induce decomposition or substitution for CO in 1^+, with the relative amount of each pathway depending on the solvent used. Figure 7 shows that the addition of a rather low concentration of $P(OBu)_3$ to **2** in CH_2Cl_2 leads to dramatic changes in the CV's. The oxidation wave for $2/2^+$ shifts negative by ca. 0.1 V and a new chemically reversible couple appears ca. 0.4 V negative of $2/2^+$; this couple is assigned to $(C_6H_6)Cr(CO)_2P(OBu)_3$. With $TBAPF_6$ as the electrolyte (Figure 7A,B) the $P(OBu)_3$ nucleophile destroys the reversiblity of the $2/2^+$ couple but does not significantly affect the peak current for the oxidation. With TBAP (Figure 7C,D) the peak current is reduced by one-third when $P(OBu)_3$ is added. It should be noted that the new couple is much less prominent when TBAP is the electrolyte. Similar results were obtained with PBu_3, except that the waves for the new couple were relatively smaller compared to the results with $P(OBu)_3$; that the new couple was due to $(C_6H_6)Cr(CO)_2PBu_3^{+,0}$ was verified by comparison to the CV of an authentic sample of $(C_6H_6)Cr(CO)_2PBu_3$.

A reasonable interpretation of the results in Figure 7 is that $P(OBu)_3$ can substitute for CO as well as induce the decomposition of 2^+ as seen with other nucleophiles (Scheme I). The mechanism is summarized by eq 2–4. Since $E_2^0 < E_1^0$, this scheme is not

$$(C_6H_6)Cr(CO)_3 \xrightleftharpoons{-e^-} (C_6H_6)Cr(CO)_3^+ \tag{2}$$

$$(C_6H_6)Cr(CO)_3^+ \xrightarrow{k',\,L} (C_6H_6)Cr(CO)_2L^+ \tag{3}$$

$$(C_6H_6)Cr(CO)_2L^+ \xrightleftharpoons{+e^-} (C_6H_6)Cr(CO)_2L \tag{4}$$

catalytic. Digital simulation as well as numerical solutions to this scheme were performed. The calculations show that the mechanistically significant feature of the CV's is the ratio of the peak current for the reduction of $(C_6H_6)Cr(CO)_2L^+$ to the peak current for the oxidation of **2**. This ratio is, of course, dependent on the magnitude of $E_1^0 - E_2^0$. For $E_1^0 - E_2^0 = +0.43$ V, which applies to the $P(OBu)_3$ reaction, this ratio is predicted to be 0.47 as long as the kinetic parameter $\psi' = k'RT/Fv > 1$ and the anodic switching potential is 0.2 V positive of the peak potential for the oxidation of **2**. The ratio in Figure 7B is 0.30, from which we conclude that the substitution reaction is accompanied by $P(OBu)_3$ induced decomposition of 2^+ as in Scheme I. The fact that the peak current for **2** oxidation in Figure 7B is not markedly increased over that in Figure 7A is not inconsistent with this conclusion.[26,28] The results with TBAP (Figure 7C,D) show clearly that reaction 3 occurs to some extent, but TBAP induced decomposition of 2^+ also takes place (as in Figure 7C). The peak current for **2** oxidation decreases from Figure 7C to Figure 7D because some of the 2^+ is trapped via reaction 3. Interestingly, CV's of $P(OBu)_3$ added to **2** in acetone/0.1 M TBAP indicate that CO substitution occurs to the virtual exclusion of the decomposition pathway in this medium. A full theoretical and experimental analysis of these and other analogous reactions will be published separately.[10]

