$$k = (i_p)_a/C^* v^{1/2} \qquad (6)$$

As can be seen in Table V, the $k$ values can be broadly categorized into two groups, those for which the observed $k$ value approaches that of ferrocene (L = $PMe_2Ph$, $PBz_3$, and $PMePh_2$) and those for which $k$ is appreciably different ($PPh_3$, $PCyPh_2$, and $PCy_2Ph$). The phosphines in the latter group all contain three very bulky cyclic groups, and the smaller $k$ values may result from significantly smaller diffusion coefficients for the compounds.

Over a range of scan rates (specified for each complex in Table V), each redox couple displayed an invariant peak potential. Consequently, for the solvent system used, with a maximum attainable oxidation state of +1, the general reaction is expected to be

$$(TMM)Fe(CO)_2L \rightarrow (TMM)Fe(CO)_2L^+ + e^- \qquad (7)$$

One would expect this process to be facilitated by the more electron-donating phosphines, but there is in fact little correlation between electron donation by the phosphine (as evidenced by IR $\nu_{CO}$ frequencies) and the mean of the observed $(E_p)_a$ and $(E_p)_c$ (which should approximate the thermodynamic $E°$ values).

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada for financial support, and Dr. Gary S. Silverman (M&T) for gifts of tertiary phosphines.

**Supplementary Material Available:** Tables of fractional coordinates and isotropic displacement parameters for all atoms (3 pages); a listing of calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

---

# Cyclic Voltammetric Study of the Metal-Centered Radicals $\{\eta^5\text{-}C_5H_5Cr(CO)_2L\}$ (L = CO, $PMe_3$, $PMe_2Ph$, $PMePh_2$, $PPh_3$) and $\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$

Kelly A. E. O'Callaghan, Stephen J. Brown, John A. Page,* and Michael C. Baird*

*Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6*

Thomas C. Richards and William E. Geiger*

*Department of Chemistry, University of Vermont, Burlington, Vermont 05405*

*Received March 14, 1991*

The results of a cyclic voltammetry study of the persistent, chromium-centered radicals $\{\eta^5\text{-}C_5H_5Cr(CO)_2L\}$ (L = CO, $PMe_3$, $PMe_2Ph$, $PMePh_2$, $PPh_3$) and $\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$ are reported. It is found that all undergo nearly reversible, 1-electron reductions to the corresponding anions, the relative ease of reduction correlating well with electron-donating abilities of the ligands, as indicated by observed values of $\nu_{CO}$. At suitable combinations of low temperature and fast scan rates, exchange between the monomeric $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ and its dimer, $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, becomes sufficiently slow relative to the time scale of the cyclic voltammetric experiment that reduction of the dimer, the predominant species in solution, is observed.

As part of growing interest in the chemistry of 17-electron organometallic compounds,[1] it has recently been shown that the metal–metal-bonded, 18-electron compounds $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ and $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ partially dissociate in solution to form the corresponding 17-electron, radical species, $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ and $\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$, respectively.[2] The two monomers are labile and react with a variety of tertiary phosphines L to form substituted 17-electron compounds of the types $\{\eta^5\text{-}C_5H_5Cr(CO)_2L\}$ and $\{\eta^5\text{-}C_5Me_5Cr(CO)_2L\}$, most of which are monomeric both in solution and in the solid state.[3] We have been investigating the physical and chemical properties of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$, and their derivatives[2a,3] and have recently reported a detailed investigation of the X-ray structures of two substituted radicals, $\{\eta^5\text{-}C_5H_5Cr(CO)_2(PPh_3)\}$ and $\{\eta^5\text{-}C_5Me_5Cr(CO)_2(PMe_3)\}$, and of the electronic structures of both the tricarbonyl and of the substituted dicarbonyl radical species, as indicated by single-crystal EPR studies and LCAO-HFS calculations.[4]

In order to gain further information concerning the electronic structures of this fascinating series of compounds, we have now also carried out a cyclic voltammetric study of the compounds $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$, and $\{\eta^5\text{-}C_5H_5Cr(CO)_2L\}$ (L = $PMe_3$, $PMe_2Ph$, $PMePh_2$, $PPh_3$) and report herein our results. Although electrochemical applications to organometallic chemistry are numerous,[5] previous electrochemical investigations of this system have been limited to a brief examination of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, for which it was con-

---

(1) (a) Astruc, D. *Chem. Rev.* **1988**, *88*, 1189. (b) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217. (c) For a number of relevant reviews, see: *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990.

(2) (a) Cooley, N. A.; Watson, K. A.; Fortier, S.; Baird, M. C. *Organometallics* **1986**, *5*, 2563. (b) McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643. (c) Jaeger, T. J.; Baird, M. C. *Organometallics* **1988**, *7*, 204.

(3) Cooley, N. A.; MacConnachie, P. F. T.; Baird, M. C. *Polyhedron* **1988**, *7*, 1965.

(4) Jaeger, T. J.; Watkins, W. C.; MacNeil, J. H.; Fortier, S.; Watson, K. A.; Hensel, K.; Preston, K. F.; Morton, J. R.; Le Page, Y.; Charland, J.-P.; Williams, A. J.; Ziegler, T. *J. Am. Chem. Soc.* **1991**, *113*, 542.

(5) (a) Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 1. (b) Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985**, *24*, 87.

0276-7333/91/2310-3119$02.50/0

**Table I. Peak Potentials (V vs Ag/AgCl/Aqueous KCl; 0.1 V/s) and $\nu_{CO}$ for the Compounds $\{\eta^5\text{-}C_5R_5Cr(CO)_2L\}^a$ ($CH_2Cl_2$)**

| compound | $\{\eta^5\text{-}C_5R_5Cr(CO)_2L\}$ reduction | $[\eta^5\text{-}C_5R_5Cr(CO)_2L]^-$ oxidation | $E^{\circ\prime}$ | $\nu_{CO}$ (cm$^{-1}$) |
|---|---|---|---|---|
| $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ | –0.30 | –0.10 | –0.21 | 2011, 1897$^b$ |
| $\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$ | –0.43 | –0.24 | –0.33 | 1993, 1892 |
| $\{\eta^5\text{-}C_5H_5Cr(CO)_2PPh_3\}$ | –0.78 | –0.62 | –0.70 | 1918, 1793 |
| $\{\eta^5\text{-}C_5H_5Cr(CO)_2PPh_2Me\}$ | –0.78 | –0.63 | –0.70 | 1915, 1787 |
| $\{\eta^5\text{-}C_5H_5Cr(CO)_2PPhMe_2\}$ | –0.81 | –0.67 | –0.74 | 1911, 1781 |
| $\{\eta^5\text{-}C_5H_5Cr(CO)_2PMe_3\}$ | –0.84 | –0.76 | –0.80 | 1910, 1778 |

$^a$ R = H, Me. $^b$ In THF; estimated from Figure 3 in ref 2b.

cluded that the electroactive species is the monomer, $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$.[6]

## Experimental Section

The compounds $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$,[3] $\{\eta^5\text{-}C_5H_5Cr(CO)_2L\}$ (L = $PMe_3$, $PMe_2Ph$, $PMePh_2$, $PPh_3$),[3] and $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$[4] were prepared by methods described previously; all reactions were carried out under nitrogen in dried, deaerated solvents. IR spectra were recorded on a Bruker IFS-85 FTIR spectrometer. Cyclic voltammograms at Queen's University were obtained with a BAS CV-1B voltammograph equipped with a Houston Instrument 100 recorder, and those at the University of Vermont were obtained with a Princeton Applied Research Model 173 potentiostat interfaced to a Nicolet digital oscilloscope (Model 4094A) and a Swan XT10 PC. Electrochemical data were normally obtained utilizing the following conditions: concentrations of test compound, 1–4 mM; $CH_2Cl_2$ or THF as solvent; 0.1 M $[Bu_4N][BF_4]$ as supporting electrolyte; Pt disk working electrode; scan rates, 0.05–0.2 V/s; experimental reference electrode, Ag/AgCl/saturated aqueous KCl. The low-temperature data on $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ were obtained with a nonaqueous Ag/AgCl electrode, against which ferrocene gave $E^{\circ\prime}$ = +0.33 V.[7]

The variable-temperature experiments on $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ were carried out inside a Vacuum Atmospheres drybox equipped with a heptane cooling bath, the temperature of which was controlled with a precision of 0.1 °C by an FTS Systems temperature controller. Voltammograms at slow scan rates were taken at a Pt disk of about 6-mm diameter (Corning Glass Works), and those at higher scan rates, with a homemade 250-μm disk prepared by sealing Pt wire (Goodfellow Metals) into soft glass.