(Mesitylene)$Cr(CO)_3$ (**3**) seems to react cleanly with alkyl phosphites. Thus, $P(OBu)_3$ or $P(OMe)_3$ at 5 × 10^{-3} M reacts with 3^+ in PC or $MeNO_2$/0.1 M TBAP to give (mesitylene)$Cr(CO)_2L^+$; CV's analogous to that shown in Figure 7B were obtained. The ratio of the peak current for the reduction of (mesitylene)$Cr(CO)_2P(OBu)_3$ + ($E_{1/2} = 0.26$ V) and the peak current for the oxidation of **3** was found to be 0.48 ± 0.03, in excellent agreement with the theoretical value of 0.47. This means that the CO substitution reaction completely accounts for the fate of 3^+. With PBu_3 (5 × 10^{-3} M), however, the relevant peak current ratio was only 0.25, substantially less than the calculated value of 0.40. This implies that PBu_3 can react with 3^+ by pathway(s) other than substitution, probably as in Scheme I. It was also observed that the i_a/i_c current ratio for (mesitylene)$Cr(CO)_2L^{+,0}$ (L = $P(OBu)_3$, PBu_3) was considerably less than unity. This is expected since neither member of this redox couple exists in the bulk solution. Calculations of this i_a/i_c ratio and its dependence on the cathodic switching potential agreed well with a series of experiments in which the switching potential was varied from 0.0 to −1.0 V (L = $P(OBu)_3$).

The caged phosphite $P(OCH_2)_3CMe$ proved to be a very interesting nucleophile. As shown in Figure 8, at a scan rate of 750 mV/s 3^+ reacts to generate a new couple with an $E_{1/2}$ about 0.1 V positive of that found with $P(OBu)_3$. This is reasonably assigned to (mesitylene)$Cr(CO)_2P(OCH_2)_3CMe$, which is harder to oxidize than the $P(OBu)_3$ analgoue because $P(OCH_2)_3CMe$ is a weaker base than $P(OBu)_3$. (The same holds true for $P(OBu)_3$ compared to PBu_3.) Figure 8A also contains a second couple at −0.05 V that becomes much more prominent at slower scan rates (Figure 8B). This couple is most likely due to formation of the disubstituted product, (mesitylene)$Cr(CO)[P(OCH_2)_3CMe]_2$, which does not have time to form at fast scan rates. Disubstitution probably occurs with $P(OCH_2)_3CMe$ but not $P(OBu)_3$ because of the former's much smaller cone angle. Indeed, this steric difference can be exploited to make mixed complexes, as illustrated

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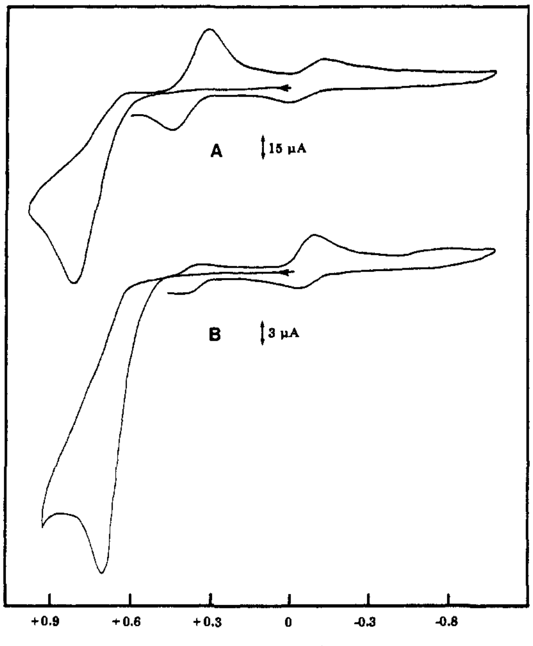

Figure 8. Cyclic voltammograms of 2×10^{-3} M (mesitylene)Cr(CO)$_3$ (**3**) and 5×10^{-3} M P(OCH$_2$)$_3$CMe at 20 °C in propylene carbonate with 0.1 M TBAP. The working electrode was a 1.6 mm platinum disk. The key is the following: (A) scan rate = 750 mV/s; (B) scan rate = 50 mV/s.