Formal potentials for the couples ($E^{\circ\prime}$; Table I and text) are reported as the mean of the cathodic and anodic peak potentials.

## Results and Discussion

**$[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$.** Cyclic voltammograms (CVs) of this compound were recorded in THF and methylene chloride under a variety of conditions. It quickly became clear from changes in the voltammograms with time that the behavior of the dimer in these solvents was complicated by disproportionation processes of the type

$$[\eta^5\text{-}C_5H_5Cr(CO)_3]_2 + S \rightarrow [\eta^5\text{-}C_5H_5Cr(CO)_3S]^+ + [\eta^5\text{-}C_5H_5Cr(CO)_3]^- \quad (1)$$

where S = solvent. Although IR spectra of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ in pure methylene chloride and THF indicated that this compound is stable in these solvents on the time scale of the CV experiments (5–30 min), the IR spectra changed noticeably when $[n\text{-}Bu_4N][BF_4]$ was added. In both solvents, albeit more so in THF, relatively intense new $\nu_{CO}$ peaks attributable[3] to $[\eta^5\text{-}C_5H_5Cr(CO)_3]^-$ appeared at about 1890 and 1790 cm$^{-1}$, and although no peaks attributable to cationic species[3] were observed, it is possible that a cationic complex of the type $[\eta^5\text{-}C_5H_5Cr(CO)_3S]^+$ would be unstable with respect to decarbonylation.

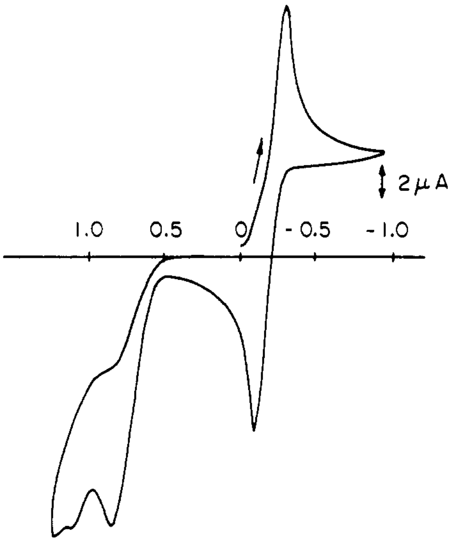

**Figure 1.** Cyclic voltammogram of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ (5 × 10$^{-3}$ M) in $CH_2Cl_2$ (scan rate 0.1 V/s).

In spite of complications arising from disproportionation, useful cyclic voltammograms of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ could be obtained by carrying out the experiments as quickly as possible; differentiation between the current peaks from starting material and from product(s) of disproportionation were made by correlating changes in the CV with absorbances in the IR spectrum of a solution during the course of an experiment. Interestingly, experiments in which $[Bu_4N][PF_6]$ was used as supporting electrolyte did not appear to result in disproportionation or other decomposition of the radical. With this supporting electrolyte, reproducible voltammograms were obtained at ambient temperature over at least 1 h in methylene chloride.

A typical CV for a freshly made sample of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ in methylene chloride at room temperature is shown in Figure 1; here, the experiment was begun at 0 V with switching at –1.0 and +1.25 V. A reversible process with $E^{\circ\prime}$ = –0.21 V as well as current peaks for irreversible oxidations at about +0.8 and +1.0 V are observed. Further experiments with the switching potential extended to –1.5 V showed no other reduction peaks for the compound, while the oxidation peaks observed were not present in the supporting electrolyte itself. A repetitive CV with switching at –1.0 and +0.2 V confirmed the reversible nature of the couple with $E^{\circ\prime}$ = –0.21 V. Comparison of the voltammogram with that for ferrocene[8] indicated that the charge-transfer process involves 1 electron per chromium. This analysis requires normalization of the peak cathodic currents with respect to the concentration of the species and assumes that the diffusion current for the electroactive species is the same as that of ferrocene.

Our results are thus in essential agreement with those of Madach and Vahrenkamp,[6] who found that a 1:2 mixture of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ and $[\eta^5\text{-}C_5H_5Cr(CO)_3]^-$ in benzonitrile gave a composite voltammetric wave with equal anodic and cathodic limiting currents and an $E_{1/2}$ of –0.17 V vs a Ag/AgCl reference electrode. The mixture also gave anodic waves with $E_{1/2}$ of +0.87 and +1.39 V representing oxidation steps of monomeric species. A CV on a solution of the anion $[\eta^5\text{-}C_5H_5Cr(CO)_3]^-$ indicated a reversible 1-

---

(6) (a) Madach, T.; Vahrenkamp, H. *Z. Naturforsch.* **1978**, *33b*, 1301. (b) Madach, T.; Vahrenkamp, H. *Z. Naturforsch.* **1979**, *34b*, 573.

(7) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461.

(8) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

electron oxidation process with $E^{\circ\prime} = -0.17$ V. Although ESR studies indicated that at equilibrium in solution only about 1% of dissolved dimer was present as monomer, the couple with $E^{\circ\prime} = -0.17$ V was thought to involve the monomer, $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$.

The behavior of the dimeric molybdenum analogue $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$, which does not dissociate significantly in solution, was found to differ significantly from that of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$. The compound $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$ is reduced irreversibly with $E_{1/2} = -0.92$ V vs a Ag/AgCl reference electrode, while the corresponding anion, $[\eta^5\text{-}C_5H_5Mo(CO)_3]^-$, is oxidized irreversibly with $E_{1/2} = 0.00$ V.[6] A recent, more detailed investigation concluded that, for both $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$ and $[\eta^5\text{-}C_5H_5W(CO)_3]_2$, reduction proceeded via an ECE mechanism involving 1-electron reductions of the dimers, cleavage of the metal-metal bonds to give the corresponding radicals and anionic species, and 1-electron reductions of the radicals.[9]

In the case of the $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$–$\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ system, the process with $E^{\circ\prime} = -0.17$ V can be attributed to a CE mechanism in which the dimer–monomer equilibration is treated as preceding a reversible electron-transfer step (eqs 2 and 3). The cathodic and anodic current peaks

$$[\eta^5\text{-}C_5H_5Cr(CO)_3]_2 \underset{k_M}{\overset{k_D}{\rightleftharpoons}} 2\{\eta^5\text{-}C_5H_5Cr(CO)_3\} \quad (2)$$

$$\{\eta^5\text{-}C_5H_5Cr(CO)_3\} + e^- \rightarrow [\eta^5\text{-}C_5H_5Cr(CO)_3]^- \quad (3)$$

then represent reduction and reoxidation of monomeric species. This conclusion requires that forward and reverse processes of eq 2 be rapid on the time scale of the electrochemical experiment, a condition qualitatively consistent with observation that monomer–dimer exchange is sufficiently rapid that the cyclopentadienyl $^1$H NMR resonances of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ and $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ coalesce well below room temperature.[2a] If this interpretation is correct, the irreversible oxidations observed at the more positive potentials in ref 6 and in this work may be attributable to oxidation of $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ and/or $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, a conclusion compatible in large part with conclusions for the molybdenum and tungsten analogues.[9]

However, by cooling the solution and/or going to faster scan rates, it should be possible to find conditions where the rate of the monomer–dimer exchange approximates the time scale of the CV experiment and where the dimer, $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, present in much higher equilibrium concentration, will be reduced. That this is so is shown in Figure 2, which presents cyclic voltammograms of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ run at −30 °C over a number of scan rates.