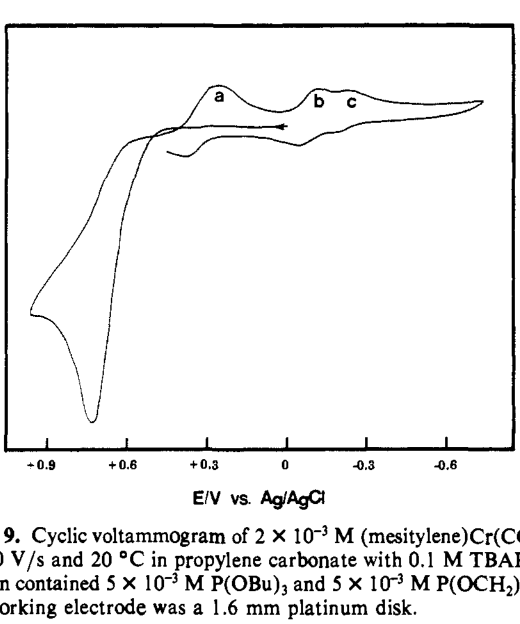

Figure 9. Cyclic voltammogram of 2×10^{-3} M (mesitylene)Cr(CO)$_3$ (**3**) at 0.20 V/s and 20 °C in propylene carbonate with 0.1 M TBAP. The solution contained 5×10^{-3} M P(OBu)$_3$ and 5×10^{-3} M P(OCH$_2$)$_3$CMe. The working electrode was a 1.6 mm platinum disk.

in Figure 9. Thus, oxidation of **3** in the presence of P(OBu)$_3$ and P(OCH$_2$)$_3$CMe gives three reversible couples in the CV, labeled **a**, **b**, and **c**. Couple **a** has a rather larger ΔE_p and occurs at a potential between that for (mesitylene)Cr(CO)$_2$P(OBu)$_3$ and (mesitylene)Cr(CO)$_2$P(OCH$_2$)$_3$CMe, and so may represent a mixture of these complexes. Couple **b** corresponds to (mesitylene)Cr(CO)[P(OCH$_2$)$_3$CMe]$_2$. Finally, couple **c** is located where one would expect to find the mixed complex (mesitylene)Cr(CO)[P(OBu)$_3$][P(OCH$_2$)$_3$CMe].

The above results show that the electroactivation to CO substitution of normally inert (arene)Cr(CO)$_3$ complexes is a facile process. In general, CO substitution that is oxidatively induced would not be expected to be catalytic because the product will have an E^0 negative of the reactant's E^0. However, this restriction may be relaxed under the proper conditions so that catalysis may still occur. We have preliminary evidence[10] that this in fact occurs with some reactions of (arene)Cr(CO)$_3$. Whether the reaction in question is catalytic or stoichiometric, it is clear that the technique of electrochemical activation is a very attractive one that may prove to be widely applicable to synthetic and mechanistic organometallic chemistry.

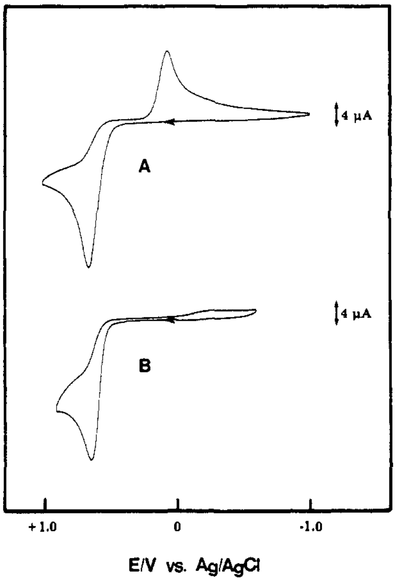

Figure 10. Cyclic voltammograms of (A) 1×10^{-3} M (mesitylene)W(CO)$_3$ (**6**) and (B) 1×10^{-3} M (mesitylene)Cr(CO)$_3$ (**3**) at 0.20 V/s and 20 °C in acetonitrile with 0.1 M TBAP. The working electrode was a 1.6 mm platinum disk.