At a scan rate of 0.05 V/s (Figure 2a), the voltammogram resembles that of a reversible couple ($\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ to $[\eta^5\text{-}C_5H_5Cr(CO)_3]^-$). At higher sweep rates (Figure 2b,c), however, the cathodic branch broadens and a new cathodic wave emerges at a scan rate of 10 V/s (Figure 2d). Further increases in scan rate lead to more negative potentials for this peak (Figure 2e), with $E_p = -1.29$ V at 50 V/s. However, the anodic peak at −0.15 V remains large, and a small cathodic peak is still present near the original reduction potential of the monomer.

Referring to Figure 2e, peaks I and II arise from the reduction of the monomer and dimer, respectively, while peak III arises from oxidation of the monomer anion. We note that peak II is in fact comparable to the reduction potentials of $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$ and $[\eta^5\text{-}C_5H_5W(CO)_3]_2$.[9]

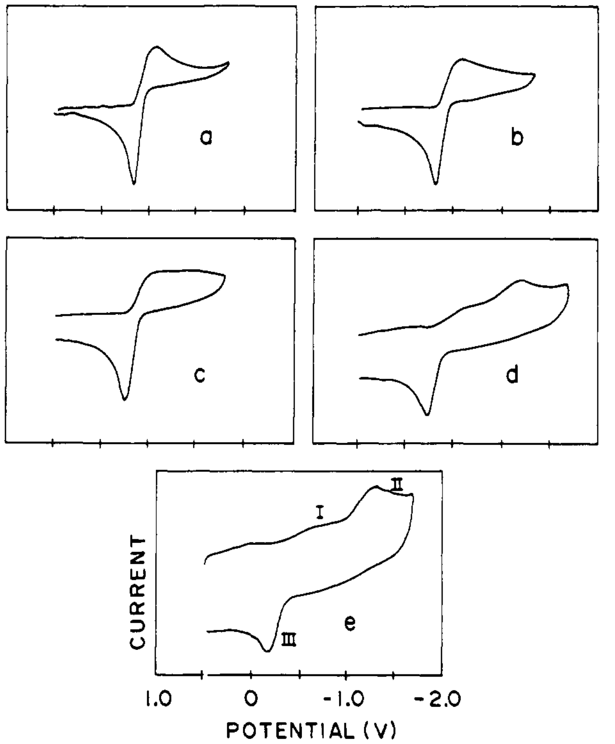

**Figure 2.** Cyclic voltammograms of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ ($1 \times 10^{-4}$ M) in $CH_2Cl_2$ at −30 °C. Scan rates: (a) 0.05 V/s; (b) 0.30 V/s; (c) 1.0 V/s; (d) 10.0 V/s; (e) 50.0 V/s. Note that the voltage scales are identical in all cases but that the current scales vary for reasons of clarity.

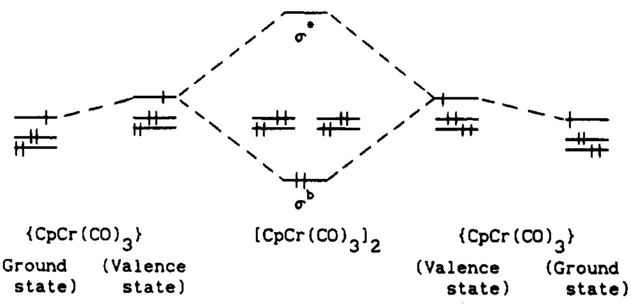

**Figure 3.** Correlation diagram for $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$.

To add further to the argument, we present in Figure 3 a diagram correlating the d orbitals during the construction of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ from two monomers, $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$, in their ground-state structures. The electronic structure of $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ in its ground state has been the subject of LCAO-HFS calculations, which suggest that the tricarbonylmetal moiety of the radical does not assume $C_{3v}$ symmetry as it does in the 18-electron analogue $\eta^5\text{-}C_5H_5Mn(CO)_3$. Instead, $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ undergoes a Jahn–Teller distortion such that the OC–Cr–CO bond angles are approximately 85°, 85°, and 110°, while the highest occupied orbitals are of essentially 3d character and are ordered as in the extremities of Figure 3.[4] To attain the structure assumed in the dimer, the monomers must distort such that the ring tilts slightly and the OC–Cr–CO bond angles become approximately 80°, 80°, and 110°.[10] While the energy requirement for this distortion has not been calculated, the facility of the monomer–dimer exchange, alluded to above, suggests that the activation energy for the process cannot be large, and thus the energy difference between the ground and the valence

---

(9) Kadish, K. M.; Lacombe, D. A.; Anderson, J. E. *Inorg. Chem.* **1986**, *25*, 2246.

(10) Adams, R. D.; Collins, D. E.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749.

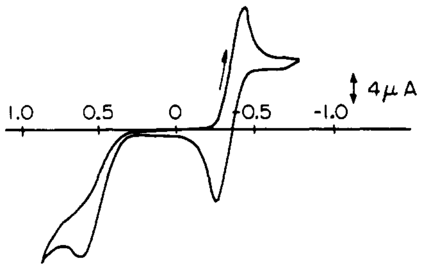

**Figure 4.** Cyclic voltammogram of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ ($5 \times 10^{-3}$ M) in $CH_2Cl_2$ (scan rate 0.2 V/s).

states of the monomer should be relatively small, as indicated in Figure 3. The $\sigma_b$–$\sigma^*$ energy gap should certainly be significantly larger, since the $\sigma_b$–$\sigma^*$ transition has been assigned to a band at 20490 cm$^{-1}$ (245 kJ mol$^{-1}$).[11]

The qualitative ordering of the frontier orbitals of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ relative to those of $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ in its ground state should therefore be essentially as in Figure 3. If so, then clearly the singly occupied orbital (SOMO) of the 17-electron compound will lie lower in energy than the lowest unoccupied orbital of the dimer, and $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ should exhibit the lower reduction potential. On the other hand, the SOMO and the nonbonding orbitals of the radical probably lie at energies comparable to those of the nonbonding 3d orbitals of the dimer. Thus, the two compounds may exhibit similar oxidation potentials, possibly rationalizing the observation of several oxidation peaks at 0.8–1.0 V.

In this context, we note that Madach and Vahrenkamp have reported an essentially linear relationship between the reduction potentials and the frequencies of the $\sigma$–$\sigma^*$ transitions of most of the metal–metal-bonded compounds $\eta^5\text{-}C_5H_5(CO)_3M\text{-}M'(CO)_3(\eta^5\text{-}C_5H_5)$ (M, M′ = Cr, Mo, W).[6b] The lone exception was the chromium dimer, $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, for which the measured reduction potential was about 0.3 V lower than anticipated on the basis of the frequency of the $\sigma$–$\sigma^*$ transition. This was taken as further evidence that the electroactive species was the monomeric $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ rather than the dimer. However, the spectroscopic data of Madach and Vahrenkamp predict an approximate reduction potential for $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ of about −0.6 V vs Ag/AgCl, reasonably close to the potential (−0.5 to −1.0 V) at which we first begin to observe definition of a cathodic wave for the dimer (see shoulders in Figure 2b,c). Considering the differences in temperature and scan rate, which can be important for irreversible processes, the observed potential for reduction of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ is now in reasonable qualitative agreement with predictions based on spectroscopic correlations.

**$[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$.** The CV of $[\eta^5\text{-}C_5Me_5Cr(CO)_3]_2$ in methylene chloride is shown in Figure 4. As with $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, a nearly reversible charge-transfer process with $E^{\circ\prime} = -0.33$ V and an irreversible oxidation step with $E_p = +0.63$ V are observed, both to more negative potentials of those for the cyclopentadienyl system in accord with the greater electron-donating ability of the $\eta^5\text{-}C_5Me_5$ ring. For reasons outlined above, it seems certain that the monomeric radical, $\{\eta^5\text{-}C_5Me_5Cr(CO)_3\}$, is the species undergoing the redox process, with $E^{\circ\prime} = -0.33$ V.