Voltammetry of (Mesitylene)W(CO)$_3$. A recent paper[18] dealing with the electrochemistry of (arene)M(CO)$_3$ (M = Cr, W) notes that (C$_6$Me$_6$)Cr(CO)$_3$ (**4**) and (C$_6$Me$_6$)W(CO)$_3$ (**5**) behave differently when oxidized in MeCN with tetraethylammonium perchlorate (TEAP) as the electrolyte. Thus, the CV of **4** at only 0.2 V/s displayed substantial chemical reversibility for the **4**/**4**$^+$ couple. On the other hand, the oxidation of **5** showed no hint of chemical reversibility even at 500 V/s. Following oxidation of **5**, the CV had a reduction peak 0.5 V or more negative of the original oxidation wave; the potential of this reduction wave was very dependent on the presence of nucleophiles. On the basis of bulk electrolysis, the oxidation of **5** was claimed to involve one electron, and accordingly the authors reached the reasonable conclusion that **5**$^+$ reacts rapidly with solvent or nucleophile to generate a radical species with an expanded coordination sphere, (C$_6$Me$_6$)W(CO)$_3$·L$^+$, which is responsible for the observed reduction wave in the CV. The authors noted that such radicals would represent a finding of fundamental significance in the general area of odd-electron organometallic reaction chemistry because of the obvious relevance to the proposed associative mechanism for ligand substitution and insertion in 17-electron complexes. For reasons outlined below, we believe that the electrochemical oxidation of (arene)W(CO)$_3$ in MeCN does not lead to observable odd-electron species and that the authors' conclusions concerning the observation of an expanded coordination sphere radical are incorrect.

Figure 10A shows the CV for the oxidation of (mesitylene)W(CO)$_3$ (**6**) in MeCN/0.1 M TBAP. This CV is almost identical with the one previously reported[18] for (C$_6$Me$_6$)W(CO)$_3$ in MeCN/0.1 M TEAP, and accordingly it seems reasonable to assume that similar chemistry obtains. We found that bulk electrolysis of **6** in MeCN with a platinum basket working electrode gave results difficult to reproduce. Sometimes the number of electrons, n, was close to 2; other experiments gave values between $n = 1$ and 2. We conclude that *on this time scale* electrode coating occurred and led in some cases to artifically low n values. This may thus account for the claim[18] that $n = 1$ for the bulk electrolysis of **5** in MeCN at a platinum electrode. Cyclic voltammetry experiments at conventional and microelectrodes established that, in fact, $n = 2$ for the oxidation of **6** in MeCN (and CH$_2$Cl$_2$). Figure 10 shows that the peak currents for the oxidation of **6** and its chromium analogue **3** are virtually identical in MeCN. It has been reported[14,15] that the oxidation of **3** in

MeCN involves two electrons, and this was confirmed by us. Since the diffusion coefficients of **3** and **6** must be very similar, it follows from the peak currents that the oxidation of **6** also involves two electrons.

CV's in CH_2Cl_2 (0.2 V/s and 1.0 x 10^{-3} M) confirmed the above results and clearly indicated the ease with which erroneous conclusions can be drawn when electrode coating occurs. On a platinum electrode the oxidation of **2** had a peak current in arbitrary units of 2.1 (TBAP, irreversible, $n = 2$) and 1.0 ($TBAPF_6$, reversible, $n = 1$). (The arbitrary units refer to a particular platinum electrode, 1.00 × 10^{-3} M electroactive species, 0.10 M electrolyte, and 0.2 V/s in CH_2Cl_2.) The **3**/**3**$^+$ couple is reversible ($n = 1$) with both TBAP and $TBAPF_6$, and in agreement with this, the peak currents were 1.08 (TBAP) and 1.02 ($TBAPF_6$). In contrast, the oxidation of **6** in CH_2Cl_2/0.1 M TBAP gave irreproducible results due to rapid electrode coating. In CH_2Cl_2/0.1 M $TBAPF_6$ the oxidation of **6** was more reproducible provided the concentration was decreased from 1.0 × 10^{-3} to 2 × 10^{-4} M, in which case the peak current averaged 1.8 (corrected to 1.0 × 10^{-3} M). Electrode coating was less of a problem on a glassy carbon electrode and the peak current ratio for **6**:**3** was 1.91:1 at a concentration of 2 × 10^{-4} M. These results clearly indicate that **6** oxidizes via a *2-electron* change in CH_2Cl_2 as well as in MeCN. The electrode coating problems evident in CH_2Cl_2 were not observed in MeCN *on the CV time scale*, presumably because of the ability of MeCN to rapidly react with **3** and **6** as oxidation occurs.

The W(II) species produced from the 2-electron oxidation of **6** in MeCN or CH_2Cl_2 most likely coordinates solvent (or electrolyte anion) to give the expanded coordination sphere previously discussed.[18] However, this species is *not* a radical, but simply an 18-electron W(II) complex, and so is not particularly relevant to odd-electron organometallic reactions. That **6** is oxidized to W(II) is consistent with the known stable complexes $(C_6Me_6)W(CO)_3X^+$ ($X = Cl^-, I^-$).[40] Finally, it is interesting to note that (arene)-$Cr(CO)_3$ and (arene)$W(CO)_3$ display major differences upon oxidation. Although both suffer 2-electron oxidation (in MeCN), the tungsten complexes seem more reluctant to decompose via loss of CO and arene, suggesting that electrochemically generated W(II) complexes may have very useful chemical applications. A detailed electrochemical study of (arene)$W(CO)_3$ complexes and their oxidatively induced reactions will be published separately.[10]

Conclusions. (1) When oxidized in dichloromethane or benzene, $(C_6H_6)Cr(CO)_3$ decomposes via an $\vec{E}C\vec{E}$ mechanism in which the chemical step is associative nucleophilic attack on $(C_6H_6)Cr(CO)_3^+$. Changing the supporting electrolyte anion from ClO_4^- to PF_6^- greatly increases the persistence of the $(C_6H_6)Cr(CO)_3^+$ radical. (2) In the presence of tertiary phosphites and phosphines, (arene)$Cr(CO)_3^+$ undergoes very rapid CO substitution. (3) (Mesitylene)$W(CO)_3$ undergoes a 2-electron oxidation in acetonitrile to give, most likely, a W(II) complex retaining the CO and arene ligands. (4) Microelectrodes under steady-state conditions are particularly useful for investigating organometallic reaction mechanisms and make it possible to obtain high-quality voltammetric data in media as nonpolar as benzene.

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Registry No. 2, 12082-08-5; **3**, 12129-67-8; **4**, 12088-11-8; **5**, 33505-53-2; **6**, 12129-69-0; $(C_6H_6)Cr(CO)_2P(OBu)_3$, 112793-59-6; (meistylene)$Cr(CO)_2P(OCH_2)_3CMe$, 112793-60-9; (mesitylene)$Cr(CO)[P(OCH_2)_3CMe]_2$, 112793-61-0; (mesitylene)$Cr(O)_2P(OBu)_3^+$, 112793-63-2; (mesitylene)$Cr(CO)[P(OBu)_3][P(OCH_2)_3CMe]$, 112793-62-1; $(C_6H_6)Cr(CO)_2PBu_3$, 12278-02-3; $(C_6H_6)Cr(CO)_2PBu_3^+$, 112793-64-3; (mesitylene)$Cr(CO)_2PBu_3$, 12278-39-6; (mesitylene)$Cr(CO)_2PBu_3^+$, 112793-65-4; MeCN, 75-05-8; MeOH, 67-56-1; H_2O, 7732-18-5; $P(OBu)_3$, 102-85-2; PBu_3, 998-40-3; $P(OMe)_3$, 121-45-9; $P(OCH_2)_3CMe$, 1449-91-8.

Supplementary Material Available: Figures giving (1) CV's for the oxidation of **2** at various scan rates in CH_2Cl_2, (2) CV of **2** in CH_2Cl_2 with 0.08 M MeCN, (3) CV's obtained by digital simulation for an $\vec{E}_1C\vec{E}_2$ mechanism with $E_1^0 - E_2^0 = 0.5$ V, (4) steady-state CV for **2** in $CH_2Cl_2/TBAPF_6$, (5) calculated steady-state voltammograms for a $\vec{E}_1C\vec{E}_2$ mechanism with $E_1^0 - E_2^0 > 0.2$ V, (6) CV's of **3** in PC with $P(OBu)_3$ or PBu_3 present, (7) CV's of **3** and **6** in $CH_2Cl_2/TBAPF_6$ at platinum and glassy carbon electrodes (8 pages). Ordering information is given on any current masthead page.