**$\{\eta^5\text{-}C_5H_5Cr(CO)_2L\}$.** Useful CVs of the compounds $\{\eta^5\text{-}C_5H_5Cr(CO)_2L\}$ (L = $PMe_3$, $PMe_2Ph$, $PMePh_2$, $PPh_3$) were obtained only in methylene chloride because of significant apparent disproportionation in THF. Even in methylene chloride, the presence of a small amount of $[\eta^5\text{-}C_5H_5Cr(CO)_3]^-$ was indicated by the observations of weak absorbances at about 1890 and 1790 cm$^{-1}$ in the IR spectra and small reduction peaks at about −0.32 V in the cyclic voltammograms. The IR spectra also exhibited weak $\nu_{CO}$ at about 1960 cm$^{-1}$, attributable to cationic species of the type $[\eta^5\text{-}C_5H_5Cr(CO)_2L_2]^+$,[3] and it appears that disproportionation of the substituted radicals is accompanied by ligand rearrangement.

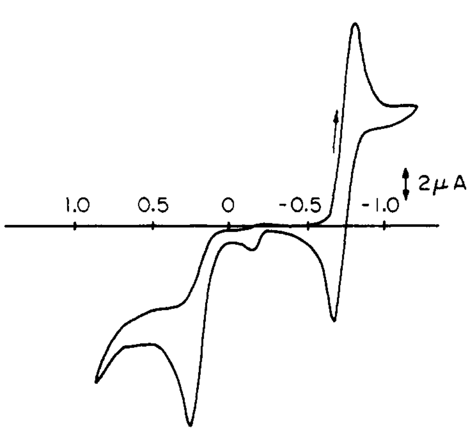

**Figure 5.** Cyclic voltammogram of $\{\eta^5\text{-}C_5H_5Cr(CO)(PMe_2Ph)\}$ ($5 \times 10^{-3}$ M) in $CH_2Cl_2$ (scan rate 0.2 V/s).

A representative CV, that of $\{\eta^5\text{-}C_5H_5Cr(CO)_2(PMe_2Ph)\}$, is shown in Figure 5; the small, reversible peak at −0.3 V, attributable to the presence of a small amount of $[\eta^5\text{-}C_5H_5Cr(CO)_3]^-$ is apparent. A nearly reversible reduction process with $E^{\circ\prime} = -0.74$ V, attributed to the 1-electron reduction of $\{\eta^5\text{-}C_5H_5Cr(CO)_2(PMe_2Ph)\}$, and an irreversible oxidation step with $E_p = +0.25$ V are also observed.

Table I lists the reduction potentials and $\nu_{CO}$ for the six substituted radicals studied here. As can be seen, there is a subtle albeit clear relationship between the ease of reduction of the chromium-centered radical species, as reflected in the reduction potentials, and "electron richness", as reflected by the carbonyl stretching frequencies.

## Summary

The 18-electron dimers $[\eta^5\text{-}C_5R_5Cr(CO)_3]_2$ (R = H, Me) dissociate to the corresponding monomeric radicals $\{\eta^5\text{-}C_5R_5Cr(CO)_3\}$ in methylene chloride solutions. Cyclic voltammograms of the solutions at ambient temperature, initiated at 0 V and switching at −1.0 and +1.5 V, exhibit reversible, 1-electron cathodic peaks at −0.30 and −0.43 V, respectively. Low-temperature, fast-scan experiments with the former system demonstrate that the monomer, not the dimer, is the electroactive species, since a peak corresponding to reduction of the dimer, $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, is observed to more cathodic potentials at −30 °C and scan rates >10 V/s. CVs of the substituted radicals, $\{\eta^5\text{-}C_5H_5Cr(CO)_2L\}$ (L = tertiary phosphine), exhibit reversible, 1-electron reductions in the range −0.78 to −0.84 V; the potentials parallel the electron richness of the radicals, as indicated by IR spectroscopy in the $\nu_{CO}$ region.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada for operating grants to M.C.B. and J.A.P. and for a Summer Undergraduate Research Fellowship to K.O. and the National Science Foundation for NSF Grant No. CHE86-03728 to W.E.G.

---

[11] Ginley, D. S.; Bock, C. R.; Wrighton, M. S. *Inorg. Chim. Acta* **1977**, *23*, 85.